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Tough and Transparent Nylon-6 Electrospun Nanofiber Reinforced Melamine–Formaldehyde Composites

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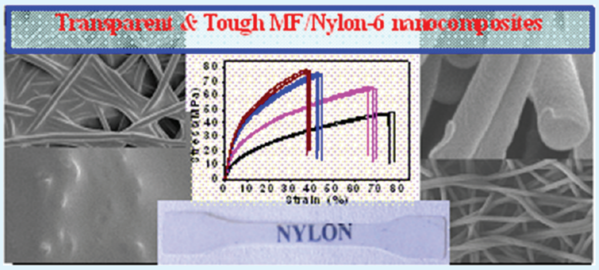
ABSTRACT: The use of nylon-6 electrospun nanofiber mats as reinforcement with synergistic effect in tensile strength and toughness for melamine–formaldehyde (MF) resin is highlighted in this article. Interestingly, there was a drastic effect of the wetting procedure of reinforcing fiber mat by the MF resin on the morphology and mechanical properties of the composites. The wetting of nylon fibers by passing through a solution of MF resin showed a core–shell morphology and a significant improvement in properties as compared to the dip-coating procedure for wetting of the fibers. Depending on the wt% of reinforcing nylon fiber mats, the composites could be considered as either fiber reinforced MF composites or MF glued nylon fibers.



KEYWORDS: *nanocomposites, mechanical properties, electrospinning, heat treatment, nanofibers*

INTRODUCTION

Melamine–formaldehyde (MF) resin and its derivatives are well-known for stiffness, hardness, strong adhesion to cellulose, and easy processing and are therefore widely applied in furniture, construction materials, tableware, adhesives, coatings, abrasive cleaner, textile treatment, and other materials requiring enhanced mechanical properties.[1−6] Pure MF resin is easily prepared from water-based melamine and formaldehyde solution by polycondensation and cross-linking during the compression molding or heating procedure,[7] but it is difficult to get the mechanical properties data of neat MF resin as it is brittle and develops extensive microcracks during sample preparation. The only data available indicated the mechanical properties of neat MF as a tensile strength of about 40 MPa and a stiffness of approximately 8–9 GPa, which implies a very low strain of less than 0.5%.[8] Different additives have been used in the past to improve the mechanical properties of MF resin, such as carbon fibers,[8] cellulose,[9] flax fibers,[10] pulp fibers,[11] carbon nanotubes,[12] and MWNT (multiwalled carbon nanotubes).[13] The resulting composites showed a higher tensile strength and modulus but nearly no increase in the elongation at break. Recently, polymer nanofibers produced by electrospinning have been attracting more and more attention for the preparation of composites. The continuous long fibers produced by electrospinning do not exhibit fiber edges (ends) and therefore lack stress concentration points in composites. During the electrospinning, the polymer molecular chains tend to align along the fiber axis as the polymer jet is drawn up to 100 000 times in less than 0.1 s. These highly molecular oriented nanofibers can provide a mechanically strong fiber for the preparation of fiber reinforced composites. Also, in most cases, electrospun nanofibers are collected in the form of a random aligned nonwoven mat with high porosity and large specific surface area. Therefore, the nanomat can be more feasibly impregnated with the resin solution and could make a remarkable improvement regarding the fracture toughness compared to the bulk film counterpart. Ramakrishna et al. pointed out in their review article that the incorporation of entangled nanofiber layers, characterized by a combination of interlocked in-plane and out-of-plane nanofibers, might contribute to improve interlaminar fracture resistance.[14] In addition, the diameters of electrospun nanofibers ranging from several to hundreds of nanometers can decrease the refractive index difference between the resin and reinforcing nanofibers, which is a significant advantage in producing transparent composites. Early reports of reinforcing effects of nanofibers in an epoxy and a rubber matrix (styrene–butadiene rubber) were contributed by Kim et al.[15] They showed an increase in Young's modulus, fracture toughness, and fracture energy of the epoxy matrix. Bergshoef et al. showed the formation of transparent epoxy composites using 4 wt % nylon-4, 6 electrospun nanofibers (30–200 nm in diameter).[16] Nylon-6 nanofibers produced by electrospinning exhibit excellent mechanical properties, such as toughness and high tensile strength,[17,18] and have also been adopted to make composites with poly(methyl methacrylate),[19] poylaniline,[20] polycaprolactone,[21] and with bis-glycidyl methacrylate/tetraglycidylmthacrylate ((BIS-GMA/TEGDMA) as dental restorative composites.[22] The field of applying electrospun nanofibers as reinforcement is still in its infancy with just a few countable reports in the literature. A recent review article[14] is a good refrence supporting this fact. In this work, we highlight the use of nylon-6 nanofibers for

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preparing very tough and transparent composites with MF resin. The importance of the fiber wetting procedure for the preparation of the corresponding composites is also emphasized. A change of the wetting method could bring about a drastic change in the morphology (from film to core−shell) of the wet fibers. Different composites with varied amounts of nylon-6 fibers generated a profile of properties. Even composites with very high amounts of fibers (nylon-6 mats) with high strength could be prepared from core−shell fiber composites. FT-IR, SEM, TGA, tensile testing, and UV−vis spectroscopy techniques were applied to determine the structure and properties of the MF/nylon-6 nanofiber composites.

EXPERIMENTAL SECTION

Materials. Nylon-6 (Ultramid B24) was kindly supplied by BASF. Melamine−formaldehyde−water solution (Madurit SMW818 75% WA) was supplied by INEOS Melamines GmbH, Germany. The solvents, formic acid (FA, ≥98 wt %) and acetic acid (AcOH, ≥98 wt %), were acquired by Sigma-Aldrich. All materials were used as received without further purification.

Electrospinning and Composite Preparation. Nylon-6 was dissolved in FA/AcOH (40/60, w/w) to form an electrospinning solution with a concentration of 20 wt %. During the electrospinning process, a high voltage electric field of 100 kV/m, by imposing a 25 kV electrical potential to a 25 cm gap between a spinneret and a rotating cylinder, was applied on the flat tip of a needle. The polymer solution was delivered by a syringe pump at a feeding rate of 0.3 mL/h, and the nylon-6 nanofibers were collected on a cylinder, which rotated at 30 rpm. The resulting nanofiber mat was cut into small samples exhibiting a size of 4.5 × 5.0 cm and dried in a vacuum oven at 80 °C for 12 h. Two different methods were used for making composites, and their respective advantages and disadvatges are discussed in the Results and Discussion section. In method 1, the dried nanofiber mats were immersed into the melamine−formaldehyde−water solutions of different concentrations (i.e., 5 wt %, 10 wt %, and 15 wt % MF in water) (method 1; dip-coating; Figure 1) which were diluted from a 75 wt % MF solution, or alternatively, MF solutions were passed through the fiber mats; i.e., a process similar to liquid filtration (method 2; Figure 2). The electrospun nanomat is kept between two Whatman qualitative filter papers (Grade 1, 11 μm) in a suction filtration flask, and MF solutions of different concentrations were passed under vacuum (about 20 bar) in different experiments.

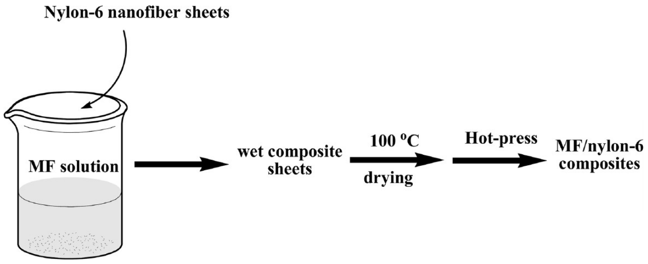


Figure 1. Schematic process for the preparation of the MF/nylon-6 nanocomposites by immersing and hot-pressing (method 1).

After wetting of the fibers (either method 1 or method 2), the sheets were dried at at 100 °C for 12 h and subsequently two impregnated and dried sheets were hot pressed at 180 °C for 10 min at a pressure of 20 MPa.[23] During the hot-pressing, the MF was polymerized and cross-linked around the nylon-6 nanofibers, resulting in composites with varying compositions. Two electrospun nylon-6 mats were also hot-pressed under similar conditions as applied for the formation of the composites and used as blank for properties comparison.

Characterization. A JSM-7500 scanning electronic microscope (SEM) was applied to investigate the morphology and structure of nylon-6 nanofibers and MF/nylon-6 nanocomposites. Prior to scanning, the specimens were sputter-coated with gold to avoid charge accumulations. Diameter distribution of the nylon-6 nanofibers was obtained by analysis of the SEM images via the ImageJ software. Mechanical properties were measured by means of a Zwick/Roell BT1-FR 0.5TN-D14 machine equipped with a 200 N KAF-TC load sensor using a stretching rate of 5 mm/min at room temperature. Dog-bone-shaped specimens were cut with a length of 3.0 cm and a width of 0.2 cm. FT-IR spectra were recorded on a Digilab Excalibur Series with an ATR unit MIRacle by Pike Technology. Transparency in the range of visible light was investigated by a Perkin-Elmer Lambda 9 UV/vis/NIR spectrophotometer operating in transmittance mode (200−800 nm). Thermal properties of the composites were evaluated on Mettler Toledo TGA/SDTA 851e at a heating rate of 10 °C/min in N_2 from 50 to 800 °C.

RESULTS AND DISCUSSION

Electrospinning is a fast and effective technology to prepare nanofibers with a diameter distribution from several to hundreds of nanometers.[24] In this work, nylon-6 nanofibers were electrospun from 20 wt % nylon FA/AcOH solutions. They comprised a smooth surface, a random alignment, and a centralized diameter distribution. As shown in Figure 3A,B, the diameter of nanofibers is mainly distributed from 186 to 221 nm and no defects such as beads, pores, or ribbons were found. For the preparation of the composites, nylon-6 nanofiber mats were impregnated with the MF water solution. This was due to (1) the high porosity and low water contact angle of nylon-6 nanofiber mats, which can be as low as 12 degrees after a contact time of 10 s[25] and (2) an improvement in wetting behavior relative to nylon-6 bulk.[26] Two different methods were used to wet the nylon fibers. The first method made use of immersing the nylon fibers in MF solutions of different

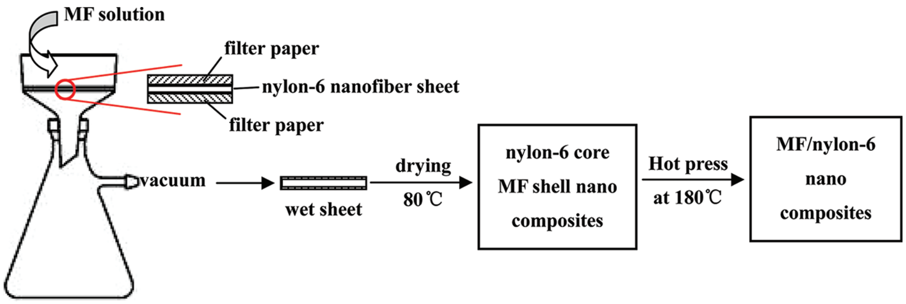


Figure 2. Schematic process for the preparation of the MF/nylon-6 nanocomposites by passing a MF solution through the nylon-6 nanomat and followed by hot-pressing (method 2).

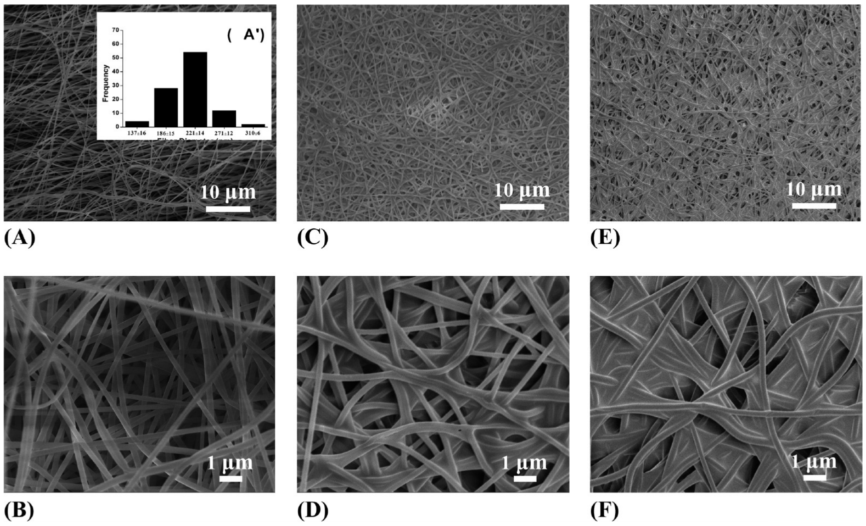


Figure 3. SEM images of (A) and (B) nylon-6 nanofibers, (C) and (D) MF/nylon-6 nanocomposite prepared by immersion into a MF solution of a concentration of 5 wt %, and (E) and (F) MF/nylon-6 nanocomposite made by immersion into a MF solution of a concentration of 15 wt %. (A′) column diagram of the diameter distribution of nylon-6 nanofibers.

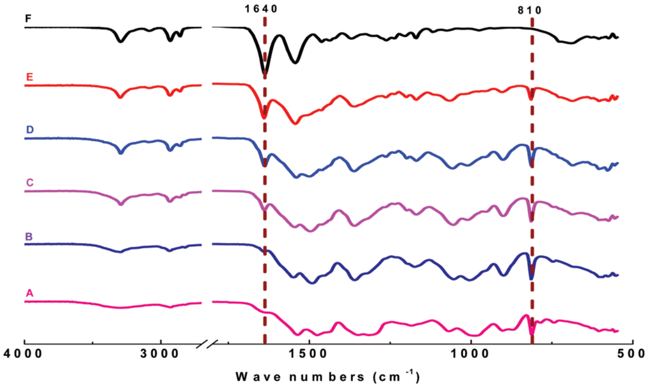


Figure 4. FT-IR spectra of composites with different contents of nylon-6 nanomat: A, 0 wt % (neat MF); B, 13 wt %; C, 26 wt %; D, 30 wt %; E, 62 wt %; F, 100 wt % (nylon-6 nanofibers).

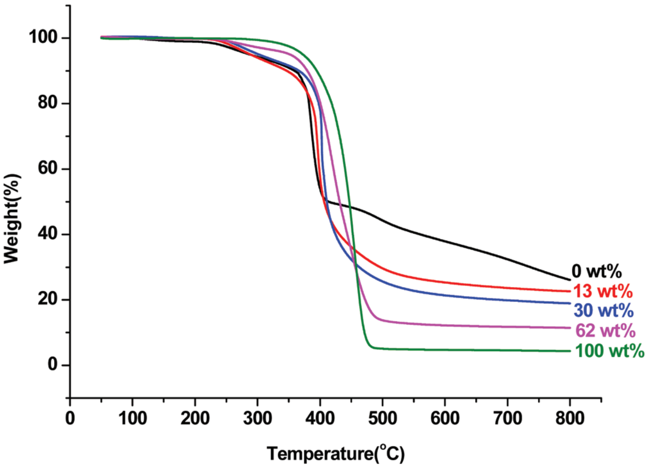


Figure 5. Thermal stabilities of pure MF resin, nylon-6 nanofiber sheets, and MF/nylon-6 nanocomposites with different amounts of nylon-6 nanofibers.

Table 1. Thermal Properties of MF/Nylon-6 Composites with Different Contents of Nylon-6 Nanomats

content (wt %)	0	13	30	62	100
$T_{5\%}$ (°C)	288	289	302	352	372
T_d (°C)	386	395	403	418	450
char yield (%)	26	23	19	11	4

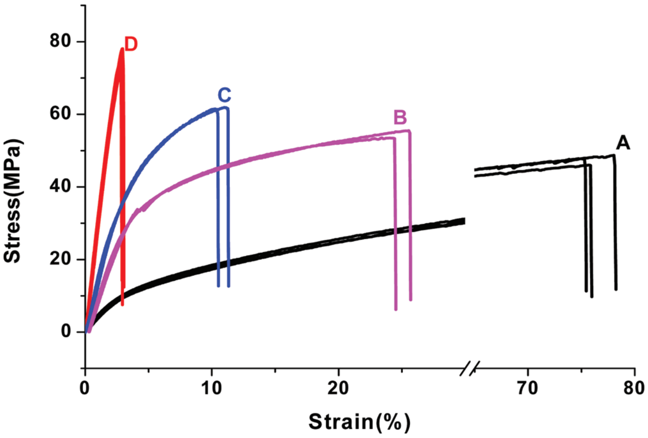


Figure 6. Typical stress−strain curves of MF/nylon-6 nanocomposites (method 1) with a content of nylon-6 in composites of (A) 100 wt %; (B) 62 wt %; (C) 30 wt %; (D) 13 wt %.

concentrations. To make composites with high amounts of MF resin, a more concentrated solution of MF was required. Different MF/nylon-6 composites with varied amounts of nylon-6 in the composite (13 wt %, 30 wt %, and 62 wt %) were prepared as determined by gravimetry.

The resulting composites depicted in Figure 3C,D exhibited quite different morphologies depending on the concentration of the respective MF solution applied. Immersion in low concentrated (5 wt %) MF solution led to deposition of MF resin on fibers. However, immersion into highly concentrated MF solutions (15 wt %) led to the deposition of MF resin both on fibers and in-between the fibers in the form of films between fibers. A small coiling of MF coated nylon fibers in composites was observed after drying at 100 °C for 12 h (Figure 3). This could be due to the different coefficient of thermal expansion between nylon-6 and MF resin.

Table 2. Mechanical Properties of MF/Nylon-6 Nanocomposites Made by Method 1 and Method 2* with Different Contents of Nylon-6 Nanofibers

nylon-6 content (wt %)	stress (MPa)	strain (%)	E modulus (2%) (GPa)	integration of stress−strain curves (MJ/m^3)	toughness (J/g)
100	47.5 ± 1.4	76.2 ± 1.6	0.37 ± 0.02	24.7 ± 0.85	21.8 ± 0.75
62	54.5 ± 1.4	24.8 ± 1.1	0.96 ± 0.09	10.7 ± 0.49	7.8 ± 0.36
30	61.7 ± 0.3	10.6 ± 0.5	1.34 ± 0.04	4.8 ± 0.33	3.6 ± 0.25
13	74.5 ± 2.9	2.85 ± 0.1	2.88 ± 0.08	1.2 ± 0.07	1.0 ± 0.05
82*	65.2 ± 1.3	67.9 ± 2.0	0.59 ± 0.23	31.6 ± 1.00	27.0 ± 0.85
72*	75.1 ± 1.0	43.4 ± 1.4	0.79 ± 0.07	23.4 ± 0.88	19.6 ± 0.74
66*	77.9 ± 0.8	38.4 ± 0.8	0.85 ± 0.05	21.3 ± 0.55	17.6 ± 0.45

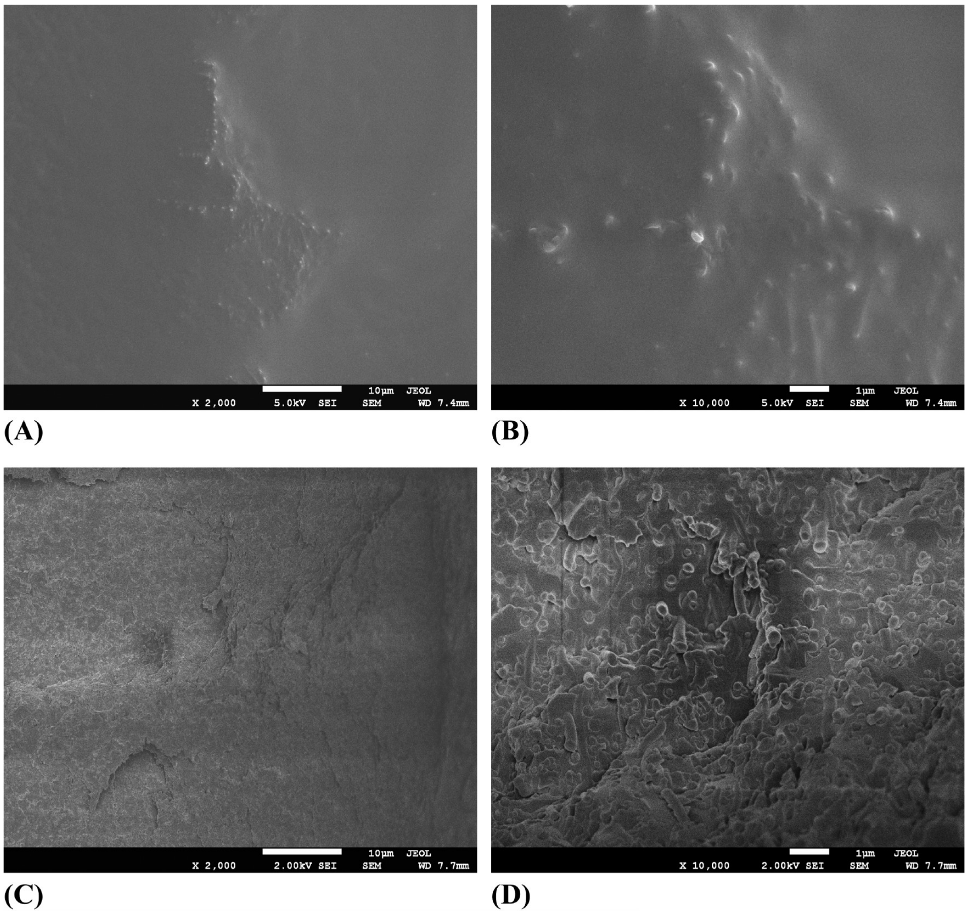


Figure 7. SEM images of fracture cross-section of composites (method 1) with a content of nylon-6 nanofibers of (A) and (B) 13 wt % and (C) and (D) 62 wt %. Scale bar: (A) and (C), 10 μm; (B) and (D), 1 μm.

FT-IR spectra of neat MF, nylon-6 nanofibers, and the MF/nylon-6 nanofiber composites are shown in Figure 4. The pure MF resin exhibited a strong and sharp peak at 810 cm^{-1}, which is characteristic for the triazine ring, while nylon-6 nanofiber sheets showed a strong band at 1640 cm^{-1}, which was due to the vibration of amide (Figure 4A,F).[27,28] Regarding MF/nylon-6 nanocomposites, according to Figure 4B−E, the characteristic peaks shown in the spectra of neat MF and nylon-6 also appeared in the spectra of MF/nylon-6 nanocomposites. The intensity of the peak at 1640 cm^{-1} became weaker, whereas the intensity of the peak at 810 cm^{-1} increased, as the content of nylon-6 nanofibers was raised in the composites. This confirmed that the integrated chemical behavior of both materials was present in the composites.

The resulting composites were investigated for their thermal stability by thermogravimetry in N_2 at a heating rate of 10 °C/min. As shown in Figure 5, all the samples exhibited an excellent heat-resistance up to at least 200 °C. As for nylon-6 nanofibers, a single step of thermal degradation was observed, while the TGA curve of the pure MF resin showed three stages of degradation. The first step of weight loss started at 210 °C and could be due to the dehydration of the uncross-linked methylol in MF resin; the second obvious degradation from 350 to 400 °C might have resulted from a decomposition of aliphatic ether group; the last slow weight loss may be due to a decomposition of the triazine. This decomposition behavior is similar to the literature for MF resins.[27] Similar trends could be found among the TGA curves of MF/nylon-6 composites. The further results are summarized in Table 1, in which $T_{5\%}$ temperature at which 5% weight loss took place, the decomposition temperature (T_d), and char yield at 800 °C are compared. As the content of nylon-6 nanofibers increased,

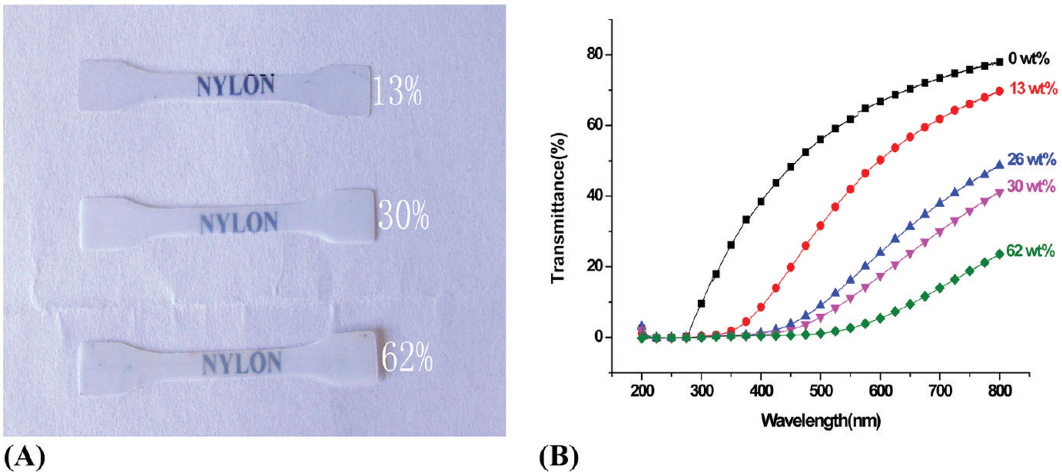
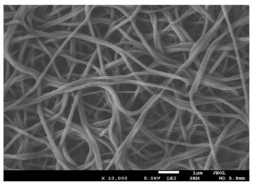
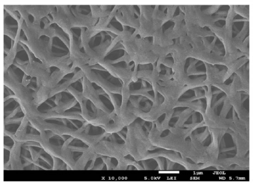
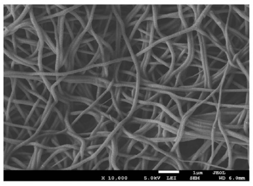
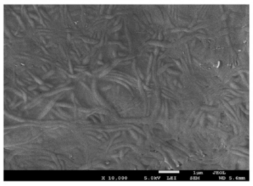
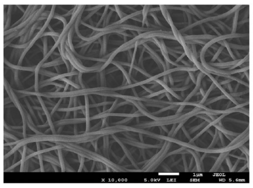
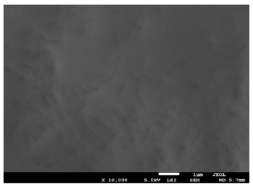
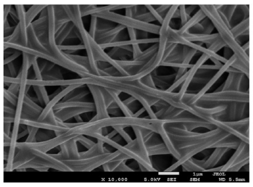
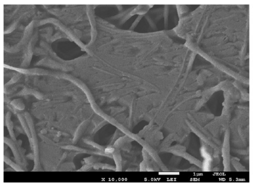


Figure 8. (A) Photographs of semitransparent composites. (B) Transmission spectra of composites with varying content of nylon-6 nanofibers.

Table 3. Morphology Comparison of the Nanocomposites with Different Content of MF before and after Hot-Pressing[a]

Composite	Before hot-pressing	After hot-pressing
1: 18 wt% MF		
2: 28 wt% MF		
3: 34 wt% MF		
4: 38 wt% MF		

[a] Scale bar = 1 μm.

$T_{5\%}$ of the composite increased from 289 to 330 °C, while T_d increased from 396 to 418 °C. However, the char yield at 800 °C showed a decrease from 23% to 12% as the amount of nylon-6 nanofibers increased and the lowest char yield for nylon-6 nanofiber mat was seen. The char yield is one of the measures of thermal stability. The thermal degradation behavior of MF resin is well-known in the literature. The degradation products are water, formaldehyde, hydrogen cyanide, carbon monoxide, and melamine. The melamine can undergo further condensation to give high molecular weight solid degradation products. According to the literature, the C−N bonds in MF char do not undergo further combustion and the composites with more MF content show, in general, more char yield.[29,30]

The mechanical properties of MF/nylon-6 nanofiber composites reinforced with different amounts of nylon-6 made by method 1 were measured. Typical stress−strain curves and the tensile properties are presented in Figure 6 and Table 2 respectively. The electrospun nylon-6 mats alone (two mats without impregnation with MF)) were also hot-pressed under similar conditions as applied for the formation of the composites and tested for mechanical properties. The compressed nylon-6 nanomat (blank) exhibited a tensile strength of 47 MPa strain at break of around 76% and toughness of around 21.8 J/g. The MF/nylon-6 composite with 13 wt % of nylon-6 comprised a very high tensile strength of 74.5 MPa and strain at break of about 3%. The reinforcement with nylon-6 nanofibers showed a synergistic effect regarding the tensile strength of the resulting composites with a value higher than those of nylon-6 nanofiber mats or MF resin. This value was nearly 2 times the strength and 6 times the strain of the pure MF resin. Further, a decrease in tensile strength and an increase in strain at break on increasing the nylon-6 content in the composites was detected, but the tensile strength is always higher compared to that of pure MF resin or nylon-6 nanofiber mats. The nylon-6 nanofibers were nonaligned and randomly distributed in the composites as shown in the Figure 3. During tensile testing, the stretching force was taken by reinforcing nylon-6 fibers and the fricton between fibers helped in delaying composite failure. Therefore, more fibers resulted in a higher strain, as shown in the tensile testing results of the composites.

Generally, cracking is one of the most important factors to affect the strength of materials.[31] Figure 7 shows SEM micrographs of the fracture cross-section of the composites with different contents of nylon-6 nanofibers. Samples with 13 wt % nanofibers comprised a smooth cross-section, and the interfaces between fibers and matrix were integrated closely. Nevertheless, a rougher morphology appeared when the content of nanofibers was increased, and many cracks could be detected (Figure 7C,D). When cracks appear, the strain energy was released in a material volume adjacent to the crack. Thus, a smaller strength was obtained upon increasing the content of fibers.

The composites prepared from MF and nylon-6 nanofibers were semitransparent as shown in Figure 8A. This appearance of the nanocomposite might be the result of the small diameter

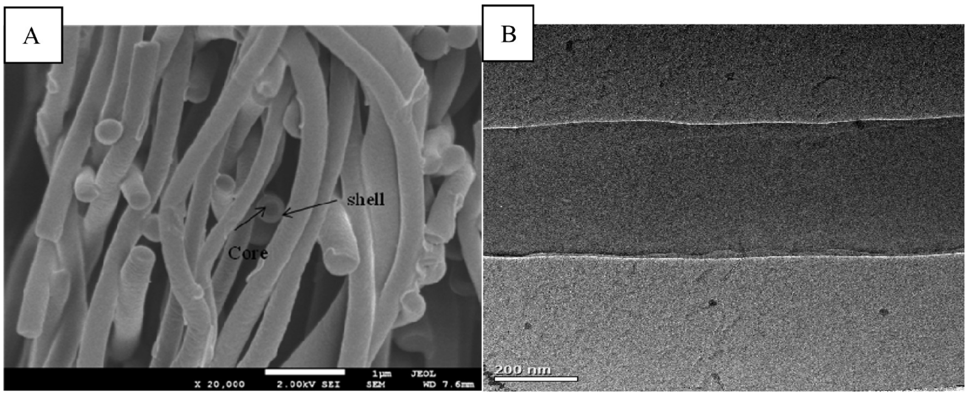


Figure 9. Core−shell structure of the nanocomposites with 66 wt % nylon fibers before hot-pressing (A) SEM (scale bar = 1 μm); (B) TEM.

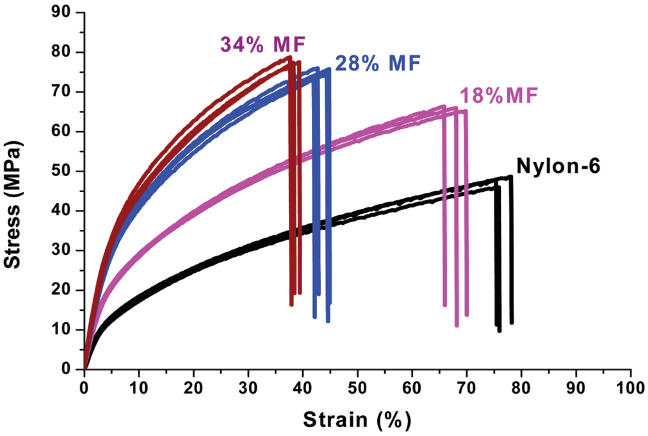


Figure 10. Typical stress−strain curves of MF/nylon-6 nanocomposites (method 2) with different contents of MF.

of nylon-6 nanofibers and nearly the same refractive index of the nylon-6 and the MF resin, 1.53 and 1.52, respectively.[32,33] However, the transparency decreased as the content of fibers was increased, which can be proved by the transmission spectra shown in Figure 8B. When the nylon-6 nanofiber content increased from 13 wt % to 62 wt %, the transmittance decreased dramatically from 70% to 24% at a wavelength of 800 nm. A higher content of nanofibers in the composite shielded the transmittance of visible light. Therefore, the composite with 13 wt % fibers, which showed a smooth cross-section, exhibited the highest transmittance of 70% (800 nm), which is only 8% less than the transmittance of pure MF, and was found to be best in terms of mechanical properties also.

As described above, the comparison of SEM pictures of composites with different amounts of nylon-6 fibers before and after hot-pressing revealed an irregular and incomplete wetting/covering of nylon-6 fibers for very high amounts of nylon-6 fibers, i.e., 62 wt %. Therefore, an attempt was also made to modify the wetting procedure of nylon-6 nanomats with MF resin for composite formation. Instead of immersing the nylon-6 nanofiber mat into the MF solution, MF solutions with different concentrations were passed through nylon-6 nanofiber mats in a process similar to liquid filtration, as depicted in Figure 2 (method 2). Afterward, two impregnated nanomats were hot-pressed together as described in the experimental part. This resulted in the generation of composites with different amounts of nylon fibers as determined by gravimetry.

The morphologies of the resulting composites are listed in Table 3. A good comparison can be found among composites 3 and 4 in Table 3. Composite 3 was prepared by passing MF solution through the nylon-6 fiber mat (method 2) whereas composite 4 was made by immersing nylon-6 fiber mat in a dilute solution of MF (method 1). Both exhibited a similar content of nylon-6, i.e., 66% and 62 wt %, respectively, as determined by gravimetry. The comparison of the respective SEM pictures clearly showed the advantage of passing MF solution through the nylon-6 mat (method 2) as the wetting procedure. In this case, the whole nylon-6 mat was completey wetted without cracks and inhomogeneous wetting. The resulting composite fibers had a core−shell morphology, as shown in Figure 9. In comparison to this, immersion of nylon-6 mat in MF solution provided an incompletely wetted mat (composite 4). This was reflected in the properties of composites as well (Figure 10 and Table 2). Composite 3 showed a significant increase regarding tensile stress (78 MPa vs 54 MPa) and elongation at break (38% vs 25%) as compared to composite 4 prepared by method 1. In addition, the composites with extremely high amounts of nylon-6 fibers (around 82 wt %) prepared by method 2 showed a significant improvement of the mechanical properties. The shell of MF resin glued the fibers together and strengthened the interface bewteen matrix (MF resin) and the reinforcing fiber (nylon-6) in composites made by method 2.

The toughness of composites is a measure of work done per unit mass to break the sample. It was determined by dividing the area under stress−strain curves with density of the composites in a similar way as reported in literature for other systems.[34] The values are tabulated in Table 2. There was a small decrease in toughness from 27 J/g (31.5 MJ/m^3) to 18 J/g (21.3 MJ/m^3) on reducing the amount of reinforcing nylon fibers from 82 to 66 wt %, but still, the values are very high in the range of elastomeric materials. For example, toughness of about 25 MJ/m^3 was reported in the literature for elastomeric polyurethane membranes.[34] The toughness values for carbon nanotubes (CNT) reinforced poly(vinyl alcohol), kevlar, and spider dragline silk are 16, 33, and 165 J/g, respectively.[35] The effect of irregular and incomplete wetting/covering of nylon-6 fibers in composites made using method 1 was also reflected in toughness values. Another good comparison between the efficiency of two wetting procedures used in this work could be entries 2 and 7 of Table 2. They both had almost the same fiber content but drastically different toughness values. The composite made by method 1 (entry 2, Table 2) was tougher than many thermoplastics (PVA = 3−4 J/g) but showed significantly less toughness as compared to the composite made using method 2.

CONCLUSIONS

MF/nylon-6 composites were prepared using electrospun nylon-6 mats as reinforcement. The reinforcement in mechanical properties of the MF resin could be seen using nylon nanofiber mats. The fiber reinforced composites showed enhanced mechanical properties in comparison to those of pure nylon-6 nanomats and the MF resin. Interestingly, there was a drastic effect of the wetting procedure of the reinforcing fiber mat by the MF resin on both morphology and mechanical properties of the composites. The wetting of nylon-6 nanofibers by passing through a solution of MF resin resulted in a core−shell morphology and a significant improvement in properties as compared to the immersion procedure for wetting of the fibers. Depending upon the wt% of reinforcing nylon nanofiber mats, the composites can be considered as either fiber reinforced MF composites or MF glued nylon fibers.

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Notes

The authors declare no competing financial interest.

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