Investigation on structure and characteristics of alpaca-based wet-spun polyacrylonitrile composite fibers by utilizing natural textile waste

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ABSTRACT: The composite alpaca/acrylic fibers were auspiciously produced through a wet spinning technique to reduce the consumption of petroleum-based polyacrylonitrile (PAN) and to enhance the thermal stability and moisture properties of the fibers. The waste alpaca fibers were converted into powder using a mechanical milling method without applying any chemicals. Alpaca powders were then blended with the PAN dope solution in different weight ratios of alpaca: PAN (10:90, 20:80, and 30:70) to wet spin the composite fibers. The Fourier transform infrared spectroscopy showed that all the composite fibers possess the functional groups of both alpaca and PAN. The nuclear magnetic resonance spectroscopy confirmed the presence of typical carbonyl carbon (C═O) and nitrile carbon (C≡N) peaks of protein and PAN, respectively. The differential scanning calorimetry and thermogravimetric analysis revealed the enhanced thermal stability of alpaca/PAN composite fibers. The moisture properties of the composite fibers were subsequently found to increase with the incorporation of alpaca, more than three times that of pure PAN fibers. These results revealed a potential green pathway to producing composite acrylic fibers with improved thermal and moisture properties by applying textile waste materials. © 2019 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2019**, *136*, 48370.

INTRODUCTION

The textile industry is one of the oldest industries in the world, which is not only fulfilling the demand for clothing but also the trend in the latest fashion.[1,2] The use of both natural and synthetic fibers is enormous in fulfilling this demand. In recent years, the production of polymeric synthetic fibers has increased rapidly, because these fibers can be tailored to the desired size, shape, and properties.[3] Nowadays, the application of fibers is not only limited to traditional apparel manufacturing but also used in energy storage, developing composite materials for reinforcement as well as functional fibers and fabrics.[4–7] These synthetic fibers application areas were found either by altering or by incorporating other functional materials into their polymeric chain. For example, it has been reported that the fibrils from poly(ethylene terephthalate) have been successfully embedded into the polymeric matrix of polypropylene (PP) by adopting the fiber spinning process, to increase the mechanical properties and foaming ability of the PP fibers.[8] Continuous bicomponent melt spun polymer optical fibers has been reported where cyclo-olefin polymer and tetrafluoroethylene–hexafluoropropylene–vinylidene fluoride terpolymer were used in the core and sheath, respectively to be used as sensors to determine the heart rate and oxygen saturation values of a human being.[9] However, the extensive use of synthetic fibers is not free from adverse environmental impact due to their petrochemical-based origin, nonbiodegradable nature, and use of various environmentally hazardous chemicals during production.[7]

After nylon and polyester, polyacrylonitrile (PAN; acrylic) is the third most widely used synthetic fiber which is synthesized from petrochemical sources.[10,11] Since production in the 1950s, acrylic has found tremendous application in clothing, industrial textiles, home textiles, and in other technical textile fields due to their versatile characteristics.[11] In addition, it is extensively used as a precursor for the production of high strength carbon fibers.[10,12,13] However, higher flammability, lower thermal stability, and moisture properties limit its further application in textile fields.[11,12] Generally, acrylic fibers are produced with at least 85% acrylonitrile monomer and the remaining 15% made up of different comonomers based on textile end-use application.[10] Acrylic fibers are mainly produced by a solution spinning process (either wet spinning or dry spinning), not melt spinning. This is due to the degradation of the acrylonitrile polymer before reaching to its melting point.[10,11] Different organic solvents, for example, dimethylformamide, dimethylacetamide, and dimethyl sulfoxide

(DMSO) is used as a solvent to produce the acrylic fibers.[14] However, among these organic solvents, DMSO is less hazardous. In wet spinning, the PAN polymers are dissolved in the solvent and then passed through the coagulation process where fiber forms due to the counter-diffusion mechanism between the solvent and nonsolvent (water) system.[15] The coagulation bath should consist of a mixture of solvent and nonsolvent, as the higher solvent ratio can redissolve the fibers while higher nonsolvent (water) content can produce fibers with larger voids that lead to fibers with low mechanical properties.[16,17]

It has already been reported that the production of acrylic fibers is possible with several physical and chemical modifications for various end uses.[18,19] Nevertheless, applying chemicals to modify the fiber properties is not free of environmental pollutions and impact on public health.[18,20] For example, different types of hazardous and toxic chemicals, consisting of halogen, phosphorus, or sulfur are used to increase the flame retardant property of the PAN fibers.[21] Therefore, it is high time to follow the eco-friendly as well as a sustainable approach to boost the thermal stability, moisture absorption, and nonflammability of acrylic fibers for different applications. Recently, a term "green-composite" or "biocomposite" has been developed where mainly cellulose-based natural fibers like cotton, hemp, and jute were mixed or blended with the synthetic materials to produce partially or completely biodegradable composite materials.[22–24] However, the application of natural protein fibers was not reported to produce these types of composites. Additionally, enhancing the flame retardancy of the fibers by increasing the thermal stability while not applying any chemicals was overlooked in the works of literature.

Alpaca fiber is an expensive and luxurious animal fiber with a protein structure similar to wool and with excellent softness, warmth, strength, and moisture properties.[25] In addition, being keratinous protein, inherently these fibers are biocompatible, biodegradable, and fire resistant.[26,27] Unfortunately, during shearing and fiber processing, around one-quarter of short and nonspinnable alpaca fibers are produced as waste and are mainly thrown in a landfill or used in the preparation of low-grade animal feed.[28] To minimize the landfilling and utilizing these valuable fibers, our group have already collected and converted these waste fibers into micrometer-sized particles in an environmentally friendly manner without altering the proteinaceous functional groups of the parent fiber.[28] We have found that while the fibers were converted into powders, the crystallinity of the powders was decreased and moisture absorption increased.[28]

This current work aims to accelerate the use of textile-based waste materials to reduce the ecological footprint and support the circular economy by using alpaca waste. Here, we have investigated the applicability of alpaca powders wet-spun with PAN polymer to enrich the thermal stability and moisture absorption properties of the alpaca/PAN composite fibers. Furthermore, the rheology of the dope solution, morphology, chemical structure, crystallinity, and mechanical properties of the wet-spun fibers were examined. To the best of our knowledge, this work represents the first attempt of applying mechanically milled alpaca powders with PAN for the production of alpaca/PAN composite fibers with improved moisture properties and thermal stability. Although there are some reports on the production of bio-based

composite fibers with enhanced functional properties, the processes described in those works are not completely free of using chemicals.[20,22,24] Hence, we assume that this study of adding plain alpaca powder (without any further chemical modification) into the polymeric chain of PAN is a combination of greener and eco-friendly procedure to enrich the functional properties of the composite fibers. Undoubtedly, this research work will lead us to a path of cleaner production of composite fibers due to adopting eco-friendly and sustainable methods.

EXPERIMENTAL

Materials
Waste alpaca fibers were provided by Nocturne Alpacas, Buckley, Victoria, Australia. PAN (molecular weight of 150,000 g mol^{-1}) was purchased from Sigma-Aldrich. DMSO of 99% purity was procured from Merck, Germany. The chemicals were used as received.

Mechanical Milling and Particle Size Measurement
The mechanical milling process of alpaca fibers to convert into powders and their particle size measurement procedure as described before.[28] Briefly, the collected waste alpaca fibers were washed with eucalyptus wool wash and water (room temperature). After drying overnight at 60 °C in an oven, the fibers were cut into snippets by using a rotary cutter mill (Pulverisette 19 from Fritsch GmbH, Germany). These snippets were converted into a slurry and spray dry powder using Attritor mill (2S, Union Process) and spray dryer (B-290; Buchi Labortechnik AG, Switzerland), respectively. Finally, the spray dried powder was processed through an air jet mill (Sturtevant Inc.) to produce the alpaca particles.[28] The distribution of volumetric particle size of the air jet-milled powder was measured where the volume median diameter of 2.5 µm was denoted as $d(0.5)$.[28] Figure 1 represents the images of alpaca fibers and particles.

Preparation of Dope Solution and Rheology Measurement
Control PAN dope solution was prepared by adding 18 wt % of PAN in DMSO by stirring (65 rpm, 60 °C) for 24 h to ensure the PAN is completely dissolved. To prepare the alpaca/PAN dope solution, first, the alpaca powder was dispersed in DMSO by sonication for 2 h, then the PAN polymer was dissolved into DMSO (containing alpaca particles) and stirred overnight at 60 °C. The blending ratio of the alpaca particle and PAN was 10:90, 20:80, and 30:70 at 18 wt % concentration of the spinning solution. Experiments on higher alpaca content (e.g., 40%) were also conducted. However, due to the presence of high solid content in the dope solution which resulted in spinneret blocking, hence spinning was not possible. In addition, a range of dope solution concentrations (%)
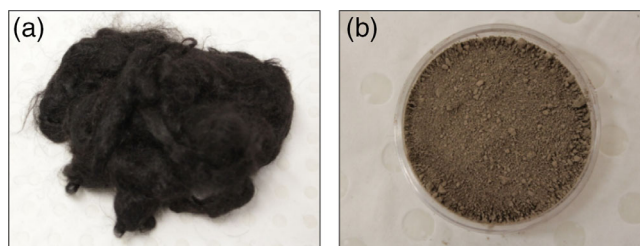

Figure 1. Images of samples: (a) alpaca fibers and (b) alpaca particles. [Color figure can be viewed at wileyonlinelibrary.com]

between 12 and 20 wt % were trialed. The 18 wt % concentration was finally found to be the best solution in terms of the viscosity and spinnability. Spinnability is the ability to produce fibers from the polymeric solution even by the use of stirring rod from a beaker.[29] It depends on various factors such as solution viscosity, extrusion ratio, and flow rate of the solution.

The corresponding composite alpaca/PAN fibers formed from the alpaca–PAN blends were termed AP (10:90), AP (20:80), and AP (30:70), respectively. A rheometer (the Discovery HR-3; TA Instruments) was used to determine the viscosity of different dope solutions. The diameter of the geometry was 40 mm with a 2° cone angle and the truncation gap was 49 μm.[30–32] The measurement was performed at 25 °C and the shear rate was between 0.1 and 100 s⁻¹. Power-law relationship of the Ostwald de Waele model [eq. (1)] was used to express the flow behavior of the dope solutions:

$$\sigma = K\gamma^n \qquad (1)$$

where σ is the shear stress in Pascal; γ is the shear rate (1/s); and K and n are the consistency index and non-Newtonian index, respectively.[33] The regression parameters of the consistency index (K) and non-Newtonian index (n) were determined by linear curve fitting.

Wet Spinning of Fibers

The wet spinning of the fibers was carried out using the Dissol (Dissol Pty. Ltd.) wet spinning line fitted with a gear pump and consists of a temperature controlled coagulation bath, a washing zone, a drying zone, and a winding zone (Figure 2). This wet spinning system is capable of spinning up to 1 L of dope solution and 3 km of filament in length at once. The dope solution was extruded through the spinneret (100 μm diameter with 100 holes) at room temperature where a mixture of DMSO and water (60:40) was used as a coagulation medium. After precipitation, the fibers were passed through the washing (ambient temperature) and stretching bath (80 °C) and wound on a spool with a total draw ratio of 4:1.

Scanning Electron Microscope

The surface and cross-sectional morphologies of the control PAN and alpaca/PAN composite fibers were observed with a Zeiss Supra 55VP scanning electron microscope (SEM), where the accelerating voltage was kept at 3 kV. Leica EM ACE600 gold coater was used to coat fibers prior to imaging.

Fourier Transform Infrared Spectroscopy

The Fourier transform infrared (FTIR) spectra analysis of all the fibers was accomplished under attenuated total reflectance mode using Vertex 70 (Bruker, Germany) spectrometer with a scan resolution of 4 cm⁻¹ and 32 scans per sample between 400 and 4000 cm⁻¹. Data were collected after baseline correction by the OPUS 5.5 software.

Nuclear Magnetic Resonance Spectroscopy

The nuclear magnetic resonance (¹H NMR) and ¹³C NMR spectra were recorded on a Bruker spectrometer, Germany. The cross-polarization magic angle spinning (CP-MAS) solid-state ¹³C NMR spectra of the samples were recorded on a 300 MHz Bruker Ascend 300 WB spectrometer by using a 4 mm rotor at spinning rate of 10 KHz and 1600 scans for each sample. Data were extracted using the TopSpin 3.2 software.

X-ray Diffraction

The crystallinity of the control PAN and composite fibers was analyzed at room temperature by X-ray diffraction (XRD) technique (X'Pert Powder; PANalytical, Netherlands) where the operating voltage and the current flow were 40 kV and 30 mA, respectively. The measurement was taken between 6 and 40°; step size was 0.013° and 250 s per step. The crystallinity index (Cr.I.) of the fibers was calculated by eq. (2):

$$\mathrm{Cr.I.} = (I_f - I_s)^*100/I_f \qquad (2)$$

where Cr.I. is the crystallinity index, I_f is the peak intensity in arbitrary units with 2θ at 17° and I_s is the peak intensity in arbitrary units with 2θ at 28.5°.[34]

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) Q200 (TA Instruments) was used to perform the DSC test. The samples (5 mg) were heated from ambient temperature to 400 °C at a heating rate of 10 °C min⁻¹ in a nitrogen atmosphere.
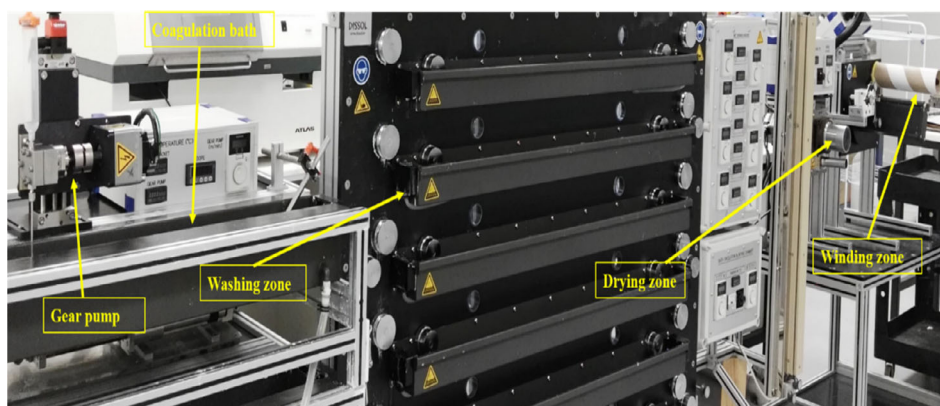

Figure 2. Dissol wet spinning machine. [Color figure can be viewed at wileyonlinelibrary.com]

Thermogravimetric Analysis

To perform the thermogravimetric analysis (TGA) TGA Q50 (TA Instruments) was used where the samples (5 mg) were heated from the ambient temperature to 600 °C at a heating rate of 10 °C min^{-1} in a nitrogen atmosphere.

Mechanical Testing

The mechanical properties (tenacity and elongation at break) of the control PAN and the alpaca/PAN composite fibers were determined by Instron 5967. To perform the mechanical testing, a load cell of 50 N, a gauge length of 100 mm, and a crosshead speed of 10 mm min^{-1} were adopted. The samples were conditioned for 48 h in a standard condition of 20 ± 2 °C and 62 ± 2% relative humidity prior to the test. The linear density of the fibers was measured in the direct system (tex) which is defined as the mass in grams per 1000 m of fiber.[35] Each fiber (control PAN and alpaca/PAN) was tested 20 times and the average of the measurements was reported for tenacity (cN/tex) and elongation at break (%) along with the standard deviation.

Moisture Properties

The moisture regain (MR) and moisture content (MC) of the fiber samples were measured in percentage by using ASTM D2495-07 (reapproved 2012).[36,37] Briefly, around 2 g of each sample was conditioned at standard atmosphere (20 ± 2 °C and 62 ± 2% relative humidity) for 48 h. The samples were weighed and dried at 110 °C for 4 hours in a laboratory conventional oven. The samples were then reweighed and the MR and MC were calculated according to eqs. (3) and (4), respectively:

$$MR\,(\%) = (M-D)/D*100 \tag{3}$$

$$MC\,(\%) = (M-D)/M*100 \tag{4}$$

where M is the weight of the conditioned sample and D is the weight of the oven-dried sample. Every sample was tested five times and the average was reported.

RESULTS AND DISCUSSION

Rheology, Morphology, and Mechanical Properties

Rheological Properties. The rheology of the dope solutions is presented in Figure 3(a). It can be seen that the control PAN had the highest viscosity among all the dope solutions and the viscosity reduced continuously with the addition of alpaca particles.[30] Furthermore, at an elevated shear rate, the viscosity of all the solutions decreased, which confirmed the shear thinning (non-Newtonian) behavior.[30,31] It has been reported that in a polymeric solution when the shear rate is low, the breakage rate of the large molecular entanglements is encountered by the formation of new molecular entanglements.[32] However, during a higher shear rate, the balance of this molecular reconstruction is hindered and the interfaces between the molecules declines resulting in lower viscosity of the solution.[32,38] Since the solutions displayed shear thinning behavior, to evaluate the spinnability of the dope solutions, the non-Newtonian index was calculated.[33] The logarithmic curves of shear stress and shear rate are shown in Figure 3(b) and the consistency index (K), non-Newtonian index (n), and correlation coefficient (R^2) are shown in Table I. The spinnability of the control PAN dope solution ($n = 0.66$) was higher than that of alpaca/PAN dope solutions and with the increase of alpaca content the spinnability reduced, as the higher the value of n, the more the spinnability of the dope solutions.[33] The alpaca particles were dispersed into the dope solution rather than complete dissolution. This could be the reason for the reduction in viscosity and non-Newtonian index (n). A similar result of reduced viscosity was found when lignin was added to PAN polymer in the preparation of lignin/PAN dope solution.[30,31]

Morphological Analysis. The longitudinal and cross-sectional SEM images of control PAN and alpaca/PAN composite fibers with different alpaca percentages are presented in Figure 4. Control PAN fibers showed a ribbon-like appearance with a smooth fiber surface, which might be the result of using DMSO and water as the precipitation bath that led to probable sulfonation of DMSO.[39] A similar effect on the surface of PAN was also reported by Kruchinin et al. where different combinations of coagulation bath were trialed but only the DMSO: water bath provided a smooth surface of PAN due to the sulfonation.[39] In addition, the cross-sectional image of the control PAN fibers showed a typical bean shape that might be due
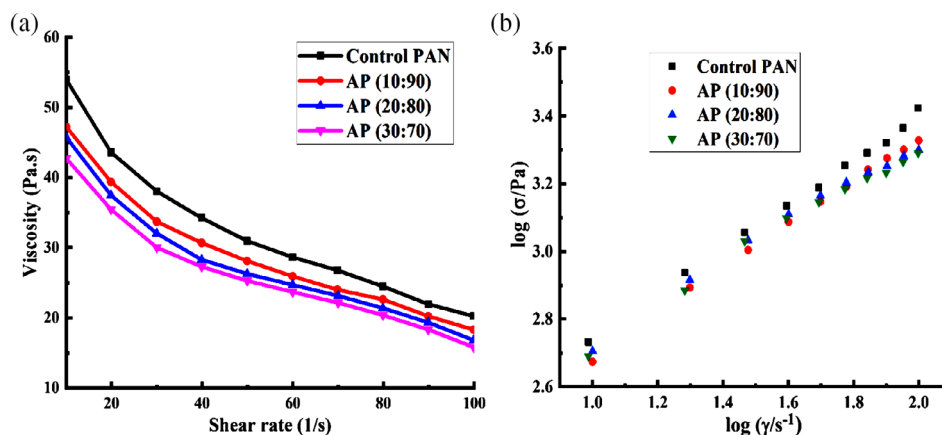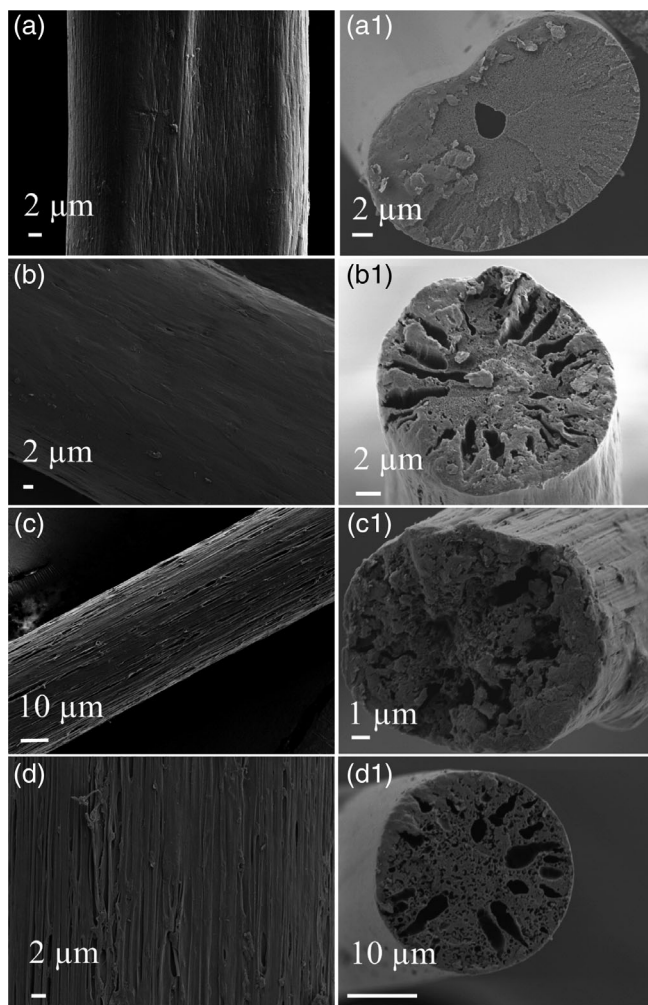

Figure 3. Viscosity versus shear rate (a) and logarithmic plots of shear stress versus shear rate (b) of 18 wt % control PAN and alpaca/PAN dope solutions. [Color figure can be viewed at wileyonlinelibrary.com]
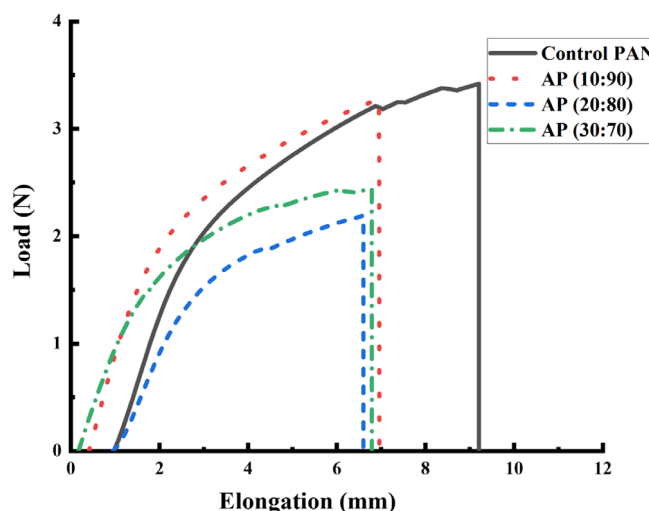
Table I. The Value of K, n, and R^2 after Fitting the Logarithmic Curves of Shear Stress and Shear Rate

Sample	Consistency index (K)	Non-Newtonian index (n)	Correlation coefficient (R^2)
Control PAN	2.07	0.66	0.99
AP (10:90)	2.04	0.65	0.99
AP (20:80)	2.14	0.59	0.99
AP (30:70)	2.14	0.58	0.99

Figure 5. The load–elongation curve of control PAN and the alpaca/PAN composite fibers. [Color figure can be viewed at wileyonlinelibrary.com]

Figure 4. Longitudinal and cross-sectional SEM images: (a-a1) control PAN, (b-b1) alpaca/PAN (10:90), (c-c1) alpaca/PAN (20:80), and (d-d1) alpaca/PAN (30:70). [Color figure can be viewed at wileyonlinelibrary.com]

surface with porous and void areas. As the alpaca particles were dispersed into the solvent rather than complete dissolution, it might be possible that during stretching of fibers from the coagulation bath to the winding spool, the striations are formed and appeared on the fiber surface.

It is known that the moisture transfer properties of alpaca fibers are higher than the acrylic fibers and has a contribution to the comfort properties.[35] However, the acrylic fibers have poor moisture transfer properties.[10,11,35] Thus, the change in morphology of the PAN by the addition of the alpaca may increase the moisture transfer properties of the acrylic fibers. We believe that both the voids and striations of the composite fibers could be able to enhance the MR of the fibers which is discussed later.

Mechanical Properties. The load–elongation curve and the average values of fiber diameter (μm), linear density (tex), tenacity (cN/tex), and elongation at break (%) of all the fibers are shown in Figure 5 and Table II, respectively. A relatively large fiber diameter ranging from around 30 to 50 μm was found in all the fibers and the linear density was approximately between 29 and 34 tex. This might be due to the lower drawing ratio during the wet spinning (draw ratio 4). The tenacity of the control PAN fiber spun in this study was 11.4 cN/tex. Similarly, the tenacity of the composite fibers was reduced by approximately 4% for AP (10:90), 31% for AP (20:80), and 41% for AP (30:70) than that of pure PAN fiber with the addition of alpaca particles. The elongation at break of the composite fibers reduced by around 25% for AP (10:90), 27% for AP (20:80), and 29% for AP (30:70) than that of the control PAN. The reason for the deterioration of the mechanical properties of the composite fibers might be due to the increased number of void formations (Figure 4) and higher fiber diameter (Table II). The presence of the voids on the surface and inner side of the fiber structure results in stress concentration when the tensile force is applied. This leads to a decrease in tenacity and finally the fiber breaks. The larger diameter of all the fibers could be another reason for the lower mechanical properties.[40] Further investigations on the modification of various wet

to the counter-diffusion mechanism of the solvent (out) and nonsolvent (in) into the coagulation bath.[30] Unexpectedly, the fibers exhibited one large (micrometer sized) and many tiny (nanosized) pores in the cross section that could be as the result of a lower draw ratio of the fibers during the spinning process (Figure 4).

When the alpaca particle was added to the PAN solution at 10, 20, and 30% weight ratios, the composite fibers exhibited almost circular cross-sectional shape having striations and nonsmooth fiber

Table II. Mechanical Properties of Control PAN and Alpaca/PAN Composite Fibers

Sample	Diameter (μm)	Linear density (tex)	Tenacity (cN/tex)	Elongation at break (%)
Control PAN	34.67 ± 2.44	29.16 ± 1.14	11.4 ± 0.20	9.21 ± 0.14
AP (10:90)	30.78 ± 2.29	28.27 ± 1.23	10.94 ± 0.31	6.95 ± 0.21
AP (20:80)	32.44 ± 2.37	31.14 ± 1.82	7.84 ± 0.38	6.79 ± 0.26
AP (30:70)	47.83 ± 2.77	33.35 ± 1.18	6.64 ± 0.26	6.59 ± 0.26

spinning parameters to wet spin the alpaca/PAN composite fibers with reduced fiber diameter and enhanced mechanical properties are currently being examined.

Chemical Structural Analysis

The chemical structures of all the fiber samples were determined by FTIR and NMR techniques, as shown in Figures 6 and 7, respectively. The protein structures of alpaca particles are primarily identified by the presence of Amide A, Amide I, Amide II, and Amide III bands. The strong and broad absorption peak at around 3300 cm^{-1} represents the presence of both N—H stretching (Amide A) and O—H stretching. The strong absorption peaks at 1540 and 1650 cm^{-1} are attributed to the methyl C—H deformation and C=O stretching that represent the Amides II and I, respectively. The components of Amide I band frequencies are very closely interrelated with the other secondary elements of proteins and it is the result of almost 80% of C=O stretching of the peptide linkage whereas the Amide II band is reflecting lower conformational sensitivity of proteins, which is primarily obtained from CN stretching vibration and NH bending.[41] In addition, the other weak band at 1240 cm^{-1} stands for the C—N and C—O stretching vibrations (Amide III).[42,43] The other two prominent peaks are at 2850 and 2930 cm^{-1}, representing the symmetric and asymmetric C—H stretching vibrations of methylene group, respectively.[44] The control PAN fiber represented its main characteristic peak at 2240 cm^{-1} assigned to the C≡N (nitrile group) and the other peaks at 1470 and 2930 cm^{-1} ascribed to the bending and stretching vibration of methylene groups, respectively.[30] Nitrile group is composed of one sigma (σ) bond and two pi (π) bonds that makes it stronger in nature. In composite fibers, all the characteristic peaks of both alpaca and PAN were observed with no further new absorption peaks. This might be due to the fact that while the alpaca powder dispersed into the PAN system it was not able to break the strong σ and π bonds to create new chemical bonds. Hence, these results recommend the proper blending of alpaca and PAN in the dope solution by avoiding any major chemical changes or deformations, which was also found in the previous works.[30,31]

On the other hand, from the solid-state ^{13}C CP-MAS NMR (Figure 7), it is evident that the alpaca particle showed the typical carbonyl carbon (C=O) peak at 174 ppm.[33] The control PAN fiber exhibited its characteristic methane carbon (CH), methylene carbon (CH$_2$), and nitrile carbon (CN) peaks at 28–29, 36–37, and 120–121 ppm, respectively.[45] From Figure 7, it can be seen that the alpaca/PAN composite fibers represent the corresponding peaks of both protein and PAN polymer. In addition, no new or additional peak was found in the NMR analysis of the composite fibers, which confirms the proper mixing of the polymers in the dope solution and further supports the findings of the FTIR analysis (Figure 6).

Thermal Properties of the Fibers

The DSC and TGA of control PAN and alpaca/PAN composite fibers are shown in Figure 8(a,b). All the fibers showed only one glass-transition temperature (T_g) between 60 and 80 °C that ultimately resembles the proper miscibility of alpaca powder and
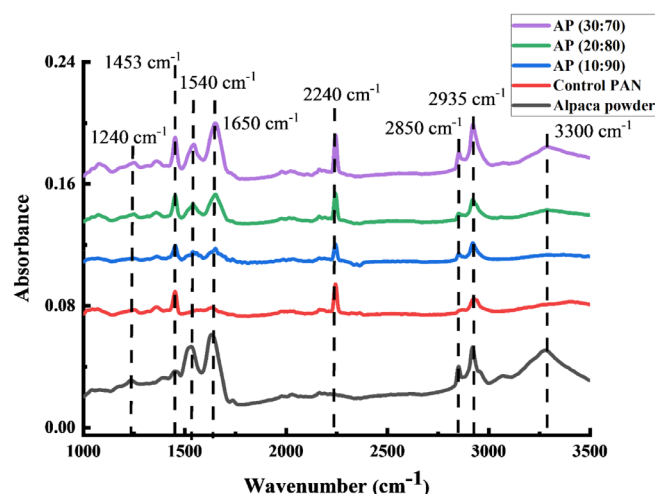

Figure 6. FTIR analysis of alpaca powder, control PAN, and alpaca/PAN composite fibers. [Color figure can be viewed at wileyonlinelibrary.com]
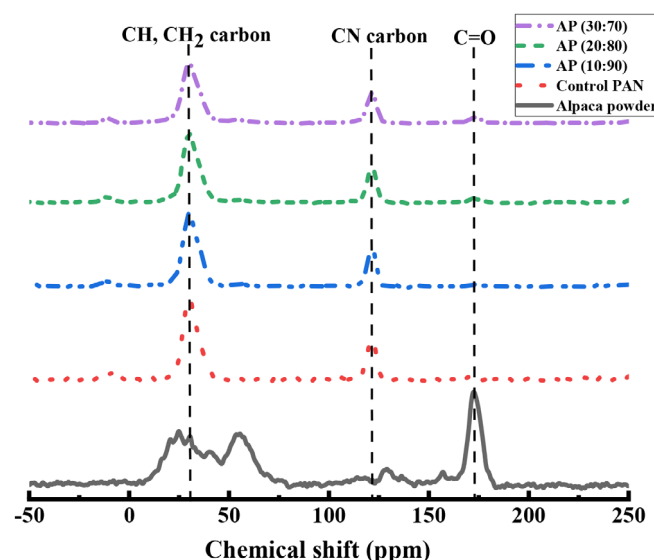

Figure 7. NMR spectroscopy of alpaca powder, control PAN, and alpaca/PAN composite fibers. [Color figure can be viewed at wileyonlinelibrary.com]
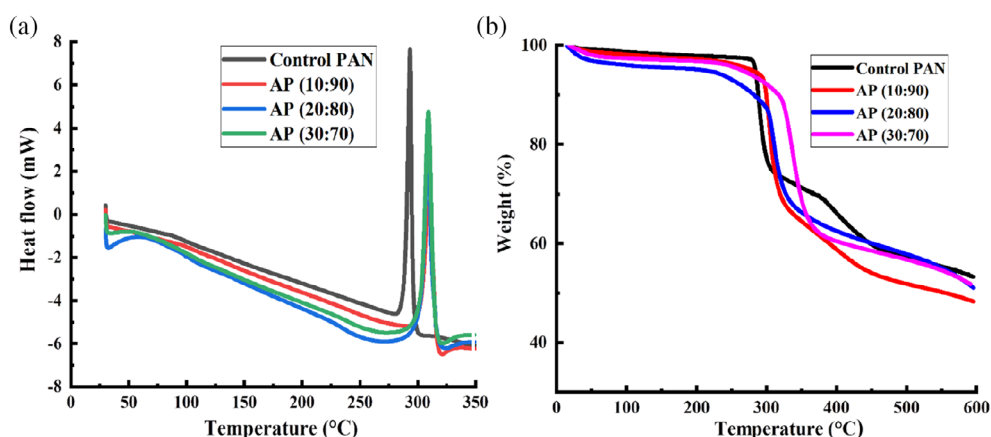
Figure 8. Thermal analysis of control PAN and alpaca/PAN composite fibers (a) DSC and (b) TGA. [Color figure can be viewed at wileyonlinelibrary.com]

PAN polymer with no phase separation during the formation of fiber.[31,46] An exothermic peak between 290 and 296 °C was evident from Figure 8(a) that corresponds to the wet-spun control PAN fibers. However, the decomposition temperature of the composite fiber with only 10% alpaca, moved to around 310 °C. This tendency might be due to the proper dispersion and physical bonding of alpaca powder into the PAN system, as previously it was found that the mechanically milled alpaca powder possess higher decomposition temperature rather than the alpaca fibers.[28] In addition, the polypeptide chains of the protein structure have tied up the flexible chain of PAN that restricts the easy movement of PAN.[46] Therefore, this phenomenon led to the increment of the decomposition temperature of the alpaca/PAN composite fibers.

Thermal degradation is an important property of polymeric materials that are determined at higher temperatures. The thermal degradation of the control PAN and alpaca/PAN composite fibers is shown in Figure 8(b). The major decomposition temperature was evident at around 286 °C in the case of control PAN

fibers where the nitrile (C—N) bonds degrade.[31,47] In addition, the second decomposition occurred at approximately 430 °C that belongs to the breakage of C—C bonds.[47] For composite fibers, it was found that the addition of only 10% alpaca powder to the PAN polymeric chain increased the thermal degradation temperature from almost 286 to 305 °C, which agrees with the study where the addition of lignin increased the degradation temperature of the lignin/PAN fibers.[31] Similarly, the addition of 30% alpaca enhanced the degradation temperature up to 320 °C, which might be due to the protein structure of the alpaca powder and large amounts of powder in the dope solution. This increment in decomposition temperature with the addition of alpaca to PAN polymer ensures the increased thermal stability of the alpaca/PAN composite fibers than that of pure PAN fibers, which is also supported by the DSC analysis [Figure 8(a)].

Crystallinity and Moisture Properties
Crystallinity of the Fibers. The diffraction patterns of control PAN and alpaca/PAN composite fibers are shown in Figure 9. The calculated Cr.I. of all the fibers is tabulated in Table III. The diffraction pattern of control PAN fiber showed a characteristic broad halo 2θ peak at 17° of the crystalline spacing of 5.2 Å and another small intensity 2θ peak at 28.5° indicating the crystalline spacing of 3.1 Å.[48] In a diffraction pattern, the halopeaks are due to the higher crystalline region whereas the broader peaks represent the lower crystalline or higher amorphous region.[40] From Table III, it can be found that the control PAN fibers showed around 55% crystallinity whereas it was gradually reduced with the increment of alpaca content in the composite fibers. As the
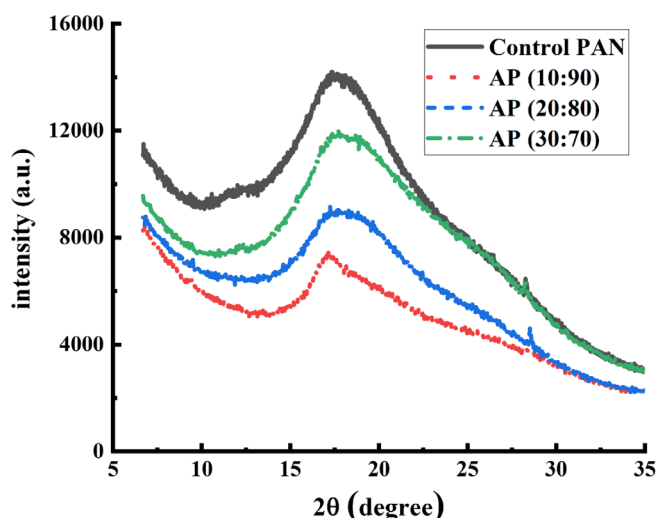

Figure 9. XRD analysis of control PAN and alpaca/PAN composite fibers. [Color figure can be viewed at wileyonlinelibrary.com]

Table III. Crystallinity Index of Control PAN and Alpaca/PAN Composite Fibers

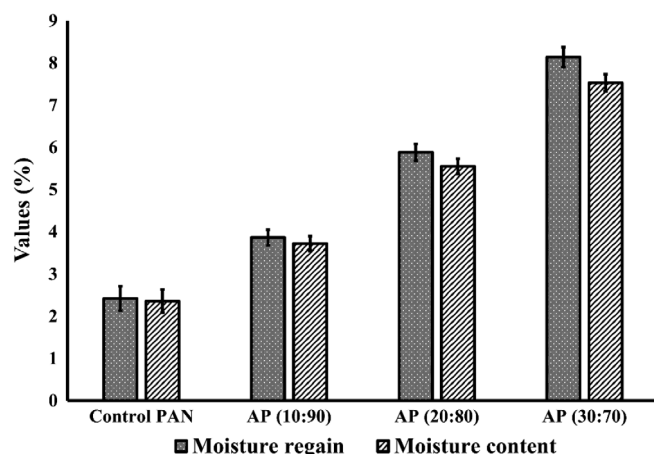| Sample	Peak intensity at 17° (I_f)	Peak intensity at 28.5° (I_s)	Cr.I. (%)
Control PAN	14 193.09	6455.41	54.51
AP (10:90)	7503.65	3820.75	49.08
AP (20:80)	9156.87	4955.32	45.88
AP (30:70)	11 991.03	6981.08	41.78

Figure 10. MR (%) and content (%) of control PAN and alpaca/PAN composite fibers. [Color figure can be viewed at wileyonlinelibrary.com]

broadness of the peak at 17° of the composite fibers increased (Figure 9), the crystallinity of the composite fibers decreased (Table III). The results are supporting literature where the lignin/PAN composite fibers exhibited lower crystallinity compared to pure PAN-based carbon fibers when the diffraction peaks of the composite fibers were broadened and less pronounced.[30] Hence, it is expected that the moisture absorption properties of the composite fibers would be enhanced because of the increased amorphous region.

Moisture Properties Analysis. The MR (%) and MC (%) of all the fibers are shown in Figure 10. It was apparent that with the incorporation of alpaca, the moisture properties of the composite fibers increased. Unlike natural fibers, synthetic fibers have low moisture properties. However, it is well known that higher regain of fiber can enhance the next to skin comfort of the wearer.[49] While the MR of alpaca fiber ranges from 14 to 16%, the MR of acrylic fibers ranges between 1.5 and 2.5%.[11,35] In this work, the MR and MC of the acrylic fiber were found to be 2.42 and 2.36%, respectively. However, when the alpaca particle was added to PAN, the composite fibers showed increased MR and MC values than that of the control PAN fibers. It was found that with the addition of 10% alpaca, the MR and MC were increased to around 60% compared to the control PAN fiber. The MR and MC were more than three times greater than the pure PAN, respectively, with the addition of 30% alpaca than that of pure acrylic fibers. While naturally, alpaca fibers are more moisture absorbent,[35] the FTIR analysis (Figure 6) showed that alpaca possesses a strong and broad —OH group that is responsible for the higher moisture absorption. In addition, the formation of porous and void areas on the surface and cross-section of the fibers as observed by SEM images (Figure 4) could also be accountable for the enhancement of the moisture properties of the composite fibers. Furthermore, the reduced crystalline area (Figure 9 and Table III) in the composite fibers is also responsible for the increment of MR (%) than that of pure PAN fibers.[50]

CONCLUSIONS

In our work, we have tried to use the eco-friendly and sustainable procedures to convert the nonspinnable waste alpaca fibers into

powders. Thereafter, these powders were blended with PAN polymer to wet spin the alpaca/PAN composite fibers with improved thermal and moisture properties for their future application. The SEM images of the control PAN fibers exhibited smooth fiber surface with typical ribbon-like shape whereas the composite fibers showed striations on the fiber surface with inner porous and void areas. The tenacity and elongation at break of the composite fibers decreased with an increasing amount of alpaca powders applied to the dope solution. No new absorption peaks appeared in the composite fibers other than the characteristics of protein and nitrile peaks through FTIR and NMR studies that ultimately confirm the proper blending and mixing between two polymers. From the DSC and TGA analyses, we have found that by adding alpaca powders the decomposition temperature was raised which confirms the increment of thermal stability of the composite fibers. It was also found that the crystallinity of the composite fibers reduced compared to the control PAN fibers with the increased alpaca content. Furthermore, with the addition of alpaca powders, the moisture properties of the composite fibers increased more than three times than that of the control PAN. The improved MRs of acrylic fibers resulting from the addition of alpaca will facilitate the use of acrylic fibers in a wide range of possible applications. From these observations, we can conclude that this work ensures the ecological reuse of textile waste materials and manufacturing of composite fibers with enhanced thermal and moisture properties while loading alpaca with the PAN polymer reduces the proportion of synthetic PAN in the dope solution.

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