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Chapter 5

LATEX-BASED NANOCOMPOSITES

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ABSTRACT

Nanoparticles have been widely used as filler in polymer because of their unique reinforcing effect. There are many compounding methods for nanocomposites. The recent development on latex nanocomposites, a group of special nanocomposites, is reviewed in this chapter. They include carbon black/latex nanocomposite, silica/latex nanocomposite, layered silicate/latex nanocomposite, ZnO/latex nanocomposite, carbon nanotube/latex nanocomposite, lignin/latex nanocomposite, starch/latex nanocomposite, nano-fiber/latex nanocomposite, and Chitin whiskers/latex nanocomposite. Advanced compounding techniques and the latest advance on these latex nanocomposites are described. The nano-reinforcing theories of latex nanocomposites are also studied.

1. INTRODUCTION

As far as the mechanical properties (tensile strength, stiffness, abrasion resistance and fatigue resistance) are concerned, most polymers do not possess practical value if they are not reinforced by fillers. For example, the pure rubber product is difficult to be made due to its high elasticity and thus has no practical value. Therefore, the exploration and development of highly effective, simple and economic reinforcing methods and agents becomes one of the...
major challenges for polymer industry. Consequently, the study on polymer reinforcement has been an important topic in polymer industry.

As well known carbon black and silica particles, particularly of nano dimension, as fillers can significantly reinforce polymer materials, including rubber [1-9]. How could carbon black and silica of nano dimension offer outstanding reinforcement in comparison to general micrometer fillers? Extensive research in recent years has significantly improved the understanding of these phenomena which are widely accepted now by researchers in polymer science. One of the most important breakthroughs is the identification of three most important factors, particle size, particle structure and surface activity influencing the reinforcing effect of the fillers. Detailed studies have been made on the influence of particle size [10], structure [11, 12], and surface [13] on the reinforcement effect. It has particularly been demonstrated that it is the particle size of nano dimension that contributed most significantly to the excellent reinforcing effect of carbon black and silica [1]. In other words, the effect of particle size is the most important among these three factors.

With the rapid advancement in science and technology, the production of all kinds of nano-particles is no longer a problem, but how to uniformly disperse the nanoparticles into polymer matrix is still a major challenge. The most common method of dispersing nanoparticles into polymer is mechanical blending [14-17]. Due to high viscosity of most polymer matrices, strong shear and tensile, and compressive forces are exerted on the agglomerates, therefore the nano-particles can be easily dispersed into polymer matrix [18]. However, there are many obvious shortcomings for this technique, such as fly dust, long mixing time, high energy consumption, and the creation of nano-aggregates or agglomerates (nano-particles directly in contact) in the nanocomposites [1], which will weaken the reinforcement effect of nano-particles and the properties of nanocomposites.

Although the properties of polymeric materials can be dramatically improved through the introduction of nanoparticles, uniformly distributing nanoparticles into polymer matrices without aggregation is still one of the most challenging issues in preparing polymer nanocomposites because the prerequisites of marked reinforcement are the uniform dispersion of nano-particles, and a certain interfacial interaction between fillers and polymer [19]. It is difficult for inorganic nano-particles to be evenly dispersed in polymer, such as rubber matrix, and attain the strong interface strength due to their surface characteristics (which generally cause the strong filler-filler interaction and weak filler-rubber interaction). Therefore, it is very important and challenging to find an economic and effective technique to improve the dispersion of nano-particles in polymer matrix and strengthen the interfacial interaction between inorganic nano-particles and polymer which enhance the structure effect of compound, reduce the hysteresis loss and improve the physical properties of composites.

As one of the most important materials, latex nanocomposites have attracted more and more attention because they usually exhibit much better performance properties when homogeneous dispersion of nanoparticles in latex matrix is achieved. Different synthesis methods are now available for the preparation of latex nanocomposite. In order to disperse particles evenly in the matrix, various nanocomposites compounding methods have been developed, such as sol-gel [20, 21], in situ polymerization [22-24], intercalation polymerization [25-27], blending as well as other methods [28]. In this chapter, recent development on latex nanocomposites is reviewed, including synthesis methods and their compounding techniques.
2. SYNTHESIS METHODS

2.1. Blending Method

Blending is one of the widely used synthesis methods, which involves mixing polymers with water slurry of nanoparticles or precursors under high shear stirring directly [28-30]. The advantage of this method is that the process is very simple and controllable while the disadvantage is that without surface treatment, some nanoparticles are hydrophobic which makes it difficult to disperse nanoparticles homogeneously into latex matrix.

2.2. Polymerization Method

There are two popular polymerization methods. The first synthetic approach mixes nanoparticle precursors with monomers, followed by simultaneous polymerization of the precursors and monomers. For example, silica composites based on polystyrene, poly(2-hydroxyethyl methacrylate) or poly(furfuryl alcohol) have been prepared via this method. The second synthetic approach is called in situ polymerization, which is carried out in the presence of nano-silica particles and either using emulsifier-free conditions, emulsions or dispersions [31, 32].

2.3. Self-Assembling Compounding Method [19, 33]

Recently a novel synthesis method called self-assembly compounding method has been developed [25]. The self-assembly is based on the electrostatic interaction of oppositely charged polyelectrolytes and is a promising method to produce latex nanocomposites. The electrostatic adsorptive interactions between latex particles and the nanoparticles are used as driving forces to ensure an effective inter-assembly at latex state. Different from other conventional methods such as intercalation and blending process, this novel process combines the self-assembly and latex compounding technique and offers a new approach to synthesize nanocomposites. The main advantage of the approach is the constraint of free movement of nanoparticles in latex matrix during the synthesis which significantly reduces the probability of particle aggregation.

3. LATEX NANOCOMPOSITES FILLED WITH INORGANIC PARTICLES AND THEIR COMPOUNDING TECHNIQUES

3.1. Carbon Black/Latex Nanocomposites

Like many other nano-materials, nano carbon black exhibits characteristics that are significantly different from those of micro-particles, such as strong absorption effect, electron tunnel effect, and unsaturated valence effect [34]. Carbon black is widely used in rubber
industry as a reinforcing agent and in the plastics industry for its antistatic [35, 36], conductive [37, 38], and UV-protective [39, 40] capacities. For example, the tensile strength of vulcanized rubber filled with fine carbon black is several or even tens times higher than that of non-reinforced rubber [1]. The general method of dispersing carbon particles into rubber is mechanical blending. Due to the high viscosity of most rubber matrix, the strong shear, tensile and compressive forces are exerted on the agglomerates; therefore carbon black nano-particles can be dispersed in rubber matrix. At the same time, the diffusion resistance from high melts viscosity can prevent dispersed nano-particles from re-agglomeration during mixing. However, there are obvious shortcomings with the blending process as described previously. This will influence the reinforcement effect of nano-particles and thus result in obvious drawback of ultimate products.

Carbon blacks are structurally complex particles containing 90-99% of carbon. The smallest dispersible units of carbon black are irregularly shaped aggregates ranging in size from 50 to 500 nm. The aggregates are composed of chemically coalesced and spherically shaped primary particles with diameter of 10-75 nm. Beyond the basic structures, aggregates of carbon black can easily form agglomerates which are physically held together [41].

Despite its hydrophobic nature, carbon black can be dispersed in water by using ionic or nonionic surfactants. In these systems, the hydrophobic parts of the surfactants adsorb onto carbon black while the hydrophilic parts interact with water, providing steric/static repulsions between carbon black aggregates. The colloidal stability of these systems depends on the amount of adsorbed surfactants and the hydrodynamic thickness of the adsorbed layer [41]. The stability of dispersed carbon black decreases upon addition of some solvents or prolonged storage due to desorption of the surfactant molecules from the carbon black surface. The surfactants or polymers that chemically linked to carbon black should provide high dispersion stability.

Since carbon black can easily be dispersed into water to produce colloidal dispersion, the production of water master batches (WMB) by directly blending rubber latex and carbon black slurry seems feasible. During solid mixing process of rubber and carbon black, productivity is improved, energy consumption is reduced, and most importantly, environmental pollution is greatly alleviated. However, the mechanical properties of vulcanized rubbers made from WMB are not ideal.

Based on this, He et al [42] recently introduced a novel way to modify carbon black. Vinyl monomers with hydrotrropic group or NaSS were in-situ grafted onto the surface of carbon black by thermo-mechanical means in non-solvent environment. Under strong shear force and higher temperature vinyl monomers were easily grafted into the surface of carbon black. The carbon black modified by thermo-mechanical means can disperse in water uniformly with higher dispersion stability. In the subsequent process, NaSS grafted hydrophilic carbon black (NaSS-g-CB) was obtained.

NaSS-g-CB was dispersed into natural rubber latex (NRL), the mixture was then coagulated. After that the process was similar to the traditional NR processing method and WMB was obtained. SEM micro-morphology (Figure 1.) shows that hydrotrropic carbon black particles were more uniformly dispersed in the NRL matrix than that of non-modified carbon black particles. And the ultimate vulcanization NR filled with these hydrophilic carbon black particles have excellent mechanical properties (Table 1).
Table 1. Tear Strength of Vulcanized NR filled by CB and NaSS-g-CB [42]

<table>
<thead>
<tr>
<th>Sample</th>
<th>CB (phr)</th>
<th>Tear Strength (KN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NRL/ NaSS-g-CB</td>
<td>10</td>
<td>41.8</td>
</tr>
<tr>
<td>NRL/ NaSS-g-CB</td>
<td>20</td>
<td>85.8</td>
</tr>
<tr>
<td>NRL/ NaSS-g-CB</td>
<td>30</td>
<td>98.1</td>
</tr>
<tr>
<td>NRL/ NaSS-g-CB</td>
<td>40</td>
<td>133.8</td>
</tr>
<tr>
<td>NRL/CB</td>
<td>40</td>
<td>52.8</td>
</tr>
<tr>
<td>NR/CB</td>
<td>40</td>
<td>52.2</td>
</tr>
</tbody>
</table>

3.2. Silica/Latex Nanocomposite

Silica is one of another widely used reinforcing fillers. Composites filled with silica exhibit better mechanical, thermal, optical properties compared with the corresponding pure composites [19, 43, 44]. The silica particles act as reinforcing agents, making the polymers harder, delivering higher strength, improving their heat distortion temperature, and lowering the coefficient of thermal expansion [45].

However, due to the strong hydrogen bonding interaction and high surface free energy, the fumed SiO$_2$ nanoparticles usually exhibit a strong tendency to form large aggregates, which lead to separation in the composites. Numerous methods have been used to solve the dispersing problem. For example, Li et al. [19] introduced a novel self assembly synthetic method by evenly dispersing SiO$_2$ nanoparticles into the NR matrix. The process of self-assembling SiO$_2$/latex nanocomposites involves two assembly steps (Figure 2). At the first stage, SiO$_2$ particles are negatively charged at a pH of 10, and act as templates to assemble the poly(diallyldimethylammoniumchloride) (PDDA) molecular chains that are positively
charged at the same pH value of 10. The driving force is the electrostatic adsorptive interaction. In the second step, the natural rubber latex particles are negatively charged. As the protein particles adsorbed on the surface of the natural rubber latex particles contain carboxyl and amino functional groups, acidic ionization of the proteins can be generated. These natural rubber latex particles with negative charges are then assembled onto the surface of the SiO₂ particles that are covered with PDDA as treated in the first stage. Finally, the SiO₂ nanoparticles are uniformly dispersed in NR matrix to form nanocomposite.

Figure 3 is the SEM micrograph of NR/SiO₂ nanocomposite. It can be seen that the SiO₂ nanoparticles are homogenously distributed throughout the NR matrix as spherical nano-clusters with an average size of 75 nm. The initial degradation temperature (T₀) and final degradation temperature (Tᶠ) and the peak degradation temperature (Tₚ) of NR/SiO₂ nanocomposite, are significantly higher than those of the pure NR (Table 2). And the degradation rates C₀ and Cᵣ (corresponding to Tᵣ and Tᵢ, respectively,) of the nanocomposite are lower than those of the pure NR, due to the retardant effect of SiO₂.

<table>
<thead>
<tr>
<th></th>
<th>T₀ (°C)</th>
<th>Tᵣ (°C)</th>
<th>Tᶠ (°C)</th>
<th>C₀ (%/°C)</th>
<th>Cᵣ (%/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>382.6</td>
<td>407.2</td>
<td>461.2</td>
<td>50.6</td>
<td>4.9</td>
</tr>
<tr>
<td>NR/SiO₂</td>
<td>400.5</td>
<td>424.2</td>
<td>476.1</td>
<td>44.6</td>
<td>10.3</td>
</tr>
</tbody>
</table>

Figure 2. The schematic of the self-assembly process [19].
3.3. Layered Silicate/Latex Nanocomposites

The research on clay as filler in polymer science has a long history. Since the diameter of over 80% of clay particles is below 20 nm, the reinforcement effect of clay can be achieved, but it cannot be compared with that of carbon and silica [1]. A series of clay/polymer nanocomposites with good performance were prepared by making use of special layer structure of clay (i.e. there are numerous layers with 1 nm thickness and 100–1000 nm width in clay particles, which tightly stack together one by one by virtue of the cation presented in inner space). But these clay/polymer composites prepared by conventional mechanical mixing are microcomposite. Hence, in order to obtain clay/polymer nanocomposites with remarkable performance, it must generate strong intercalating force to drive macromolecules into inner space of clay layers [14]. At present, the preparation methods of clay/polymer nanocomposites are in situ polymerization [24, 46], liquid rubber reaction, polymer melt intercalation [26], polymer solution intercalation [47], and polymer latex compounding [48-50]. In this Chapter we mainly focus on the polymer latex compounding methods.

Because the sheet shaped fillers have large aspect ratio, it strongly limits the deformation of macromolecules due to a highly efficient stress transfer. As a result, the composite possesses high modulus, stiffness, strength [10, 51], low elasticity and large permanent set, and has excellent resistance to gas permeation [52-54], solvent swelling, oil-proof, vibration-absorption, flame resistance [55], and heat resistance [17].

However, the improvement in mechanical property has not been as good as expected. There are two reasons for this. One is the clay exfoliation, which is quite difficult to achieve in rubber unless using expensive in situ polymerization. The other is the weak interfacial
strength/toughness unless a chemical reaction happens between the clay and rubber molecules.

There are three main strategies reported to prepare rubber/clay nanocomposites, that is, melt intercalation, solution intercalation, and emulsion compounding. Among these, emulsion compounding has advantages over the other two because of its environmental friendliness and simple processing procedure.

Ma et al. [54] used emulsion compounding methods to produce an exfoliated styrene butadiene rubber(SBR)/clay nanocomposite by mixing organic modified clay suspension with SBR latex. The mixture was then coagulated by diluted H$_2$SO$_4$ solution and washed with water until neutral. The experimental results showed that there are significant improvements in mechanical properties. Transmission electron microscopy (TEM) analysis of the intercalation/exfoliation phenomena is shown in Figure 4, which proves that both exfoliation and a strong interface play critical roles in nano reinforcement.

![Figure 4. TEM image of a SBR/allylamine (AA)-clay nanocomposite, revealing the disorderly exfoliated silicate layer structure in SBR: (a) low magnification TEM micrograph for the SBR/AA-clay nanocomposite, in which exfoliated nanolayers are observed; (b) a typical aggregate observed at higher magnification with a disorderly exfoliated structure [54].](image)

3.4. ZnO/latex Nanocomposites

Besides carbon black and silica, other inorganic nano-particles were developed and commercialized, such as ZnO, TiO$_2$, Mg(OH)$_2$, AL(OH)$_3$, and Fe$_3$O$_4$. Many researchers investigated the properties of polymers filled with these novel particles. Experimental results proved that the reinforcement effect of these nano-particles was much better than that of conventional argil, talc micro-reinforcing fillers, even without surface treatment.

Nano-ZnO, as one of the multifunctional inorganic nanoparticles, has drawn increasing attention in recent years due to its significant physical and chemical properties, such as high
chemical stability, low dielectric constant, large electromechanical coupling coefficient, high luminous transmittance, high catalysis activity, intensive ultraviolet and infrared absorption [29]. Zinc oxide can react with accessory ingredients and accelerators to form organic zinc salts, which can further improve the activity accelerators. Decreasing the particle size of zinc oxide and increasing the surface area can increase the reaction activity. The experimental results demonstrated that when the dosage of nano-ZnO was half of micro-ZnO, the curability and mechanical properties of composites with nano-ZnO reached the same level as those of composites with macro-ZnO, which could greatly reduce the cost and was beneficial to environmental protection [1].

Owing to the functional properties of nano-ZnO, it can potentially be applied as catalysts [56], gas sensors, semiconductors, varistors [57, 58], piezoelectric devices, field-emission displays and UV-shielding [59, 60] materials. The introduction of nano-ZnO into polymers could improve the mechanical and optical properties of the polymers due to a strong interfacial interaction between the organic polymer and the inorganic nanoparticles and nanoparticle’s small size and large specific area, and quantum effect, respectively. Consequently, these nanocomposites could be widely applied in coatings, rubbers, plastics, sealants, fibers and other fields.

Xiong et al. [29] prepared poly(styrene butylacrylate) latex/nano-ZnO composites by blending poly(styrene butylacrylate) latex with a water slurry of nano-ZnO particles which have a diameter ranging from 60nm, 100nm to micron scale and defined as samples A1, A2 and A3, respectively. The tensile strength (Table 3), UV and NIR shielding properties (Figure 5) of the nanocomposite increase with an increasing nano-ZnO content.

Table 3. Mechanical Properties of Pure, A1, A2 and A3 Samples [29]

<table>
<thead>
<tr>
<th>Samples</th>
<th>Content of ZnO(%)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>0 wt</td>
<td>2.30</td>
<td>448.4</td>
</tr>
<tr>
<td></td>
<td>3 wt</td>
<td>4.63</td>
<td>374.5</td>
</tr>
<tr>
<td>A1</td>
<td>5 wt</td>
<td>4.83</td>
<td>390.6</td>
</tr>
<tr>
<td></td>
<td>7 wt</td>
<td>4.95</td>
<td>389.9</td>
</tr>
<tr>
<td></td>
<td>9 wt</td>
<td>5.04</td>
<td>385.8</td>
</tr>
<tr>
<td></td>
<td>3 wt</td>
<td>4.96</td>
<td>369.2</td>
</tr>
<tr>
<td>A2</td>
<td>5 wt</td>
<td>5.03</td>
<td>367.5</td>
</tr>
<tr>
<td></td>
<td>7 wt</td>
<td>5.18</td>
<td>371.9</td>
</tr>
<tr>
<td></td>
<td>9 wt</td>
<td>5.33</td>
<td>389.9</td>
</tr>
<tr>
<td>A3</td>
<td>3 wt</td>
<td>3.54</td>
<td>394.8</td>
</tr>
<tr>
<td></td>
<td>5 wt</td>
<td>4.13</td>
<td>387.6</td>
</tr>
<tr>
<td></td>
<td>7 wt</td>
<td>4.30</td>
<td>388.2</td>
</tr>
<tr>
<td></td>
<td>9 wt</td>
<td>4.57</td>
<td>377.2</td>
</tr>
</tbody>
</table>

Xiong et al. [29] prepared poly(styrene butylacrylate) latex/nano-ZnO composites by blending poly(styrene butylacrylate) latex with a water slurry of nano-ZnO particles which have a diameter ranging from 60nm, 100nm to micron scale and defined as samples A1, A2 and A3, respectively. The tensile strength (Table 3), UV and NIR shielding properties (Figure 5) of the nanocomposite increase with an increasing nano-ZnO content.
Recently, Gatos et al. [61] produced nanocomposites by mixing boehmite aluminas with polyurethane (PU) latex. The mechanical performance, thermal stability, water uptake and dielectric response of these nanocomposites were investigated, as a function of the nominal nanoparticle size of the boehmites. The stiffness, determined by tensile experiment and
dynamic mechanical thermal analysis (DMTA), was enhanced with decreasing particle size at the same filler content. The composite with 25 nm boehmite alumina has the highest improvement in modulus, however, at cost of thermal stability compared to those with 90 nm and 220 nm boehmite alumina. The water uptake increases with the addition of fillers; however, the effect becomes less significant when the size of alumina particles increases. The dielectric response of the nanocomposites was examined by means of broadband dielectric spectroscopy in the frequency range $10^3$–$10^7$ Hz, at ambient temperature. Three distinct relaxation modes were recorded in the spectra of all systems. They were attributed to interfacial polarization, glass transition (α-relaxation) and movement of polar side groups (β-relaxation).

3.5. Carbon Nanotube/Latex Nanocomposite

Ever since the first scientific report of carbon nanotubes (CNTs) in 1991, carbon nanotubes become a world research focus in recent 15 years [62, 63]. According to its structure it can be divided into single-walled carbon nanotubes (SWTs) and multi-walled carbon nanotubes. CNTs have attracted enormous interest owing to their potential applications in field-emission devices, electronics, fibers, composites, sensors, detectors, capacitors, hydrogen storage media, and fuel cell, and so on [37, 64]. Recent work has demonstrated how nanocomposites of polymers and CNTs offer the advantages of polymers, such as optical clarity, viscoelasticity and good barrier properties, combined with the strength and high thermal and electrical conductivity of CNTs [65, 66].

Single-walled carbon nanotubes (SWNTs) remain an interesting filler material for polymers due to their large aspect ratio, small diameter and relatively large length, high elastic modulus [67], high intrinsic electrical conductivity [68, 69] and high thermal conductivity and their surprising high malleability and elastic deformation. The malleability of nanotubes is 200 times of other fibers, which makes them easily restore their original shape without any destruction after removing the exerted high pressure [1]. SWNT-filled polymers are a unique class of composites due to their ability to achieve significant enhancements with a very low filler concentration. Significant improvements in thermal transport, electrical conductivity, and mechanical properties of polymers have been achieved with the addition of less than 1 wt% SWNTs [66].

Vandervorst et al. [64] used latex processing and functionalized SWNTs to create crack-free, water-resistant, and optically clear nanocomposite coatings. In this approach, there is no requirement for adding surfactant or emulsifier. Nanocomposites with carbon nanotubes exhibit high electrical and thermal conductivity and enhanced mechanical properties.

4. Latex Nanocomposites Filled with Organic Particles and their Compounding Methods

In last few decades, the development of biodegradable polymers, based on renewable resources, has attracted increasing interest because of environmental pollution and the petroleum crisis. Many organic particles, such as starch, fiber, lignin and chitin whiskers,
have been used to substitute inorganic particles in polymer reinforcement. Great efforts have been made in organic-particle modification and compounding methods in order to achieve homogeneous dispersion.

4.1. Starch/Latex Nanocomposites

In comparison with inorganic particles, such as carbon black and silica, starch is a renewable natural product with the following advantages: low density [70], cost-effectiveness, abundant supply, and environmental amity. Therefore it is widely used in food, paper-making [71, 72], fine chemicals, and packing material [73, 74] industry. Given the declining storage of petroleum, much effort has been devoted to develop starch-based polymers: that is, chemically modified starch being used as a matrix or filler. This promising technology has been attracting an increasing attention, since it provides an environmentally friendly alternative to the present petroleum-based plastics.

In the past, some researchers used resorcinol-formaldehyde (RF) to modify starch xanthate/rubber composites to improve interfacial strength, but the result was not as good as expected. In order to achieve fine dispersion of starch in rubber matrix, Tang et al. [75] and Angellier et al. [76] developed a novel dispersion technique — the latex compounding method. This method was to mix rubber latex with starch paste and then coagulate the mixture. The method has two merits:

1. water is an excellent medium to dissociate the hydrogen bonding of starch, and
2. most rubbers have a latex form.

In comparison with previous direct compounding techniques, this method can produce smaller size of starch granules and help homogeneous dispersion.

4.2. Nano-Fiber/Latex Nanocomposites

To take the advantage of the biomass, fibrous cellulose (e.g., wood, coir, pineapple, sisal) is gaining ever more attention as a reinforcing agent in polymer matrices [77, 78]. Short fibers are particularly interesting because of their great reinforcing potential and their ability to make recyclable composites with thermoplastic matrices. However, in accordance with the reinforcement theory, this interesting potential cannot be fully exploited without:

1. an adequate interfacial adhesion between fibers and matrix,
2. an optimized fiber aspect ratio length to diameter ratio (L/D), and
3. an acceptable dispersion level of the fibers into the matrix phase.

Unfortunately, materials properties such as high viscosity of the molten polymer and systematic formation of hydrogen bonds between cellulose fibers usually lead to heterogeneous dispersion with the formation of cellulose aggregates. Otherwise, a decrease of the L/D ratio is frequently occurred by fiber breakage during the mixing step. Moreover, these thermoplastic matrices and hydrophilic cellulose fillers usually result in composites with poor
performance. Many investigations have shown that the use of various surface treatments applied onto cellulose fibers or chemical modifications of the matrix (e.g., by addition of maleic anhydride) can improve the dispersion and the mechanical properties of the composites (i.e., tensile strength, and impact strength) [70].

The preparation methods include direct blend, for example attapulgite/rubber nanocomposites, electric nano-fiber/rubber nanocomposites and nano-whisker/rubber nanocomposites by traditional mechanical mixing processing; in-situ polymerization, in which rigid monomers in-situ condensation polymerize in styrene-butadiene block copolymers (SBS) to improve the modulus and heat resistance [79], and solution blend coprecipitation, which prepares poly(p-phenylene terephthalamide) (PPTA)/ Nitrile rubber (NBR) molecular composites by blending PPTA and NBR in solution. Obviously, compared to other preparations, direct solution blending is a simple and promising method to prepare fibrous nanocomposites.

Hajji et al [78] produced cellulose whisker/latex nanocomposite by adopting a water suspension mixing procedure instead of using compatibilizing agents. Cellulose whiskers have been used to reinforce a copolymer matrix prepared from a latex phase (i.e., water suspension of polymer spheres with low viscosity) to process nanocomposites with quasi-isotropic mechanical properties to improve the dispersion quality and limit the degradation of the whisker aspect ratio during the compounding step.

4.3. Lignin/Latex Nanocomposites

Lignin is a waste material, and can be largely extracted from waste solution originating from paper making. It is a kind of renewable reinforcing filler for polymer. The mechanical properties of composites that filled with lignin can be significantly improved due to lignin’s multifunction, high-impact strength, thermal resistance, and biodegradable properties [80, 81].

Lignin is the reinforcing part of plant, composed of C, H and O elements, as the form of aromatic compound of phenylpropyl units connected by —O—, —C—C—. It can be dissolved during papermaking, and its molecular weight is from several hundred to several million. Lignin can be precipitated out by acid from its lye, but the diameter of lignin particles is relatively large (2~50μm) by precipitating method, and cannot evidently decrease even by further grinding.

The preparation of lignin nano-reinforcing (more accurately fine-reinforcing) rubber is through coprecipitation [1]. It dissolves the lignin into lye, then mixes the lye with latex, and lastly coagulates them together by acid. The composite obtained by this way has light color, low density, and higher physical and mechanical properties than those of rubber with furnace carbon black. In addition, the mixing time is greatly shortened, and the size of dispersed lignin particles in rubber is below 100nm.

Lignin is independent of petroleum resources and the polymer reinforced with it has good surface properties, low density, the same strength as polymer filled with carbon black, and a certain level of flame resistance. Now much of the work related to polymer–lignin products has focused on increasing the reactivity of the lignin by modifying specific reactive groups, such as carboxyl and hydroxypropyl groups. Especially, hydroxyalkylation of lignin has been recognized as a promising technique for overcoming the frequently observed adverse effect of
lignin on mechanical properties of solid polymer materials. This kind of materials have wide applications in various industry, and therefore will be of great interest to researchers [70, 80].

4.4. Chitin Whiskers /Latex Nanocomposite

Chitin whiskers are very promising reinforcing materials for polymer because of their high stiffness and strength [82]. Owing to their small diameter, whiskers are nearly free of internal defects, thereby yielding strength close to the maximum theoretical value predicted by the theory of elasticity. The extent of their reinforcement depends on many factors, such as the nature of the matrix, the generation of a strong polymer matrix interface through physicochemical bonding, the aspect ratio, and dispersion of the whiskers in the matrix. Compared with inorganic whiskers, whiskers from renewable resources have advantages such as renewability, low cost, easy availability, good biocompatibility, and easy modification by chemical and mechanical methods. Chitin, from shellfish, insects, and microorganisms, is the second most abundant structural biopolymer. Chitin whiskers have been used as a new kind of nanofillers in both synthetic polymeric matrices and natural ones [82]. Utilizing natural fillers from renewable resources not only contributes to a healthy ecosystem but also makes them economically interesting for industrial applications due to the high performance of the resulting composites.

Nair et al.[82-84] produced nanocomposite materials from a colloidal suspension of chitin whiskers as the reinforcing phase and latex of both unvulcanized and prevulcanized natural rubber as the matrix. The chitin whiskers, prepared by acid hydrolysis of chitin from crab shell, consisted of slender parallelepiped rods with an aspect ratio close to 16. After the two aqueous suspensions were mixed and stirred, solid composite films were obtained either by freeze-drying and hot-pressing or by casting and evaporating. The processing and swelling behavior of composite films were evaluated. The resistance against swelling in an organic solvent medium is a good evidence that a rigid chitin network exists. The diffusion coefficient, bound rubber content, and relative weight loss also supported the presence of a three-dimensional chitin network within the evaporated samples. The mechanical behavior of the composites gives additional insight and evidence for this fact.

5. THE NANO-REINFORCING THEORIES

Why can the filler with small particle size offer the polymer significant reinforcement effect? Is the reinforcing effect improved with the decrease of particle size? What role does the interface play in the reinforcement? Many theories have been developed in order to explain the phenomenon. Some representing theories are briefly described.

5.1. The Surface Structure Model

The surface of active fillers is not smooth, and the surface structure has marked effects on the reinforcement. Three reinforcing mechanisms originated from different scales are
involved. In the range of small scale (less than 100 nm), due to the multi-dimensions of surface structure of fillers, the shape and activity of the fillers play an important role in the physical and chemical interactions between fillers and polymers. At the intermediate scale, particle agglomerates and gel cause reinforcement. In a large scale, filler networks exhibit reinforcement. At the low loading content, the diameter of dispersion phase is very small, and therefore the reinforcing mechanism is absorption. At the high loading content, hydrodynamic reinforcement play a main role, and the deformation and rupture of branched agglomerate dissipate energy [85].

5.2. Mechanical Model

In this model, the polymer-aggregate of fillers and aggregate-aggregate interactions are taken into consideration. The polymer-aggregate interaction can be represented by a linear spring-dumper system; the force of neighboring aggregates is the London-vander waals interaction, the magnitude of which decreases with the seventh power of the distance, which can be represented by a non-linear elastic spring. When the elastomer is stretched, the agglomerate-polymer interaction makes the agglomerates move to new rest positions. The model includes the following main points [86]:

1. the linear viscoelastic behavior of the polymer matrix and the nonlinear elastic behavior of agglomerates contribute to the complex modulus;
2. upon deformation, the polymer pulls agglomerate apart, while the London-van der waals force pushes them together;
3. due to the London-van der waals force, a pair of aggregates have two stable equilibrium points, combination or separation state; and
4. the transition of agglomerates from combination to separation state is the reason that the complex modulus decreases with the increase of shear rate.

6. CONCLUSION

As one of the most important materials, latex nanocomposites have attracted more and more attention because of their simple compounding methods, uniform nanoparticle dispersion in latex matrix, unique properties, and wide range of applications. Great achievements have been made to prepare latex nanocomposites. However, much more efforts have to be done to modify the surface of organic or inorganic particles so as to further improve the nano-dispersion phase in polymer matrix and it is still a long way to develop a valid reinforcement mechanism in the future.

The fundamental understanding of the interaction between fillers and latex molecules will play an important role in developing novel compounding methods. This includes the understanding of the materials properties at molecular level, the forces existing during the compounding, the validation of theoretical models. There are many mature and emerging techniques to facilitate the development of theoretical models. For example, various forces at molecular level can be measured with equipment such as atomic force microscope; the
assembly process can be monitored with techniques including small angle X-ray scattering and small angle neutron scattering. All these advanced technologies will significantly enhance the understanding of filler-latex interaction, which consequently contribute significantly to the development of latex-based nanocomposites with greatly improved properties.

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