SELF-HEALING SUPRAMOLECULAR POLYMER
NANOCOMPOSITES

by

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Submitted in fulfilment of the requirements for the degree of

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This thesis is dedicated to my teachers and my family with love and gratitude.
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ABSTRACT

Supramolecular chemistry is an evidence of how research with a real-world focus can be productively employed for innovations with high commercial and academic value. The ultimate aim of this branch of chemistry is to attain control over the non-covalent molecular interactions. On the other hand, a rapidly rising field of polymer technology is that of nanocomposites that can be prepared by dispersing nanometre sized particulate material throughout a host polymer matrix. Such nanocomposites can demonstrate superior chemical or physical properties compared with conventional polymer composites, and often these improved properties can be attained using a moderately small quantity of nanoparticles. However, nanocomposite materials can be subject to failure due to damage initiated by various external factors.

Here we propose the synthesis of novel polymer nanocomposites that assemble together via hydrogen bonds and thus obtain nanocomposites with reversible hydrogen bonds. They are synthesised from simple fatty acid derivatives, amines and urea by the vigilant utilisation of hydrogen bonding Along with conventional properties these systems can associate together upon damage, i.e. they can self-heal at room temperature or at slightly elevated temperatures. These materials are believed to be having extensive range of future applications. Moreover, we study the factors which affect the chain formation and cross linking mechanism. As a special property, these materials can be repetitively processed and reused. The self-healing abilities, the easy synthesis approach, and a cost effective technique makes these polymers a better choice for commercial use. In accordance with the work described in this thesis it provides information of a self-healing nanocomposite wherein the functional groups form non-covalent bonding interactions between the macromolecule, crosslinking agent, and a nanofiller dispersed in the matrix.

In general, this thesis contributed to the fundamental understanding that generally relates to a supramolecular polymer nanocomposite and to a process for the preparation of these polymer nanocomposites having some desired properties like self-healing ability.
PUBLICATION LISTING

PATENTS:


▪ Self-healing polymers and process for the preparation thereof, *United States Provisional Application Number 61/499,884; filed on 22nd June 2011.*

▪ Self-healing polymer nanocomposite and process for the preparation thereof, *Australian Provisional Application Number 20100905099; filed on 17November 2010.*

CONFERENCES:


▪ Conference Attended: *Third International Conference on Self-Healing Materials* (3ICSHM) conference 27th-29th June, University of Bristol, Bath, United Kingdom, 2011.
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<tr>
<td>C25A</td>
<td>Cloisite 25A nanoclay</td>
</tr>
<tr>
<td>C30B</td>
<td>Cloisite 30B nanoclay</td>
</tr>
<tr>
<td>CNa+ / Na-MMT</td>
<td>Cloisite Na+ nanoclay</td>
</tr>
<tr>
<td>DCP</td>
<td>Dicyclopentadiene</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<tr>
<td>FTIR-ATR</td>
<td>Fourier Transform Infrared-Attenuated Total Reflectance</td>
</tr>
<tr>
<td>MMT</td>
<td>Montmorillonite</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi Walled Carbon nanotube</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>SAXS</td>
<td>Small angle X-ray diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SMP</td>
<td>Supramolecular polymer</td>
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<tr>
<td>SMPA</td>
<td>Supramolecular polymer with C25A</td>
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<tr>
<td>SMPB</td>
<td>Supramolecular polymer with C30B</td>
</tr>
<tr>
<td>SMPNa+</td>
<td>Supramolecular polymer with CNa+</td>
</tr>
<tr>
<td>SWCNT</td>
<td>Single Walled Carbon nanotube</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>Tg</td>
<td>Glass Transition Temperature</td>
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1 INTRODUCTION

The entire range of known chemical phenomenon is observed to be occurring due to either attractive or repulsive molecular interactions. These interactions include London dispersion forces, hydrophobic interactions and dipole-dipole interactions. Apart from these there are other molecular interactions possible that can bring the molecules back together reversibly such as $\pi$-stacking, inclusion complexes, coordination bonds and the hydrogen bonds. These non-covalent chemical interactions are generally discussed in the window of supramolecular chemistry. Understanding the various factors governing the formation of non-covalent interactions and the environment required for such formations form the basis of supramolecular chemistry. The two significant properties that determine a supramolecular interaction are the strength of the chemical interaction and the kinetics of interaction. Understanding these components form the characteristic of supramolecular interactions.

Polymer dynamics and physical interactions were analysed to form higher cross linking of molecules which are responsible for the high mobility of the polymer chains and thus allowing them to form reversible chemical interactions. These reversible interactions can be used to meet the high but unmet demands of the polymer and plastics industry for materials with the ability to heal and restore the original material properties when damage occurs through thermal, mechanical, ballistic or other means. This research project therefore aimed to design and discover novel self-healing polymer materials with higher levels of molecular mobility to overcome this issue. The present invention relates to self-healing polymer nanocomposites. The polymer nanocomposites of the invention include a cross-linked matrix and nanofiller dispersed in the matrix. Upon damage or failure of the nanocomposites material, they self-heals without the need or use of chemical reactants to promote the damage repair. This thesis generally relates to self-healing polymer nanocomposites and to a process for the preparation of the
self-healing polymer nanocomposites. Due to their versatility, such polymers are very desirable and are estimated of huge commercial interest. This class of material is largely unexplored and should be broadly applied to many product requirements.

It was Jean Marie Lehn in 1993 firstly reported the utilisation of hydrogen bonds to form supramolecular polymers [1]. Later many different types of interactions were revealed but hydrogen bonding stood out due to its unique characteristics in terms of its strength and kinetics. The reversible chemical interactions that help to form polymeric structures can resemble polymer moieties which are traditionally available. Pristine or organically modified nanoclays can be used and the dispersion of the clay in the polymer can be evaluated. A study between the self-healing behaviour of the polymer, clay morphology, the development of polymer matrices, polarity, concentration, molecular weight, pH and temperature at polymerisation, branching, cross linking degree, and crystallinity could give better understanding of the interaction chemistry. Thus it is possible to produce self-healing nanocomposite materials from polymers with a mixture of functional properties together with the self-healing ability, making this material unique.

This technology could develop a major breakthrough due to its impact on polymer research. This technological leap combines the mechanical strength and stiffness with molecular mobility resulting in unlimited repairs to damaged plastics. This project is trying to optimise the material properties and self-healing ability of the polymer nanocomposites. We will use available polymeric materials, and introduce for e.g. nanoclays, carbon fibre and carbon nanotube particles into the polymer to increase the stiffness and make them useful for high performance practical applications. It is anticipated that further enhancement of this technology may also yield materials with useful static load bearing capabilities. Moreover, these advanced polymers will have enhanced overall material properties along with its capability for further improvement. This dissertation is discussing the consequences of hydrogen bonding interaction in main rather than its origin which has helped to explore new and specific functions to the polymers.

The scope of this work was decided to be focused upon the following research gaps by making a significant contribution towards the field of material science
where there is only a very few research projects are done on supramolecular polymer systems that are having repairable capability. Thus the project aimed at addressing the following research questions:

- **Question 1**: Can novel nano-modified polymer matrix be made with combined characteristics of nanocomposites and self-healing polymers?

- **Question 2**: What are the methods and models that can be developed for the prediction of properties of nanocomposites consisting of reversible hydrogen bonds?

- **Question 3**: How does the polymer nanocomposite matrix is driven by the molecular structure of nanofillers and molecular structure of monomers?

### 1.1 Objectives

The objective of this thesis is to acquire a better understanding of the hydrogen bonding chemistry in supramolecular polymers through elucidating a structure-property relationship. This was scaled up to the production of a series of polymer nanocomposites having unique properties. To accomplish these developments, broader aims given below were investigated:

- Investigate various mixing techniques and processing techniques for the preparations of polymer nanocomposites.

- Study the effect of molecular structure of monomers and nanoclays on the formation of polymer nanocomposites by understanding of the type of dispersion of nanoclay platelets into polymer galleries.

- Develop a structure-property relationship to help the prediction of final product properties.

- Evaluate the healing and repairing capabilities of the polymer by studying the reversible hydrogen bonding.
1.2 Thesis Outline

Apart from this chapter 1, this thesis comprises other seven chapters as described below.

Chapter 2 is a detailed review of the recent developments published on supramolecular polymers, self-healing polymers and nanocomposites. A variety of synthesis and fabrication approaches in making self-healing polymers and nanocomposites along with its characterisation techniques are illustrated.

Chapter 3 specifics all the materials, methods and techniques used for the synthesis. It also briefly describes the instruments and characterisation techniques used in developing an understanding the morphological and material characteristics of synthesised polymers.

Chapter 4 mainly describes the processing conditions and techniques which are used to optimise and develop a feasible process that can be carried out in a chemistry laboratory. The effects of molecular structure of monomers used are also discussed on the perspective of the formation of supramolecular polymers.

Chapter 5 deals with the effect of nanofillers and its modifiers in the formation of supramolecular polymers. This has been connected with chapter 4 to develop a strategy for the selection of monomers and nanofillers while synthesising polymer nanocomposites.

Chapter 6 deals with preparation of ideal polymer nanocomposites using optimised processing conditions described in chapter 4 and optimised molecular structures described in chapter 5. The materials are studied for their ability to repair their damages.

Chapter 7 gives a general discussion of the aspects revealed in the technical chapters.

Chapter 8 concludes the complete work done in this project leading to suggestions for future work.
CHAPTER TWO

2 LITERATURE REVIEW

The world of material science comprises of a very diverse spectra of compounds such as polymers. The polymers have a massively familiar ability to stand for a huge diversity of applications. For the very reason it is quite expected that the polymer research will give way to more novel innovations that can represent the employment of polymer molecules for the creation of smart polymer materials. These processes will follow a realistic understanding of basic processes within the polymer structure variations. The correct methods of analysis with the huge range of polymers and sophisticated characterisation techniques will largely give out towards the arena of supramolecular polymers.

The outstanding innovative research outcomes from the field of science and technology are greatly exiting in multiple ways. These outcomes are obviously the creative outcomes of many collaborative initiatives from interdisciplinary fields of technology, sciences and engineering. The past decade saw the wonderful growth in the development of smart materials. It is known that a smart material is one which can alter its functional material property according to application requirements. Also these smart materials have potential to be used in materials that need considerable engineering changes.

Here we discuss about the materials that can exhibit healing responses upon a given stimulus. The materials of that category have got many practical applications including increased life time. Such materials can find their potential application in coating technologies and many others. To make these materials practically useful they must have the capability to withstand mechanical load so that they are not very prone to cracks even at a regular usage which will lead to the materials permanent failure. The small cracks are the precursors to major failures because the detection techniques used to find cracks may not be successful always. Later these cracks will grow which will end up where the mechanical properties cannot be restored. On the other hand if the cracks were identified and welded together to restore its functionality, the chances of another
failure of the same material from the same point are more likely to occur. This will in turn lead to an irreversible failure of material. These issues were identified by the research community in materials engineering to explore further and develop new materials were crack formations can either be delayed or repaired much before the total irreversible failure. Thus the polymers having a cross-linked network were imagined and thought to make this a reality. Those materials were called as smart ones as they can delay the micro crack formation or they will be capable enough to repair the small cracks by themselves. There were few different approaches were the healing can be achieved by intrinsic or extrinsic means. The intrinsic means involve the healing happened by the reversible bonds of the polymer while the extrinsic healing was obtained by the aid of healing agents which are already added along with the polymer. The world of self-healing materials is a moderately new research field having a history of its own for just two decades. The Third International Conference on Self-healing materials was conducted in Bath, United Kingdom from 27th to 29th June 2011 following its success after the previous conferences.

Very interestingly patents, peer reviewed journal articles and reviews are being coming out in big numbers every year on the different fields of self-healing materials. Basically all of them have a chemical synthesis and smart engineering background to prove its practical applications and scope. Here we are going to discuss in short detail and review the work done on various self-healing materials studied in past two decades by giving a special prominence given to current trends from last three year published works and by including some prospective future ways.

2.1 Supramolecular Polymers and Self-Healable Materials

A large number of compounds fall under the category of polymers. These compounds are often described to be associated to themselves or to other compounds through its molecules with the help of chemical bonds. Conventionally the molecules are interconnected by covalent bonds. The concept of supramolecular chemistry is based on the chemistry beyond these conventional chemical interactions. Therefore these is not related to just molecules but are related with the properties of moieties of molecules that are held together by weak
interactions. Supramolecular chemistry is said that molecules are to supramolecules as atoms are to molecules. All the fundamental knowledge of kinetics, thermodynamics, intermolecular interactions, and organic synthesis are employed here to make a real contribution to the supramolecular chemistry[1].

The atoms of highly electronegative elements such as fluorine, oxygen or nitrogen gets bonded with hydrogen atom, the designed molecule is polar. Then the electronegative atom of the molecule will form a weak bond with hydrogen atom to be called as a hydrogen bonding. There are two types of hydrogen bonding such as intermolecular and intramolecular hydrogen bonding. Hydrogen bonding has important effect on many physical and chemical properties of compounds.

It is hard or not practically possible to extend the life time of a polymer composite material once after it gets damaged. The best possible method known is to monitor the material performance continuously and run an on-site in-situ repair process. This process could remove the possibility of total replacement of component and will give an enhanced life time. However, this method has got its own limitations where the strategies for the repair mechanism have to design differently for various materials according to its use and functional life time. The welding process of cut surfaces is a known technique where polymer surfaces were melted about its glass transition temperature and kept in contact for longer period so that the pristine mechanical strength are restored. The problem with this technique is that the welded part will remain the weakest part to occur damage for another time at the same point and thus this technique cannot prove itself as an efficient one to repair cracks in polymer surfaces. Thus this approach will be the one which needs the human or mechanical intervention on continuous basis that can ensure a temporary answer to the issue which in turn will highly influence the maintenance cost of the polymer product. This led the researchers to find better and cost effective approaches towards the concept of self-healing polymers.

2.1.1 Measurement of Self-Healing Process

It is important to develop a general and applicable mode to govern the healing efficiency of self-healing polymers in a quantitative manner. For that pieces were damaged and healed purposefully. Then conducted stress–strain experiments on ‘original’ and ‘healed’ samples, and the healing efficiency was expressed using
tensile strength as a measure of the efficiency of a component and was calculated using the equation:

\[
\text{Healing efficiency} = 100\% \times \frac{\text{tensile strength healed}}{\text{tensile strength original}} \rightarrow \text{Equation (1)}
\]

Here tensile strength healed is the tensile strength of the healed sample set and tensile strength original is the tensile strength of the original sample set[2]. This actually made the extent of quantification of healing process.

2.2 Well-Known Self-Healing Approaches for Polymers

A number of engineering and synthesis approaches on the self-healing polymers were discovered in a short period of time during the last two decades which are discussed here.

2.2.1 Hollow Glass Fiber

The significance of using fiber in polymers has greatly known for its improved mechanical strength and other physical properties including thermal stability. This technique is therefore used for the synthesis of materials with tailor made properties. However, delamination is a problem for this class of materials to perform and thus prone to damage is identified as the major disadvantage. The reinforcing fiber along with healing agent can give the polymer material a better mechanical strength along with a promise to repair its damage by the release of healing agent. This would give the material another attractive property to perform better for longer periods of time. The fibres additives can be glass fibres or carbon fibres to make these polymer composites.

This technique of using glass fibres has proven to give enhanced performance in material properties with dependable strength to all parts of the polymer. The major advantage of this technique is the possibility to create plastics with adjustable mechanical properties by adjusting the thickness of glass walls or the area of hollow space. Another major benefit offered hereby this technology is the use of the hollow space to be filled with a healing agent (unreacted monomer) which will be released when the glass fiber will break upon a mechanical stimulus. This will enable healing agent to polymerise and to initiate a repair to the damaged systems as shown in Figure 2.1.
The best known study to start the concept of self-repairing polymer composites were Dry et al [4] and later by Li et al [5] on a cement based composite. Motuku et al [6] later tried this technology of releasing chemicals from the polymer matrix to fix its structure on polymeric materials. He also identified that glass fibres are finest and appropriate choice for this purpose as other options like polymer tubes will fail at instances where it need to break for the controlled release of monomers. In order to apply these technique perpendicular fibres filled with polymer and hardener were inserted into the composite matrix. The major problem that encounter with this technique is the engineering concerns of using hollow fibres and its handling while on composite preparation. A series of practical approaches had to be worked out while this technique was used including the overall properties of the hollow fibres and the resin used in these fiber. A vacuum assisted method was proposed by Bleasy et al [3] to help these issues which later became a widely used approach. There were a number of studies published to establish a relationship between the dilutions of solvent to help the filling of glass fibres. It was also interesting to see the scientific correlations made to discuss the favourable and unwanted reactions that could happen chemically between the solvent and unreacted healing agent. These studies would enable the design and engineering concepts of the self-healing techniques of polymer composites work effectively.
The other concerns in the engineering include the strength of glass fiber as they have to survive the composite preparation without any damage, to protect the unreacted healing agents contained in the glass fibre. The effect of glass fiber diameter was studied by Hucker et al [7] to prove its better compressive strength which is obtained by the increased storage of liquid material inside the hollow fiber. Methods to promote the breakage of fiber were outlined by Dry and Sottos by the application of a coating which is brittle on the fiber surface[4]. All these better explain the diversity of parameters to be explored to achieve the better use of hollow glass fibres.

Now the other major concern is the capability of the resin used inside the hollow fibres which is either the solvent or resin or the monomer. The liquid have to reach the damaged site to initiate the healing process. For this the properties including the viscosity and related parameters need to be understood correctly. The work by Bleay et al [3] showed that cyanoacrylate system has to withstand substantial problems where the healing agent gets cured even before reaching the damaged site. Brilliant approaches towards this issue were made by various research groups across the globe. The usage of dyes in the liquid form along with the composite preparation [8-10] helped to identify the mechanisms of resin flow and its dynamics while on the repair-damage process [8, 9, 11]. It has to be ensured using the dyes that have the unreacted monomer will reach damage site correctly to polymerise and give the composite material its pristine mechanical strength and other properties.

Thus there was a whole set of various parameters needed to establish the efficient and feasible engineering strategies for this technology. Moreover, there were other concerns on the special orientation of glass fibres, the size and shape of these fibres. By considering the final aim of all these steps is to ensure a better mechanical strength and intrinsic self-repairing capability. It was found out by Jang et al that the arrangement of fibres with in the polymer matrix affect the response to the polymer upon a damage [12]. The spacing between the fibres was also an area of interest which later proved that the mechanical properties had a clear effect to show their greater healing abilities [6]. These concerns in terms of the design parameters raise the biggest challenge towards the tailor made polymer
composites that can be used for the specific needs. It is needed to be admitted that a lot of studies done on this technology were all focused on the possibility of this technique which made it a more quantitative study area. However, there were few studies done to show the reduction of mechanical stability, at least at initial stages when the hollow glass fibres were used to establish self-healing ability [3-6, 8, 10-16]. Those studies quantitatively compare the reduction in mechanical strength when used in glass fiber reinforced polymer and carbon fiber reinforced polymer. It also establishes the level of recovery of its original mechanical strength once after the self-healing process is over. So it is important to explore the scientific capabilities of these classes of polymer composite materials.

2.2.2 Healing Via Microencapsulation Technique

As we have discussed the hollow glass fiber and its engineering concerns causing the practical limitations, ongoing research for alternative technologies to employ self-healing phenomenon. Thus the alternative idea of using additional components that can be used as a part of the polymer matrix came in. The encapsulates can be rubber or glass fillers. It was described that the fracture toughness can be improved for an epoxy composite system without having an adverse effect on mechanical properties [17, 18]. These studies were recommended in some earlier works published in 1980s [19, 20]. The reality of making more complexity towards the synthesis of this system cannot be ruled out. Some studies shows that the complexity includes poor adhesion within the polymer matrix and voids caused within the polymer matrix [20-22]. However, there were researches done to show increased adhesion and mechanical properties like fracture toughness even after encapsulation techniques were employed [21]. The special options other than these conventional glass or rubber fillers are microcapsules, by the use of which tougher and lightweight polymer materials can be synthesised. The most significant advantage of microcapsules is their capability to carry healing agents inside them. These microcapsules can break upon the trigger of damage on the polymer body to release the healing agent to initiate a repairing process which will make it efficient. On the other hand, these techniques also have to go through many engineering concerns being a polymer product demanding specific functionalities.
2.2.2.1 Synthesis of Microcapsules

The general technique known for microcapsule synthesis is the emulsion polymerisation technique [22, 23]. Mostly, the systems studied present the use of the urea-formaldehyde microcapsules which contain dicyclopentadiene healing agent. The in-situ reaction process in water phase between urea and formaldehyde will produce highly cross linking pre-polymer. They will form the shell walls of the microcapsules. After that process the nanoparticles of pre-polymer will adhere to the microcapsule to give them an uneven surface morphology. This uneven and rough surface will help the adhesion of these microcapsules while on polymer processing.

![Microcapsules](image)

Figure 2. 2 Microcapsules breakage mechanism was studied to understand the stress state produced by a planar crack. The left figure represents to a three times stiffer inclusion while the other figure denotes the inclusion which is three times compliant [24, 25].

The healing processes in these types of polymers are basically triggered by damage or crack occurring on the polymer matrix. This crack will initiate the breaking of microcapsules to release the encapsulated healing agent to come out. Thus the breakages of the microcapsules are highly mandatory for the healing process to occur. This arena of self-healing polymers were studied by Keller and Sottos [24-26] to establish a connection between the strength of microcapsule walls and the strength of area around the microcapsules.

A description of the effect of high elastic modulus of microcapsules in the polymer material was studied. That study proved that this higher modulus will rebound the crack propagation in the matric which in turn will fail the microcapsule breakage as given in Figure 2.2. This study helped to elucidate and develop an optimum strength ratio between the microcapsule walls and polymer
matrix so that the healing process can happen upon the trigger of a mechanical failure.

There are lots of other factors to be considered while designing microcapsule embedded self-healing polymer systems. The important among them are the wall thickness and size. The optimum thickness outlined by research studies is 150-230 nm. This is because of the concern over when microcapsules are not breaking of wall because of too strong capsule wall and break easily due to thin walls, are both not ideal. Another important factor is the size of the microcapsules which actually determine toughness of polymer and amount of filling in microcapsules. The healing agent quantity which is going to act upon the healing process will be determined by the amount of fillings inside. Different processing aids can be used to vary the size of microcapsules like the agitation speed. It is optimised ideally on a broad range of 200-2000 rpm. There are a lot of studies which actually validates the size of microcapsule in the vicinity of its performance [23, 27].

There are proven studies explaining that larger microcapsules will give better healing efficiency which may be due to the higher amount of healing agents released upon their breakage. On the other hand, smaller microcapsules are also explained to serve with better toughening characteristics when checked at poorer concentrations [23, 28]. In the advanced studies the precession based works done by scientists calculations were made in terms of determining the amount of content of microcapsules and the microcapsule sizes in connection with the damage area of a polymer composite sample [24, 25, 28, 29]. The comparison was obtained by comparing manually injecting the required amount of healing agent against the volume obtained by the breaking of microcapsules. Various techniques can be used to make microcapsules. They involve mini-encapsulation and ultrasonication techniques. The obtained capsules is having a high content of healing agent inside and to the best result they all proved to be breakable at testing conditions [30]. Thus obtained nano capsules have clear ability to impart self-healing to functional polymer materials.

Over the concerns towards the design of microcapsules, then come the healing agent and its activity to make the healing process a reality. The relationship with the crack propagation speed and healing efficiency was studied by Jones et al
[31] where he clarifies that when the speed is too high then the healing process will be slow. This study also relates the curing speed of the healing agent and its effect on the efficiency on healing by comparing a fast and slow curing mechanism. Thus it may be indicative of the fact that the careful control of these parameters can ensure a higher level of self-healing ability on composite materials.

### 2.2.2.2 Dicyclopentadiene/Grubb's Catalyst Microcapsule System

So far after its potential in self-healing polymer materials were identified, they remain the most popular and explored system in that area. This system uses dicyclopentadiene as the microcapsule healing agent and ruthenium (IV) catalyst in the polymer matrix which works through a ring opening metathesis polymerization mechanism. There were a number of studies on this concept to compare the benefit and problems associated, the alternate approaches, and modifications were discussed. Among them the most studied one is the work done by White et al [24] that uses the catalyst in the polymer matrix which will come in contact with healing agents from microcapsules when polymer matrix is under a mechanical damage. Figure 2.3 represents a schematic way towards this approach. When the catalyst reacts with the healing agent the polymerisation will occur to repair the polymer which in turn will keep the material strength and life term unaffected.

The cost effective choice dicyclopentadiene made it suitable for all sorts of fundamental research. The capability to Grubbs catalyst to support olefine metathesis for a wide range of functional group ensures it adaptability towards the technology. The healing performance given by this technique was apparently good to give about 60% of healing competence which made it a major breakthrough towards the invention of self-healing polymer systems. This work has given way to a number of further research outcomes from the pioneer group and from other research groups around the globe.
A structural composite material containing an encapsulated healing agent and a catalyst which can enable polymerization process. 

Later the pioneer group tested the technology feasibility to address one of the major issues with the polymer composites which is the delamination [32, 33]. As given in Figure 2.4 three sets of samples were prepared and healing efficiency was compared against the 2001 study from the same group. It was observed that the healing efficiencies were effectively increased to a sensible level. The feasibility studies were finding success on self-healing composite technology and researchers [34] found their scope on exploring the mechanical properties of the same systems. A correlation between the microcapsule concentration and its mechanical strength was driven out. Moreover the effect of particle size of catalyst was studied according to its effect on the mechanical strength. The studies were done on healed and original samples. The optimised conditions elucidated were to use 2.5wt% catalyst and 5% microcapsules to get a healing efficiency of around 90%. An in-situ polymerisation technique was employed for synthesis.

Even though the results were promising the scientists were not happy about the cost effectiveness of this system as Grubbs catalyst was very expensive. Also the possibility of using alternate sources of healing agents was also considered by many researchers to try better healing efficiency and cost effectiveness.
Figure 2.4 Three different types of samples were studied. (a) Manually catalysed healing agent is injected into cracked area. (b) Healing agent alone was injected on to a polymer matrix which has got catalyst embedded on it. (c) polymer matrix having microcapsules containing healing agent and catalyst are both embedded to exhibit an autonomous healing process [33].

2.2.2.3 Monomers as Tools for Healing In Microcapsule Approach

The most widely studied system in microcapsule approach is the one which uses dicyclopentadiene (DCP) as the healing agent. Thus the importance given to DCP and its isomeric forms were also studied [35] to examine the effect of fast healing and the selection of isomer. It was studied and described that the exo-isomer functions better as it experience faster polymerisation compared to the endo-isomer which is commercially easily available. The reasons for this better polymerisation reaction while comparing with the two isomers are explained to be due to the steric interactions. The interest to find alternative sources for monomers to be used in self-healing composite systems were on-going all the time and thus emerged another candidate which was the ethylidene norbornene. The approach had complexities involved such as the product polymer had less mechanical properties compared to the previous ones using dicyclopentadiene. Thus the possibility of using both monomers together as a blend was given a trial by Liu et al. that helped to increase the rate in which the polymerisation occurred [36]. This approach gave additional benefit of testing the polymer at a wide range of temperatures. Moreover the approach kept almost all the benefit of it’s mechanical properties as well. The optimised ratio between dicyclopentadiene and norborane was 1:3 to give the best possible properties.

2.2.2.4 Catalyst for Polymerisation

The use of a catalyst in self-healing polymer systems was studied quite extensively. The great concern over this study was obviously on the choice of
catalyst systems. The commonly used catalyst was the Grubb’s catalyst. This catalyst will start losing their activity on long exposure to atmospheric air and moisture. Another case where the catalyst lose it activity was when it gets exposed to Diethylenetriamine (DETA) which is a component used for curing in composites. Moreover, there were concerns raised by Kessler et al on the agglomeration issues of this catalyst [33, 37]. It is described that the different morphological forms of the catalyst has very high impact on the effect of dissolution and self-healing performance of the material. For instance the deactivation was faster and activity was higher when small catalyst particles are used in the polymer matrix.

The high deactivation was due to its high reactivity with DETA and larger activity was due to more surface area. These issues were tried to be addressed by Rule et al [38] where the research was oriented in protecting the catalyst from getting deactivated by external agents like amines. The solution found was to coat the catalyst surface with paraffin before embedding into the polymer matrix. It was found that only 9% of activity is affected by the amines when the amine was later brought into reaction with this catalyst. It was also shown that the paraffin wax will get melted first for the healing process to take place. It is also described that the wax helped in uniform healing to be performed on the polymer matrix. Also the healing efficiency has kept very high by using a lower percentage of catalyst and that is always highly cost effective [39].

This study lead its way to another very interesting work published by Wilson et al to try the concept of this wax coated catalyst in another polymer system where vinyl groups and peroxide moieties were present. The effect of using endo-dicyclopentadiene and exo- dicyclopentadiene in the system was explored to validate its capacity to give better healing efficiency. It was proved that the exo-dicyclopentadiene systems showed better and efficient healing behaviours for the same level of catalyst used. The peroxide moieties were tested against the wax coated catalyst particles and found to be working well for longer ties without loss in activity. It was also believed that the smaller catalyst coated with wax melted faster to give better healing uniformity and efficiency. Thus the first generation
Grubbs catalyst was explored and proved in many ways to be performing well toward the self-healing capabilities on a polymer system [40, 41].

Later different other catalyst were tried to be used as the possible alternatives for first generation Grubbs catalyst. The parameters that have to meet while performing the comparison test includes the stability of catalyst in different resins, its possible temperature ranges and thermal stability, overall activity and life time, readiness to initiate polymerisation reactions etc. The second and first generation Grubb’s catalyst were compared on these parameters and found that the first generation Grubb’s catalyst is showing a better performance in terms of faster polymerisation rate. When compared the thermal stabilities, second-generation Grubbs' catalyst showed better performance than the first generation and Hoyveda-Grubbs' catalyst which showed an efficient thermal aided healing at around 125°C. On a cost effective perspective Tungsten (VI) catalysts were tried an alternative for Grubbs catalyst [42].

All these remarkable studies gave way to the exploration towards the raise of substitutes for healing agents and catalysts in self-healing polymer systems. However some of the new catalyst and healing agents were showing self-healing capabilities but were not so good when coming to the restoration of mechanical strength. This may be accounted due to the lack of proper bonding between these molecules and polymer matrix. Additional steps were taken to address these issues by giving better mechanical string, keeping wax covered catalyst for long hours etc. It is important to say that the design and engineering mechanisms involved in the research and development based on microcapsules was amazing. It has to understand that it is not only the perfect combination of catalyst and healing agent is working out but the various design and chemistry involved parameters determine the self-healing behaviours of polymer systems. All these mentioned approaches and parameters must be carefully addressed along with the right selection of catalyst to get a perfect self-healing polymer system.

2.2.3 Polydimethylsiloxane Self-Healing System

While the overall interest of scientific field was to develop on DCP based self-healing systems, the other possible approaches were started to be explored. The
major issues faced by the previous system were the coating related problems on catalyst surface and the less stable catalyst under the presence of healing agents were tried to be addressed across the wider research community. Another self-healing polymer as an alternative to Grubbs catalyst and DCP system was put forward by Cho et al [43] which was based on the catalytic reactions of organotin on a poly(dimethylsiloxane) (PDMS) system. One of the major advantages of this system over the Grubbs catalyst system is its stability towards moisture. In fact the reaction in this system will initiate upon the presence of water only. Another advantage of this approach is the better dispersion of healing agent that can be directly spread on polymer matrix. This will allow the better dispersion and thereby uniform healing efficiency. Thus it is considered that this organotin system is more practically feasible considering its better action towards water and healing performance.

This system was practically more approachable due to its general capabilities to work as same as any other self-healing polymer system and also due to its stability towards wet conditions and high temperature environments. The healing mechanisms were simple as explained by other systems such as the propagation of a crack is the trigger for healing to occur. Once crack occurs, the ruptured microcapsule will allow the contact of the catalyst with the drops of healing agent which are phase separated to allow healing process to occur that will in turn regain the lost mechanical properties of polymeric material. Despite of these advantages these systems can ensure another advantage which is the cost effectiveness by using low cost and easily available raw materials. However, the problems associated with this system are that the healing efficiency was counted to be low compared to other systems. This low performance was attributed to the bad adhesion properties between the healing agent and the polymer matrix. This problem was tried to deal with adding adhesion promoting additives to the polymer matrix which was proved to provide double healing efficiency [43]. The optimised condition were set at using 3.6wt% microcapsules and 4% adhesion promoter to obtain about 24% of healing recovery when 12wt% PDMS was used. This approach was proved to help to slow down the crack propagation on a polymer matrix to a significant level.
However, this innovation is considered to be an important achievement as this material can exhibit its self-healing properties to improve the life of polymer materials under destructive and challenging conditions in a cost effective way. According to Keller [44] who did a follow up study on the same PDMs based self-healing system but by introducing two different microcapsules where one is a resin microcapsule and another a initiator microcapsule along with platinum catalyst. Thus this system expects the polymer to release by itself to initiate an in-situ healing process when crack occur on the polymer matrix. This approach gave a healed material; which looks attractive like the starting one and by giving an average healing efficiency of about 75%. As a matter of interest this efficiency was achieved with the use of only 10% of the healing resin and 5% microcapsules. In some case studies it was also observed that a 100% healing efficiency is possible when the healing tear path was deviated. This accomplishment is attributed to the similarities of chemical counterparts of polymer matrix and healed part. Another advantage of using microcapsule are well explained in this study by showing better tear tolerance which can contribute to its use in energy absorbing conditions.

Lately they further investigated the self-healing capabilities of these polymer systems [45] by determining the self-healing on the basis of adhesion between healing agent and polymer matrix. It is generally considered that the under fatigue bearing conditions, the self-healing abilities have to undergo some challenges. But in the here explained system cracks were healed and mechanical strength was regained by this adhesion based bonding mechanism. However, the mechanism is very complex to be materialised on a fatigue bearing testing condition to be practically functionalised because of the inclusion of various steps like adhesive bonding, protection off crack point, synthetic crack closing etc.

2.2.4 Epoxy-Hardener Based Self-Healing System

Amongst various approaches towards the polymer systems that can restore their properties on damage the self-healing polymer systems based on uncured epoxy is an important one.
Later on another research outcome, the idea of using epoxy as a healing agent was proposed. The healing agent will be encapsulated as an embedding in the polymer matrix. It is hoped that this material will keep all the characteristics of a composite material and at the same time ensure a mechanical strength recovery [46, 47]. To reach to the better and efficient healing efficiency of this polymer a hardener material is also integrated into the polymer. The mechanism works closer to the microcapsule based self-healing approach. Here the encapsulated epoxy capsules will get ruptured upon a mechanical damage to the polymer matrix which will release the healing agent out to be in touch with the hardener. This will polymerise the uncured epoxy resin and the healing process occurs.

2.2.5 Solvent Aided Healing

Another approach towards the self-healing polymer technology aided with the help of encapsulated technologies is the self-healing polymers working by the entrapment of solvents. This approach is studied to be accomplished through various steps which includes surface reorganization, diffusion, surface advance, wetting and randomization [48]. These polymers were capable of exhibiting healing at room temperatures. The major drawback of this technology was evaluated to be its healing efficiency issues by showing poor retrieval of mechanical power.

The healing competence was highly depending on the solvent polarities and the aprotic solvents were performing well. This was attributed to the existence of more hydrogen bonding groups by the presence of hydroxide groups. The healing efficiencies were highly altered from 38% to 82% due to the variation in the selection of solvents and its polarity.

2.2.6 Microvasular Approach

After several trials on the hollow fibre and microcapsule based research on self-healing polymers, the research community around the globe was simultaneously exploring other systems that can mimic nature for repairing its damage. This lead towards the attention on self-healing based on micro vascular networks. The incapability of multiple healing on the same crack point was the major disadvantage for the hollow fibre and microcapsule approach. This problem occurs through the extra draining out of the healable components from the
polymer matrix. This issue can be rectified by engineering a controlled discharge of the healing agent from the polymer matrix. The flow should be controlled and at the same time continuous. Scientists always get inspiration from nature and here also it’s a similar story. The plants and animals have an in built sensing system towards damage on its any of the body part to trigger a healing process. This is capable due to the presence of an interconnected micro vascular network inside the body of the plant or animal. The design of a similar network with healing agent inside to use in a polymer matrix can be a smarter option to find solution for the aimed healing process.

This technology was basically inspired from the animal kingdom where blood remains clot-free in the veins of body network in a three dimensional fashion as a fluid. Any damage caused on the body will initiate the flow of blood to clot and heals the damage [49]. One recent study on this consideration which could gain attention amongst scientific community was by Toohey et al [50] who used the DCP healing agent and a catalyst system to perform the healing process by actively using these in a microvasular substrate where the channels are filled with DCP as shown in Figure 2.5. The healing efficiency achieved was around 70% and the recyclability of healing efficiency was up to seven times. But there was a clear indication to prove the dependency of the available catalyst in the layer to activate the healing process. If the catalyst present is used up, then the healing efficiency seems to have diminished even if there is an uninterrupted flow of healing agent.

There were similar approaches of microvasular networking in the polymers around the same period of the previous mentioned invention. Thus on a similar timeframe, on another study it was reported about the feasibility of another approach where a sandwich structure composite was designed which can show high mechanical stability. A three dimensional vascular network with their channels filled with healing agents was introduced into the sandwich structure which can allow the polymer to heal multiple times upon a damage. The healing mechanism will be similar to the conventional ones where the pre-mixed resin healing agent and hardener will be released upon a mechanical stimulus. But it
was also revealed that the efficiency of healing was only achieved by around 50% of the total samples.

![Image of a microvasular network, from inspiration to application: (a) graphic of the vasculature; (b) schematic showing microvasular substrate can aid self-healing process in composite structures; (c) coating on the material, and cracks propagation are shown; (d) healed material, having a surface with surplus healing agent [50].]](image)

**Figure 2.5** Microvasular network, from inspiration to application: (a) graphic of the vasculature; (b) schematic showing microvasular substrate can aid self-healing process in composite structures; (c) coating on the material, and cracks propagation are shown; (d) healed material, having a surface with surplus healing agent [50].

It was observed from the well healed samples that the mixing up of the components in the vascular system as a result of the impact helped in achieving a better efficiency. Also the improperly healed ones had a history of uneven mixing of healing agents due to an improper release of healing agent. There are a lot more studies going on till date based on mechanical stimuli responsive self-healing polymer systems.

### 2.3 Reversible Supramolecular Polymer Networks

The scientists around the world are historically known to be passionate about exploring the very details about the supramolecular interactions in polymers. For instance the hydrogen bonding interactions are widely studied in various approaches in the polymer chemistry. The spot-light significance of this hydrogen bonding networking is its natural reversibility. The researchers were always trying to avoid this significance for the better usability of the polymer material in high strength applications. However, in the world of self-healing materials, this characteristic was tried to be used in favour to employ multiple healing times in a self-healing polymer material [51, 52].
2.3.1 Hydrogen Bonding Networks for Self-Healing Polymers

The self-reversibility of hydrogen bonding systems and its directionality are the capabilities which were explored by Cordier et al. to bring the design and develop self-healing elastomer polymer systems which gathered considerable attention in scientific field [53-57]. Unlike the other self-healing polymer systems reported so far, not any catalyst or resins were used here but the healing process was triggered by bringing the cut surfaces together to facilitate a contact between each other. This contact will be enough for the polymer to initiate the healing process and recover its material properties to behave like a new material again. The elastic properties were designed for the polymers by the selection of amido imidazolidone and urea molecules. These molecules allowed the formation of supramolecular network which can exhibit a higher strain rate and elongations which are 500% and 300% respectively. Along with the fact that this self-healing polymer system does not use any chemical species, another astonishing advancement on this technique was its capability to heal its damages at room temperature. The contact hours that the cut surfaces were kept together seemed to have a higher relation with the healing efficiency, i.e. the higher the contact time the higher the recovered mechanical strength. The healing times were repeatedly tried to prove that this hydrogen bonding polymer system can be healed multiple times at room temperature.

2.3.2 Metal-Ligand Coordinated Self-Healing Polymers

In the concept of supramolecular interactions to help self-healing in polymers, the co-ordination chemistry between metals and ligand has been worked out for a successful research filed. This was a polymer system which consists of irreversible covalent bonds and some reversible hydrogen bonding interactions [57]. These multiple variety of interactive bonds will help towards the better stability and improved mechanical strength of the polymer matrix. This would enable the reversible bonds to reform its links upon breakage due to mechanical load. The chemical bond forming material was pyridine- methacrylates groups and networks present in the polymer which is a bi-functional compound of platinum and palladium. This kind of system which contains both types of bonds
will be a future field of investigation for the generation of self-healing materials which works on a mechanical stimulus.

2.3.3 Thermo Reversible Diels-Alder Polymers

The Diels-Alder (DA) system works in some contradiction towards the widely known self-healing systems. The self-healing is not relied just on any healing agent. Thus the possibilities towards this approach got a huge interest from researchers around the globe which is discussed here. The most widely studied polymer systems that use the reversibility of co-valent bonds are the Diels-Alder (DA) cycloaddition reactions. The versatile nature of hydrogen bonds is where they can show its natural reversible nature that is quite different from the co-valent bonds where the reversibility is less. Therefore it was appropriate to develop polymers that work on co-valent bond interactions but have the goodness of hydrogen bonding reversibility. The first of its kind was successfully tried to be the DA reactions. The researchers explained the formation of cyclohexane having new carbon-carbon bonds which are formed from conjugated dienes and dienophiles. This reaction is an important one across the people who are doing chemistry research because the main constituents responsible for the reaction can be changed to design polymers of specific characteristics. Another peculiarity of this reaction scheme is its response to the thermal energy where it can alter the final product behaviour and characteristics [58]. Thus the concept of thermal reversibility aided self-healing polymer systems were possible to be discovered in the light of DA reactions. This concept was later elaborated by studying the stereochemistry (cis and trans forms) or by varying the pedant groups to the polymer backbone so that the final polymer will behave differently to thermal stimuli. This gave new polymers including thermally responsive gels, elastomeric polymers; hydrogels etc. [2]. Another study by Chen et al [59] incorporated furan and maleimide species with the polymer to employ DA reaction.

2.3.4 Furan/Maleimide Polymer System

This system proposed by Chen et al comprises of two kinds of monomers and the reaction was proposed to be happening by the formation of a polymer network through co-valent bond interactions which are reversible in nature.
This makes it enable to be self-healing where the DA reactions occur when the crack occurs on the polymer matrix. This crack will exhibit the active functional groups to healing process and the properties of the undamaged materials are retrieved back after the mending process. The polymer studied here resembles to epoxy polymer materials in mechanical stability and thereby can be used in high performance applications. This polymer material was thermally healable at around a moderate temperature range which is between 120-150°C and the healing efficiency was given at around 57%. The healing process explains the total healing was not achievable because of the breakage of test specimens into two separate parts which is shown in Figure 2.6.

One of the major advantages shown by this reversible DA self-healing system is its healing capability given for repeated and multiple times which is practically useful as it can help significantly towards the total life time of the polymer. This invention could get considerable attention from the scientific world around. However, some of the drawbacks that this study always carried includes the melting point of the monomer, healing ability less than multiple times and use of solvents. These problems were addressed along with an improved mechanical strength on a later study by the same research group. Another major leap in the engineering design was implemented to keep the test specimen a single piece even after the breakage occurred. This was attained by drilling a hole on the polymer.

Figure 2.6  (A) Fracture toughness testing to validate healing efficiency. (B) Cracked specimen ready for thermal treatment. (C) Thermally treated specimen. (D) SEM image of the healed specimen. (E) Scale up picture of the boxed area in (D) [59].
surface which will end the crack propagation which will in turn gave a better healing efficiency of around 80%. Another advantage over the prior art was the efficiency to perform multiple healings on the same sample.

This modified system was also showing healing capabilities which were thermally aided at around the similar temperature range which is 120-150°C. These studies were later explored further to understand and optimise the temperature and time needed for the self-healing process to happen on the polymer matrix [60]. Thus the ideal temperature was discovered to be between 85-95°C for a time period of four minutes. Interestingly the healing efficiency was approaching 100% after several cycles of repeated breaking and healing process.

2.3.5 Self-Healing Through Embedded Particles

After quantifying the issues associated with the use of liquid healing agents in the self-healing systems there were a great deal of efforts towards the discovery alternate techniques and resources to employ self-healing in polymers. One prominent approach among them was the use of processing that involved the use of solid state particles that can perform best to its ability. The careful fabrication of the system itself was the major challenge in the design path of the previous systems. Overall in the previous systems, even after the careful fabrication the system have to withstand and survive any mechanical damages so that the used in liquid resin should not flow out and drained.

However, the concept of using solid particles work on the basis of the some inorganic particles which are used into the composite material while fabrication. The solid particles can be used directly into the composite material. These were used as coatings on metallic surface to protect them from corrosion. Initially there been computational studies in 2004 and later real time studies in 2007 were conducted on this concept where self-assembling nanoparticles were used which will act as a protective cover over the polymer surface [61, 62]. This concept works on the basis that nanoparticles and polymer matrix work in conjugation to act as a thin film on a damaged surface. The computational work demonstrated the automatic drive by the solid particles when the polymer surface was damaged to perform a localised healing process. The real time experimental works on this
direction involved the use of a resin which is a combination of a thermoplastic and thermosetting resin. On the breakage of the polymer matrix the resin will flow into crack to initiate a healing process. However this technology required a thermal stimulus for the healing to happen to call it a thermally aided healing. A recovery of about 70% was achieved using this mechanism. Again the healing efficiency and the thermal stimulus were highly related that the higher the thermal energy, higher the healing. A modification to this approach was tried by the same research team where a remarkable advantage was shown on its repeated healing efficiency which was tried over cycles during the experiment.

2.3.6 Electrical Stimulus Aided Self-Healing Polymers

A different initiate towards the design and development of self-healing polymers was the one which uses electrical impulse to employ a self-healing phenomenon in polymers. This technology is totally different on its approach beginning from its design. A thermally and electrically conductive material is embedded or incorporated in the polymer matrix while on fabrication. Later when a crack occurs on the polymer matrix, the electric stimulus is applied. This will naturally develop heat energy on the polymer body as the pathway for the travel of electrons is limited due to the crack. Thus the developed heat energy from the resistance suffered by the electrons will initiate the healing process at the damaged site which will later re-establish the mechanical and electrical properties of the polymer. This technology also enables the detection of micro cracks which are usually invisible to any human inspections to help the early action towards the healing process [63].

2.3.7 Carbon based healable polymer composites

Carbon fibre reinforced polymers are known to the material research and polymer research too. They are materials important to high performance applications including the aerospace industry. They can be good counter parts for the metal composites where the fiber reinforced composite offer good mechanical strength and light weight. Along with these advantages they can conduct electricity which is tuneable for specific applications like in the applications where fibres wanted to generate heat from within either through resistance or through dielectric hysteresis.
This technique was successfully acknowledged by Wang et al in 2007. He tried the mechanism on a healable polymer which contains a Diels-Alder based healing material and was tried in a composite that can produce heat intrinsically [64]. Thus it contributed to the discovery towards a carbon fiber reinforced polymer that can repair its damages at given electric stimuli and similar conditions. Around a year after this technique was reported Park et al [65] published the worked out possibility of a composite material that can self-heal with the aid of a resistive heating by electricity. These composites used polymers based on dicyclopentadiene systems that were used on an epoxy system. The healing action was performed quickly on testing condition in around a minute time at around 70-100 ºC. The healing efficiency was good that it left the damaged polymer with less uncured sites. Thus this system claimed it application towards aerospace industry as a carbon fiber reinforced polymer that can repair its damages with the aid of thermal energy produced by electrical impulses.

2.3.8 Self-Healing In Polymers through Shape Memory Alloys

Certain metals and its alloys were studied for their shape memory abilities while heated over prolonged time. Here an approach from this metallurgical research field is considered into the inter-disciplinary material science research to benefit the self-healing polymers. These metal alloys show shape memory behaviours when the phase change occurs from austenitic phase to a martensitic phase and are called shape memory alloys (SMA).

On a very interesting work by Kirby et al in 2008 [66] the SMA was used in a polymer matrix where it could successfully exhibit its self-healing capabilities through resistive heating. Kirby used Ni/Ti/Cu combination to make alloys that were embedded in an epoxy matrix having Grubbs catalyst already embedded in them. The study was performed after creating cracks on the polymer surface and injecting healing agents like dicyclopentadiene on a controlled level. Later the polymer matrix was heated to activate the SMA wires by heating them at 80ºC for about 30minutes. After heating the SMA wires were subject to contraction and lead to the closing of crack mouth. This lead to the decrease in the volume of healing agent to be used at the crack contributing towards a better healing efficiency as shown in Figure 2.7.
The healing effectiveness were benefitted at large by the use of SMA wires when compared against the study done by Kessler et al [33, 66] which was not using any SMA wires. This technique helped in better ways for improved adhesion and performance and thereby greater efficiency of around 77% compared to 44% obtained without using SMA wires. The maximum efficacy shown was up to 98% being the fact that the design and fabrication remains complex.

2.3.9 Electromagnetic Self-Healing Using Magnetic Particles

Electromagnetic induction can be induced to the polymer matric where magnetic particles are used while fabricating them. Heat energy was used to activate them which were produced by remote methods. The magnetic particle oscillates to produce heat energy and this heat energy produced is required to be dissipated. This technique was already reported to be used in biomedical applications to treat tumours [67]. The incorporation of a polymer matrix was considered to dissipate the energy. This concept was combined with shape memory polymer systems to develop a self-healing system by Schmidt [68]. The technique works on the basis that the embedded magnetic particles will generate heat energy on by the activation of electromagnetic field. This will later recovers the shape of the polymer through its shape memory properties.
2.3.10 Ballistic Self-Healing Ionomers

The ionic interactions are considered to be reversible chemical interactions in the field of chemistry. They are very capable of forming reversibly cross-linking interactions by ionic bonds. Thus the concept that the ionic interactions are possible candidates in polymers to help restore the ruptured bonds in polymer and thereby the mechanical strength and other properties. Increasing the ion content from the minimal 15% to any higher value had shown direct increase in the magnitude of overall properties of the polymer like its high impact toughness, high tensile strength and high fracture toughness [69, 70]. This was explained that as the ionic content increases, the chances of the ionic cluster formation is increased which will lead to better cross-link formation with in the polymer matrix.

A material of this kind over its puncture repairing ability was studied by Kalista et al. He studied the commercially available polymer containing different ratios of methacrylic acid for its healing efficiency after a puncture. The puncture was made using projectiles [71]. At given impact strength, the material seems to be more viscoelastic at a higher temperature of 90ºC. The formed puncture was sealed by the viscoelasticity and then the ionic cross-linkings can regain the mechanical properties of the material with no healing of polymer sample. But at room temperature, the projectile test left the polymer healed with a minor scar and with the puncture sealed proving its self-healing capability. This is been explained that the healing happens in two stages where the first one is a ‘snap-back’ of the polymer and second is an elastic recovery that helps the healing which is a material property through the intermolecular interactions and diffusion mechanism. Thus the inventors explain that the combination of ‘snap-back’ and right choice of molecular chemistry makes the material healing. On a chemistry point of view the inclusion of more acid groups were confirmed to be favouring the puncture healing on a large scale.

Later the influence of the “snap-back” mechanism and temperature were explored by Kalista and Ward [72]. The influence of heat was tested by conducting a test using a saw. The sawing action had imparted the dissipation of heat energy on the polymer cut surface due to friction leaving it in a molten state and healing soon
after its being cut. The requirement for high heat energy was confirmed by cutting
the polymer on a smooth way to produce less friction by employing a razor blade
where healing was not happening. Low temperature studies at -30°C were also
done to prove the outcome of using high temperature. Moreover snap-back
phenomenon described was also experimented using nails which were compelled
through pieces of polymer. No healing was observed on these samples proving the
effect of the high energy reversal happened after the projectile motion.

2.3.11 Photolytic Healing in Polymers

The covalent bond chemistry is applied to a new level over the cycloaddition
reactions. The initiator used in these reactions will be a perfectly custom made
light source i.e. photo-initiated reactions. When compared to chemically run
reactions, the photo initiated ones are cheap, simpler and are green techniques.

The cycloaddition reactions in polymer compounds are based on olefins forming
cyclobutadiene when exposed to light source. These cyclobutadienes can be
converted gain to their starting materials by the reversible reaction used by light
energy at optimum frequencies. The crack propagation recovery in polymers was
tried by Chung et al in 2004 using a photochemical treatment method. 136
Cinnamoyl groups were incorporated into the polymer system which transform to
cyclobutane dimers by cycloaddition reactions. The ring strain of dimers was
accounted for the healing characteristics of this polymer system. It was identified
using infrared spectroscopic techniques that The C=C bonds and carbonyl bonds
are responsible for the reformation of structure networks inside the polymer which
in turn will restore the mechanical assets of the polymer upon damage. The
healing efficiency reported for this system was 14% at its best upon a photolytic
healing which can be considered low while around 25% upon the combination of
thermal and photolytic methods. In 2011 Burnworth et al reported an optically
healable metalosupramolecular polymer which mend polymer using light. The
metal–ligand sites are electronically excited to produce heat. This will lead to the
disconnection of the metal–ligand bonds to affect the molecular mass and
viscosity to allow a healing process in the polymer [73, 74].
2.4. Polymer-Clay Nanocomposites

The clays are small crystalline particles of aluminosilicate which when made in various compositions result in different clays with distinguishable properties. From the basic structure the iron and magnesium can be substituted by alkalis and alkaline earth elements. The silicon-oxygen unit is a tetrahedron, and then four oxygen atoms surround the central silicon.

<table>
<thead>
<tr>
<th>Clay</th>
<th>Chemical formula</th>
<th>CEC (mequiv/100g)</th>
<th>Particle length (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite</td>
<td>(Na,Ca)0.33(Al,Mg)₂(Si₄O₁₀)(OH)₂·nH₂O</td>
<td>110</td>
<td>100-150</td>
</tr>
<tr>
<td>Hectorite</td>
<td>Na₀.₄Mg₂.₇Li₀.₃Si₄O₁₀(OH)₂</td>
<td>120</td>
<td>200-300</td>
</tr>
<tr>
<td>Saponite</td>
<td>Ca₀.₂₅(Mg,Fe)₃((Si,Al)₄O₁₀)(OH)₂·n(H₂O)</td>
<td>86.6</td>
<td>50-60</td>
</tr>
</tbody>
</table>

M – monovalent cation; x – degree of isomorphous substitution; CEC – cation exchange capacity.

Table 2.1 Chemical formulations and distinguishing parameters of commonly used 2:1 phyllosilicates [75].

Hexagonal rings are formed by tetrahedral and the pattern gets repeated until it forms a sheet. This happens again when Aluminium combines with oxygen to form an octahedron where Aluminium is at the centre to form a closely packed two-dimensional sheet. The clay structure can be basically divided into two which are kaolinite and pyrophyllite. The first one Kaolinite is 1:1 type of non-swelling dioctahedral clay. It is a sheet of alumina octahedral deskbound on top of a sheet of silica tetrahedral. The oxygen atoms of silica are pooled with the aluminium atoms of the top layer. The second type of clay is of the pyrophyllite (smectite) which is 2:1 type. The two parent materials are pyrophyllite and talc, with alumina and magnesia, respectively, in the central layer. Polymer clay nanocomposites used to get prepared in clays belong to the 2:1 layered structure type. The most commonly used layered silicates clays are Montmorillonite,
Hectorite, and Saponite. Table 2.1 gives the general detail of the chemical formula and characteristic factors of these phyllosilicates clays. Among them Montmorillonite is one of the most remarkably and extensively used for the provision of polymer nanocomposite synthesis.

2.4.1 Montmorillonite

The montmorillonite (MMT) clays come from the smectite family of clays. The structure of them comprises of layers one octahedral alumina sheet sandwiched between two tetrahedral silica sheets. Stacking up of the silicate layers traces towards a regular van der Waals gap among the layers. The aluminium ions present over the octahedral layers of montmorillonite are subjected to substitution by magnesium or other divalent ions. This substitution will reduce negative charges that are compensated by cations existing in in the interlayer. These MMT clays are very popular for its use as filler for reinforcing purpose in polymeric compounds. These clays composed of plates which will have thickness of about 1nm and cross dimensionally measure more than 30nm. These clays have high aspect ratio, high availability, cheap and are easy to functionalise for its various applications in polymer science [76-78]. As given in Figure 2.8, the octahedral layer is fused in between the two tetrahedral sheets which are held by week van der Waals bonds [79]. The magnesium ions can be substituted with Al$^{3+}$ and Fe$^{3+}$ which can then leave excess negative charge on the surface of the octahedral layer. So for to actively keep the layers of the clay together, the Na$^+$, Li$^+$, K$^+$, Ca$^+$ will balance across the negative charges.

2.4.2 Morphology of Polymer Nanocomposites

In a polymer nanocomposite there are basically three possible structural forms. This depends on the degree of polymerisation and the level into which the clay and polymer are penetrated into each other. A conventionally formed composite will have properties and structures similar to that of a micro composite where it will have an ordered and arranged structure for the clay platelets. When polymer chains are penetrated into the clay platelets to have an increased clay platelet distance and give multilayer morphology, they will be called as an intercalated structure. The only difference between an intercalated and exfoliated structure is in the arrangement of clay platelets where in exfoliated the clay platelets will be
delaminated from one another and are disseminated throughout the polymer matrix.

![Molecular scheme of montmorillonite clay](image)

**Figure 2.8** The molecular scheme of montmorillonite clay (top right). Different morphologies met in a polymer-layered silicate nanocomposites and the schematic sketch of three achievable forms of polymer nanocomposites [80].

It is illustrated in Figure 2.8 the simple possible morphologies and changes occur when a polymer MMT system is formed. Mostly the polymer nanocomposites will be formed out of the combination of intercalated and exfoliated structures.

### 2.4.3 Commercial Montmorillonite Clays

The use of pristine and modified montmorillonite clays in the field of polymer technology to improve the polymer-clay interaction is well known these days. A wide range of research has also been done on the modification of the clay surfaces of MMT clays [81-83]. The commonly used and widely available forms of the commercial MMT are the sodium salt (Cloisite Na+) of MMT, Cloisite 30B and Cloisite 25A [83-89]. They are readily available from Southern Clay Products Inc. Cloisite Na+ is a natural sodium montmorillonite clay containing no organic modifier. Cloisite 25A is organically modified clay which is improved with dimethyl, dehydrogenated tallow, 2-ethylexyl quaternary ammonium salt (2MHTL8). Cloisite 30B is an organically modified clay which is improved with methyl, tallow, bis-2- hydroxyethyl, quaternary ammonium salt (MT2EtOH). The surfactants in the surface modified clays are generally believed to have catalytic effects where the effect towards the catalytic contribution is expecting to be a weak for the Cloisite clays. Also the surfactants are believed to contribute towards
the hydroxyl initiation reaction of OH groups [90-94]. Thus the choices of nanoclays are very important in the design of nanocomposites as they largely affect the morphology of polymer nanocomposites. The selection of surfactants of the organoclay also influences the polymerisation reactions as reported by Tolle and Anderson [95]. The surfactants that exfoliate slowly are capable for network formation [85]. The characteristic behaviour of MMT nanoclays surfactants will obviously influence the nanoclays dispersion to get corresponding nanocomposites structures. Moreover, the processing methodology will also affect the nanocomposites morphology. Because of these reasons a few of nanoclays are selected to be used in this study to discuss in detail and compare different morphologies.

2.4.4 Polymer Montmorillonite Clay Nanocomposites

The term 'nanocomposite' was first introduced during 1980's by Komarneni. The definition referred to composites including more than one solid phase (amorphous, crystalline or semicrystalline) and filler of at least one dimension in the nano size range [96]. Having used this term for more than thirty years, now the term is widely recognised as the combination of a nano sized filler ranging between 1- 100 nm (spherical, platelet or tubular) in a polymeric matrix. These nanoparticles in polymer matrix have the ability to give it large surface areas and improved properties that are different from pure polymer matrixes.

2.4.5 Structure-Property Relationship of Polymer/MMT Nanocomposites

More than thirty years before Toyota [97, 98] revealed a polymer clay nanocomposites system with improved mechanical properties through an exfoliated structure obtained in Nylon6/MMT (4.2wt %) nanocomposites. Only a few quantity (usually measured in weight %) of silicate is consistently disseminated in the polymer medium. During moulding, the nanocomposites exhibit loftier characteristics and properties when compared to pristine material. Apparently due to the contribution towards the overall material properties of polymers the research interest in the same field is getting enhanced considerably which reflects in the number of research articles coming out, reaching several hundred in few years [99]. Other enhancements reported through exfoliated polymer/MMT nanocomposites structures include thermal stability and solvent
uptake [100], optical clearness [101], flame retardancy [102] and also the gas and liquid barrier properties [103-106].

2.4.6 Processing of Clay Nanocomposites

Mixing together of the different matrixes is an essential tool for propagating clay dispersion. The processing of the mixing up a polymer matrix and nanoclays to form new polymer nanocomposites having new functionalised surfaces and improved properties have a great role in defining the ultimate morphology in polymer nanocomposites.

2.4.6.1 Preparation Routes

The preparation of polymer/clay nanocomposites can be accomplished through three different routes; melt intercalation, solution blending and in-situ polymerisation.

2.4.6.1.1 Melt Intercalation

In this process the thermoplastic polymer and nanoclay are combined and will be annealed at the polymer's softening point. Either intercalated or exfoliated nanocomposites can be formed when clay galleries get diffused by the polymer chains. This is known to be as an environmentally benign process due to the fact that no organic solvents are used for this process [78, 107, 108]. Further polymer processing techniques such as extrusion and injection moulding can be successfully engaged on these polymers [109, 110]. Various conventional polymers such as polystyrene, nylon [107-114], and polypropylene [107, 108] have been produced through the melt intercalation process. This technique was employed in this study which is discussed in the following chapters.

2.4.6.1.2 Solution Blending

The technique of solution blending is associated with the addition of a polar solvent such as water or chloroform [78] to solvate clay platelets. The principle is that the used solvents will break down the weak van der Waals forces that exist between platelets and will enable better clay dispersion. An example is use of acetone solvent to employ clay dispersion during mixing to give its good compatibility, low boiling point and relatively low toxicity [115, 116]. However it is considered that traces of acetone can lead to an incompletely cured polymer
nanocomposite, paying to the decreased mechanical properties [117]. It is also considered that the use of solvents can make porosity in the polymer material to adversely affect the life of polymer [118].

2.4.6.1.3 In-Situ Polymerisation

In-situ polymerisation is a technique that can be used in the preparation of both thermoplastics and thermosets [119]. The platelets of clay materials are swollen by liquid monomers (or monomers) to diffuse polymer chains into clay platelet galleries. The incorporation of a curing agent or in some cases heat/radiation, initiates polymerisation. It was the in-situ polymerisation method invented by Toyota lead to the formation of Nylon 6/MMT nanocomposites [86, 97, 98, 111]. This invention opened way to research on other thermoplastic systems such as polystyrene [120] and polypropylene [93, 121], and thermoset epoxies [122-124]. In-situ polymerisation is a main mixing method employed to form polymer-clay nanocomposites and will therefore be employed in this study.

2.4.6.2 Mechanical Processing Techniques

Various additional forms of processing (mechanical) instigated to support in the dispersion of MMT clay platelets include, shear mixing, ultrasonic vibration and mechanical mixing [125-127].

2.4.6.2.1 Shear Mixing

This method includes high shear mixing [128], extrusion and roll milling [129]. This technique has got the benefit of reduced resin viscosity in polymer/clay nanocomposites polymer. This reduced resin viscosity enables chain diffusion into gallery spacing and increases the clay dispersion. However, it is proved that shear forces applied on the clay platelets can prompt the clay platelet damage, giving a reduction in the aspect ratio of the clay and this high shear forces can also lead to re-agglomeration [130]. Moreover, these heavy shear forces can lead to the degradation of MMT surfactant of the nanocomposites by breaking the carbon-carbon bonds rather than delaminating the clay platelets [131, 132] contributing to the depletion in its overall properties.
2.4.6.2.2 Ultrasonic Vibration

Ultrasonic vibration is broadly used as a technique to disperse clay in polymer matrix to form polymer nanocomposites [128]. This technique is otherwise known as sonication. It is a destructive technique by applying high intensity ultrasound waves under a liquid polymer medium. A high control over the sonication process is required as it is highly dependent on few factors like ultrasonic frequency, power and mixing time. Cavitation effect is created using sound waves to make varying pressure cycles that can break down clay agglomerates to get better dispersion into polymer. High and precise control is required over the heat energy used, as a localised heat that could form within the polymer/MMT mixture will lead to self-polymerisation in thermoset resins which is not ideal [133, 134].

2.4.6.2.3 Mechanical Mixing

The mechanical mixing consists of a low shear stirring mechanism for example hand mixing or via a magnetic stirrer. The dispersion in a polymer in clay platelets through this process is said to be highly reliant on the design of impeller, the speed of mixing and temperature used for synthesis. The infrastructural requirements and thereby the cost required [135, 136] to set up this mechanical mixing system was low and thereby it widely used in the preparation polymer-clay nanocomposites and therefore used in this study.

2.4.7 Nanocomposite Characterisation Techniques

There is a shortage of dependability and steadiness in the known and practised characterisation techniques to explain the nanocomposite formation and degree of clay dispersion in the polymer matrix. Transition electron microscopy (TEM) and X-ray diffraction (XRD) analysis has delivered scientists with acceptable level of evidences to understand and clarify the structure of polymer/MMT nanocomposites [137, 138]. Moreover, confirmatory characterisation experiments have been explored using techniques such as Optical microscopy, Scanning electron microscopy (SEM), Small angle X-ray diffraction (SAXS) and nuclear magnetic resonance (NMR) techniques to understand the formation of polymer nanocomposite and also in analysing the clay dispersion and distribution in the polymer matrix.
Scanning electron microscopic (SEM) techniques are currently being used to investigate clay distribution. SEM is used to estimate the polymer nanocomposites topography on a micro scale which can be well down to the resolution of 1nm. It is highly important to have adequate evidence from this technique to pronounce a nanocomposite structure as exfoliated with confidence. The level of intercalation of nano clays into the polymer material can be determined by the XRD spectrum. It is commonly between 2° (2θ) and 10° (2θ) the characteristic crystallographic peaks for the clay can be observed. These peaks can also give information about the clay structure present in the polymer nanocomposites. The shape, position and intensity studies are needed to be done for these evaluations. An intercalated/flocculated clay structure will give two peaks in an XRD as given in Figure 2.9.

![Figure 2.9](image)

**Figure 2.9** (a) WAXD patterns and (b) TEM pictures of three types of polymer nanocomposites [75].

Also an exfoliated structure where the polymer chains entered into clay galleries to get a disordered orientation is implied when there is a reduction in intensity or absence of a basal reflection [76]. As discussed earlier a multiplicity of structures are possible and are obtained when a MMT clay is incorporated in a polymer matrix to form a polymer/MMT nanocomposites as displayed in Figure 2.9. TEM data can be used to support the XRD results. The TEM studies will reveal the internal structure of the sample where individual platelets can be closely observed to study the interface between the polymer and clay platelets. Mostly XRD and TEM are used together to characterise the nanocomposite polymer materials.
However, discretely the data from these techniques can be conflicting with each other to create unreliable circumstances and for the very same reason it is highly important to use other characterisation tools for the purpose of cross checking and confirming the distribution and alignment of nanoclays platelets in the polymer nanocomposite. We have used SAXS data to resolve this problem. Thus here in our study for the characterisation of polymer/MMT nanocomposites, the surface morphology was established through SEM and exfoliation of film was established through XRD and SAXS. These are the key techniques hired by material scientists to analyse polymer/MMT nanocomposites [77, 129].

FTIR spectroscopy is another powerful characterisation tool to study nanocomposite structures. The positions of peaks for distinctive functional groups that are affected by presence of MMT nanoclays are studied here. Also the formation of characteristic infrared bands for different functional groups involved in the polymer formation and its changes will give key evidences. In order to confirm the assumption that the interface between the polymer and nanoclay makes the formation of polymer/MMT nanocomposite, the condition of polymer and nanoclays can be studied using FTIR spectroscopy. Evidences of different clay loading conditions and reaction conditions can be generated using FTIR spectroscopy.

Solid state NMR spectroscopy is used here in characterising the polymer/MMT nanocomposite morphology. Generally speaking solid state NMR spectroscopy is largely used as a conventional and proven tool to identify and distinguish the chemical molecules and its structures. Only a few studies are done by applying NMR as a tool to analyse polymer/MMT nanocomposites [139-141]. Those studies successfully used the technique to understand the level that the nanoclays platelet gets dispersed in the nanocomposite and also they suggested a theoretical relationship between the clay dispersion and relaxation times. Here in this study we mainly used solid state NMR spectroscopy to identify the chemical species and its interactions.

Thus all these techniques (SEM, XRD, SAXS, NMR, FTIR and optical microscopy) are required here to be functioning together here to study the polymer/MMT nanocomposites and factors affecting their formation.
2.5. Summary

From the above discussion, it is evident that the factors governing the formation of self-healing polymer materials and polymer nanocomposites are many such as physical and thermo physical properties of starting materials, synthesis approaches, temperature, pressure, other thermo physical parameters and operating conditions. Self-healing polymers have already shown great applications in many functional areas. Even though the widespread research that has been done in this area, there are numerous significant concerns still remain unclear, especially in the area of forming a nanocomposite polymer that can be self-healing by employing hydrogen bonding interactions. A large portion of the published literature on polymer clay nanocomposites accents on the synthesis and characterisation of polymer nanocomposites. Thus the preparation of polymer-clay nanocomposites remains a well-studied area in literature. It is now essential to perform research issues on novel applications, scale-up, and industrial processing of nanocomposites, including control of morphology, and specific performance.

The research in the field of supramolecular polymers that can self-heal its damages is quite far-reaching and is interesting. New research methodologies and research paths are being explored every now and then. The optimistic research in the field of hydrogen bonding chemistry is being discussed in the following chapters that start with the synthesis path ways and then extending to characterisation, experimenting and validating the healing efficiency. We believe that a remarkable contribution towards the field of polymer nanocomposite will be accomplished by fulfilling this work.
CHAPTER THREE

3 MATERIALS AND METHODOLOGY

In this chapter, all materials used in this research work are listed. Experimental procedures and characterisation techniques are also described in detail.

3.1 Materials

The polyacid monomers consisting of sebacic acid, maleic acid, fumaric acid, malonic acid, glutaric acid, pimelic acid, azelaic acid polyethylene glycol diacid, and isophthalic acid. The polyamine monomer used was mainly diethylenetriamine. The crosslinking agents used was urea. The details with chemical structure are given in Table 3.1. These chemicals were obtained from Sigma Aldrich Co., whereas the montmorillonite clays cloisite25A, cloisite30B and CloisiteNa⁺ were obtained from Southern clay products, Inc. All the chemicals were used as received. All these were used without further purification.

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Chemical / molecular formula/ structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malonic acid</td>
<td>CH₂(COOH)₂</td>
</tr>
<tr>
<td>C₃H₄O₄</td>
<td></td>
</tr>
<tr>
<td>Glutaric acid</td>
<td>HOOC(CH₂)₃COOH</td>
</tr>
<tr>
<td>C₅H₈O₄</td>
<td></td>
</tr>
<tr>
<td>Pimelic acid</td>
<td>HO₂C(CH₂)₇CO₂H</td>
</tr>
<tr>
<td>C₇H₁₂O₄</td>
<td></td>
</tr>
<tr>
<td>Azelaic acid</td>
<td>HO₂C(CH₂)₉CO₂H</td>
</tr>
</tbody>
</table>

43
<table>
<thead>
<tr>
<th>Chemical</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sebacic acid</td>
<td>HO₂C(CH₂)₆CO₂H</td>
</tr>
<tr>
<td>C₁₀H₁₈O₄</td>
<td></td>
</tr>
<tr>
<td>Isophthalic acid</td>
<td>C₆H₄-1,3-(CO₂H)₂</td>
</tr>
<tr>
<td>Dimer acid, hydrogenated</td>
<td>Dimerised fatty acids</td>
</tr>
<tr>
<td>Dimer acid, hydrogenated</td>
<td></td>
</tr>
<tr>
<td>PEG-600 diacid</td>
<td>HOOCC₂(OCH₂CH₂)ₙOCH₂COOH</td>
</tr>
<tr>
<td>Diethylenetriamine</td>
<td>(NH₂CH₂CH₂)₂NH</td>
</tr>
<tr>
<td>D-Sorbitol</td>
<td>C₆H₁₄O₆</td>
</tr>
<tr>
<td>Urea</td>
<td>NH₂CONH₂</td>
</tr>
<tr>
<td>Butadiene - dicarboxy</td>
<td>HO₂C(CH₂CH=CHCH₂)ₙCO₂H</td>
</tr>
<tr>
<td>terminated</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1 The used chemicals and its details
3.2 Preparation of Supramolecular Polymer

It is known from the extensively studied methodologies for the synthesis of polymer-clay nanocomposites, either the in-situ polymerization or the melt mixing techniques of the monomer and nanofillers seems to be efficient in accomplishing desired morphology such as exfoliation or intercalation of the clay platelets into the matrix of the polymer. All percentages used herein are percentages based on weight by weight (% w/w), unless otherwise indicated. The resultant macromolecule is condensation polymer, where the macromolecule are formed when compatible reactive functional groups present in one or more monomers react to join together via molecular interactions and liberate a small molecule, such as water. The cross-linked matrix of the nanocomposite may include any type of macromolecule containing suitable functional groups. Synthetic macromolecules may be formed using a number of different techniques, including free radical, ionic, ring opening, allyl addition or condensation polymerisation techniques. Here in this thesis we describe synthetically prepared macromolecules that can be obtained from the polymerisation of a single monomer, or from two or more co-monomers.

3.2.1 General Procedure for the Preparation of Polymer Nanocomposites

The supramolecular polymers described in this thesis are prepared using a one pot, two-step procedure in the absence of added solvent and under an inert atmosphere at controlled temperature. The reaction was conducted in a three neck round bottom flask with the provision for mechanical stirring. To a stirred solution of polyamine monomer under a nitrogen atmosphere maintained under reflux, a polyacid monomer was added in a slow fashion over a period of 30 minutes. The mixture was turbid at room temperature and was heated to 100-120°C under nitrogen flow. It was then heated for 1 hour under same gas flow and temperature which turned to a viscous solution. The resulting condensation product was a macromolecule polymer, known as a pre-polymer. To the hot mixture of pre-polymer, crosslinking agent and selected nanofiller of choice was then added. As the reaction mixture is stirred, it is observed that gaseous ammonia is given off (verified with pH paper), accompanied by foaming of the reaction medium. When the ammonia being given off decreases, the reaction
mixture was then heated to 165°C by 5°C increments every 60 minutes maintaining the same gas flow. Once the whole content of the reactor had raised, the reaction mixture becomes difficult to stir and the stirring was stopped. The resulting viscoelastic material was then cooled to 100°C and quickly collected while it is still hot and elastic. Once the material cooled to room temperature, it was then placed in a vacuum oven at 70 °C (vacuum of 5 mmHg) in order to remove any remaining ammonia. The resulting polymer nanocomposite material obtained is hydraulically pressed, at 70 ºC, in the form of plates that are 1 to 3 mm thick. The polymers formed are usually pale yellow or orange in colour, at room temperature and at elevated temperatures. The resulting product was characterized to identify it as nanocomposites and as SMP if montmorillonite clay is not used. The samples were then characterised using the techniques described later in this chapter.

### 3.2.1.1 Example: Pristine Layered Silicate Nanocomposite

The pristine layered silicate was used in this example and it was Cloisite Na⁺. Nanocomposites containing layered silicate montmorillonite were formed by mixing 10.3 g (50.9 mmol) of sebacic acid and 8.99 g (87 mmol) of diethylenetriamine in a 100 ml round bottom flask. The flask was fitted with a condenser and flushed with nitrogen gas to sustain an inert atmosphere. The contents were magnetically stirred at 120 °C (oil bath) for 4 hours. The mixture was then cooled to 90 °C. To the reaction mixture 4.9 g (81.5 mmol) of urea and 0.95 g Cloisite Na⁺ was added.

The forming of reaction mixture along with evolution of ammonia was observed at 140°C. The temperature was increased to 175°C at a slow increment rate of 5°C per hour after the ammonia evolution has dropped down significantly. The reaction mixture was left at 175°C for 12 hours for the completion of reaction. When there was no phase separation in the reaction mixture the following procedure was used for getting the nanocomposite formed. The reaction mixture was transferred to a sheet of Teflon while hot at room temperature. The material obtained was hot pressed at 70°C for 5 minutes to form sheets of 3 mm thickness. This polymer named SMPNa⁺ is studied for its material characteristics in chapter 6 of this thesis.
3.3 Details of Steps in the Synthesis

The details of synthesis steps and methods adapted are described here under this heading. The process involves two main reaction steps which are in sequence. The sequence is described as given in the following two steps.

3.3.1 Step 1: Formation of Pre-Polymer

The supramolecular material was synthesized in two steps. The goal of the first step is to produce an assembly of linear and branched oligomers bearing hydrogen bonding capable functional groups at all its extremities which we called pre-polymers. This was realized by reacting Polyacid monomer with polyamine monomer. This reaction is highly influenced by temperature. This reaction possibly involves sequential steps which proceed as the temperature is raised. The relative reactivity of the primary and secondary amino groups of polyamine monomers depends on the thermal reaction conditions and concentration of reactants. The products and intermediates vary, depending on the reaction conditions used. The details of this reaction are discussed in the coming chapters of this thesis.

3.3.2 Step 2: Formation of Supramolecular Polymer Nanocomposite

The ability of polymers to form well-distinct nanostructures has been exploited in the group of nanocomposites by combining the pre-polymer with other nanoparticles. In the present study, in order to improve the mechanical properties of the self-healing polymer to make it practically more important we have used pristine montmorillonite clays and its organic modified versions with quaternary ammonium salts which are very cheap and abundantly available.

The mixture of pre-polymer with urea and montmorillonite nanoclay was heated under a nitrogen flow and then the temperature was raised in a controlled fashion for the completion of reaction. At that stage the reaction mixture becomes viscoelastic and starts to rise up in the reaction vessel. This step is supposed to have transformed all the possible functional groups into supramolecular polymer moieties capable of forming hydrogen bonds. Once the whole content of the reactor had risen in the reaction vessel, the stirring was stopped and the viscous material was quickly removed from the reaction vessel while it was still hot. Then
films were formed out using hydraulic press. The prepared films will have the physical and chemical characteristics of conventional polymer materials when tested at room temperature. However, when these polymers were tested in the presence of hydrogen bond breaking solvents or at elevated temperatures they exhibited the physical and chemical characteristics of low molecular weight materials. The system did not crystallize and there was no macroscopic phase separation. The final product will be checked for its solubility on conventional solvents. The initial finding was based on the fact that it will remain insoluble in almost all other organic solvents.

3.4 Characterisations Techniques Used

Various characterisation techniques are used in this study to understand the different characteristics of reactants and products.

3.4.1 Scanning Electron Microscopy (SEM)

The nanoclays and polymers were observed with scanning electron microscopy (Leica S440). The samples were coated with platinum for 60 seconds. The imaging was conducted at a voltage between 15 kV at working distance of 6-10mm. The average images were taken determined on at least 100 nanometre measurements. SEM EDX was performed on a JOEL JSM7500FA cold field emission gun microscope.

3.4.2 Optical Microscopy

Optical microscopy was used to analyse the morphology and self-healing capability of these nanocomposite polymers using a Nikon TS100 optical microscope. The polymer was spread as thin films on the glass slides and dried in a vacuum oven.

3.4.3 Mechanical Testing

For the mechanical property studies, tensile properties of the nanocomposite were measured on a Lloyd LR 30 K testing machine. The tests were conducted on specimens which were technically made according to ASTM standard D 638-03. The tests were conducted at room temperature. At least five specimens were tested to obtain the average values of tensile properties for the entire
nanocomposites and its healed samples. All error bars used in this report are one standard deviation on either side of the mean.

Differential mechanical analysis was carried out on a dynamic mechanical thermal analyser (DMTA) on a TA Q800 machine with a TA universal analysis 2000 v4.5A software at compression mode. The test was a stress-strain experiment at room temperature. The frequency used was 1.0 Hz and the force ramp rate was 0.01N/sec. The round specimen dimensions were 3.5mm×15mm. The relaxation modulus, displacement were measured on the application of static load from 0.001 to 18 N. Circular disk shaped sample specimens were used. The glass transition temperature was observed to be at the peak maximum of tan δ curve.

3.4.4 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) experiments were carried out using a TA Q200 differential scanning calorimeter instrument. The measurement was performed using 5–10 mg of the sample under an atmosphere of nitrogen atmosphere. The samples were first heated to 170 ºC and held at that temperature for 3 min to remove the thermal history. Subsequently, the samples were cooled to -50 ºC at the rate of 10 ºC per minute, held for 5 min and again heated to 170 ºC at 20 ºC per minute. The glass transition temperature \(T_g\) was taken as the midpoint of the second heating scan of the plot in the DSC thermograms. The accuracy term of ±1 ºC is used throughout the thesis where ever glass transition values are given unless stated otherwise.

3.4.5 Fourier Transform Infrared Spectroscopy (FTIR)

The Fourier transform infrared attenuated total reflection spectroscopy (FTIR-ATR) of all the samples was measured on a Bruker Vetex-70 FTIR spectrometer. The spectra were recorded at the average of 32 scans in the standard wave number range of 400–4000 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\).

3.4.6 X-ray Diffraction (XRD)

X-ray diffraction measurements were carried out on a Philips PW1140/90 X-ray diffractometer with Cu K\(\alpha\) radiation target at 25 mA and 40 kV; scan rate of 1 deg/min; step size of 0.02 degree; 20 scan range from 2 to 80. D-spacing values
are calculated using Bragg’s law \( n\lambda = 2dsin\theta \), where \( \lambda \) is the wavelength of 1.54nm, and \( \theta \) is the angle measured. 001 and 002 peaks are analysed by software analysis. An accuracy term of ±0.00001 nm is used throughout the thesis where ever d spacing values are given unless stated otherwise.

3.4.7 Small Angle X-ray Scattering (SAXS)

SAXS measurements were performed at the Australian Synchrotron on the small/wide angle X-ray scattering beam-line using an undulator foundation that permitted capacity at a very high flux. A minimum q limit (0.012 nm\(^{-1}\)) was used to obtain a good flux through moderate scattering angles. The intensity profiles were understood by plotting scattering intensity (I) versus scattering vector, \( q = (4/\lambda) \sin (\theta/2) \) where \( \theta \) is the scattering angle).

3.4.8 Nuclear Magnetic Resonance Spectroscopy (NMR)

\(^1\)H and \(^{13}\)C NMR spectra were collected on a Jeol Eclipse JNM-EX400 MHz spectrometer. Samples were dissolved in CD\(_3\)OD. Proton signals reported as chemical shift \( \sigma \) (ppm). The carbon signals were recorded as chemical shift \( \sigma \) (ppm).

3.4.9 Thermo Gravimetric Analysis (TGA)

The Thermo gravimetric analysis (TGA) measurements were carrying out to determine the thermal stability of the samples using a NETZSCH STA 409 PC/PG instrument. Initially, the sample was heated under Argon atmosphere up to 900 °C for nanoclays and 600 °C for polymers. The heating rate was 10 °C /min. For each sample, three tests were carried out under the same heating rate and the temperatures were reproducible. Experiments were conducted in an inert atmosphere under Nitrogen gas at a flow rate of 30 ml/minute.
4 EFFECT OF PROCESSING CONDITIONS AND MOLECULAR STRUCTURES ON THE FORMATION OF SUPRAMOLECULAR POLYMERS

4.1 Introduction

The engineering of supramolecular polymeric materials is now extensively recognized as a new branch of polymer technology. The versatility of the material properties given by supramolecular polymers has given them much attention[142]. The tuneable and reversible molecular interactions of these materials are responsible for their fascinating properties. A small change in the reaction temperature range or even a slight change in the monomer structure will contribute to the generation of new material properties to these materials. The molecules controlled by supramolecular interactions are basically governed by the interaction between the monomers responsible for this formation. Their properties are often highly responsive towards the influence of reaction medium solvent, heat, light, presence of catalyst, molecular structure, chemical reaction parameters etc. This property makes the materials capable of design friendly towards special requirements of temperature and other physical properties. This efficiency of the supramolecular polymer makes them capable of being used in an extensive range of real-world applications. The huge and ever-growing area of supramolecular polymer discusses different kinds of molecular interactions generally focused on non-covalent bonding chemistry including hydrogen bonding[143, 144] nucleobase stacking[145], metal–ligand interactions [146, 147], and hydrophobic effects[148].

The vast majority of studies on molecular interactions which are noncovalent in nature are generally carried out on hydrogen bonding or ionic interactions. The design and development of hydrogen bonding chemistry to work on supramolecular polymers have attracted a significant deal of attention from research community over the earlier few years [54, 149-153]. Thus there have
been a number of studies done over the past decades to develop new supramolecular polymers with tailored physical and chemical properties. Numerous research publications on supramolecular polymers detailing hydrogen bonding chemistry[154] and its interactions have been reported previously[52, 155].

However, there noted a gap in the literature to discuss the factors such as molecular structure of monomers and processing conditions used for the polymer synthesis that governs the formation of supramolecular polymers which are interacted mainly using hydrogen bonds. In this chapter, various hydrogen bonding systems are evaluated on the basis of the molecular structure of the monomers, reacting components and synthesis methodology. Also the synthesis parameters to obtain an ideal supramolecular polymer system are also studied here. A carboxylic acid and amine based system is considered for the study and supramolecular polymers were formed out of various combinations. Various synthesis approaches, different molecular structures, behaviour and characteristics of formed hydrogen bonds are mainly studied here.

4.2 Hydrogen Bonding in Polymers

The cross-linked matrix of the nanocomposite discussed in this study is a polymer matrix which is formed from a macromolecule and a crosslinking agent. In forming the matrix, macromolecule chains interact with a crosslinking agent to form a three-dimensional polymer network. In the cross-linked matrix of the nanocomposites, the macromolecule interacts with the crosslinking agent by non-covalent bonding interactions. The crosslinking agent extends between chains of the macromolecule to provide intermolecular links between the chains. These three-dimensional polymer networks may be considered a supramolecular network that is held together by non-covalent bonds. Accordingly, the cross-linked matrix is predominately held together by non-covalent bonds. It is desirable that the noncovalent bonds between the macromolecule and the crosslinking agent be hydrogen bonds. However, it is contemplated that other types of non-covalent bonding interactions, such as electrostatic or ionic bonding interactions, may occur in addition to, or instead of, hydrogen bonds.
The macromolecule used in the cross-linked matrix of the self-healing nanocomposite includes a multitude of organic functional groups. The macromolecule includes at least two functional groups and may include three, four or more, functional groups. The number of functional groups in the macromolecule may depend on the type of monomer used to prepare the macromolecule, as well as macromolecule’s molecular structure. The functional groups may be included in the backbone structure of the macromolecule, or they may be pendant functional groups attached to the backbone. The functional groups enable the macromolecule to interact with the crosslinking agent by non-covalent bonding interactions. These non-covalent bond interactions between the macromolecule and the crosslinking agent form hydrogen bonds where they are formed between the macromolecule and the crosslinking agent, it is desirable for the macromolecule to include hydrogen donating functional groups, hydrogen accepting functional groups, or a mixture of such groups. The functional groups containing a hydrogen atom bonded to an electronegative atom (such as nitrogen or oxygen) can act as hydrogen bond donors, while functional groups containing an atom with a lone pair of electrons can act as hydrogen bond acceptors. Direct interactions between the donor group and acceptor group of chemical functional groups results in the formation of hydrogen bonds.

Thus the functional groups for macromolecules need to be carefully selected from the group of halogen, oxygen, and nitrogen containing functional groups. This chapter discusses the functional groups of the macromolecules consisting of hydroxyl, amine, and carbonyl containing functional groups. The functional groups of the macromolecule may each be of the same type of functional group, or alternatively, they may be a mixture of different types of functional group. The functional groups of the macromolecule that contain carbonyl functional groups includes the moiety C=O. It is believed that the C=O moiety of carbonyl containing functional groups can act as hydrogen bond acceptors for the development of hydrogen bonds, as the oxygen atom of the carbonyl group contains a lone pair of electrons.
4.3 Polymerisation of Monomers

The macromolecules that are formed when compatible reactive functional groups present in one or more monomers react to join together via a covalent bond and liberate a small molecule, such as water. Such macromolecule can be called as condensation polymers. For instance in this study, the carboxylic acid functional groups can react with amine functional groups to make amide functional groups, with the loss of water. Other compatible reactive functional groups such as hydroxyl, carboxylic acid, carboxylic acid halide, ester, anhydride, amine and amide functional groups, which are contained in monomers capable of participating in condensation reactions, are capable of producing condensation polymers. The macromolecule includes at least one condensation polymer of polyamides and polyesters. The polyamides include a multiplicity of amide functional groups, while polyesters include a plurality of ester functional groups. The macromolecule may be prepared from the polymerisation of a single type of monomer, or from the polymerisation of two or more co-monomers.

When a single monomer is used to form the condensation polymer, typically two or more compatible reactive functional groups are confined in the same monomer unit. The compatible reactive functional groups in the monomer are usually of different types; however they are capable of reacting with one another under condensation polymerisation reaction conditions to produce the desired condensation polymer. Examples of a monomer containing two different types of reactive functional group include hydroxy-acids, which contain a carboxylic acid and a hydroxyl functional group, and amino acids, which contain functional groups such as carboxylic acid and amines. When two or more co-monomers are used to form the condensation polymer, one co-monomer unit can contain one type of reactive functional group, while another co-monomer unit contains an altered type of reactive functional group. The reactive functional groups of each of the co-monomers are compatible with one another and are able to react together under conditions of condensation polymerisation. Generally, each monomer unit includes two or more reactive functional groups. This enables to conclude at the point that at least two reactive functional groups are required in each monomer unit to enable the co-monomers to link together in the macromolecule chain.
4.3.1 Structure of Macromolecule

In forming macromolecules by condensation polymerisation, the nature of the reactive functional group in each monomer unit is important to the polymerisation reaction. The structure of the remaining portion of the monomer unit however is less critical. As a result, this attributes and contemplates to the fact that a variety of different moieties may be present in the remainder of each monomer unit.

As discussed earlier the macromolecule in the cross-linked matrix is formed from the condensation polymerisation of a monomer including at least two compatible reactive functional groups. A macromolecule in accordance with this study may have a monomer unit having a structure of Formula (I) as given in Figure 4.1 below:

\[ \text{A} \quad \text{R}^1 \quad \text{X} \quad \text{m} \]

Where
X is selected from the group consisting of O and N;
A is selected from the group consisting of O and NHR, where R is H or Alkyl;
R1 represents the monomer unit; and
m represents the number of repeating units for the monomer and is at least 2.

Figure 4.1  Formula (I)

It is to be summarised that in another case, the macromolecule in the cross-linked matrix is formed from the condensation polymerisation of at least two co-monomers. In this project, each co-monomer includes at least two reactive functional groups that are compatible with the reactive functional groups of the other co-monomer.

Each co-monomer provides a repeating monomer unit in the resulting macromolecule. A macromolecule described here may have a repeating unit having a structure of Formula (II) as given in the Figure 4.2 below:
Where
X at each occurrence is independently selected from the group consisting of O and N;
A at each occurrence is independently selected from the group consisting of O and NR, where R is H or alkyl;
R1 represents the first monomer unit;
R2 represents the second monomer unit;
m represents the number of repeating units for the first monomer and is at least 1;
and n represents the number of repeating units for the second monomer and is at least 1.

Figure 4.2 Formula (II)

From the $^1H$ NMR spectroscopy given in Figure 4.3 it is evident that the newly synthesised macromolecules were formed with a repeating unit having a structure of Formula (I) or Formula (II) may be polyesters or polyamides.

Figure 4.3 $^1H$ NMR plot showing the formation of condensation polymer by reacting a carboxylic acid and an amine.
It is therefore concluded that to be desirable for at least one of the groups R1 and R2 in a repeating unit of Formula (I) or (II) to include a moiety having at least 4 carbon atoms. The use of monomers containing at least 4 carbon atoms to prepare the macromolecule can desirably enable better physical properties to be imparted to the macromolecule initially, and later to the nanocomposites as well. For example, bulk physical properties such as physical state (i.e. liquid to solid state) of the nanocomposite, and thereby the hardness, density, tensile strength and young’s modulus-like properties of the nanocomposite may be influenced by the nature of the monomer used to prepare the macromolecule used in the cross-linked matrix of the nanocomposite.

Also it is discovered to be desirable for at least one of the groups R1 and R2 to include a moiety having at least one unsaturation. Nanocomposites formed with a macromolecule including at least one unsaturation in the polymer chain display different mechanical properties.

4.3.2 Molecular Interactions of Functional Groups

The macromolecule is derived from a comonomer containing two or more carboxylic acid functional groups, i.e. a polyacid monomer and a co-monomer containing two or more amine functional groups, i.e. a polyamine monomer. Here, the carboxylic acid containing comonomer is capable of reacting with the amine containing co-monomer to form an oligomer, with an amide linkage between the monomer units of the oligomer. The oligomer, which now has a terminal carboxylic acid group and a terminal amine group, may subsequently react with further monomer units bearing an amine or carboxylic acid group so as to form one or more further amide linkages (amide functional groups) in the polymer backbone and extend the length of the macromolecule chain.

Mixtures of two or more of the above polyacid monomers and/or two or more of the above polyamine monomers may be used to prepare macromolecules suitable for inclusion in a nanocomposite described here. The use of mixtures of monomers may allow the properties of the macromolecule and resulting nanocomposite language to be tailored for particular applications. For example, it has been found that a macromolecule formed by reacting a polyamine monomer
with a mixture of Glutaric acid and Pimelic acid exhibits elastic properties. Thus, a nanocomposite formed with such a macromolecule may exhibit shape memory properties as well as self-healing properties. For the scope of this study, a macromolecule is formed from the polymerisation of a dicarboxylic acid monomer and a diamine or a triamine monomer.

To provide the cross-linked matrix of the nanocomposite described, the functional groups of the macromolecule interact with functional groups present in a crosslinking agent by non-covalent bonding interactions. The bonding interactions result in the formation of a cross-linked matrix that is predominantly held together by intermolecular non-covalent bonds between the crosslinking agent and at two chains of the macromolecule. The intermolecular non-covalent bonding interaction is reversible. Accordingly, reversible crosslinks are formed between the macromolecule and crosslinking agent. It is one advantage that upon disruption of the non-covalent bonding interactions, the reversible crosslinks between the macromolecule and crosslinking agent are able to readily re-form under appropriate conditions.

4.3.3 Molecular Interactions of Cross-Linking Agent

In order to interact with the macromolecule, the crosslinking agent includes functional groups which are capable of participating in non-covalent bonding interactions. Accordingly, the crosslinking agent ideally should include functional groups that are capable of participating in non-covalent bonding interactions with the functional groups of the macromolecule. Desirably, the functional groups of the crosslinking are terminal functional groups as such groups would be more readily available for interaction with the macromolecule.

The non-covalent bonding interaction between the crosslinking agent and the functional groups of the macromolecule forms hydrogen bonds. Where hydrogen bonds are formed, it is desirable for the crosslinking agent to include hydrogen donating functional groups, hydrogen accepting functional groups, or a mixture of such groups. The features of functional group that is present in the crosslinking agent may be dictated by the features of functional group present in the macromolecule. For example, where the macromolecule includes hydrogen bond
acceptor groups, it would be desirable for the crosslinking agent to include hydrogen bond donating groups to ensure that a hydrogen bond can then be formed between the crosslinking agent and the macromolecule. Conversely, where the macromolecule includes hydrogen bond donor groups, the crosslinking agent may include hydrogen bond accepting groups.

The functional groups contained in the crosslinking agent can be a halogen, oxygen, or nitrogen containing functional groups for the effective supramolecular interactions. The functional groups of the crosslinking agent may be independently hydroxyl, amine, and carbonyl containing functional groups. The functional groups of the crosslinking agent may each be of the same type of functional group, or alternatively, they may be a mixture of different types of functional group. The functional groups of the crosslinking agent consisted of amine and amide functional groups. Amine and amide functional groups can contain the moiety $-\text{NHR}$. The moiety $-\text{NHR}$ is capable of acting as a hydrogen bond donor in the formation of hydrogen bonds, as it contains a hydrogen atom bonded to an electronegative nitrogen atom.

The cross-linked matrix of the nanocomposite include any type of crosslinking agent, provided the crosslinking agent contains suitable functional groups that are capable of participating in non-covalent bonding interacting with the functional groups of the macromolecule. The cross-linked matrix includes one type of crosslinking agent or in an alternative case; the cross-linked matrix includes a mixture of two or more different types of crosslinking agents. The cross-linked matrix of the nanocomposite of the may include at least one diamide crosslinking agent. Diamide crosslinking agents include two $-\text{NHR}$ functional groups, which are each capable of interacting with the functional groups of the macromolecule. Examples of diamide crosslinking agents include urea, 1,3-dimethylurea, 1,1-diethyl urea etc. Mixtures of diamide crosslinking agents may be present in the cross-linked matrix. In the nanocomposite, the macromolecule and the crosslinking agent are held together in mutual association in the cross-linked matrix by hydrogen bonds. An example of a hydrogen bonded cross-linked matrix that is formed with a polyamide macromolecule and urea crosslinking agent is shown in Figure 4.4.
The association between the macromolecule and the crosslinking agent results in the formation of reversible crosslinks in the matrix. The number of crosslinks and crosslink density can be varied to obtain a matrix and nanocomposite of desired characteristics.

![Chemical Structure](image)

*Figure 4.4* The synthetic strategy for generation of supramolecular hydrogen bonding cross links formed between the pre-polymer and urea. The dotted lines represent the hydrogen bonds connecting the pre-polymer chains and urea to form the networking of the hydrogen bonded polymer.

A variation in the number or density of crosslinks may be achieved by varying the concentration and/or type of crosslinking agent used to prepare the cross-linked matrix.

### 4.3.4 Molecular Interactions of Nanofillers

On a major step for improving the material properties of the hydrogen bonded polymer, nanofiller were selected as candidates that can be get incorporated into the polymer. When the nanofiller include a plurality of nanoparticles, the type of nanoparticles necessary for a nanocomposite can differ conditional to the nature of the polymer matrix. Nanoparticles can help to impart desirable physical, mechanical and thermal properties to the nanocomposite [75, 156-159]. The nanofiller can be either carbon nanotubes or montmorillonite clays. Among new generation of nanofiller is the carbon nanotubes (CNTs), which exist as single walled or multi-walled. We preferred to use some multi walled carbon nanotubes as these structures are known for their application in nanomedicine. They have economical and safe properties that can be used in gene and drug delivery[79].
As another candidate of nanofillers, the nanoclay particles were used for the preparation of the nanocomposite as either pristine montmorillonite clay or organically-modified montmorillonite clay. The nanoclay capable of cation exchange is montmorillonite, such as Na+ montmorillonite. Such nanoclays can provide nanocomposites with cation exchange capacity, which may be useful in some biomedical applications. Organically-modified clays are clays modified with one or more functional groups. Organically-modified clays may be clays modified with hydroxyl (-OH) groups, which can enhance the hydrogen bonding capacity of the supramolecular polymer. The organically-modified clays are clays modified with one or more organic cations. In another case, the organically-modified clays are clays modified with one or more alkoxylated ammonium compounds. Alkoxylated ammonium compounds may include 2 to 10 carbon atoms. Also the nanofiller have layered silicate structure which have a as part of their molecular structure have (SiO4)n4-repeating units. Layered silicates may contain separate platelet units that are closely arranged and kept together. It is assumed that upon being dispersed through the cross-linked matrix material, the layered silicate particles that exfoliate or delaminate to deliver minor aggregates in the matrix material.

4.4 Development of Synthesis Methodology

A through literature study and reading gave light towards the synthesis of a supramolecular polymer composition from carboxylic acid and amine combinations. The candidates for the reaction were selected according to the chemical structure and reaction hypothesis[119].

4.4.1 Dependence of the Molecular Structure on Polymer Morphology

The initial consideration was on the selection of monomers that have hydrogen bonding capable functional groups along the carbon chain. Thus the first reaction started with roughly weighed quantities of monomers by adding dimer acid which is also known as "dimerised fatty acids" is not one specific molecule, it will not have a discrete molecular formula or structure. In general, these are dicarboxylic acids, but sigma Aldrich do not provide for specific components of this material and thus cannot state the actual concentrations of specific monomers (8-10 gram) to DETA (2-3 ml) in a 100 ml beaker. Slowly a gel like material was formed with
evolution of a stinking smell. Then urea was added and later the reaction mixture was kept in oil bath at 40°C. Colour less highly viscous and sticky material was obtained as produced from this reaction trial which is shown in Figure 4.5.

On a second approach towards macromolecular formation, butadiene dicarboxy terminated was used along with the previous reaction mixture to provide better opportunities for more molecular interactions. But the resultant material properties were not as expected. On another exercise, molecular combinations involving alcohol functional groups were realised by using D-Sorbitol which also was not giving any desired products. These experiments brought to the conclusion towards the necessity for optimising the reaction conditions and stoichiometry. Isophthalic acid and PEG-600 diacid were other candidates used in the experimentation but did not form desired products. Thus a series of reactions were conducted keeping a proper material balance. This process ended up with optimised reaction conditions which are given in Table 4.1.

While carrying out the process of the synthesis, a macromolecule including a range of functional groups, a crosslinking agent including a variety of functional groups, and a nanofiller in a reaction vessel; forming non-covalent bonds between the functional groups of the macromolecule and crosslinking agent in the presence of the nanofiller to provide a nanocomposite including a cross-linked matrix and a nanofiller dispersed in the matrix. Prior to its interaction with the crosslinking agent, the macromolecule may be regarded as pre-polymer, which is useful for the formation of the cross-linked matrix of the supramolecular polymer.

![Figure 4.5](image_url)  
*Figure 4.5*  (a) Physical form of polymer formed by reacting dimer acid with amine and urea. (b) & (c) the polymer is a sticky visco-elastic material.
However, following the interaction of the macromolecule with the crosslinking agent, a polymer host matrix is then generated. In the process, a macromolecule is formed in the reaction vessel. The process included the step of reacting a single monomer having two or more compatible reactive functional groups in the reaction vessel under conditions allowing condensation of the two or more reactive functional groups to form the macromolecule in the reaction vessel. Also the step of reacting two or more co-monomers (e.g. a first monomer and a second monomer) having compatible reactive functional groups in the reaction vessel under conditions allowing condensation of the two or more monomers to form the macromolecule within the same reaction vessel. The molecular chain length influences the polymer morphology. Carboxylic acid with carbon chain length less than 5 such as Glutaric acid will give viscous polymer which will flow indicating that they will fail to exhibit any structural characteristics. Introduction of aromatic rings, dienes (butadiene - dicarboxy terminated) cannot help cross linking.

The reaction conditions required for condensation polymerisation of appropriate monomers to form the macromolecule was optimised through the approach of trial and error. Such condensation polymerisation conditions may be dictated by the nature of the monomers used to form the macromolecule. With polycondensation reactions it is possible to some extent to control the molecular weight of the resulting macromolecule, its degree of branching (through control of monomer functionality) and its end group functionality by adjustment of the molar ratios and the functionality of the monomers used in the reaction[160]. Where the macromolecule was be prepared by mixing a polyacid monomer and a polyamine monomer together with heating and continued stirring, a condensate such as water may be liberated from the reaction between the polyacid and the polyamine and if desired, the condensate may be removed from the reaction mixture using techniques such as distillation. To promote further reaction to produce a higher molecular weight macromolecule the temperature may be increased and vacuum applied.

While carrying out the process of the synthesis, the macromolecule and the crosslinking agent are then treated under conditions allowing the formation of
non-covalent bonds. The process includes the step of heating the reaction vessel containing the macromolecule, crosslinking agent and nanofiller. A polyamide macromolecule is formed by reacting a polyacid monomer with a polyaniline monomer at a temperature range varying from about 100°C to about 120°C for a time period in the range of from about 1 to 2 hours. Further, after the addition of crosslinking agent and nanofiller, the reaction vessel may be heated for a sufficient time to form the supramolecular polymer which needs to be optimised. Usually the reaction vessel is heated for a period in the range of from about 12 to 17 hours to form the nanocomposite.

4.4.2 Dependence of the Type of Nanofiller on Polymer Morphology

Our step of preparing a supramolecular nanocomposite include synthesising the macromolecule in the reaction vessel, then adding a crosslinking agent to the vessel after the desired macromolecule has been synthesised. In order to provide the formation of cross linking through hydrogen bonding a crosslinking agent in the reaction vessel, the process of the may include the step of adding a crosslinking agent to the reaction vessel. An excess of crosslinking agent, relative to the amount of macromolecule, is added to the reaction vessel. An excess of crosslinking agent may be used to ensure that the cross-linked matrix is formed. The amount of crosslinking agent employed in the formation of the polymer matrix was optimised to be at least 25%, which is relative to the weight of macromolecule pre-polymer.

The process of finding the optimum level of nanoclay to be used to get the ambient properties that fit with the primary focus of this study was done. It was evidenced that the nanofiller may be present in an ideal nanocomposite in an amount in the range of from about 1% to about 10% by weight of the nanocomposite. Higher concentrations of nanofiller may provide a more brittle nanocomposite than if a lower concentration of nanofiller is used. However, lower concentration of nanoclays will also remain a bad initiative as it could not bring any desired properties to the final product such as firmness. The optimised process includes the step of adding nanofiller to the reaction vessel. Suitable nanoparticles that may be used in the process are nanoclay particles. The nanoclay particles may be derived from pristine clays or organically-modified clays or
carbon nanotubes. The nanoclay particles are montmorillonite particles. In the present study we use very thin platelets of clay that are dispersed in the cross-linked matrix material. To disperse the nanofiller throughout the cross-linked matrix it may be desirable to disperse the nanofiller in a composition including a macromolecule and a crosslinking agent, then treat the resulting nanofiller containing mixture under conditions allowing formation of non-covalent bonds between the macromolecule and the crosslinking agent. The nanofiller may be added to the reaction vessel at approximately the same time as the crosslinking agent. An amount of nanofiller in the range of from about 3% to about 5% by weight by be added to the reaction vessel which is relative to the weight of macromolecule pre-polymer.

On another experiment smaller CNTs were used to see the effect of nanofiller size on the formation of nanocomposite. The possibility of synthesising supramolecular polymer nanocomposite containing carbon nanotubes as nanofiller was firstly explored. The aim was to obtain structure that can be an intercalated structure, an exfoliated structure, or a flocculated structure. The formations of these nanocomposites were analysed using techniques such as SAXS. Two different types of carbon nanotubes were used such as single walled carbon nanotubes and multi-walled carbon nanotubes. The SAXS data given by both Figure 4.6 and Figure 4.7 reveals that incorporation of carbon nanotubes into the supramolecular polymer does not gave the formation of a nanocomposite. Thus a careful selection of another type of nanofiller is required to produce polymer nanocomposite of desired properties.
Figure 4.6  *SAXS plot showing the inclusion of multi-walled carbon nanotubes to polymer*

Figure 4.6 and Figure 4.7 shows that the obtained morphology such as exfoliation or intercalation does not have any influence while using carbon nanotubes.

The peaks incorporated CNTs in the polymer neither shift its position nor disappeared indicating that CNTs are not intercalated or exfoliated in the polymer.
The nature of the physical and chemical interfaces between the nanoclay particles and the cross-linked matrix can influence the structure of the nanocomposite and consequently, the mechanical properties of the nanocomposite. Following the general procedure and optimised conditions described above, a series of polymer nanocomposites were prepared using the components detailed in Table 3.1 of previous chapter to understand the influence of carbon chain length on the overall properties of polymer nanocomposites. Moreover a range of nanofillers were also used to combine with the polymers to make nanocomposites. Different types of pristine and organically modified montmorillonite nanoclays were used as nanofillers. This is discussed in the next chapter of this thesis. A comparative polymer matrix without nanofiller (SMP) was also prepared for comparative experiments. The desire of the functional groups of the macromolecule and the crosslinking agent to associate by intermolecular hydrogen bonds can provide the driving force for the formation of the nanocomposites.

4.5 Optimisation of Synthesis/Process Methods

The process of the synthesis includes the optimisation of the heating step of the reaction vessel containing the macromolecule, crosslinking agent and nanofiller. The reaction mixture may be heated at a temperature in the range from room temperature to a maximum about 200°C for the completion of reaction. The mixture may also be stirred to disperse the nanofiller in the mixture at the optimised temperature range of each step for a time period of about 12 hours. The completion of reaction was verified using NMR technique as given in Figure 4.8. The characteristic peak positions for the molecular entities for the reaction after 5 minutes are as follows. $^1$H NMR (400MHz, CD$_3$OD)δ (ppm): 1.31(4H,s); 1.58(2H,s); 2.1(2H,m); 2.7-2.8 (NHCH$_2$CH$_2$NH$_2$,m); 3.3-3.5(C(O)NHCH$_2$CH$_2$NH,m). The molecular ineractions have made significant changes after a reaction time of about 12 hours. A large number of new peaks at corresponding positions for 2.7-2.8 (NHCH$_2$CH$_2$NH$_2$m); 3.3-3.5(C(O)NHCH$_2$CH$_2$NH,m) are attributed to the formation of new molecules and new molecular cross links and this further evidences the reactions with carbonyl and amine functional groups.

When the mixture of macromolecule, crosslinking agent and nanofiller is heated at elevated temperature, any excess crosslinking agent may be present would be
decomposed and removed. An exemplary crosslinking agent is a diamide crosslinking agent, such as urea. When is used as the crosslinking agent, excess urea may be decomposed to ammonia and isocyanic acid. The decomposition products may then be removed from the mixture[161, 162]. In another aspect of the synthesis and process for the preparation of the supramolecular polymers includes the association of molecular moieties by hydrogen bonding. This process was optimised to be having requirement of providing a mixture including a first monomer including at least two reactive functional groups, a second monomer including at least two reactive functional groups that are compatible with the reactive functional groups of the first monomer. On another requirement a crosslinking agent and nanofiller including functional groups must be present.

![Figure 4.8](image)

**Figure 4.8**  NMR spectra showing the completion of reaction. After 12 hours new molecular moieties are clearly demonstrating the formation of supramolecular polymer.

These reacting candidates can be mixed and reacted in a single reaction vessel; reacting the first monomer and the second monomer under conditions of condensation polymerisation to form a macromolecule; and forming non-covalent bonds between the functional groups of the macromolecule and the functional groups of the crosslinking agent in the presence of the nanofiller to provide a supramolecular polymer including a cross-linked matrix and nanofiller dispersed in the matrix. In such cases, the supramolecular polymer having lot of hydrogen bonding moieties may be formed in situ, in a single step process, in the single
reaction vessel. Supramolecular polymers produced via a single step procedure involving the in situ synthesis of a macromolecule in the presence of the crosslinking agent and nanofiller may exhibit different physical, thermal and mechanical properties when compared to the supramolecular polymer produced in a two-step method with a pre-formed macromolecule. It is has been found that nanocomposites formed from the in situ polymerisation of monomers in the presence of a crosslinking agent and nanofiller can be more viscous than nanocomposites produced using a preformed macromolecule that is subsequently cross-linked in the presence of nanofiller. An exemplary incarnation of the process of the synthesis that utilise the reactants and reaction conditions are detailed in Table 4.1.

<table>
<thead>
<tr>
<th>Amount of Carboxylic acid</th>
<th>50 mmol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of Amine</td>
<td>80 mmol</td>
</tr>
<tr>
<td>Amount of Urea</td>
<td>25 % of pre-polymer</td>
</tr>
<tr>
<td>Amount of nanofiller</td>
<td>3-5 % of pre-polymer</td>
</tr>
<tr>
<td>Reaction time for the formation of pre-polymer</td>
<td>3-5 hours</td>
</tr>
<tr>
<td>Reaction time for the formation of supramolecular polymer</td>
<td>8-12 hours</td>
</tr>
<tr>
<td>Reaction temperature for the formation of pre-polymer</td>
<td>100-120 °C</td>
</tr>
<tr>
<td>Reaction time for the formation of supramolecular polymer</td>
<td>140-180 °C</td>
</tr>
</tbody>
</table>

*Table 4.1*  Optimised reactants and reaction conditions
While processes of the synthesis may employ a solvent, it is desirable that processes described herein be free of added solvent. Accordingly, the supramolecular polymer can be formed without the use of a solvent. However, processes of the synthesis may be carried out using the optimised condition given in Table 4.1, the presence of a relatively small amount of water or alcohol, which may be generated as a by-product of a condensation reaction used to prepare the macromolecule.

4.5.1 Solvent-Free Two-Step One-Pot Synthesis of Nanocomposite

Thus after optimising the reaction conditions the reaction was conducted in a three neck round bottom flask with a provision for mechanical stirring. To a stirring solution of amine (80 mmol) under a nitrogen atmosphere maintained under reflux, dicarboxylic acid was added (50 mmol) in a slow fashion over a period of 30 minutes. The mixture was turbid at room temperature and was heated to 100-120°C under nitrogen flow. It was then heated for 2 hour under same gas flow and temperature which turned to a yellow coloured viscous solution. The resulting product was called as a pre-polymer. To the hot mixture of pre-polymer, solid urea (which is 25% of pre-polymer) and the nanofiller (which are about 3% of pre-polymer) were then added and temperature was increased. It was observed that gaseous ammonia was given off (verified with PH paper), accompanied by foaming of the reaction medium as given in Figure 4.9.

When ammonia being given off decreases, it was then heated to 165°C by 5°C increments every 60 minutes maintaining the same gas flow. Once the whole content of the reactor had raised the reaction mixture becomes difficult to stir and then string was stopped. The visco-elastic material was then cooled to 100°C which was quickly collected out while it is still hot and elastic. Once cooled to room temperature, it was then placed in a vacuum oven for 48 hours at 70°C. (Vacuum of 5 mmHg) in order to evacuate the ammonia. This step is considered to have more significance en the synthesis methodology. The polymers formed are usually orange or yellow in colour, at room temperature and elevated temperatures. The resulting product was characterized to identify it as supramolecular polymer nanocomposite and as supramolecular polymer (SMP) if montmorillonite clay is not used.
Figure 4.9  Photos of the polymer synthesis (a), reaction when started by mixing carboxylic acid and amine in an oil bath at room temperature (b), when reaction was at 100-120 °C, the acid and amine are reacted to form homogenous mixture with good stirring was possible (c), when reaction was at 145-160 °C when the entire content had risen in the reaction vessel, the stirring was stopped and the viscous polymer material was formed (d), final product hydraulically pressed and shaped into rectangular slab form.

4.5.2 Solvent-Free In-situ One-Pot Synthesis of Nanocomposite

To a stirring solution of amine (80 mmol) under a nitrogen atmosphere maintained under reflux, dicarboxylic acid was added (50 mmol), solid urea (which is 25% of pre-polymer, calculated value) and the nanofiller (which is about 3% of pre-polymer, calculated value) in a slow fashion over a period of 30 minutes. The mixture was turbid at room temperature and was heated to 165 °C by 5 °C increments every 60 minutes under nitrogen flow. It was then heated for 12 hours under same gas flow and temperature which turned to a yellow coloured viscous solution. It was observed that gaseous ammonia was given off at around 140-145 °C (verified with pH paper), accompanied by foaming of the reaction medium. When ammonia being given off decreases, it was then heated to 165 °C maintaining the same gas flow. Once the whole content of the reactor had raised the reaction mixture becomes difficult to stir and then stirring was stopped. The visco-elastic material was then cooled to 100 °C which was quickly collected out while it is still hot and elastic. Once cooled to room temperature, it was then placed in a vacuum oven for 48 hours week at 70 °C (vacuum of 5 mmHg) in order to evacuate the ammonia. This step is considered to have more significance on the synthesis methodology.
4.6 Importance of Optimising Processing Parameters

It is observed that the glass transition temperature of the polymer samples which are treated in vacuum have improved significantly.

4.6.1 Vacuum Treatment and Glass Transition Temperature

The increase in the glass transition temperature with vacuum treatment is evaluated for two types of polymer nanocomposites. As given in Figure 4.10 the vacuum treatment have improved the glass transition temperature of Glutaric acid based nanocomposite by 7°C. To confirm this concept another set of nanocomposites with a higher carbon chain length such as Pimelic acid based nanocomposites was prepared and vacuum treated to check its thermal behaviour. It is observed that the glass transition temperature was increased by 16°C as shown in Figure 4.11. This bigger difference is attributed to the effect of longer carbon chain and this factor is considered for discussion in the next chapter of this thesis. The improvement with vacuum treatment can probably be explained by the enhanced stability of lower molecular weight compounds.

![Figure 4.10](compare DSC results obtained for the Glutaric acid based nanocomposites to explain the effect of vacuum treatment on the Tg.)
This trial and error based method used in the present work describes a facile method for the formation of a supramolecular polymer that can associate together using hydrogen bonds through an in-situ process in a single reaction pot. We optimised the process steps via two approaches. The first one was a single-step procedure, involving the in situ polymerisation of appropriate monomers in the presence of a crosslinking agent and nanofiller to produce the supramolecular polymer in a single step. In another approach, the process of the synthesis is a two-step procedure, which involves formation of a macromolecule in a first step, then crosslinking of the pre-formed macromolecule in the presence of nanofiller in a subsequent step, to produce the supramolecular polymer. The pre-formed macromolecule may be optionally isolated during the two-step procedure.

4.6.2 Polymerisation Technique and Glass Transition Temperature

The optimisation of process methodology was based on the primary objective of the project to develop a strategy that can improve the thermal stability of polymers. It is observed from the Figure 4.12 that the glass transition temperature varies with the difference in the difference in process steps.

\[ \text{Figure 4.11 compares DSC results obtained for the Pimelic acid based pre-polymer SMP to explain the effect of vacuum treatment on the Tg.} \]
The two-step approach seems to have improved contribution towards the higher glass transition temperature of the polymers. This contributes towards the possibility of tuning the polymer properties with the help of processing aids. The difference in the glass transition temperature is around 7°C higher for the polymer which is made through a two-step synthesis method compared to the other which was made through an in-situ process technique. It is an advantage of the process that the supramolecular polymer can be prepared in a relatively simple method that employs fewer steps than other methods described in the literature [53, 149, 163]. As a result, the process described here may be more commercially feasible than other methods for producing supramolecular polymer materials that uses hydrogen bonds for its association.

4.6.3 Effect of Polymerisation Technique on the Polymer Morphology

Figure 4.13 describes the XRD study performed to understand the morphology of the synthesised polymer. The process was carried out in two different ways and the effect of processing is considered to be an important factor that determines the type of polymer morphology formed.
Figure 4.13 compares XRD results of montmorillonite nanoclay, and its nanocomposites obtained through the single-step process, and two-step process. Here the figure 4.13 compares the diffraction peaks of montmorillonite nanoclay with its corresponding nanocomposites which were produced through two different techniques. In both single step and two-step process, the peaks are shifted towards the higher diffraction angle. The broad characteristic peak of nanoclay has been disappeared in the nanocomposites while showing small peaks towards a higher diffraction angle which are indicated by coloured arrows in Figure 4.13. This is attributed to the fact that a better case of exfoliation or intercalation is shown by both cases. However, the two step process gives a sharp peak indicating chances of more intercalated morphology.

Figure 4.14  SEM images and EDX analysis evidences the amorphous nature of the supramolecular polymer formed.
One advantage of the supramolecular polymer is that its properties can be tuned to suit particular applications. For example, the nanocomposite may be a mouldable nanocomposite, or it may be a brittle nanocomposite. Adjustments in the physical properties of the nanocomposite may be obtained by varying the type and concentration of nanofiller in the nanocomposite, as well as by varying the nature of the macromolecule and crosslinking agent used in the cross-linked matrix of the nanocomposite. The cross linked polymer matrix will have an amorphous surface as given in SEM images of Figure 4.14. The supramolecular polymer can be formed in the form of a liquid, such as a viscous liquid. If required some of the supramolecular polymers can be converted to a liquid when heated at an elevated temperature. For example, the polymer will flow like a liquid at a temperature range of 160-180°C. This may be useful where it is desired to prepare products by moulding techniques such as injection moulding. The fluidity of the material makes it promising to control the rate of this process and also to replicate the details of the mould. Also the polymer can be made in the form of a solid.

4.7 Conclusions

This chapter investigated on the optimisation of process methodology for the synthesis of supramolecular polymers and elucidated a structure-property relationship for the formation for polymer nanocomposites. The expertise control over synthetic organic chemistry rules are understood to be very important. Systematic experimentation has revealed that the right selection of starting materials including the carboxylic acids, amines, nanoclays and crosslinking agents can prepare polymers having unique properties.

The molecular study found that the macromolecule is derived from a comonomer containing two or more carboxylic acid functional groups (a polyacid monomer) and a co-monomer containing two or more amine functional groups (a polyamine monomer). The macromolecule in the cross-linked matrix is formed from the condensation polymerisation of a monomer including at least two compatible reactive functional groups. It is therefore concluded that the use of monomers containing at least 4 carbon atoms to prepare the macromolecule can desirably enable better physical properties to be imparted to the macromolecule initially,
and later to the nanocomposites as well. Also it is discovered to be desirable for use of molecular groups having at least one unsaturation. Nanocomposites formed with a macromolecule including at least one unsaturation in the polymer chain may display different mechanical strength properties. The selection of monomer unit was based on the criteria of having at least two or more reactive functional groups. This enables to conclude at the point that at least two reactive functional groups are required in each monomer unit to enable the co-monomers to link together in the macromolecule chain.

The minimum carbon chain length of dicarboxylic acid is 5 (Glutaric acid) to require to form polymers having the characteristics of nanocomposites. Less than five carbon atoms will give viscous polymer which can flow. Introduction of aromatic rings (Phthalic acid), dienes (butadiene - dicarboxy terminated) cannot help cross linking. So they will give low mechanical strength polymer. It was observed that the elastic property of the polymer loses after C7 (Pimelic acid). It is determined for the selection of cross-linked matrix of the nanocomposite that it should include at least one diamide crosslinking agent. Diamide crosslinking agents include two -NHR functional groups, which are each capable of interacting with the functional groups of the macromolecule. A variation in the number or density of crosslinks may be achieved by varying the concentration and/or type of crosslinking agent used to prepare the cross-linked matrix. On another requirement for the effective formation of supramolecular polymer nanocomposite, nanofiller must be present and the presence of the nanofiller can provide a supramolecular polymer. The best step of preparing a supramolecular nanocomposite include synthesising the macromolecule in the reaction vessel, then adding a crosslinking agent to the reaction vessel after the desired macromolecule has been synthesised in a two-step process, in the single reaction vessel. Nanoclays that are dispersed in polymer matrix can radically donate to various properties of nanocomposites such as mechanical strength, thermal and chemical stability etc. Addition of nanoclays along with urea gives better nanocomposite than adding them all together at the beginning.

Without wanting to be restricted by theory, it is assumed that hydrogen bonds can promote the supramolecular interactions and thereby better capability of the nanocomposite to exhibit other superior properties. As a result, the process
described a method for producing supramolecular polymer materials that uses hydrogen bonds for its association. This concept is discussed in the next chapter by systematically studying the relations between molecular structure of monomers and other reactants. Furthermore, the effect of nanoclay interactions and type of modifiers used in the clay to the property of nanocomposite are elucidated. We have used various techniques such as FTIR-ATR, SEM, DMA, NMR, DSC and TGA to study these molecular bonding interactions in detail.
CHAPTER FIVE

5 THE EFFECT OF NANOCLAY AND ITS MODIFIERS ON THE FORMATION OF SUPRAMOLECULAR POLYMERS

5.1 Introduction

Chapter four demonstrated that the selection of monomer having molecular structure capable of hydrogen bonding can enhance the dispersion of nanofiller in a viscous polymer. The polymer nanocomposite includes nanofiller dispersed in the matrix. The term “nanofiller” refers to a material with at least one dimension in the nanometre scale. Desirably, the nanofiller can be compatible with, and is capable of being substantially homogeneously dispersed in the cross-linked matrix of the macromolecule. Accordingly, it is desirable that little or no phase separation of the nanofiller from the macromolecule matrix be observed. The type of nanofiller and its properties may influence the properties of the resulting nanocomposite. Nanoparticles are particles of a material that have a size measured on the nanometre scale. Nanoparticles may have a size of from about 1 nm up to about 1000 nm [164, 165].

Any type of nanofiller conventionally employed in the preparation of nanocomposites may be used. Some specific examples of nanofiller that may be used to in the formation of nanocomposite described in this thesis include the following Nanofibers, such as carbon nanofibers or ceramic nanofibers. Graphitic nanofiller, such as pristine graphite and modified graphite, Nano sheets, such as graphite Nano platelets or graphite flakes, graphene, Stacked graphene sheets, Carbon nanotubes and inorganic nanotubes, Nanotube / nanofiber compositions, POSS (Polyhedral oligomeric silsesquioxanes), Metal phosphates, such as Zr(HPO4)2, Layered double hydroxides, such as Mg6Al2(OH)16CO3, Nanocalcium, such as calcium carbonate nanoparticles, Cellulose Nano whiskers, Metal chalcogenides such as (PbS)1.18(TiS2)2, MoS2, Nanoparticles, such as nanoclay particles and layered silicate particles including montmorillonite, hectorite, saponite, fluoroamica, fluorohectorite,vermiculite, kaolinite, magadiite.
The nanoparticle dispersion is reported to be enhanced by the use of certain type of montmorillonite nanoclays [166]. Incorporating montmorillonite nanoclays may further increase the clay dispersion in the supramolecular polymer. This chapter will investigate whether the selection of nanofiller based on its molecular structure and hydrogen bonding capability will help the dispersion of nanofiller and formation of supramolecular polymers.

5.2. Synthesis of Nanocomposite

The basic chemicals used include polyacid monomer, polyamine monomer, Nanofiller and crosslinking agent. Table 5.1 gives the overall distribution of polymer and polymer nanocomposites prepared to study the effect of molecular interactions that lead to the formation of them. This table also shows the list of polymer matrix without nanofiller (SMP) and polymer nanocomposites prepared using the components to understand the influence of carbon chain length on the overall properties of polymer nanocomposites. The last chapter has discussed the effect of polyacid structure on the formation of supramolecular polymers and discussed the use of CNTs as nanofillers in the formation of nanocomposite. It was out of the scope of this study to explore the possibility of using more than a few nanofillers. Thus three different types of commercially available montmorillonite clays such as cloisite25A (C25A), cloisite30B (C30B) and Cloisite Na⁺ (CNa⁺) were used in this study. The details of these nanoclays are detailed in table 5.2. All the chemicals were used as received. All these were used without further purification.

The supramolecular polymers were synthesised through a two-step one-pot synthesis approach just as discussed in the previous chapter. These supramolecular polymers were prepared by the condensation of carboxylic acid with amines in the first step to produce a pre-polymer followed by a reaction of pre-polymer in the presence of urea using the optimised conditions given in the last chapter. These materials do not require any solvent for the polymerization processes. The reaction was done in an inert nitrogen atmosphere with a regulated temperature control. The reaction was conducted in a three neck round bottom flask with a provision for mechanical stirring. To a stirring solution of poly amine
under nitrogen atmosphere maintained under reflux, acid was added in a slow fashion.

<table>
<thead>
<tr>
<th>Example No</th>
<th>Polyacid monomer</th>
<th>Polyamine monomer</th>
<th>Crosslinking agent</th>
<th>Nanofiller</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Malonic acid</td>
<td>DETA</td>
<td>Urea</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Malonic acid</td>
<td>DETA</td>
<td>Urea</td>
<td>Cloisite 25A</td>
</tr>
<tr>
<td>3</td>
<td>Malonic acid</td>
<td>DETA</td>
<td>Urea</td>
<td>Cloisite 30B</td>
</tr>
<tr>
<td>4</td>
<td>Malonic acid</td>
<td>DETA</td>
<td>Urea</td>
<td>Cloisite Na+</td>
</tr>
<tr>
<td>5</td>
<td>Glutaric acid</td>
<td>DETA</td>
<td>Urea</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Glutaric acid</td>
<td>DETA</td>
<td>Urea</td>
<td>Cloisite 25A</td>
</tr>
<tr>
<td>7</td>
<td>Glutaric acid</td>
<td>DETA</td>
<td>Urea</td>
<td>Cloisite 30B</td>
</tr>
<tr>
<td>8</td>
<td>Glutaric acid</td>
<td>DETA</td>
<td>Urea</td>
<td>Cloisite Na+</td>
</tr>
<tr>
<td>9</td>
<td>Pimelic acid</td>
<td>DETA</td>
<td>Urea</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>Pimelic acid</td>
<td>DETA</td>
<td>Urea</td>
<td>Cloisite 25A</td>
</tr>
<tr>
<td>11</td>
<td>Pimelic acid</td>
<td>DETA</td>
<td>Urea</td>
<td>Cloisite 30B</td>
</tr>
<tr>
<td>12</td>
<td>Pimelic acid</td>
<td>DETA</td>
<td>Urea</td>
<td>Cloisite Na+</td>
</tr>
<tr>
<td>13</td>
<td>Azelaic acid</td>
<td>DETA</td>
<td>Urea</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>Azelaic acid</td>
<td>DETA</td>
<td>Urea</td>
<td>Cloisite 25A</td>
</tr>
<tr>
<td>15</td>
<td>Azelaic acid</td>
<td>DETA</td>
<td>Urea</td>
<td>Cloisite 30B</td>
</tr>
<tr>
<td>16</td>
<td>Azelaic acid</td>
<td>DETA</td>
<td>Urea</td>
<td>Cloisite Na+</td>
</tr>
</tbody>
</table>

**Table 5.1** The list of polymer matrix without nanofiller (SMP) and polymer nanocomposites prepared using the components to understand the influence of carbon chain length on the overall properties of polymer nanocomposites.
While the reaction mixture was turbid at room temperature it turns to clear viscous polymer when heated under nitrogen flow. Later it was heated under same gas flow and temperature which turned to a yellow coloured viscous solution. The resulting product was called as a pre-polymer. To the hot mixture of pre-polymer, solid urea and the nanofiller were then added and temperature was increased. It will be then observed that gaseous ammonia is given off accompanied by foaming of the reaction medium. When the release of ammonia decreases, it was then heated to higher temperature maintaining the same gas flow to ensure the completion of the polymerisation reaction. Once the whole content of the reactor had raised the reaction mixture becomes difficult to stir and then string was stopped. The visco-elastic product was then cooled and was quickly collected out while it is still hot and elastic. The product was treated with vacuum and hydraulically pressed to form thin sheets. The resulting product was characterized to identify it as nanocomposite or as a standard pristine polymer.

5.3 Morphology of Nanoclays and its Nanocomposites

Once the nanocomposites are prepared according to the optimised methods, the factors affecting the influencing the formation are evaluated. The main techniques used in the characterisation of morphology of the nanocomposites are XRD, SAXS and SEM. These methods are used to understand the significance of clay structures and its modifiers in determining the structure and morphology of final nanocomposite. The Figure 5.1 and table 5.2 describe the details of commercial nanofillers used. It is important to understand the structural nature of organic modifiers present in the montmorillonite nanoclays. It is as given below:

![Chemical structures of organic modifiers of Cloisite 25A and Cloisite 30B.](image)

**Figure 5.1** Chemical structures of organic modifiers of Cloisite 25A and Cloisite 30B.
These studies will also help to understand the degree of dispersion of montmorillonite particles in the polymer matrix.

<table>
<thead>
<tr>
<th>Organo Clay Powder</th>
<th>Organo Clay Powder Acronym</th>
<th>Organic Modifier Acronym</th>
<th>CEC (meg/100 g clay)</th>
<th>Organic Modifier Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cloisite Na⁺</td>
<td>(CNa⁺)</td>
<td>None</td>
<td>92</td>
<td>Nil</td>
</tr>
<tr>
<td>Cloisite 25A</td>
<td>(C25A)</td>
<td>2MHTL8</td>
<td>95</td>
<td>Dimethyl, dehydrogenated tallow, 2-ethylhexyl quaternary ammonium salt</td>
</tr>
<tr>
<td>Cloisite 30B</td>
<td>(C30B)</td>
<td>MT2EtOH</td>
<td>90</td>
<td>Methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium salt</td>
</tr>
</tbody>
</table>

*Table 5.2 The details of nanofiller used in the synthesis and its organic modifiers.*

5.3.1 X-Ray Diffraction and Small Angle X-Ray Diffraction

Both XRD and SAXS techniques are known to be powerful tools to characterise the formation of nanocomposites and its morphology.

5.3.1.1 X-Ray Diffraction Scattering

X-ray diffraction can be used to determine the morphology of montmorillonite nanoclays. This is possible for the nanofiller in a powder form or in a compounded polymer form. The fundamental principle of working is based on the fact that the incident X-rays that fall on the clay or polymer sample will get reflected from each layer. This reflection will have a direct relationship with the angle $\theta$ and spacing between the layers in the clay or polymer. The diffraction peaks at smaller angles are calculated using its relation with the interlayer spacing as per the Bragg's law, $\lambda=2dsin\theta$, where $\theta$ is the diffraction angle, $\lambda$ is the X-ray wavelength and $d$ is the diffraction plane spacing.
The d-spacing values of the montmorillonite nanoclays are measured using an X-ray diffraction technique as is shown in Figure 5.2. The molecular chains of organic modifier will make the clay platelet gallery of montmorillonite to get intercalated or expanded. The thereby increased clay spacing has become evident through the XRD of montmorillonite clays. The pattern of curves will be usually be determined by the organoclay interactions and the interlayer distance of the clay platelets. Nanoclays Cloisite 25A and Cloisite 30B have different types of organic modifiers present in them which is evident by the diffraction peaks.

![XRD pattern of Cloisite Na+, Cloisite 25A, Cloisite 30B nanoclays.](image)

**Figure 5.2**  
XRD pattern of Cloisite Na+, Cloisite 25A, Cloisite 30B nanoclays.

The peaks correspond to the (001) plane reflection of the clay, the d001 peak of montmorillonite at 2θ = 4.2 (C25A), and 4.8 (C30B). The peak location change from 4.2 to 4.8 in modified clays may be due to the presence of different levels of ammonium salts present in them. While the pristine montmorillonite nanoclay gives it peak at 2θ = 7.4 (CNa+), corresponds to 1.19 nm interlayer spacing. This attributes to the fact that Cloisite Na+ is a natural montmorillonite with a small percentage of modifying ammonium salts. Thus, the clay modification of the nanocomposite polymer is responsible for the swelling of the clay galleries.

All these three nanoclays were used in the synthesis to form polymer nanocomposites. Typical examples of the XRD results of these supramolecular
nanocomposites are given in the Figure 5.3. The lowest chain length dicarboxylic acid Malonic acid could not form any polymer with firm physical structure than viscous polymers. Therefore polymer nanocomposites made out of other dicarboxylic acids were studied here. Figure 5.3 represents the peak positions of sodium Montmorilinite nanoclay and various nanocomposites produced using different polyacids. It is quite evident from the shift in the peak position for the nanoclay that the clay galleries are intercalated or exfoliated in the polymer matrix when formed.

![XRD pattern showing the formation of nanocomposites which used Cloisite Na+ montmorillonite nanoclays.](image)

For the Glutaric acid nanocomposite the diffraction peak was nearly disappeared indicating that Na-MMT has clay layers which are exfoliated in the polymer matrix. For the nanocomposites based on Azelaic acid and Pimelic acid which have higher chain length the diffraction peak shifted to smaller angle while and has become more narrower in its width indicating an intercalation of clay layers. This information is directing towards bringing out the clear relation between the carboxylic acid chain length and the type of montmorilinite nanoclay used in the given reaction system.

Thus it was decided to study the nanocomposites by using other types of montmorilinite nanoclays to elucidate this relationship. We have two
montmorilinite nanoclays under consideration which can be used to make nanocomposites from carboxylic acids of increasing chain length. The first one of this series was to use cloisite 25A nanocomposite and then using the cloisite 30B. The nanoclays containing organically modified surfactants contribute toward the formation of nanocomposites. Figure 5.4 shows that the characteristic peak for the Cloisite 25A nanoclays has been almost disappeared in the nanocomposites. This can be qualified to the exfoliation of nanoclays in the nanocomposite matrix. While using organically modified montmorillonite nanoclay C25A the results were surprising while we obtained better exfoliation of the clay into the polymer chains. The broad characteristic peak of C25A has been disappeared in the nanocomposites while showing small humps towards a higher diffraction angle. This is attributed to the fact that a better case of exfoliation is shown by these nanocomposites may be contributed by the organic modifier present in C25A montmorillonite nanoclay.

![Figure 5.4](image)

**Figure 5.4** XRD pattern showing the formation of nanocomposites which used Cloisite 25A montmorillonite nanoclays.

In the same platform of study by comparing carboxylic acid chain length and type of montmorillonite nanoclay, another exercise was to use nanoclay with a functional group that has the capability of forming hydrogen bonding interactions. This is believed to provide a better molecular level interaction in the polymer
nanocomposite and thereby by achieving a better exfoliation of nanoclay layers into the polymer chains. Thus nanoclay C30B containing organic modifier MT2EtOH helps towards the formation of corresponding nanocomposites. As given in figure 5.5, there is either a significant shift in the characteristic peak for the nanoclays or there is a disappearance of the peaks. Both of these characters evidence the formation of nanocomposites. The molecular chains of organic modifier which are used to modify the montmorillonite nanoclays will get intercalated and expanded into the clay galleries. The characteristic diffraction peak of C30B ($d_{001}$) plane appears at $2\theta = 4.8$, C25A ($d_{001}$) plane appears at $2\theta = 4.2$, CNa$^+$ ($d_{001}$) plane appears at $2\theta = 7.3$. The clay spacing has been increased in all the nanocomposites formed is evident by the shift or disappearance of diffraction peaks.

![XRD pattern showing the formation of nanocomposites which used Cloisite 30B montmorillonite nanoclays.](image)

**Figure 5.5** XRD pattern showing the formation of nanocomposites which used Cloisite 30B montmorillonite nanoclays.

Here the general case was similar as of using the Na-MMT nanoclays where Glutaric acid based nanocomposites gave an exfoliated morphology while the higher chain length Azelaic and Pimelic acids gave intercalated morphology.

The shift of diffraction peaks to higher values in C25A nanocomposites (Fig. 5.4) and C30B nanocomposites (Fig. 5.5) indicate the decrease in interlayer spacing[167]. While the shifting of diffraction peak to a lower value for
nanocomposite corresponding to CNa⁺ nanocomposites evidences the increased interlayer spacing in the polymer/MMT matrices (Fig. 5.3). Thus it appears that the interlaying spacing is highly altered in all the nanocomposites compared to the presence of nanoclays. This was recognized as the proof of the intercalation or exfoliation of the molecular chains of polymer into the silicate galleries of nanoclays to form multilayered structures. These multilayers may have been formed by various layers of polymer and layered nanoclay particles and its molecular chains.

As discussed in the literature review, XRD technique alone cannot reveal the complete morphology of the nanocomposites. So addition techniques such as SEM and SAXS are used to complement the diffraction experiments.

### 5.3.1.2 Small Angle X-Ray Scattering

Since the X-ray diffraction pattern can reveal only the basal reflections of the nanocomposite, and it was observed that characteristic peaks for montmorillonite clays had disappeared in some of the nanocomposites, further attempts to understand the morphology of nanocomposites are made using SAXS technique. The presence of quaternary ammonium ions as modifiers in C25A and C30B might have helped towards the lower viscosity observed during synthesis for those nanocomposites.

It will be easy for the polymer to penetrate deep into the clay galleries if the viscosity is lower. This would probably explain the formation of intercalated clay morphology for CNa⁺ nanocomposites and exfoliated morphology using modified nanoclays which is proved by XRD measurements. The cross checking with SAXS technique identifies the characteristic peaks for the nanoclays which is shown in Figure 5.6. A similar disappearance of characteristic peak of C30B in its corresponding nanocomposites was seen in Figure 5.9 indicating the formation of nanocomposites. CNa⁺ and its nanocomposite are given in figure 5.7 where disappearance of nanoclay peak is observed. This case was repeated for C25A and its nanocomposite as given in Figure 5.8.
Figure 5.6  Small angle X-ray scattering data showing the characteristic peaks of all the montmorillonite clays.

Figure 5.7  Small angle X-ray scattering data showing the formation of nanocomposites which used Cloisite Na+ montmorillonite as nanofiller.
Figure 5.8  Small angle X-ray scattering data showing the formation of nanocomposites which used Cloisite 25A montmorillonite as nanofiller.

An each set of nanocomposite made using different nanoclays are plotted along with the corresponding nanoclays to confirm the formation of nanocomposites.

Figure 5.9  Small angle X-ray scattering data showing the formation of nanocomposites which used Cloisite 30B montmorillonite as nanofiller.

While nanocomposite were formed, it is observed that the three dimensional nanoclay particles are spread all over the polymer matrix. This is evident through
the disappearance of characteristic peaks of nanoclays in their corresponding nanocomposites. This observation is in absolute agreement with data observed from XRD measurements. It is also important to note that it is not just the diffraction plane spacing the only component to determine the morphology of nanocomposite. So SEM micrographs were taken and analysed to understand the nanocomposite morphology better.

5.3.2 Scanning Electron Microscope Studies

The evidences from the SEM micrographs given from figures 5.10, 5.11, 5.12 gives the morphology of nanoclays C25A, C30B and CNa⁺ respectively.

![SEM images and EDX analysis of Cloisite 25A montmorillonite clay](image)

**Figure 5.10**  *SEM images and EDX analysis of Cloisite 25A montmorillonite clay*
Figure 5.11  SEM images and EDX analysis of Cloisite 30B montmorillonite clay

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>Wt% Sigma</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>50.24</td>
<td>0.64</td>
</tr>
<tr>
<td>Mg</td>
<td>1.37</td>
<td>0.08</td>
</tr>
<tr>
<td>Al</td>
<td>11.63</td>
<td>0.19</td>
</tr>
<tr>
<td>Si</td>
<td>27.19</td>
<td>0.37</td>
</tr>
<tr>
<td>Fe</td>
<td>3.36</td>
<td>0.21</td>
</tr>
<tr>
<td>Zr</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Pt</td>
<td>6.2</td>
<td>1.1</td>
</tr>
<tr>
<td>Total:</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.12  SEM images and EDX analysis of Cloisite Na+ montmorillonite clay

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>Wt% Sigma</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>48.96</td>
<td>0.5</td>
</tr>
<tr>
<td>Na</td>
<td>2.1</td>
<td>0.08</td>
</tr>
<tr>
<td>Mg</td>
<td>1.25</td>
<td>0.07</td>
</tr>
<tr>
<td>Al</td>
<td>11.31</td>
<td>0.16</td>
</tr>
<tr>
<td>Si</td>
<td>27.78</td>
<td>0.3</td>
</tr>
<tr>
<td>Ca</td>
<td>0.33</td>
<td>0.07</td>
</tr>
<tr>
<td>Fe</td>
<td>3.71</td>
<td>0.18</td>
</tr>
<tr>
<td>Zr</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Pt</td>
<td>4.55</td>
<td>0.86</td>
</tr>
<tr>
<td>Total:</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>
It can be demonstrated from the SEM images and EDX analysis of the montmorillonite nanoclays that clay structures are crystalline in nature. Also it reveals the elemental composition of the nanoclays. The presence of elemental traces of sodium in $\text{CNa}^+$ is proven by EDX analysis.

Thus it can be estimated from the morphological analysis of montmorillonite nanoclays that the molecular interaction formed between the polymer matrix and nanofiller are the key factors leading the morphology of polymer nanocomposites to give an intercalated or exfoliated clay structure in the polymer matrix. The interactions can be either chemically bonded or through hydrogen bonds which are studied using spectroscopic techniques.

5.4 Spectroscopic Studies

We have employed the use of NMR and FTIR-ATR spectroscopic techniques to ensure the formation of nanocomposites and the effect of nanoclays on their formation. These techniques are already been proven as suitable characterisation techniques in detecting chemical molecules and their reaction interfaces.

5.4.1 $^1H$ NMR Spectroscopy

Solid state NMR spectroscopy is used in characterising the polymer/MMT nanocomposite morphology. Generally, this technique is largely used as a conventional and proven tool to identify and distinguish the chemical molecules and its structures. Only a few studies are done by applying NMR as a tool to analyse polymer/MMT nanocomposites.

It is quite notable the effect of addition of nanoclays into the reaction mixture by showed the interaction of $-\text{NHCH}_2\text{CH}_2\text{NH}_2-$ groups and appearance of new molecular moieties with carbonyl interactions. Thus the NMR spectra given in Figure 5.13 can showed the significance of the effect of incorporation of montmorillonite nanoclays into the polymer matrix by effectively providing new molecular cross links.
Figure 5.13 $^1$H NMR plot showing the effect of addition of nanofiller on the formation of supramolecular polymer

$^1$H NMR (400MHz, CD$_3$OD)$\delta$ (ppm): 1.29(4H,s); 1.52(2H,s);2.3(2H,m); 2.7-2.8 (NHCH$_2$CH$_2$NH$_2$,m); 3.3-3.5(C(O) NHCH$_2$CH$_2$NH,m).

Formations of new molecular entities are observed after the addition of nanoclays. This indicates that the reactive functional groups of nanoclays have effectively reacted with polymer end groups. The formation of these new molecular interaction and possibility of hydrogen bonding interactions are further studied with the help of FTIR-ATR technique.

5.4.2 FTIR-ATR Spectroscopy

FTIR-ATR is a great tool to probe hydrogen bonding in polymers. The characteristic spectral bands of the Si–O–Si stretching vibration, Al–O and the Si–O bending vibration of the montmorillonite nanoclays are seen at 1010 cm$^{-1}$ for C25A and C30B, 1020 cm$^{-1}$ for CNa$^+$ as given in Figure 5.14 and Figure 5.15. These peaks are further observed for their corresponding nanocomposites as well which are due to the stretching vibration contributed by the Si–O–Si interactions. Moreover the intercalations of polymer chains into the clay gallery of montmorillonite are observed by the stretching vibration of Al–O and the Si–O bending vibration of montmorillonite.
Figure 5.14 FTIR-ATR spectrum to show the Si–O–Si stretching vibration, Al–O and the Si–O bending vibration of nanoclays.

It is intended that the peak positions for characteristic functional moieties should be similar to the standard polymer compound. This can be a proof to the segmented structure of the nanocomposite that should not get affected by the presence of montmorillonite irrespective of the presence of the organic modifiers present in them.

Thus it is also expected for the nanocomposites that, with respect to symmetric and anti-symmetric stretching vibrations of the OH group in the polymer and nanoclay respectively a broad peak would get develop. Also the bigger intensity of C30B nanoclay with more number of hydroxyl functional groups is supposed to form more hydrogen bonded stretching vibrations [168]. The broad peaks observed for the nanocomposites at 3600cm⁻¹ denote the presence of strong –NH groups and these are attributed to the development of hydroxyl groups (–OH).
Figure 5.15  FTIR-ATR spectra of Cloisite 30B, Cloisite 25A and Cloisite Na+ nanoclays.

The free hydroxyl groups are supposed to show peaks at 3600 cm\(^{-1}\). The broad peak in 3180 to 3580 cm\(^{-1}\) region shows the formation of new hydrogen bonding interaction.

The presence of dominant peaks in the spectral region of 1500 to 1800 cm\(^{-1}\) proves the presence of lots of C=O and C=C interactions which is given in Figure 5.16 and Figure 5.17 shows the FTIR-ATR spectra of C25A based nanocomposites showing the amide region vibrations between 1450-1 and 1850 cm\(^{-1}\). The nanocomposites formed from Glutaric acid and various montmorillonite nanoclays are studied for the effect of organic modifiers present in the clay and clays itself.

From the FTIR-ATR spectroscopic studies conducted on these samples the results are as shown in Figure 5.17. This further evidences the formation of multiple interactions between carbonyl groups and hydroxyl groups. The hydrogen bonding interactions are believed to loosen the C=O bonds of the carbonyl groups (C=O…H-O). This shows the CH vibration available in the region of 2750cm\(^{-1}\) and 3100 cm\(^{-1}\) and carbonyl stretching vibration available between 1400cm\(^{-1}\) and 1800 cm\(^{-1}\).
When analysing the lower spectral region, the C=O stretching frequency is observed at 1650 cm\(^{-1}\) and another peak at 1615 cm\(^{-1}\) shows the C=C stretching frequency. The peaks observed between 1150 and 1320 cm\(^{-1}\) are responsible for the C-O-C stretching vibrations. Also there are a few C-O stretching peaks seen in
the 1000 to 1250 cm\(^{-1}\) range. The extra hydroxyl ions present in the organic
modifies (2MHTL8 and MT2EtOH) nanoclays C25A and C30B may give extra
C=O stretching and O-H bending vibrations so as to provide hydrogen bonding
capability with the carbonyl groups of carboxylic acids [118, 169]. While the
natural montmorillonite CNa\(^+\) have the Na\(^+\) ions that may get replaced by H\(^+\) ions,
this exchange behaviour can increase the number of nonionised carbonyl groups (-
COOH) and not by any specific interaction prevail between nanoclay and
nanocomposite.

The CH\(-\) vibrations are clearly observed at around 2800 to 3000 cm\(^{-1}\) for all
nanoclays and nanocomposites which had remained unchanged during the
incorporation of nanoclays into the polymer matrix. This tells that the C-H
functional groups do not directly involve in the hydrogen bonding interactions
while forming a new polymer by using the nanoclays. Figure 5.18 FTIR-ATR
spectra of C25A based nanocomposites showing the symmetrical and
antisymmetric –C-H vibrations.

![Figure 5.18 FTIR-ATR spectra of C25A based nanocomposites showing the
symmetrical and antisymmetric –C-H vibrations.](image)

These are in agreement with the \(^1\)H NMR studies to prove that the addition of
nanoclays have triggered the formation of new molecular moieties and the
functional groups of nanoclays have effectively reacted with polymer end groups to form supramolecular moieties. Thus FTIR-ATR technique gives clear evidences about the formation of many active supramolecular interactions in the polymer nanocomposite.

5.5 Thermal Studies

One of the important characteristic used to analyse the improvement of polymer before and after the addition of nanoclays is the thermal properties. It’s been evaluated using two methods such as thermo gravimetric analysis and differential scanning calorimetric analysis.

5.5.1 Dependence of Nanoclay Type on Glass Transition Temperature

Differential Scanning Calorimetric technique was used as a tool to study the thermal properties of the polymers. A number of relationships in the properties of the nanocomposites are evaluated by the glass transition temperature, \( T_g \). This is because a few constituents in the polymers play an important role in increasing the thermal stability of the polymer. All the samples were tested and evaluated at the same conditions. A series of dicarboxylic acids were used along with a series of nanoclays to form their corresponding nanocomposites.

![DSC results](image)

Figure 5.19 Compares the DSC results obtained for the nanocomposites made from a cross-linked polymer matrix including pre-polymers derived from Azelaic dicarboxylic acid (SMP of AA) monomers and contain C25A, C30B and CNa+ nanoclays.
The test results for the pristine polymer which do not have any nanofiller SMP, Azelaic acid based nanocomposite which uses C25A nanoclay AA/C25A, nanocomposite which uses C30B nanoclay AA/C30B and nanocomposite which uses CNa+ nanoclay AA/CNa+ are shown in Figure 5.19. The Tg values are reported in the same figure. The glass transition (Tg) temperature of both compounds AA/C25A and AA/C30B were observed at 27 °C, AA/ CNa+ exhibited Tg at 34 °C while SMP the pristine compound gave Tg peak at 30 °C respectively. The DSC results show how glass transition temperature (Tg) varies for the different nanocomposites. It is highly interesting to note that for a Azelaic acid based nanocomposite, the Tg of pristine polymers SMP AA are higher by 4 °C for CNa+ based nanocomposite while it is decreased by 4 °C for the nanocomposites based on organically modified nanoclays.

The effect of nanoclay on the glass transition temperature is explained here. The chain length of the carboxylic acid is slightly varied and nanocomposites using Pimelic acid are made to confirm the effect of nanoclays which is given in Figure 5.20.

![Figure 5.20](image)

**Figure 5.20** compares DSC results obtained for the nanocomposites made from a cross-linked polymer matrix including pre-polymers derived from Pimelic dicarboxylic acid pre-polymer (PA-SMP) and corresponding C25A, C30B and CNa+ nanoclays.
While for a nanocomposite series based on Pimelic acid the case is totally different where the neat polymer has a higher Tg of 72±1 °C. However the carboxylic acid chain length might have contributed the higher Tg when compared against Azelaic acid based nanocomposite counterparts. However when mixed with nanoclays the Tg has come down to a comparable value. It can be seen that nanocomposite with higher chain length has a lower glass transition temperature. This fact is been further studied against the dependence of carboxylic acid chain length by using C25A nanoclay as shown in the figure given below Figure 5.21.

It compares DSC results obtained for the nanocomposites contain C25A nanoclay and a cross-linked polymer matrix including pre-polymers derived from dicarboxylic acid monomers of varying chain length. The DSC results show how glass transition temperature (Tg) varies for the different nanocomposites.

![DSC comparison of glass transition temperature (Tg) for different nanocomposites based on Cloisite 25A nanoclays.](image)

**Figure 5.21** DSC comparison of glass transition temperature (Tg) for different nanocomposites based on Cloisite 25A nanoclays.

The nanocomposite with the natural montmorillonite is showing a higher Tg than the nanocomposite with the modified montmorillonite. Among the modified ones, C30B nanoclay based nanocomposites have a higher Tg. The effect of nanoclay on the glass transition temperature is explained here. The chain length of the carboxylic acid is slightly varied and nanocomposites using Glutaric acid are made to confirm the effect of nanoclays which is given in Figure 5.22.
Figure 5.22 compares DSC results obtained for the nanocomposites made from a cross-linked polymer matrix including derived from Glutaric dicarboxylic acid and corresponding C25A, C30B and CNa+ nanoclays.

These facts are consistent with data from XRD and FTIR spectrum that the hydrogen bonding effects are higher when carbonyl groups in carboxylic acid are used along with the nanoclays with functional groups capable of hydrogen bonding. In borderer terms the increased glass transition temperature of the polymer nanocomposites may be attributed to (i) the influence of small amounts of well distributed nanoclay on the polymer matrix (ii) the existence of the intercalated or exfoliated polymer chains inside the nanoclay galleries that limit the polymer chain movements. These can be described on the basis of mobility of the nanoclay chains within the polymer matrix layers.

5.5.2 Dependence of Nanoclay Type on Thermal Degradation

Thermo gravimetric analysis (TGA) provides information on the thermal strength and thermal degradation behaviour of the polymer nanocomposites. The formation of volatile materials upon heating the polymer will contribute to the weight loss of the polymer which was studied. The results of TGA analysis of the macromolecule pre polymer, pristine (SMP) and clay modified nanocomposites. The thermo-gravimetric analysis and related studies conducted on a non-oxidative Nitrogen atmosphere at a heating rate of 10°C/min and data provides evidence on
the subject of their thermal stability and thermal degradation characteristics of the polymer nanocomposites.

![TGA plots of montmorillonite nanoclays](image)

**Figure 5.23** TGA plots of montmorillonite nanoclays

In this study, the indicators for the thermal permanence for the polymer compound are the peak decomposition temperatures (the thermal point where the maximum rate of decomposition occurs), and the equivalent peak decomposition rates (prevailing rate at which particular peak decomposition temperature occurs) were also considered. On a typical exercise, the onset temperature of thermal degradation and the yield of charred residue for nanoclays were calculated at 900°C and 600°C for nanocomposites. The TGA measurements of montmorillonite nanoclays with different contents are shown in Figure 5.23. The thermal decomposition passes through different steps in different clays. In the first step, up to 250°C, there is nearly no difference between the thermal stability of all the three nanoclays.

For the modified nanoclays Cloisite 25A and Cloisite 30B, the second decomposition starts after that due to the elimination of organic side-groups at lower temperature, which occurred at 250-450°C showing a major weight loss in this range. And finally the third step after that at around 500°C due to the decomposition of main chains. However for the unmodified Cloisite Na⁺ nanoclay
the first stage continues up to around 550°C and then a major decomposition occurring between 500-700°C. The improvement of thermal stability of nanocomposites is thus expected to be given by those which are made from Cloisite Na⁺ nanoclay. The initial peaks observed for all the clays are the elimination of the free and water molecules which are trapped inside the clay and the later peaks observed are due to the dissociation of surfactant molecules.

While studying the nanocomposites prepared from shortest chain length to longest chain length ones, it goes in the order of Glutaric acid, Pimelic acid and Azelaic acid. All of these studies compare nanocomposites made using different nanoclays. Firstly, as given in Figure 5.24, the commencement of the degradation of pristine nanocomposite (SMP GA) occurred at nearly 70 °C and extreme degradation happened at around 450 °C. The incorporation of any of the given three montmorillonite nanoclay into the pristine nanocomposite decreased the initiation of degradation considerably.

Figure 5.24 TGA comparison of degradation of nanocomposites prepared using Glutaric acid and three different nanoclays.

Nonetheless, the degradation temperatures at its maximum were marginally increased to 450 and 460°C for GA/CNa+ and GA/C25A respectively while it was decreased to 435 °C for GA/C30B.
Figure 5.25  *TGA comparison of degradation of nanocomposites prepared using Pimelic acid and three different nanoclays.*

Thus, it can be determined for this case that the incorporation of natural montmorillonite did not influence to change the temperature of maximum degradation while C25A has contributed to a slight increase and C30B to a slight decrease in the temperatures of degradation. For another case where different montmorillonite nanoclays were used along with a higher chain length carboxylic acid which is Pimelic acid. The initiation of thermal degradation of pristine nanocomposite (SMP PA) was observed to happen at around 90 °C and maximum thermal degradation befallen at 475 °C as shown in Figure 5.25.

The incorporation of relative montmorillonite nanoclays into the pristine nanocomposite decreased the start of degradation PA/CNa⁺ and PA/C30B considerably while the change for PA/C25A is just marginal. However, the maximum degradation temperatures of almost all nanocomposites are comparable with the pristine polymer to remain at around 475 °C. The maximum degradation temperature PA/CNa⁺ has slightly increased by 5°C to get degrade at 480 °C. This thermal behaviour indicate to the higher dependence carboxylic acid’s increasing chain length and type of nanoclay used in imparting better thermal stability for supramolecular polymers.
This concept is developed further by using an even higher chain length by selecting Azelaic acid along with three montmorillonite nanoclays C25A, C30B and CNa+ to produce nanocomposites AA/CNa+, AA/C30B and AA/C25A which were compared against their pristine polymer SMP AA. The start of thermal degradation of pristine nanocomposite (SMP AA) was observed to happen at around 135 ºC and the peak maximum degradation befallen at 495 ºC. This is a greater improvement achieved by increasing the chain length of carboxylic acid as shown in Figure 5.26.

The maximum degradation temperatures of degradation for AA/CNa+ and AA/C25A nanocomposites are comparable with the pristine polymer which was at 495 ºC. This temperature has come down for AA/C30B nanocomposite to 485 ºC. The perceived rises in the thermal permanence of nanocomposites were contributed by the high thermal stability of montmorillonite nanoclays and the interfacial reactions amongst the nanoclay layers and the polymer medium through the process of intercalation or exfoliation.

![TGA comparison of degradation of nanocomposites prepared using Azelaic acid and three different nanoclays.](image)

**Figure 5.26**  *TGA comparison of degradation of nanocomposites prepared using Azelaic acid and three different nanoclays.*

The increased chain length of carboxylic acids has helped in achieving better intercalated polymer chains. The direct exposure of these polymer chains were highly restricted by the nanoclay layers which also may help in improving the
thermal stability. It is also observed that addition of montmorillonite nanoclay has contributed significantly towards the improvement of initial degradation temperature. This was achieved by the control of out-diffusion of many volatile components from the nanocomposites. A summary of the onset temperatures of different nanocomposites and their corresponding standard polymers are given in table 5.3.

<table>
<thead>
<tr>
<th></th>
<th>SMP</th>
<th>CNa⁺</th>
<th>C25A</th>
<th>C30B</th>
</tr>
</thead>
<tbody>
<tr>
<td>GA</td>
<td>70</td>
<td>190</td>
<td>130</td>
<td>170</td>
</tr>
<tr>
<td>PA</td>
<td>90</td>
<td>220</td>
<td>140</td>
<td>210</td>
</tr>
<tr>
<td>AA</td>
<td>135</td>
<td>225</td>
<td>150</td>
<td>230</td>
</tr>
</tbody>
</table>

Table 5.3: Onset temperatures of nanocomposites and their stand polymers

The temperature of 50% mass loss (T50%) is given in the Figure 5.27. The nanocomposites contain C30B nanoclay and a cross-linked polymer matrix including pre-polymers derived from dicarboxylic acid monomers of varying chain length are compared. Also the thermogram compares the decomposition temperatures of the different nanocomposites. The temperature at which 50% mass loss occurs (T 50%) is also given in the figure.

Figure 5.27 TGA thermogram comparing degree of degradation of nanocomposites based on Cloisite 30B nanoclays.
The higher dependence of the molecular chain length is explained using the Figure 5.27 such that it is obvious that the longer chain length polymer nanocomposite made using Azelaic acid has the higher thermal stability.

5.6 Montmorillonite Clay Distribution in the Nanocomposite

From the XRD, SAXS, NMR and SEM characterisation techniques, along with the process methods optimised in the previous chapter, it was confirmed that the reaction conditions were good enough to produce polymer nanocomposites from dicarboxylic acids. Here in this chapter, the effect of the use of various montmorillonite nanoclays are compared against the formation of supramolecular polymers. The ensured advantage of the practised process method was the formation of nanocomposite. It is illustrated in Figure 5.28 about the simple possible changes occur when a polymer/MMT system is formed.

*Figure 5.28* Scheme representing the microstructure formation inside a polymer/clay nanocomposite through the interactions occurs between polymer and nanoclay.

Mostly the polymer nanocomposites will be formed out of the combination of intercalated and exfoliated structures. Either an intercalated or exfoliated morphology is achieved while synthesising the nanocomposites. The only
difference between an intercalated and exfoliated structure is in the arrangement of clay platelets where in exfoliated the clay platelets will be delaminated from one another and are disseminated throughout the polymer matrix. Three commercially available functionalised clays were used in this study. The purpose of incorporation of these nanoclays into the polymer matrix is to tune the material properties like thermal stability according to the requirements. It is confirmed by the characteristic techniques that non-covalent molecular interactions such as hydrogen bonding prevail in the polymer nanocomposites. Material property such as the high dependence on temperature was intrigued in the polymer as a result of the reversibility of the molecular interactions by hydrogen bonds. Also an exfoliated structure where the polymer chains entered into clay galleries to get a disordered orientation is implied. As discussed earlier a multiplicity of structures are possible and are obtained when a MMT clay is incorporated in a polymer matrix to form a polymer/MMT nanocomposites as displayed in Figure 5.28. It is highly important to have adequate evidence from this technique to pronounce a nanocomposite structure as exfoliated with confidence. The level of intercalation of nano clays into the polymer material has been determined and discussed earlier in this chapter.

5.7 Conclusions

A series of different montmorillonite nanoclays were used to synthesise a series of polymers and they were evaluated for the formation of nanocomposites. The formed polymers were analysed for its morphologies to confirm the production of nanocomposites by effectively using a simple solvent free synthesis methodology. A structure-property relationship was established for the effective selection of monomers and nanofillers while preparing supramolecular polymer nanocomposites.

The supramolecular polymer nanocomposites can be synthesised by using montmorillonite nanoclays containing diverse organic modifiers. It is concluded that the incorporation of nanoclays improved the polymer matrix-nanofiller interaction. It is also observed that the clay with lowest amount of organic modifier such as ammonium salts increased the thermal strength of the polymer nanocomposites. The intercalation was more favoured when montmorillonite
nanoclays with large d_{001} was used. The clays with large d_{001} presented larger thermal stability because the polymer-montmorillonite surface interaction is higher due to the absence of modifier ammonium salts on the surface of nanoclays. It is confirmed from XRD, SAXS, NMR and SEM studies that polymer nanocomposites proved the formation of exfoliated nanocomposites for Cloisite 25A and Cloisite 30B whereas for Cloisite Na\(^+\) there could be the formation of intercalating structure. The highest thermal stability is achieved for polymer nanocomposites which are intercalated into Na-MMT nanoclays and synthesised from dicarboxylic acids of higher chain length.
CHAPTER SIX

6 REPAIRABLE POLYMER NANOCOMPOSITES

6.1 Introduction

Biological systems have the inbuilt property to repair themselves after being injured. Motivated from this fact, a material that can naturally correct its damage caused by normal usage could lower production expenses of a large number of commercial products and industrial processes. They can provide lengthier lifetime, reduce the ineffectiveness caused by dreadful conditions, as well as avoid expenses and accidents incurred by material letdown [170]. Inspired from these concepts and after the first experiments in this direction of engineering materials nearly a decade ago, it can be concluded that research in the field of self-healing polymers, defined as a “material where damage powers a healing response,” has been added as a new research area across the whole scientific world ranging from chemistry to engineering [171]. The mechanical damage in plants is healed by regulatory molecules like nitric oxide, binders or wax which might potentiate the healing responses leading to a rapid restoration of the damaged tissue [172], whereas in human body the blood coagulation on skin soon after a cut occurred was contributed by two major facets of the clotting mechanism – the platelets, and the thrombin system [173].

Among polymer systems, the work by White et al[24] was not the first ever done work on self-healing polymers but that work involved the concept of encapsulated microcapsules system which gave a major breakthrough and stimulated further work in this area. There occurred various successful approaches including the investigation of a reaction which is thermally reversible like the Diels–Alder (DA) reaction used for self-healing applications to give thermally re-mendable cross-linking materials by Chen et al [59], dicyclopentadiene/Grubbs catalyst system [2], poly(dimethylsiloxane)/tin catalyst system [35], epoxy/hardener system [174], solvent encapsulation [175], isocyanate encapsulate system [176], etc. The known supramolecular network through hydrogen bonding [177], which recently
revealed a self-healing elastomer system [178]. We employ a similar type of approach to use hydrogen bonding chemistry to fetch self-healing efficiency in polymer nanocomposites but through a simpler and solvent free approach. The self-healing elastomer system revealed by Cordier et al was unique where it reveals a polymer material which can repair its cut by merely pressing the broken ends together for a few minutes. It was a solvent involved process which uses EMPOL 1016 (mixture of monoacid, diacid and triacid along with polyacids) as the starting material. Self-repairing composition comprising of molecules of vegetable fat and crosslinking agents have diamide, urea functional groups which use hydrogen bonding, co-valent bonding and water molecules in forming self-healing polymer composition. However a full repair required up to six hours of bonding. A damaged sample could be left overnight before being repaired, although it would exhibit fewer elastic properties, because some of the detached bonds had connected to their neighbours. We also use hydrogen bonding in forming self-healing polymer composition, but disclose the use of nanofiller that gives the resultant polymer nanocomposite the flexibility of tailor made mechanical and physical properties. Our materials do not change its properties over time through the successful incorporation of nanoclays into the macromolecule to give polymer nanocomposite with no elastic properties. We work out a simple solvent free process which uses only diacid instead of the mixture of acids to give a self-healing polymer that can repair its cuts in less time.

Meanwhile, self-healing epoxy composites [52], and metal-ligand coordination approach [179], are worth to be remembered here. Also an elastic polymer matrix was reported to provide protection at the site of damage through expelling biocide [180]. The well-known Diels-Alder chemistry resulted in approaches involving furan-maleimide and dicyclopentadiene systems [181], which directed to a polymer network formation by reversibly cross-linked covalent bonds. Recently significant interest was developed in the self-healing property research of carbon fiber composites [182], shape memory alloys [183] and organometallic polymers [183]. Polymer composite materials which can self-heal by inductive heating with the help of incorporated magnetic compounds was another approach [184]. An altered form of reversible chemical interaction was the ionic interactions [185]. In another work amalgamated cinnamoyl groups into a polymer matrix, lead to
CHAPTER SIX

photo-chemically prompted healing of the materials [70]. Oxetane-substituted chitosan polyurethane networks were reported to be healed by ultraviolet (UV) light exposure [186]. A new approach where optical light was used to utilize to heal the damage sites on supramolecular polymer networks [73], was articulated recently. On another recent study self-healing nanocomposite hydrogels were reported that do not use any healing agent and cuts on polymer surface will recombine by just contacting the cut surfaces together at mildly elevated temperatures [187]. Thus a through literature study and optimised reaction parameters which are discussed in earlier chapters 4 and 5 of this thesis helped in predicting the structure-property relationship of polymer nanocomposites. The polymer nanocomposites with reversible hydrogen bonding ability with longest chain length was assumed to bring repairing capabilities to the polymer. The available dicarbixylic acid with longest carbon chain was sebacic acid and thus it was decided to use as the candidate for synthesising polymer nanocomposites. Also the use of three different types of montmorilinite nanoclays was also studied.

6.2 Synthesis of Self-Healing Polymer Nanocomposite

Polymer/layer-silicate nanocomposites defined as compositions that bring more than one property improvement to a particular function have captivated considerable interest of material scientists and manufacturers. The commercial and technical importance of nanocomposites is easily understood by their commercial and technical applications which run from automotive industry to drink packaging. The basic example on this regard was done by Toyota motor company on the synthesis of clay-nylon nanocomposites and this may be the largely studied system till date [188]. Hydrogen bonded brush polymers to form nanocomposites with the self-healing capability were synthesised using solvents employing the relatively complex ATRP techniques [189].

The aim of this study is to give birth to a new class of self-healing materials, i.e., self-healing polymer nanocomposites through a feasible technique. We employ a most fascinating aspect of supramolecular chemistry which focuses particularly on the synthesis of self-healing polymer which heals quickly in room temperature without being aided by any material or energy. For simplicity, the present work strategy involves a one-pot, two-step in-situ synthesis method by using the
condensation of carboxylic acid with amines to form a pre-polymer in the initial step followed by the cross-linking of the pre-polymer in the presence of urea. The selection of these components was driven by their capabilities to serve specific tasks.

Figure 6.1 Synthesis of the supramolecular pre-polymer from fatty acid and amine followed by crosslinking with urea.
The resultant supramolecular polymer material (standard self-healing polymer) shows the fascinating characteristic of fast self-healing capability; but with poor mechanical properties which hardly holds it vital for any practical use. Thus considering the industrial potential, a successful scheme to improve the material properties of this self-healing polymer was developed with montmorillonite clays in the polymer medium through a melt mixing polymerisation technique. As given in Figure 6.1 the reaction of fatty acids, amine and urea proceeds in two main sequential steps as the temperature is elevated. The first step (Figure 6.1 S1.A) illustrates the synthesis of pre-polymer in which the carboxylic acid was reacted with amine. The goal of the second step (Figure 6.1 S1.B) is to transform all possible functional groups into new moieties capable of forming hydrogen bonds. This was realized by reacting the pre-polymer with urea.

The urea can certainly interact with amino group giving way to the formation of 1, 3 dialkyl ureas or 1, 1 dialkyl ureas with excellent product yield of 95% [190, 191]. Thus the networks are allowed to crosslink and form self-assembling polymeric material. A set of controlled experiments were carried out on specimens as listed in previous chapter. The desired material with good product yield is one of the significance of this reaction. The thermal reaction conditions serve to be key factor that controls the reactivity of the primary and secondary amino groups of diethylenetriamine with fatty acids. In the absence of solvents, 1, 3 diamides will be the main product. This may be due to the steric reasons that the primary amines are more reactive than the secondary amines. This was further verified using $^1$H and $^{13}$C nuclear magnetic resonance techniques as shown in Figure 6.9.

Further, an effort has been made by using the clay in an in-situ formation of polymer nanocomposites by intercalating the clay gallery gaps by the polymer. This allows the controlled research for the synthesis of multifunctional materials with customized material properties. The ability of polymers to form well-distinct nanostructures has been exploited in the bracket of self-healing polymer nanocomposites by combining the polymer with nanoparticles that would not usually form nanostructures. Recently, the mixture of montmorillonite nanoclay with polyurethane in a selective solvent condition has led to the enlargement of a
high performance elastomer [192]. In the present study, without using any solvent we have developed self-healing polymer nanocomposite using montmorillonite clays which were either pristine or organically modified with quaternary ammonium salts that are cheap and abundantly available.

Table 6.1 details of stoichiometries of materials used for synthesis are given in previous chapter of this thesis. The compound SMPNa⁺ contains natural sodium montmorillonite with no organic modifier in it of which 3% clay loading in the master batch was added into the Sebacic acid-DETA reaction mixture. The compound SMPA contains nanoclay with organic modifier 2MHTL8 (dimethyl, dehydrogenated tallow, 2-ethylhexyl quaternary ammonium salt), 3% clay was loaded in the master batch was added into the sebacic acid-DETA reaction mixture. The compound SMPB contains nanoclay with organic modifier MT2EtOH (methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium salt), 3 wt. % clay was loaded in the master batch was added into the sebacic acid-DETA reaction mixture.

<table>
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<th>SMPB</th>
<th>SMPNa⁺</th>
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<tbody>
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<tr>
<td>DETA (mmol)</td>
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<tr>
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<td>-</td>
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<td>&gt;95</td>
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</tr>
</tbody>
</table>

*Table 6.1* the stoichiometries of materials used for the synthesis of supramolecular polymer pre-polymer, SMP (standard self-healing polymer), SMPA, SMPB and SMPNa⁺ nanocomposites.

### 6.3 Self-Healing Studies

The healable polymers that are made of supramolecular networks are considered well and treated as future materials that can address the damage issues in polymers. A big deal of global attention is focused on this research field recently.
These attempts were concentrated on fibre reinforced polymer nanocomposites. It has become an engineering requirement for polymer materials to consider seriously about its reparability and reusability. There exists a gap in the literature to explore nanoclay based polymer nanocomposites having the capability to repair its damages.

We are exploring our research in this window to develop novel polymer materials that are healable supramolecular polymer nanocomposites. The Polyacid-polyamine combinations optimised in earlier chapters of this thesis are used to determine the key factors in governing the selection of candidates used for synthesis. The highest chain lengths to lowest chain length dicarboxylic acids are studies for the effects on the formation of nanocomposite in the previous chapters. Also the type of montmorillonite nanoclays and their influences on the formation of nanocomposite are also studied well in the previous chapters.

Thus we decided to use the natural montmorillonite nanoclay as nanofiller that is expected to be get intercalated into the polymer matrix. Also other organically modified nanoclays are used because they have shown a high level of exfoliation into the polymer matrix and they can alter the self-healing ability of polymer nanocomposites. Organically-modified clays may be clays modified with hydroxyl (-OH) groups, which can enhance the hydrogen bonding capacity of the self-healing nanocomposite. The presence of hydroxy groups (-OH) in nanofillers such as MT2EtOH (FTIR spectrum; Fig 6.12) can enhance hydrogen bonding interactions between the nanofiller and the polymer matrix. While coming to the thermal stability just as discussed in the previous chapters a higher chain length dicarboxylic acid such as sebacic acid was decided to be used to conduct the further studies. The welding process of cut surfaces is a known technique where polymer surfaces were melted about its glass transition temperature and kept in contact for longer period so that the pristine mechanical strength are restored. The problem with this technique is that the welded part will remain the weakest part to occur damage for another time at the same point and thus this technique cannot prove itself as an efficient one to repair cracks in polymer surfaces. Thus this approach will be the one which needs the human or mechanical intervention on continuous basis that can ensure a temporary answer to the issue which in turn will highly influence the maintenance cost of the polymer product.
Figure 6.2 Optical microscope images of a polymer SMP taken (a) 2, (b) 10, (c) 20, (d) 40, (e) 60 and (f) 90 seconds after a cut is made on the surface of the nanocomposite. The composition of this nanocomposite was sebacic acid/DETA/Urea.

The networks were allowed to crosslink and form polymeric material; then intentionally damaged by creating a scratch. Figure 6.2 demonstrates the healing of a mechanical damage created on nanocomposite polymer SMP. The digital photos of sebacic acid/DETA/Urea/CNa+ is given in appendix figure 1.

Figure 6.3 Self-healing efficiency of nanocomposite polymer. Optical microscopic images of a deliberately damaged nanocomposite specimen after (a) less than a 1 minute, (b) after 3 minutes, (c) after 5 minutes, (d) after 7 minutes (e) after 8 minutes, and (f) after 15 minutes. The rapid self-healing capability of the nanocomposite once after a cut is made on its surface is visually demonstrated. The scratch was made on its surface. The composition of this nanocomposite was sebacic acid/DETA/Urea/C25A.
This standard polymer was exfoliated with C25A and healing on its surface was studied using optical microscopic technique as given in Figure 6.3. When the damaged area was left to expose at room temperature the damaged area gradually vanished. The self-healing of the supramolecular nanocomposite polymer was estimated by making a small mark at the centre of the sample with a surgical blade attached to a calliper, and then damaged by cutting the samples to a depth of nearly 60–80% of their thickness, which allowed for specific depth control of known length ‘l’ at room temperature.

The healing ability is an inbuilt material response rather than by design. It occurs automatically and instantaneously without any manual involvement indicating the existence of an automatic self-healing behaviour. The self-healing capability of the nanocomposite made with C30B when a cut is made on its surface is visually demonstrated in Figure 6.4.

![Figure 6.4](image)

**Figure 6.4** Self-healing efficiency of nanocomposite polymer. Optical microscopic images of a deliberately damaged nanocomposite specimen after (a) less than a 1 minute, (b) after 5 minutes, (c) after 6 minutes, (d) after 7 minutes (e) after 8 minutes, and (f) after 15 minutes. The composition of this nanocomposite was sebacic acid/DETA/Urea/C30B.

Even though the cut is made at micrometre or even smaller scales, the actual act of cracking is in molecular level. To determine the mechanism of self-healing and improved mechanical strength we used controlled characterisation techniques such as dynamic mechanical analysis as shown in Figure 6.13, along with the hold of more characterisation techniques like thermal analysis involving thermal gravimetric analysis results Figure 6.15 and differential scanning calorimetry.
results given in Figure 6.17, Attenuated total reflectance-infrared spectra given in Figure 6.10, nuclear magnetic resonance spectra given in Figure 6.9. Moreover the self-healing process is better demonstrated with the help of digital photos given in Figure 6.7. Material properties including the stability to higher temperatures and mechanical material goods of the resulting nanocomposites (SMPNa⁺, SMPA and SMPB) were also evaluated and compared to that of the nanoclay unfilled polymer compound (SMP).

6.4 Thermo Reversible Self-Healing Polymers

The comparable efficiency of ‘original’ polymer nanocomposite, and ‘healed’ polymer nanocomposite after a cut was made in the original nanocomposite and then healed at 90 ºC for 5 minutes followed by air cooling for 15 minutes. As shown in Figure 6.6 and Figure 6.7, the nanocomposite retained its physical shape, material characteristics after damaged and healed. They also exhibited temperature-responsive self-healing behaviour. The study of SMPNa⁺ showed an 81% healing efficiency by use of a thermal energy (85-95 ºC). The scheme below show the hydrogen bonding while heating and cooling the polymer nanocomposites is shown in Figure 6.5. which is reproduced from K J Lee et al [149].

![Figure 6.5](image)

*Figure 6.5  Schematic drawing of the polymer nanocomposites which are associated via hydrogen bonds while at (a) low and (b) high temperatures.*
The present study enables the damage to be repaired as the interfaces are brought together in close proximity. Desirably, the interfaces are brought into direct contact with one another. The self-healing nanocomposite may exhibit autonomic mending by thermal treatments and promote repair of the damage site. The self-healing capability of the supramolecular polymer nanocomposite described here is promoted by the noncovalent bonding interactions between the macromolecule and the crosslinking agent used to form the cross-linked matrix of the nanocomposite. The noncovalent bonding interactions provide reversible crosslinks in the polymer matrix.

Thus this approach will be the one which needs the human or mechanical intervention on continuous basis that can ensure a temporary answer to the issue which in turn will highly influence the maintenance cost of the polymer product. The beneficial part of the polymer nanocomposite described here is its capability to have the similar strength at the healed parts of the polymer rather than being the weakest site.

Figure 6.6  SEM micrographs showing the healing process of SMPNa+. (a) Fresh polymer after deliberately damaged, (b) after healing performed at 90 °C for 1 minute, (c) after healing performed at 90 °C for 3 minutes (d) after healing performed at 90 °C for 5 minutes and cooled in air.

The self-healing nanocomposite advantageously is capable of repeated self-healing. That is, the nanocomposite is re-mendable and may undergo repeated
damage and repair at the same site without substantial loss or compromise of the physical and mechanical properties of the nanocomposite.

![Figure 6.7](image)

**Figure 6.7** The digital photos of thermo reversible self-healing polymer SMPNa+ before, while and after a cut is made on its surface is demonstrated. (a) Fresh polymer, (b) after the polymer been deliberately damaged, (c) after healing performed at 90 °C for 5 minutes and cooled in air. The composition of this nanocomposite was sebacic acid/DETA/Urea/CNa+.

The welding process of cut surfaces is a known technique where polymer surfaces were melted about its glass transition temperature and kept in contact for longer period so that the pristine mechanical strength are restored. The problem with this technique is that the welded part will remain the weakest part to occur damage for another time at the same point and thus this technique cannot prove itself as an efficient one to repair cracks in polymer surfaces. Upon failure or damage of the nanocomposite, crosslinks present in the matrix may be broken or disrupted as a result of the stress suffered by the nanocomposite during fracture or damage. The ability to reform the crosslinks through reestablishment of the non-covalent bonding interactions enables the nanocomposite to be repaired. Accordingly, this is an impressive characteristic of the nanocomposites that they can repair its damages more than once.

These polymers can heal their cracks or damages through a mild thermal treatment at a temperature in the range which will go up to a maximum of about 90°C. The type of conditions under which the supramolecular polymer nanocomposite exhibits self-healing capability may be influenced by the nanofiller. Where the nanofiller used is montmorillonite nanoclay particles, varying the type of nanoparticles used can allow the nanocomposite to exhibit self-healing capabilities under different conditions. This is evidenced by forming nanocomposite including organically-modified nanoclay particles may exhibit self-healing at ambient room temperature, while another nanocomposite of the
including nanoclay particles derived from pristine clays may exhibit self-healing at an elevated temperature.

Functional groups on the nanoparticles may also influence self-healing behaviour if such groups are capable of participating in non-covalent bonding interactions. The polymer chains in the thermally healable polymer can be reconstructed and redesigned to any shape of choice. The 100% recyclability of this polymer system using thermal energy is a major advanced while considered in combination with the repairing ability. This property may be attributed to the fact that hydrogen bonds associate while cooling down the polymer and dissociate when temperature is applied as shown in Figure 6.5. These advancements can be considered as major improvements while designing a thermosetting polymer.

6.5 Morphology of Polymer Nanocomposites

As described in previous chapter, the primary techniques used for the characterisation of the polymer nanocomposites are XRD, SAXS, SEM, optical microscopy and NMR. These methods have been used to investigate and confirm the formation of nanocomposites and understand more about the clay distribution throughout the polymer matrix during the formation of nanocomposite. Thermal and mechanical studies were also employed to understand how the structural differences of polymer and organoclay affect the physical properties of polymer nanocomposites.

6.5.1 X-Ray Diffraction Studies

The X-ray diffraction (XRD) patterns of montmorillonite nanoclays and montmorillonite modified polymer nanocomposites are shown in Figure 6.8. The molecular chains of organic modifier will make the clay platelet gallery of montmorillonite to get either intercalated or exfoliated morphology depending on the type of nanoclay used. The thereby increased clay spacing has become evident through the XRD of montmorillonite clays and their corresponding nanocomposites. The pattern of curves will be usually analysed according to polymer matrix and the organoclay interactions.
Figure 6.8 Characteristic XRD patterns of base material (SMP), montmorillonite clays (CNa+, C25A & C30B) and nanocomposites produced from them (SMPNa+, SMPA and SMPB respectively). The XRD pattern clearly indicates the total shift in SMPNa+ and absence of diffraction peaks for montmorillonite clays in SMPA and SMPB compounds, indicating the formation of delaminated nanocomposites.

The peaks correspond to the peak of pristine montmorillonite at 2\(\theta\) = 4.2 (C25A), and 4.8 (C30B) relates to 1.8 nm interlayer spacing for SMPS, SMPSA and SMPSB nanocomposite compounds. While 2\(\theta\) = 7.4 (CNa+) corresponds to 1.19±0.01 nm interlayer spacing which was completely shifted to 1.39±0.01 nm interlayer spacing in the diffraction peaks of SMPNa+ nanocomposite compound, demonstrating the silicate layer are entirely intercalated to form polymer nanocomposites.

The inset peak shown in Figure 6.8 shows a peak for the montmorillonite clay at 21.7 and this corresponds to the inter gallery spacing of 1.4±0.01 nm which is being shifted to 19.7. Moreover, the characteristic peaks of C25A corresponding to 1.86±0.01 nm and of C30B at 1.85±0.01 nm are completely disappeared in SMPS, SMPSA and SMPSB. This is also a clear indication of exfoliated montmorillonite nanoclay into the delaminated polymer matrix. Thus, the clay alteration of the polymer nanocomposite is accountable for the swelling of the clay platelets.

The varying different peak positions for the pristine montmorillonite CNa+ and its modified versions indicate the fact that the organic modifiers used in the
nanoclays C30B and C25A create exfoliated clay galleries. The addition of these nanoclays into the polymer matrix form nanocomposites with exfoliated molecular chains in polymer. These molecular interactions between the nanoclay and polymer matrix determine the gallery spacing in these supramolecular polymers. The broad characteristic peak of nanoclays has been disappeared in the nanocomposites while showing small humps towards a higher diffraction angle. This is attributed to the fact that a better case of exfoliation is shown by these nanocomposites may be contributed by the organic modifier present in C25A montmorillonite nanoclay.

Compound C30B have hydroxyl bonding groups in the nanoclay matrix which can increase the polymer matrix-filler interaction to enhance the dispersal of the nanofillers and thereby the material properties. Moreover the pre-polymer, unreacted urea, bridging urea, hydroxyl groups of nanoclays etc. all is ready to form hydrogen bonds within the nanocomposites. This enables the association of molecules to each other by hydrogen bonds and demonstrates the magnificent self-healing properties at room temperature.

6.6 Spectroscopic Studies

The better understanding of the molecular level interactions are made through NMR spectroscopic techniques and functional group wise interactions are elucidated here using the FTIR technique.

6.6.1 Nuclear Magnetic Resonance Spectroscopy

Solid state NMR spectroscopy was used here in characterising the polymer/MMT nanocomposite morphology. Generally speaking solid state NMR spectroscopy is largely used as a conventional and proven tool to identify and distinguish the chemical molecules and its structures. Only a few studies are done by applying NMR as a tool to analyse polymer/MMT nanocomposites [139-141]. Those studies successfully used the technique to understand the level that the nanoclays platelet gets dispersed in the nanocomposite and also they suggested a theoretical relationship between the clay dispersion and relaxation times. Here in this study we mainly used solid state NMR spectroscopy to identify the chemical species and its interactions. Samples were dissolved in CD3OD. Proton signals reported
as chemical shift \( \sigma \) (ppm). The carbon signals were recorded as chemical shift \( \sigma \) (ppm). The identified peak positions corresponding to the molecular interactions from NMR spectroscopy are given under Figure 6.9

![Figure 6.9](image)

**Figure 6.9** \(^1\)H and \(^{13}\)C NMR spectroscopic peaks of the pristine self-healing polymer.

\(^1\)H NMR (400MHz, CD\(_3\)OD)\( \delta \) (ppm): 1.29(4H,s); 1.52(2H,s);2.3(2H,m); 2.7-2.8 (NHCH\(_2\)CH\(_2\)NH\(_2\),m); 3.3-3.5(C(O) NHCH\(_2\)CH\(_2\)NH,m).

\(^{13}\)C NMR (400 MHz, CD\(_3\)OD) \( \delta \) (ppm): 164.4 (C=O amide), 175.2 (C(N)N imidazoline), 48.3 (CONH-CH\(_2\)-CH\(_2\)-NH), 42.7 (NCH\(_2\)CH\(_2\)N imidazoline), 36.9 (CH\(_2\)-CONH), 29.5-28.7(CH\(_2\) and CH), 26.3 (CH\(_2\)-CH\(_2\)-CONH).

### 6.6.2 FTIR-ATR Spectroscopy

**FTIR-ATR** spectroscopy is an efficient method to gain better understanding the H-bonding and encapsulation process of nanoclay particles into the polymer compound (polymer compound into the silica surface) while on the process of insitu-polymerisation of the nanocomposites. The positions of peaks for distinctive functional groups that are affected by presence of MMT nanoclays are studied here. Also the formation of characteristic infrared bands for different functional groups involved in the polymer formation and its changes will give key evidences. In order to confirm the assumption that the interface between the
polymer and nanoclay makes the formation of polymer/MMT nanocomposite, the condition of polymer and nanoclays can be studied using FTIR spectroscopy. The process of polymer grafting into the modified silica surface is mapped out here on the basis of the hydrogen-bonding interactions amongst the pre-polymer, standard polymer (SMP), organo modified montmorillonite nanocomposites (SMPA, SMPB) and montmorillonite nanocomposites (SMPNa+) in the FTIR spectrum is given here. Demonstrating the FTIR-ATR study for SMPA, SMPB and SMPNa+ samples in Figure 6.10 and Figure 6.11 it shows that the carbonyl band is probably seen to be in the 1605-1650 cm\(^{-1}\) region and the amide bands of urea are at 1560-1530 cm\(^{-1}\). The Symmetrical and asymmetrical \(-\text{CH–}\) vibrations are observed at 2750 and 3100 cm\(^{-1}\).

The FTIR-ATR spectrum of polymer nanocomposite showed a peak at 3265 cm\(^{-1}\) which is corresponding to the N–H hydrogen bonds and peak at 3295 cm\(^{-1}\) peak indicates that of free N–H groups. Peaks at 1655 cm\(^{-1}\) shows the effect of hydrogen bonding C=O group and analysing the peak position at 1630 cm\(^{-1}\) gives information for free C=O.

![Figure 6.10](image)

*Figure 6.10*  FTIR-ATR spectra of pre-polymer, pristine SMP and modified nanocomposite compounds SMPNa+, SMPA and SMPB.
The stretching vibration of Si–O–Si, Al–O by the polymer nanocomposites gave characteristic peaks at 1060, 920 cm\(^{-1}\). The montmorillonite gave bending vibrations for its Si–O to give peaks at 670 cm\(^{-1}\). These characteristics evidence the intercalation of polymer chains into the montmorillonite clay gallery.

**Figure 6.11** FTIR-ATR spectra of, pristine SMP and modified nanocomposite compounds SMPA and SMPB showing the symmetrical and antisymmetric –C-H vibrations.

**Figure 6.12** FTIR-ATR spectra of, pristine SMP and modified nanocomposite compounds SMPA and SMPB showing the SiO-H bonds.
As shown in Figure 6.12, the nanocomposites show the following characteristic bands at 3600–3900 cm⁻¹ analogous to the OH stretching of Si-OH groups. The water molecules trapped in interlayers of the nanoclay contribute to the peaks at 1640 cm⁻¹ due to the deformation vibrations and 1030 cm⁻¹ due to asymmetric Si-O-Si stretching.

Thus it is found that the characteristic peak positions for functional groups are similar with the standard polymer compound, indicating that the polymer nanocomposites segmented structure has not been interrupted by the montmorillonite nanoclays and its organic modifiers. Broad peaks developed in compound SMPA and SMPB, with respect to anti-symmetric and symmetric stretching vibrations of the hydrogen bonding groups. It was observed that SMPA with less number of hydrogen bonding groups have less intense peaks compared to SMPB with the bigger intensity peak in explains to the hydrogen bonded stretching vibrations. This was also evidenced these compounds quick self-healing capability at room temperatures. Thus the spectroscopic studies of these polymers confirmed the presence hydrogen bonding interactions and explain the provision of anchor groups for further functionalization.

### 6.7 Mechanical Properties

Dynamic mechanical analysis was used as an effective resource to study the transition and relaxation behaviour of polymer systems. The DMA curves illustrating the time dependence of relaxation modulus clearly compares the effect that the addition of nanoclay into the polymer compound SMP, the polymer matrix has made to change progressively the mechanical properties of compound SMPNa⁺, SMPA and SMPB. Figure 6.13 better explains the comparison of mechanical strength of nanocomposites SMPNa⁺, SMPA and SMPB to the base material SMP and confirms the fact the addition of clay has a significant role in improving the mechanical properties. Different type of nanoclay has varying effect on the mechanical properties can also be understood from this study.

The mechanical property relaxation modulus is the variation in stress while retaining a constant strain in a given time. The mechanical strength of SMPNa⁺, SMPA and SMPB nanocomposites have significantly varied compared to pristine
SMP, representing that the layered silicate has an improved purpose on the polymeric matrix. The layered silicates perform as high aspect ratio strengthening, comparable to fibres inside a fibre-reinforced plastic, and consequently vary the mechanical strength of the standard polymer SMP. By the addition of organically modified nanoclays the decreased the mechanical strength of the SMPB and SMPA can be due to the incompatibility of polymer with C30B and C25A clays. On the contrary Na-MMT (CNa⁺ montmorillonite) layers present in SMPNa⁺ were intercalated in the polymer matrix to enhance its mechanical properties when the clay was added through a two-step approach. The two-step involves the addition of nanoclays to the pre-polymer at an elevated temperature. The relaxation modulus of SMP gradually starts to decay while the nanocomposites give an adjusting or a linear nature of relaxation modulus for a given time. This is the major difference in the mechanical property of these various polymer networks. At the points of time when the exponential decay of relaxation modulus of polymer domain gets noticeable, the following assumptions can be made for relative decrease of the relaxation modulus.

According to the Figure 6.13 the dotted lines illustrates in the steadily decreasing relaxation modulus of the base material SMP as a function of time while the solid lines on either sides of it shows the enhanced relaxation modulus of SMPNa⁺ or

![Figure 6.13](image)

**Figure 6.13** DMA test results showing the relaxation modulus as a function of time which proves that the diverse variations in mechanical strength of nanocomposites (SMPNa⁺, SMPA and SMPB) as a comparison between the standard polymer material SMP.
the decreased relaxation modulus for the SMPA and SMPB nanocomposites. The lower inset picture shows the schematic representation of DMA compression test on the supramolecular polymer sample. The relaxation modulus of nanocomposites with 3 wt. % montmorillonite loading has different effects on incorporation of different organic modifiers in the nanoclay matrix. Whilst the nanocomposites with same 3 wt. % montmorillonite loading with different organo modifiers 2MHTL8 in SMPA and MT2EtOH in SMPB or none in SMPNa+ shows a difference. The detailed structure of these organo modifiers are given in chapter 5 in Figure 5.1 and Table 5.2. The SMPB behaves with more strength compared to SMPA, which may be probably due to the silicate clays with -OH groups in it have more hydrogen bonding and high activity begin to aggregate along with the abundant montmorillonite which results the outstanding combination of material goods such as improved mechanical strength and rapid self-healing capability. The nanocomposite SMPNa+ with sodium montmorillonite nanoclay gave a linear straight line indicating its stronger and stiffer nature and there by higher modulus.

The SMPNa+ was excellent in demonstrating temperature stimuli responsive behaviour enables calling it a thermo-reversible self-healing polymer capability. Typically at 70-90 °C and 30 seconds processing time these nanocomposites display properties such as remelt ability, reprocess ability and recyclability. After slowly cooling to room temperature (100-120 min) a rigid structural polymer network can be attained because of the regeneration of the cross links. In this process the polymer chains are capable of reconstructing or remodelling themselves into any desired physical shape. Beside the self-healing capability, these nanocomposites show other properties such as re-cyclability and re-networkability. This could be very convenient choices form an economic point of view. The mechanical properties were also studied before and after the self-healing process was employed to show that the nanocomposites retain its mechanical strength after healing any crack which was vertical to the tensile direction on its surface as shown in Figure 6.14.

Giving mechanical properties similar to commonly available polymer materials, it is indicated that these materials can be used as potential substitutes for the existing conventional polymers. It is also observed from the mechanical testing
that it gave almost the same performance even after a healing step has been performed on the polymer surface. From Figure 6.14 and Table 6.2, it explains that the mechanical property of supramolecular polymer SMPNa⁺ by plotting a comparison between the mechanical strength of original and healed sample. To determine the healing efficiency of self-healing nanocomposite SMPNa⁺ in a quantitative manner, pieces were damaged and healed as described above. We conducted stress–strain experiments on ‘original’ and ‘healed’ samples, and the healing efficiency was expressed using tensile strength as a measure of the efficiency of a component and was calculated using the equation (1) given below:

\[
\text{Healing efficiency} = 100\% \frac{\text{tensile strength healed}}{\text{tensile strength original}} \rightarrow \text{Equation (1)}
\]

Here tensile strength healed is the tensile strength of the healed sample set and tensile strength original is the tensile strength of the original sample set.

![Figure 6.14](image) Representative stress-strain curve on a tensile testing machine for original and healed nanocomposite SMPNa⁺ specimen which exhibits a thermo reversible self-healing behaviour. The curves demonstrate the comparable efficiency of the healed nanocomposite polymer with the original nanocomposite polymer, even after a cut and healing was performed on it. The healing was done at 90 ºC for 5 minutes and it was later cooled in air for 15 minutes.

Employing a thermal stimulus that range from 80-90 ºC these polymers exhibited a healing efficiency of approximately 81%, which is considered significant for a polymer nanocomposite without using any additional components for the healing
process. In summary, this study demonstrates a solvent free, high yielding in-situ synthesis method which gave birth to two types of novel repairable nanocomposites that exhibit the self-healing ability at room temperature without employing healing agents or external stimuli. A strategy to increase the physical, thermal and mechanical properties of these compounds was also recommended by the incorporation of nanoclays into the polymer matrix.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation-to-Break (%)</th>
<th>Young’s modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>3.2 ±2.5</td>
<td>12.9±0.5</td>
<td>125.5±0.4</td>
</tr>
<tr>
<td>Healed</td>
<td>2.7±2.8</td>
<td>13.5±0.2</td>
<td>154.4±0.7</td>
</tr>
</tbody>
</table>

Table 6.2  Tensile Test Data

It is proven that structural modification of polymer nanocomposites are related to polymer molecular networks and that are quite related to the physical and mechanical properties. The enhanced matrix-filler interaction enables better dispersion of the nanofiller to construct hydrogen bonding groups in the supramolecular polymer matrix. This can improve the thermal and other material properties of the self-healing polymer nanocomposite. Moreover, other than the organically modified nanoclays the Na-MMT layers were intercalated during polymerisation which increases the thermal stability and gives enhanced mechanical properties along with thermo-reversible self-healing ability. This method can be used to produce structure responsive self-healing materials with improved thermal and mechanical properties.

Perhaps the most exceptional characteristic of this repairable polymer system is its capability to undergo the healing step multiple times, without significant loss in activity. This will meaningfully extend the lifetime of the polymer. This aspect of the work will need further experimentation to prove and can be considered as an objective for future development. Supramolecular materials of this type have potential applications in adhesives and coating technologies. The further improvements in physical and mechanical properties are under exploration.
6.8 Thermal Studies of Polymer Nanocomposite

6.8.1 Thermo Gravimetric Analysis

The TGA data provides information regarding their thermal stability and thermal degradation behaviour of nanocomposites. The TGA data provides evidence about their thermal permanence and thermal degradation behaviour of polymer nanocomposites. The TGA examination of the pre-polymer, pristine (SMP) and clay modified polymer nanocomposites (SMPNa⁺, SMPA, SMPB) is shown in Figure 6.15 and Table 6.3 lists the thermal degradation, onset temperature and the yield of charred residue at 900°C. In this study, the indicators for the thermal permanence for the polymer compound are the peak decomposition temperatures (the thermal point where the maximum rate of decomposition occurs), and the equivalent peak decomposition rates (prevailing rate at a particular peak decomposition temperature) were also tabulated.

![Figure 6.15 Typical TGA curves for pre-polymer, pristine self-healing polymer SMP and modified nanocomposite compounds SMPNa⁺, SMPA and SMPB.](image)

The peak decomposition temperature of the SMP is almost same as that of compound SMPNa⁺. In this study, there was a decrease for peak decomposition rate for the compounds SMPA and SMPB. This enhancement in thermal stability is due to improved polymer-filler contact through either intercalation or exfoliation, or both together of the montmorillonite clay into the polymer matrix.
Thus it is evident that for given clay loading with the increased presence of OH-groups the peak decomposition rate will gets decreased. The role of hydrogen bonding groups on the thermal decomposition developments at equivalent montmorillonite loading of 3% was compared for polymer nanocomposites SMPA and SMPB. The clay layers intercalated within the montmorillonite gallery (compounds SMPA and SMPB) effects greater thermal stability than standard compound. Compounds SMPA and SMPB) effects greater thermal stability than standard compound. The clay modified polymer nanocomposites SMPNa+, SMPA and SMPB which degrades a little quicker than standard compound SMP. This is attributed to the fact that nano-sized organic particles are be likely to get degraded before the polymer, triggering a weight loss in the polymer nanocomposites. In the meantime, it is established that the onset temperature of thermal degradation has decreased more with the clay loading, due to the type of organic modifier used in clay also affects the degradation temperature of polymer nanocomposite.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Pre-Polymer</th>
<th>SMP(Standard)</th>
<th>SMPNa⁺</th>
<th>SMPA</th>
<th>SMPB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onset Degradation Temperature (°C)</td>
<td>285</td>
<td>415</td>
<td>420</td>
<td>440</td>
<td>450</td>
</tr>
<tr>
<td>Residual mass 900°C (%)</td>
<td>18</td>
<td>11</td>
<td>8</td>
<td>6</td>
<td>7</td>
</tr>
</tbody>
</table>

**Table 6.3 TGA Data of polymer nanocomposites**

Consequently, the thermal resistance of SMPA nanocomposites contains 2MHTL8 organo modifier is lower than that of SMPB which contains MT2EtOH as organo modifier. After a complete degradation above 400°C of the clay particles, the clay modified polymer nanocomposites exhibit developed thermal strength compared to pristine compounds which may be due to the presence of silicate clay. However, the volume of residue is varying by the type of clay modifier present in the polymer nanocomposite matrix.
The reason for that may be due to the reassociating silicate layers that may happen on the surface of the polymer nanocomposites. This layer may degrade on thermal exposure. The greater insulation property of silicate clay helps in acting as a mass-transport barrier against the formation of volatile products and at the same time to act as an insulator thereby increasing the thermal stability.

Moreover, the start of breakdown of pristine polymer nanocomposite SMP was observed to happen at about 165 °C and extreme degradation happened at around 290 °C. The integration of C25A nanoclay to the pristine polymer have shown to reduce the initiation temperature because of the existence of residual polymer of lower molecular weight. The extreme breakdown temperatures for nanocomposites SMPA and SMPB were improved to 440 °C and 450 °C respectively. Normally it is assumed that the integration of inorganic constituents to polymers could enhance its various material properties including their thermal strength.

![Figure 6.16](image.png)

*Figure 6.16 shows the T50% of dicarboxylic acid based nanocomposites made using C30B nanoclay compared to other carboxylic acids.*

The survival of residue at 900°C in the TGA curves is credited to the existence of the inorganic clay in polymer nanocomposites. It is believed that intercalated polymer chains into clay layers can avoid direct contact of those chains to thermal
impact. Thus the exfoliation of nanoclay layers into the polymer matrix are well accounted to the increase in the thermal stability of polymer nanocomposites.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Glutaric acid</th>
<th>Pimelic acid</th>
<th>Azelaic acid</th>
<th>Sebacic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>T15% (°C)</td>
<td>422</td>
<td>458</td>
<td>463</td>
<td>465</td>
</tr>
</tbody>
</table>

*Table 6.4: T15% value of dicarboxylic acid based nanocomposites made using C30B nanoclay*

This is in accordance with the increasing order of carboxylic acid chain length. This can probably be attributed to the fact that higher chain length will favour higher thermal stability. This is possible by the better intercalation of molecular chains of nanoclays and carboxylic acids. Figure 6.16, shows the T50% of dicarboxylic acid based nanocomposites made using C30B nanoclay compared against each other. Also a table 6.4 with T15% values give shows the decomposition temperature or in other words the thermal stability goes in the following order.

Glutaric acid < Pimelic acid < Azelaic acid < Sebacic acid.

### 6.8.2 Differential Scanning Calorimetric Studies

The thermal properties of the polymers were measured by DSC technique too. TA Q200 differential scanning calorimeter instrument was used to carry out the Differential scanning calorimetric (DSC) experiments. The measurement was conducted using 5–10 mg of the polymer sample under nitrogen atmosphere. On an initial step, the samples were heated to 170 °C and were kept isothermal there for 3 min to eliminate any thermal history if present. Later, the samples were cooled to -70 °C at a rate of 10 °C per minute, kept isothermal for 5 min and further heated to 170 °C at 20 °C per minute. The glass transition temperature (Tg) was calculated as the middle point of the second heating scan of the plot in the DSC thermo grams. All the samples were tested at similar test conditions. The test results for the Pristine SMP, montmorillonite nanoclay modified SMPA, SMPB and SMPNa+ polymer nanocomposite samples are shown in Figure 6.17.
The DSC results show how glass transition temperature (Tg) varies for the different nanocomposites. The glass transition temperatures (Tg) of samples are indicated in the graph. The heating rate of 20 °C/min is used for all samples. The study of glass transition temperature, (Tg) was identified to be important as the presence of some components will affect the structure of molecules and thereby the thermal stabilities. The glass transition (Tg) temperature of compound SMPB was observed at 24 °C, SMPA exhibited Tg at 30.5 °C while SMPNa+ gave Tg peak at 18.5 °C and for the pristine compound SMP at 26 °C, respectively. These can be explained on the basis of easy mobility of the clay chains within the polymer matrix layers thus ascertaining the intercalated nature of the organically modified nanoclay nanocomposites. The Tg of SMPNa+ as compared to SMPA is lower. This is attributed to the higher thermal stability of the organic modifier, present in Cloisite 25A, which is single tallow with an ethylhexyl group. As the reviewer suggested, this will be applicable to explain the differences of glass transition temperature of other polymer systems too.

![Figure 6.17 DSC thermogram comparing DSC results obtained for the nanocomposites made from a cross-linked polymer matrix including pre-polymers derived from Sebacic dicarboxylic acid pre-polymer, standard polymer SMP, nanocomposites corresponding to C25A, C30B and CNa+ nanoclays.](image)

The pre-polymer gave a Tg peak at -5.5±1 °C. A further conclusion regarding the glass transition temperature of all polymer nanocomposites discussed over chapter 4,5 and 6 is given in appendix table 1. In borderer terms the increased glass
transition temperature of the polymer nanocomposites may be attributed to (i) the influence of small amounts of well distributed nanoclay on the polymer matrix (ii) the existence of the intercalated or exfoliated polymer chains inside the nanoclay galleries that limit the polymer chain movements. These can be described on the basis of mobility of the nanoclay chains within the polymer matrix layers.

6.9 Conclusions

Self-healing materials belong to the family of advanced materials that have the capability to repair damage. Here we report self-healing polymer nanocomposites which were not reported in literature till date. Such products may be vulnerable to damage such as cracks or failure due to the product being subjected to continued mechanical stress or from being in continued contact with liquids or other materials. In such circumstances it may be difficult to detect when the product has sustained damage. The inclusion of the nanocomposite in such products means that the products would have the ability to self-heal in a rapid and autonomous manner. We describe the in-situ synthesis of self-healing polymer nanocomposites based on nanoclays and supramolecular polymer network which is intelligent for its rapid self-healing capability. The damage interfaces can be welded together effectively at room temperature very rapidly, in less than fifteen minute time without using any healing agents or external stimuli. This process can be repeated to heal cracks many times. The nanocomposites show enhanced mechanical strength, which makes them practically useful as a new type of self-healing materials in diverse fields such as coatings, adhesives, packing and biomedical applications.

These polymers can repair the damages within a time period from about 12 minutes to about 15 minutes depending upon the type of material synthesized and type of candidates used in the polymer formulation. For instance some of the polymers can repair its damage quite rapidly. Temperature may play a role in healing time, with higher temperatures supporting faster healing processes and shorter healing time. Healing time and temperature may also have an influence on the mechanical properties of the healed nanocomposite. For example, the strength of healed nanocomposite material could increase with healing temperature and healing time which can be considered as a future focus of this work. The healing
 capability of these polymer nanocomposites may be observed visually, using techniques such as optical microscopy and digital photography. Other techniques may also be used. The self-healing properties of the polymer nanocomposite can be tuneable. Tuneable self-healing properties may be obtained by altering the macromolecule, crosslinking agent and/or nanofiller present in the nanocomposite. For example, organically modified nanoclays may provide polymer nanocomposites with decreased mechanical strength, while unmodified nanoclays may provide polymer nanocomposites with increased mechanical strength, compared to a base polymer matrix with no nanofiller. Accordingly, the choice of nanofiller can enable the mechanical properties of the polymer nanocomposite to be adjusted to suit particular applications. Self-healing properties may also be adjusted by varying the relative proportions of these components in the nanocomposite. The self-healing polymer nanocomposite is capable of being reconstructed or remodelled from one physical shape into another, desired physical shape. Accordingly, beside the self-healing capability, the polymer nanocomposites described here exhibit properties of recyclability or rework ability, which could provide advantages from an economic point of view. The self-healing product may take on a variety of forms as the nanocomposite is capable of being moulded or shaped to adopt a desired form. The ability to alter the physical shape of the nanocomposite may be influenced by the types of monomers used to form the macromolecule employed in the nanocomposite. i.e. higher the chain length of the dicarboxylic acid the better will be the corresponding nanocomposites material properties.

These materials can be potentially used as self-healing coatings. The self-healing coating may be in the form of a film that is applied to a substrate surface. For example, the self-healing coating may be in the form of a self-healing paint coating. Such coatings may be susceptible to damage from scrapes or scratches and the ability of the coating to self-heal autonomously could represent a significant advantage. Also the polymer nanocomposites can be used in a wide range of applications due to the ability to tune the properties of the nanocomposite to suit a particular application. This study can also be considered as a developed strategy to advantageously enhance the tensile strength according to the requirement. Nanocomposites with favourable tensile properties may be used to
construct biomedical materials or products suitable for use in humans and other animals. The polymer nanocomposites may also be used to in the preparation products such as high performance parts, cosmetics, dental materials, toys or seals. The patents filed from the developments of this technology will help a commercially feasible process for producing a novel class of self-healing materials.
CHAPTER SEVEN

7 GENERAL DISCUSSION

The fundamental purpose of this chapter is to discuss the work directed towards the hydrogen bonding chemistry of supramolecular polymers in this thesis as a whole with a particular emphasis on the innovative knowledge established as well discuss the research question in this very broad field that remained unattended. This chapter will also consider a constructive approach towards the preliminary results from the characterisation studies. This study demonstrated that XRD studies alone cannot provide sufficient evidences to characterise and understand the bulk morphology of the polymer nanocomposites. This is been complemented by SAXS, SEM, FTIR, NMR and optical microscopic studies to characterise the morphology of exfoliated or intercalated structures of polymer nanocomposites and starting materials. Later the thermal and mechanical abilities of the polymer are evaluated using relevant techniques such as DMA, TGA and DSC. Analysis of these data when drawn together to generate insights toward the selection of monomers and nanoclays while designing polymer nanocomposites that has the capability of forming reversible hydrogen bonds. Also the influence of the molecular structure of monomers and nanoclays over the performance and properties of the polymer nanocomposites are elucidated here. Significant consideration towards the optimisation of process methods was given which helped the timely and successful completion of the project. All these approaches and methods combined to acquire a greater level of appreciation towards the formation of polymer nanocomposites that can reversibly associate together to give novel polymer materials with self-healing property.

In this chapter, the given discussion is based on the significance of optimising the process and synthesis conditions, facts about the selections of nanoclays and their dispersion in the polymer matrix, property study in connection to the structure of the polymer nanocomposites formed.
7.1. Importance of Optimising Process Conditions

Generally, the selection of monomer unit was based on the criteria of having at least two or more reactive functional groups. This enables to conclude at the point that at least two reactive functional groups are required in each monomer unit to enable the co-monomers to link together in the macromolecule chain. A variety of different moieties may be present in the remainder of each monomer unit. The macromolecule in the cross-linked matrix is formed from the condensation polymerisation of a monomer including at least two compatible reactive functional groups. It is therefore concluded that the use of monomers containing at least 4 carbon atoms to prepare the macromolecule can desirably enable better physical properties to be imparted to the macromolecule initially, and later to the nanocomposites as well. Also it is discovered to be desirable for use of molecular groups having at least one unsaturation. Nanocomposites formed with a macromolecule without at least one unsaturation in the polymer chain may display different mechanical strength properties (e.g. lower mechanical strength).

The macromolecule is derived from a co-monomer containing two or more carboxylic acid functional groups (a polyacid monomer) and a co-monomer containing two or more amine functional groups (a polyamine monomer). Here, the carboxylic acid containing co-monomer is capable of reacting with the amine containing co-monomer to form an oligomer, with an amide linkage between the monomer units of the oligomer. The oligomer, which then has a terminal carboxylic acid group and a terminal amine group, may subsequently react with further monomer units bearing an amine or carboxylic acid group so as to form one or more further amide linkages (amide functional groups). This process will happen in the polymer backbone and extend the length of the macromolecule chain. The reaction is desirably carried out under condensation polymerisation conditions.

In another aspect of the synthesis and process for the preparation of the supramolecular polymers includes the association of molecular moieties by hydrogen bonding. On another requirement a nanofiller must also be present. These reacting candidates can be mixed and reacted in a single reaction vessel;
reacting the first monomer and the second monomer to form a macromolecule; and forming non-covalent bonds between the functional groups of the macromolecule. The functional groups of the crosslinking agent in the presence of the nanofiller provide a supramolecular polymer with nanofiller dispersed in the matrix. In such cases, the supramolecular polymer having lots of hydrogen bonding moieties may be formed in a single step process, in the single reaction vessel.

The nature of functional group that is present in the crosslinking agent may be dictated by the nature of functional group present in the macromolecule. For example, where the macromolecule includes hydrogen bond acceptor groups, it would be desirable for the crosslinking agent to include hydrogen bond donating groups to ensure that a hydrogen bond can then be formed between the crosslinking agent and the macromolecule. Conversely, where the macromolecule includes hydrogen bond donor groups, the crosslinking agent may include hydrogen bond accepting groups. The cross-linked matrix of the nanocomposite include any type of crosslinking agent, provided the crosslinking agent contains suitable functional groups that are capable of participating in non-covalent bonding interacting with the functional groups of the macromolecule. The cross-linked matrix includes one type of crosslinking agent or in an alternative case; the cross-linked matrix includes a mixture of two or more different types of crosslinking agents. The cross-linked matrix of the nanocomposite should include at least one diamide crosslinking agent. Diamide crosslinking agents include two -NHR functional groups, which are each capable of interacting with the functional groups of the macromolecule.

In order to interact with the macromolecule, the crosslinking agent includes a multitude of functional groups which are capable of participating in non-covalent bonding interactions. The macromolecule is formed in the reaction vessel, the crosslinking agent may be added before, during or after the macromolecule is formed in the vessel. But our step of preparing a supramolecular nanocomposite include synthesising the macromolecule in the reaction vessel, then adding a crosslinking agent to the vessel after the desired macromolecule has been synthesised. It is an advantage of the process of one or more aspects of the invention that the supramolecular polymer can be prepared in a relatively simple
method that employs fewer steps than other methods described in the literature. As a result, the process described here may be more commercially feasible than other methods for producing supramolecular polymer materials that uses hydrogen bonds for its association.

![Figure 7.1](Image)

Figure 7.1 Hydrogen bonding possibilities while forming supramolecular polymer where (a) urea and amide (-CONH), (b) amide group of polymer (-CONH), and interaction of carbonyl group of carboxylic acid (-COOH)

The three probable forms of hydrogen bonding formations for supramolecular polymer formations are demonstrated in figure 7.1. The possibilities are (a) urea and amide (-CONH), (b) amide group of polymer (-CONH), and interaction of carbonyl group of carboxylic acid (-COOH). Thus it is possible that there are monomeric and dimeric forms of hydrogen bonding possible while forming supramolecular polymers.

The atoms of highly electronegative elements such as fluorine, oxygen or nitrogen gets bonded with hydrogen atom, the designed molecule is polar. Then the electronegative atom of the molecule will form a weak bond with hydrogen atom to be called as a hydrogen bonding. There are two types of hydrogen bonding such as intermolecular and intramolecular hydrogen bonding. Hydrogen bonding has important effect on many physical and chemical properties of compounds. It is one advantage that upon disruption of the non-covalent bonding interactions, the
reversible crosslinks between the macromolecule and crosslinking agent are able to readily re-form under appropriate conditions. In the nanocomposite, the macromolecule and the crosslinking agent are held together in mutual association in the cross-linked matrix by hydrogen bonds such as the hydrogen bonded cross-linked matrix that is formed with a polyamide macromolecule and urea crosslinking agent. The number of crosslinks and crosslink density can be varied to obtain a matrix and nanocomposite of desired characteristics. A variation in the number or density of crosslinks may be achieved by varying the concentration and/or type of crosslinking agent used to prepare the cross-linked matrix.

The increase in the glass transition temperature with vacuum treatment is evaluated for two types of polymer nanocomposites. The vacuum treatment has improved the glass transition temperature which is attributed to the effect of longer carbon chain. The improvement with vacuum treatment can probably be explained by the enhanced stability of lower molecular weight compounds. This trial and error based method used in the present work describes a facile method for the formation of a supramolecular polymer that can associate together using hydrogen bonds through an in-situ process in a single reaction pot. We optimised the process steps via two approaches. The first one was a single-step procedure, involving the in situ polymerisation of appropriate monomers in the presence of a crosslinking agent and nanofiller to produce the supramolecular polymer in a single step. In another approach, the process of the synthesis is a two-step procedure, which involves formation of a macromolecule in a first step, then crosslinking of the pre-formed macromolecule in the presence of nanofiller in a subsequent step, to produce the supramolecular polymer. The pre-formed macromolecule may be optionally isolated during the two-step procedure.

The optimisation of process methodology was based on the primary objective of the project to develop a strategy that can improve the thermal stability of polymers. The two-step approach seems to have improved contribution towards the higher glass transition temperature of the polymers. This contributes towards the possibility of tuning the polymer properties with the help of processing aids. The difference in the glass transition temperature for the polymer which is made through a two-step synthesis method compared to the other which was made through an in-situ process technique. It is an advantage of the process that the
supramolecular polymer can be prepared in a relatively simple method that employs fewer steps than other methods known. As a result, the process described here may be more commercially feasible than other methods for producing supramolecular polymer materials that uses hydrogen bonds for its association.

One advantage of the supramolecular polymer is that its properties can be tuned to suit particular applications. For example, the nanocomposite may be a mouldable nanocomposite, or it may be brittle nanocomposite. Adjustments in the physical properties of the nanocomposite may be obtained by varying the type and concentration of nanofiller in the nanocomposite, as well as by varying the nature of the macromolecule and crosslinking agent used in the cross-linked matrix of the nanocomposite. The supramolecular polymer can be formed in the form of a liquid, such as a viscous liquid. If required some of the supramolecular polymers can be converted to a liquid when heated at an elevated temperature. For example, the polymer will flow like a liquid at a temperature range of 160-180°C. This may be useful where it is desired to prepare products by moulding techniques such as injection moulding. The fluidity of the material makes it promising to control the rate of this process and also to replicate the details of the mould. Also the material can be made in the form of a firm polymer.

7.2. Characterisation of Clay Dispersion in Nanocomposites

Various characterisation techniques are used to integrate the properties of reactants used and products yielded for the synthesis described herein. The shift of diffraction peaks to higher values in nanocomposites using organically modified montmorillonite nanoclays indicate the decrease in interlayer spacing. While the shifting of diffraction peak to a lower value for nanocomposite corresponding to nanocomposites using natural montmorillonite nanoclays evidences the increased interlayer spacing in the polymer/MMT matrices. Thus it appears that the interlaying spacing is highly altered in all the nanocomposites compared to the pure nanoclays. This was recognized as the proof of the intercalation or exfoliation of the molecular chains of polymer into the silicate galleries of nanoclays to form multilayered structures. When montmorillonite nanoclays were modified by organic modifier, the gallery of montmorillonite were either
intercalated or expanded by the long molecular chains of the organic modifier. This theory serves as the evidence for the increased clay spacing upon the addition of the modifier between the nanoclay platelets. The interaction between the polymer matrix and the organoclay highly depend upon the clay gallery spacing of organoclay in polymer nanocomposites. These multilayers may have been formed by various layers of polymer and layered silicate molecules. These facts have been confirmed using XRD technique and further complete morphology of the nanocomposites were techniques such as SEM and SAXS are used to complement the diffraction experiments.

The hydrogen bonding capabilities are described in this thesis with the help of FTIR spectroscopy. The characteristic peak positions for functional groups are similar with the standard polymer compound, indicating that the polymer nanocomposites segmented structure has not been interrupted by the montmorillonite nanoclays and its organic modifiers. Thus these polymers confirmed the presence hydrogen bonding interactions and explain the provision of anchor groups for further functionalization.

7.3. Properties of Nanoclay Dispersed Polymer Nanocomposites

To provide the cross-linked matrix of the nanocomposite described in this thesis, the functional groups of the macromolecule interact with functional groups present in a crosslinking agent by non-covalent bonding interactions. The bonding interactions result in the formation of a cross-linked matrix that is predominantly held together by intermolecular non-covalent bonds between the crosslinking agent and at the chains of the macromolecule. The intermolecular non-covalent bonding interaction is reversible. Accordingly, reversible crosslinks are formed between the macromolecule and crosslinking agent. It is one advantage that upon disruption of the non-covalent bonding interactions, the reversible crosslinks between the macromolecule and crosslinking agent are able to readily re-form under appropriate conditions.

It is believed that the C=O moiety of carbonyl containing functional groups can act as hydrogen bond acceptors for the formation of hydrogen bonds, as the oxygen atom of the carbonyl group contains a lone pair of electrons. Where
hydrogen bonds are formed between the macromolecule and the crosslinking agent, it is desirable for the macromolecule to include hydrogen donating functional groups, hydrogen accepting functional groups, or a mixture of such groups. The functional groups containing a hydrogen atom bonded to an electronegative atom (such as nitrogen or oxygen) can act as hydrogen bond donors, while functional groups containing an atom with a lone pair of electrons can act as hydrogen bond acceptors. Direct interactions between a hydrogen bond donor group and a hydrogen bond acceptor group results in the formation of a hydrogen bond.

One advantage of the supramolecular polymer is that its properties can be tuned to suit particular applications. For example, the nanocomposite may be a mouldable nanocomposite, or it may be brittle nanocomposite. Adjustments in the physical properties of the nanocomposite may be obtained by varying the type and/or concentration of nanofiller in the nanocomposite, as well as by varying the nature of the macromolecule and/or crosslinking agent used in the cross-linked matrix of the nanocomposite. It is observed that a nanocomposite comprising of organically-modified nanoclay particles may exhibit self-healing at ambient room temperature, while a nanocomposite of the invention including nanoclay particles derived from pristine clays may exhibit self-healing at an elevated temperature. This can be attributed the structure-property relationship of the nanocomposites. Functional groups on the nanoparticles may also influence self-healing behaviour if such groups are capable of participating in non-covalent bonding interactions.

The self-healing properties of the polymer nanocomposite can be tuneable. Organically modified nanoclays may provide polymer nanocomposites with decreased mechanical strength, while unmodified nanoclays may provide polymer nanocomposites with increased mechanical strength, compared to a base polymer matrix with no nanofiller. Accordingly, the choice of nanofiller can enable the mechanical properties of the polymer nanocomposite to be adjusted to suit particular applications. Self-healing properties may also be adjusted by varying the relative proportions of these components in the nanocomposite. The optical microscope and SEM images demonstrate the self-healing capability of the nanocomposite following mechanical damage. This thesis describes both types of
polymers that exhibit healing response automatically without any manual involvement and healing ability exhibited upon use of a thermal energy, indicating the existence of an automatic and thermo-reversible healing behaviour.

The self-healing polymer nanocomposite is capable of being reconstructed or remodelled from one physical shape into another, desired physical shape. Accordingly, beside the self-healing capability, the polymer nanocomposites described in this work exhibits properties of recyclability or rework ability, which could provide advantages from an economic point of view. The carbon chain length influences activity. The minimum carbon chain length is 5 (Glutaric acid) to required get properties such as self-healing and elasticity. Less than C5 (such as Malonic acid) will give viscous polymer which can flow indicating that they will fail to exhibit self-healing and elastic characteristics. Introduction of aromatic rings, dienes (butadiene - dicarboxy terminated) cannot help cross linking. So they will give low mechanical strength polymer. Elastic property loses after C7 (Pimelic acid) but retains self-healing ability. Further experimentation on this (which was not the primary objective of this study) will be required as a future objective to estimate this. However, it is obvious that the expertise control over synthetic organic chemistry rules is very important. Nanoclays that are exfoliated in polymer matrix can radically donate to various properties of nanocomposites such as mechanical strength, thermal and chemical stability etc. Addition of nanoclays along with urea gives better nanocomposite than adding them all together at the beginning. The robust (OH…OH) molecular interactions promote hydrogen bonding between the montmorillonite nanoclay and polymer. Moreover, if higher the chain lengths of dicarboxylic acid monomer, the mobility of the polymer chains are reduced by the high molecular interactions.

The enhancement in thermal stability is due to improved polymer filler contact through the either intercalation or exfoliation, or both together of the montmorillonite clay into the polymer matrix. Thus it is evident that for given clay loading with increase in hydrogen bonding, the peak decomposition rate will gets decreased. Nanocomposites prepared with different polyamide macromolecules were also characterised by DSC, and TGA. These results are then checked in agreement with the results obtained from DMA. These results from
these techniques indicate that thermal stability of nanocomposite can vary when different pre-polymers are used. These studies provided information on the thermal stability and thermal degradation behaviour of the polymer nanocomposites. It was observed that the peak decomposition temperature of SMP is almost same as that of its nanocomposites prepared using natural montmorillonite nanoclays. However, thermal properties changed in case of nanocomposites prepared from organically modified montmorillonite nanoclays, suggesting that the type of organic modifier can affect thermal decomposition trends. The observed increase in the thermal stability of nanocomposites may be due to the high thermal stability of clay and the interfacial reactions between the clay layers and the polymer matrix through intercalation/ exfoliation. It can be also be explained on the basis of easy mobility of the clay chains within the polymer matrix layers thereby demonstrating the intercalated nature of the modified clay nanocomposites.

Bulk physical properties such as physical state (i.e. liquid to solid state) of the nanocomposite, and thereby the hardness, density, tensile strength and Young’s modulus-like properties of the nanocomposite may be influenced by the nature of the monomer or monomers used to prepare the macromolecule used in the cross-linked matrix of the nanocomposite. It is believed that hydrogen bonds can promote the self-healing capability of the nanocomposites. The desire of the functional groups of the macromolecule and the crosslinking agent to associate by intermolecular hydrogen bonds can provide the driving force for nanocomposite. It is confirmed that the addition of nanoclay has a significant role in altering mechanical properties. It was observed that polymer nanocomposites with the same 3 wt. % nanoclay loading but with different organo-modifiers or no organic modifier show a difference in behaviour as C30B based nanocomposites behaves with more strength compared to C25A based nanocomposites, which may be due to the presence of -OH groups in C30B were providing greater hydrogen bonding capability. The nanocomposite based on CNa+ which is the sodium montmorillonite natural nanoclay that get intercalated into the polymer chains exhibited a linear straight line indicating its stronger and stiffer nature and thereby higher modulus.
Polymer nanocomposites described in this thesis can be used in a wide range of applications due to the ability to tune the properties of the nanocomposite to suit a particular application. Polymer nanocomposites described in this thesis may be used to in the preparation products such as high performance parts, adhesives, coatings, cosmetics, dental materials, toys or seals. Such products may be vulnerable to damage such as cracks or failure due to the product being subjected to continued mechanical stress or from being in continued contact with liquids or other materials. These materials can be potentially used as self-healing coatings. The self-healing coating may be in the form of a film that is applied to a substrate surface. For example, the self-healing coating may be in the form of a self-healing paint coating. Such coatings may be susceptible to damage from scrapes or scratches and the ability of the coating to self-heal autonomously could represent a significant advantage.
8 CONCLUSIONS AND FUTURE RESEARCH

8.1 Conclusions

The effect of hydrogen bonding in supramolecular polymers by the appropriate selection of functional groups and processing conditions were investigated in this study. Characterisation techniques were used to scrutinise the level and type of clay dispersion occurred in bulk and localised regions of nanocomposites. The key findings from the study are listed below where the common subject is the elucidation of structure-property relationships.

i. Polymer nanocomposites can successfully synthesised with combined goodness of self-healing polymers and nanocomposites. A solvent free one-pot two-step synthesis methodology is developed and optimised for the production of supramolecular polymer nanocomposites.

ii. It is concluded that the incorporation of montmorillonite nanoclays improved the hydrogen bonding interactions in the polymer matrix. A structure-property relationship was established for the effective selection of montmorillonite nanooclays while preparing supramolecular polymer nanocomposites. The highest thermal and mechanical stability was achieved for polymer nanocomposites which was intercalated into Na-MMT nanoclays and synthesised from dicarboxylic acids of higher chain length.

iii. The minimum carbon chain length of five is required for dicarboxylic acid to form supramolecular polymer nanocomposites. The formation of exfoliated nanocomposites can be achieved for organically modified montmorillonite nanoclays whereas for the formation of intercalating structure can be achieved by using natural montmorillonite nanoclay.

These results show that in order to improve the self-healing ability of clay nanocomposite, the type of montmorillonite and type of polyacid monomers must be predetermined. Optimising material and processing parameters that can reduce self-healing time and increase the mechanical strength.
8.2 Suggestions for Future Research

Polymer nanocomposites described in this thesis can be used in a wide range of applications due to the ability to tune their properties to suit particular application and may be used to in the preparation products. Thus this technology can be suggested for the exploration towards some future research as follows.

i. The outstanding shape memory properties exhibited by few polymers can be explored further as possible candidates for self-healing polymers with shape memory abilities.

ii. The self-healing nanocomposite of the invention may be used along with conventional additives, such as plasticizers, antioxidants, and colorants. Such additives may be included in the nanocomposite where it is desired to customise the nanocomposite for a particular application.

iii. Exploration of characterisation techniques such as insitu-NMR for the better understanding of molecular interactions in detail which can complement the XRD, SAXS and optical microscopy results.

iv. Further optimisation of process conditions and improvement in mechanical properties can facilitate towards polymers which can be scaled up for component manufacture.

v. Formation of repairable polymer system having capability to undergo healing step multiple times, without significant low in activity.
Appendix figure 1: the digital photos of thermo reversible self-healing polymer SMPNa+ after a cut is made on its surface is demonstrated. (a) polymer after been deliberately damaged, (b) after healing performed at 90 °C for 1 minutes and cooled in air (c) after healing performed at 90 °C for 3 minutes and cooled in air (c) after healing performed at 90 °C for 5 minutes and cooled in air. The composition of this nanocomposite was sebacic acid/DETA/Urea/CNa+. 
<table>
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<tr>
<th></th>
<th>Tg of SMP (°C)</th>
<th>Tg of CNa⁺ nanocomposite (°C)</th>
<th>Tg of C25A nanocomposite (°C)</th>
<th>Tg of C30B nanocomposite (°C)</th>
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*Appendix table 1: DSC comparison of glass transition temperature (Tg) for different nanocomposites out of the combination of all nanoclays and carboxylic acid studied.*
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