Preparation of Cellulose Nanofibers Reinforced Polyether-b-Amide Nanocomposite

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A new kind of thermoplastic elastomer nanocomposite reinforced with cellulose nanofibers has been reported. The aim of this investigation was to study the interaction and dispersion of cellulose nanofibers into the Pebax matrix. These copolymers are considered as polyether-b-amide thermoplastic elastomers. They are from renewable resources, and their hydrophilic character allows them to interact with nanocellulose. The interaction and reinforcement effect of nanocellulose at 3 levels of nanocellulose, (1%, 3%, and 5%), were examined by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), and other mechanical tests. The results achieved from these tests indicated appropriate effects of cellulose nanofibers for the strong interaction and close contact with the polyamide phase of the Pebax polymer *via* strong hydrogen bonding.

Key words: Thermoplastic elastomer; cellulose nanofiber; Nanocomposite; Pebax

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INTRODUCTION

Interest in nanocomposites has increased markedly in recent years due to the great potential associated with this relatively new group of materials. Nanocomposites are usually defined as a combination of two or more materials, or phases, in which one of the phases has at least one dimension in the nanometer range (1 nm to 100 nm) (Oksman *et al.* 2006; Sorrentino *et al.* 2007).

The development of biodegradable materials from renewable sources, such as cellulose, is increasing because of their availability, low price, and abundance in nature (Cheriana *et al.* 2011). New properties and functions are required for the next generation of cellulose fiber composites, and such features can be displayed by nanocellulose fiber. Among different kinds of nanocellulose materials, cellulose nanofibrils are ideal candidates for their reinforcing role due to the properties such as low density, high aspect ratio, high surface area, and modifiable surface properties because of reactive OH side groups. Cellulose nanofibers produced by grinding are fundamentally different from cellulose nanowhiskers in terms of their entanglement, morphology, production process, and yield. In particular, the difference in entanglement can be attributed to the difference between the aspect ratios of cellulose nanowhiskers and of cellulose nanofibers produced by grinding. Grinding is simpler, cheaper, and faster than acid hydrolysis, bacterial synthesis or electrospinning, and it is a one-step, high-yield process (Yousefi *et al.* 2011).

Advantages in the use of cellulose nanofibrils are related not only to their useful, unsurpassed, physical and chemical properties, but also to their biodegradability, renewability, sustainability, abundance, and high biocompatibility (Brinchi *et al.* 2013).

In recent years, great emphasis has been given to the development of composites based on renewable resources. In this research, the authors selected Pebax copolymers as the composite matrix. Pebax is a polyether-b-amide thermoplastic elastomer that has a hydrophilic character (not water-soluable), which is the source of compatibility between cellulose fibers and the polymer. The Pebax copolymer consists of rigid polyamide segments, acting as physical cross-links, and flexible polyether segments. Its properties depend on the polyether/polyamide ratio (Fakirov 2005; Sliwa *et al.* 2012). Qua and Hornsby (2011) worked on reinforcing Polyamid-6 by nanocellulose, but there is no report about preparing a nanocomposite by Pebax reinforced with nanocellulose.

Furthermore, another reason to select this polymer is that it comes from renewable resources. This is a great advantage because the authors' final objective is to elaborate on a composite mainly derived from natural resources, *i.e.* bio-based composites. The characteristics of the polymer, in particular its elastomeric properties and hydrophilic character, define it as a technical polymer (Capadona *et al.* 2007).

The main challenge with nanoparticles is related to their homogeneous dispersion and distribution within a polymeric matrix, which may affect the final properties. Homogeneous dispersion and distribution of cellulose nanofibers is difficult to achieve by means of traditional melt processing techniques. The dispersing medium has to be evaporated during extrusion, which places demands on the screw configuration and the venting/vacuum capability during extrusion (Bondeson and Oksman 2007; Lemahieu et al. 2011). As the dispersing medium is evaporated, there is a high tendency of nanocellulose fibers to form agglomerates, partly as a consequence of the presence of hydroxyl groups on the particle surfaces and their high specific surface area (Capadona et al. 2007, 2009). For this reason, the most common method used in the preparation of cellulose nanocomposites is solution casting. Another drawback using nanocellulose fibers is the difficulty to disperse them uniformly in non-polar medium because of their polar surface (Oksman et al. 2006). So, most researchers are focused on a water-soluble polymeric matrix, considering the hydrophilic character of cellulose for the easier dispersion of cellulose (Oksman et al. 2006; Bondeson and Oksman 2007; Chen et al. 2009; Alain Dufresne 2010; Lemahieu et al. 2011; Zhou et al. 2012; Tang et al. 2015; Pracella et al 2014; Trifol et al. 2016; Haafiz et al. 2016; Ivdre et al. 2016; Khoo et al. 2016; Sethi et al. 2017).

The main aim of this study was to investigate the possibility of producing a nanocellulose composite with a non-water-soluble polymer matrix (Pebax). The authors report on the preparation of thermoplastic elastomer composites reinforced with cellulose nanofibers. Then, the effects of the cellulose nanofibers loadings and the compatibility between the cellulose nanofibers and Pebax matrix were evaluated by differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and mechanical tests. The results indicated appropriate effects of nanocellulose for good interaction and close contact between the nanocellulose and polyamide phase of the Pebax polymer.

EXPERIMENTAL

Materials

Polyether block amide Pebax® 55R53 SP 01 (density 1.03 g cm⁻³, melting point 167 °C), a thermoplastic elastomer based on renewable resources was supplied by Arkema (Colombes Cedex, France) in granule form. The benzyl alcohol used in this work was purchased from Merck (Darmstadt, Germany).

In this research the raw material was pure commercial cellulose fibers of softwood, purchased from Nano Novin Polymer Co. Cellulose nanofibers were prepared from long fiber α -cellulose pulp by a super-grinding procedure. At first, long fiber α -cellulose pulp was rinsed with distilled water 3 times and then placed in a 5% concentration of potassium hydroxide (KOH) solution for 1 h at 80 °C under mechanical stirring. After this alkaline treatment, α -cellulose suspension with a 1% concentration was prepared and then passed 3 times through the super-grinding disk machine (MKCA6-3; Masuko Sangyo Co., Ltd., Kawaguchi, Japan) to produce cellulose nanofibers. The super-grinding disk machine consisted of a static and a rotating grinder disk. The grinding stone was SiC and its diameter was 6 inches. The time and speed of grinding were 40 g/hour and 1800 rpm, respectively. The energy consumption of the grinder was 25 KWh/Kg and the nano-size fibers in gel form were achieved.

Preparation of nanocomposites

Pebax has a high chemical resistance to various chemicals and solvents, because of its structure as a block-copolymer of poly-amide and polyether. The authors found that benzyl alcohol was a good solvent for Pebax. A specific amount of Pebax was dissolved in benzyl alcohol (with a ratio of 6.6% solvent to 100% polymer) at 100 °C for 3.5 h under mechanical stirring. The solution of polyether block amide copolymers was prepared.

The solvent exchange method has been used to change the water of nanocellulose suspension to benzyl alcohol by a series of centrifugation steps. The nanocellulose suspension was centrifuged at 10,000 rpm and 20 °C for 5 min, and the water was replaced with ethanol. This process was repeated 3 times. This procedure was applied again, and the ethanol was replaced with benzyl alcohol. This process was also repeated 3 times. Then, a different amount of Pebax and nanofibers with the benzyl alcohol base were mixed together, followed by mechanical stirring for 10 min at 60 °C to prepare a masterbatch. The masterbatches were poured onto petri dishes and oven-dried at 90 °C for approximately 3 days to evaporate the solvent.

Preparation of samples

The Pebax granules and masterbatches were oven-dried at 75 °C for 8 h to remove the absorbed water before preparation of samples. The nanocomposite samples were obtained by adding the masterbatch to the required amount of Pebax granules and then melted and blended in a small capacity internal mixer (Model 815802, Brabender Technologie GmbH & Co. KG, Duisburg, Germany). This minimized the loss of masterbatch that may occur in a high volume mixer and also promoted its homogeneous distribution into the Pebax matrix. The heating temperature and rotational speed of the screws were set at 180 °C and 60 rpm, respectively, for 10 min. The mixed materials were compression molded using a Nautilus hot press (Villeurbanne, France). The material was placed between metal plates of the press, preheated in contact mode without pressure at 190 °C for 5 min, pressed with 15 MPa for 1 min at 190 °C, and then cooled under the same pressure. Formulations of the samples and abbreviations used for the respective mixtures prepared are given in Table 1.

Code Content	Pebax	1% CNF ^a	3% CNF	5% CNF
Pebax Polymer (%)	100	99	97	95
Nanocellulose (%)	0	1	3	5

Table 1. Formulation and Appreviations Used for Mixtures Prepar	ulation and Abbreviations Used for Mixtures Prepa	ures Prepare	Used for Mixtu	Abbreviations	and	. Formulation	Table 1
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*Note: a CNF= Cellulose Nanofibrils composite

Methods

Differential scanning calorimetry analysis (DSC)

The DSC experiments were conducted on a differential scanning calorimeter 131 (Setaram Instrumentation, Caluire, France). Sample sizes of approximately 10 mg were sealed in aluminum-crimped pans. As per ASTM D3418 (2015), the samples were heated at the rate of 10 °C/min⁻¹ under an inert nitrogen atmosphere. At first, the samples were heated from 25 °C to 200 °C, then cooled from 200 °C to 25 °C, and then reheated to 200 °C. The first heating cycle was intended to remove any prior thermal history that resulted from the process of composite manufacture.

Mechanical testing

The tensile properties were measured according to ASTM D638 (2010), using a Santam machine (Model STM-So, Santam Company, Tehran, Iran). The crosshead speed during the tension testing was 50 mm/min⁻¹. A Zwick impact tester (Model 5102, Zwick GmbH & Co. KG, Ulm, Germany) was used for the Izod impact test. All of the samples were notched in the center of one longitudinal side according to ASTM D256 (2010). For each treatment, 3 replications were tested.

Morphological study

The SEM micrographs of the surfaces that were fractured in liquid nitrogen were taken using a scanning electron microscope (Model AIS2100 Seron Technology, Gyeonggi-do, Korea). The samples were mounted onto a SEM holder using double-sided electrically conducting carbon adhesive tabs to prevent a surface charge on the specimens when exposed to the electron beam.

The morphology of the prepared nanocellulose was examined *via* Atomic Force Microscopy (AFM), which was performed by an SII Nanonavi E-sweep microscope (SII Nanotechnology, Inc., Tokyo, Japan) in dynamic force mode at 25 °C. The Si probe was an SI-DF20 (SII Nanotechnology, Inc., Tokyo, Japan) with a spring constant of 18 N/m and a frequency of 138 kHz.

FTIR analysis

The FTIR analysis was performed by means of a Thermo Nicolet Nexus 870 FTIR (Nicolet Instrument Corporation, Madison, USA) instrument to analyze the interaction between the nanocellulose and the matrix. The samples were scanned in the frequency range 500 cm⁻¹ to 4000 cm⁻¹ at a resolution of 4 cm⁻¹. Thin films of nanocomposite were prepared for the FTIR analysis.

RESULTS AND DISCUSSION

Mechanical Analysis

The results from tensile testing and Izod impact resistance are given in Table 2. As shown, the Young's modulus increased with the cellulose nanofiber content up to 3%, but at the higher nanofiber concentrations (5%), an increase of the Young's modulus did not happen as remarkably as was expected. The Young's modulus for the sample containing 3% nanocellulose was 5.96 times higher than the pure Pebax (the ratio of composite modulus / modulus of pure Pebax). As expected, the elongation at break was reduced with increased cellulose nanofibers (Cheriana et al. 2011). The impact resistance exhibited a trend similar to Young's modulus and showed an improvement of 51.62 J M⁻¹ for the 3% sample, which was 1.81 times higher than that of the pure Pebax. The improvements of the tensile and impact properties may have been ascribed to the aspect ratio, nucleation effects, higher modulus of the cellulose nanofibers, and the strong interaction between the Pebax matrix and nanocomposite (Dogan and McHugh 2007; Hubbe et al. 2008; Ten et al. 2010). The filler orientation and distribution plays an important role in realizing the concept of aspect ratio (Jiang et al. 2007; Chen et al. 2009; Malmstrom and Carlmark 2012). The maximum improvement in properties of the composites occurs when there is just enough filler in the matrix that they can form a continuous structure (Reddy et al. 2013). This is also known as the percolation threshold; the enhancement is influenced by the proper dispersion of filler within the matrix (Reddy et al. 2013). In the present research, the most effective content of nanocellulose was 3%. It seemed that the small decrease in the Young's modulus of the 5% nanocomposite in comparison with the 3% nanocomposite was most likely due to agglomeration phenomena of the nanocellulose into the polymer matrix, as observed by the SEM image. The variation of Young's modulus, observed for the samples in the range from 1% to 5% nanocellulose, was close to what was reported for other nanocomposites systems reinforced with cellulose nanofibers and cellulose nanocrystals (Xu et al. 2013; Pracella et al. 2014).

Code	Young's Modulus (MPa)	Elongation at Break (%)	Impact Resistance (J M ⁻¹)
Pebax	16.82	501.8	63.08
1% CNF	18.1	318.9	71.28
3% CNF	100.28	191.3	114.7
5% CNF	82.39	123.3	103.94

 Table 2. Mechanical Properties of Pebax and Nanocomposites

FTIR Analysis

Figure 1 shows the spectra for nanocomposite samples, Pebax, and nanocellulose. The most prominent FTIR peaks in Pebax were observed at 1234 cm⁻¹ (attributed to stretching vibration of C-O group in chain), 1377 cm⁻¹ to 1455 cm⁻¹ (related to stretching vibration of C-H bonds of CH₂ groups), 1734 cm⁻¹ (related to C=O stretching vibration of the carbonyl group), 2982 cm⁻¹ (attributed to stretching vibration of C-H of CH₂ groups) and 3445 cm⁻¹ (related for stretching vibration of the N-H group).

The most important FTIR peaks for nanocellulose were observed at 750 cm⁻¹ (related to stretching vibration of C-H bonds in aromatic ring), 1050 cm^{-1} to 1200 cm^{-1} , and 1600 cm^{-1} to 1650 cm^{-1} (related to the stretching vibration of the C-O group, which are

many in quantity in nanocellulose), 2100 cm^{-1} to 2200 cm^{-1} (related to C-C stretching vibration) and a broad peak in the range 3300 cm^{-1} to 3500 cm^{-1} (related to O-H stretching vibration in the nanocellulose structure).

The main peaks in 3 various nanocomposites, Pebax and nanocellulose are listed in Table 3 for better comparison. According to Table 3, every nanocomposite has its own peaks, related to its raw materials, which shows main functional groups.

Mixture	Wave number (cm ⁻¹)	Functional group*
	1234	C-Op
Pebax	1455-1377	C-H _p (aliphatic)
	1734	C=Op
	2982	C-H _p
	3445	N-H _p
	750	C-H _n (ring)
Colluloso popofibor	1600-1650 and 1050-1200	C-O _n
Cellulose nanoliber	2100-2200	C-C _n (ring)
	3300-3500	O-H _n
	756	C-Hn (ring)
	1185	C-O _{p,n}
	1485	C-H _p (aliphatic)
Pehay+1% CNF	1624	C-On
	1701-1770	C=Op
	2032	C-C _n (ring)
	2903-3080	C-H _p
	3429-3683	N-H _{n,p} and OH
	730	C-H _n (ring)
	1079	C-O _{p,n}
	1540	C-H _p (aliphatic)
Dobox 20/ CNE	1692	C-O _n
Pebax+3% CNF	1740	C=Op
	2073	C-C _n (ring)
	2923	C-H _p
	3670	N-H _{n,p} and OH
	744	C-H _n (ring)
	1066-1165	C-O _{p,n}
	1454	C-H _p (aliphatic)
Pebax+5% CNF	1733	C=Op
	2062	C-C _n (ring)
	2959	C-H _p
	3666	N-H _{p,n} and OH

Table 3. Comparison the Wavenumber Values of Nanocomposites in
Comparison to the Raw Materials

*Index p is related to the functional group or bond in Pebax structure and n is related to the functional group of cellulose nanofiber

The FTIR analysis confirmed the presence of Pebax and nanocellulose in nanocomposites and showed that the composition of Pebax could be affected by the content of cellulose nanofiber.



Fig. 1. FTIR spectra of Pebax, CNF, Pebax with 1% CNF, Pebax with 3% CNF, Pebax with 5%

Morphology of Pebax Nanocomposites

The diameters of 30 cellulose nanofibers were calculated using a Digimizer (MedCalc Software Co.) on the phase micrograph of AFM (Fig 2). Based on the calculation, the average diameter of CNF obtained was 35 ± 10 nm.



Fig. 2. AFM image of pure nanocellulose fibers

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The morphology of the nanocomposite and dispersion of cellulose nanofiber into the Pebax matrix was investigated by SEM. Figures 3 through 6 show the cryogenically fractured surfaces of Pebax and the related nanocomposite reinforced with different amounts of cellulose nanofibers. Cellulose nanofibers appear as white dots during the SEM imaging. Cellulose nanofibers of almost uniform size were observed. The fractured surface of the Pebax matrix was smooth and uniform.



Fig. 3. SEM of Pebax

The SEM images for the nanocomposite with 1% and 3% of nanocellulose (Figs. 4 and 5) indicated that the cellulose nanofibers (white dots) were dispersed homogeneously within the Pebax matrix. This could have been ascribed to a good interaction between the nanocellulose and polyamide phase of the Pebax matrix.



Fig. 4. SEM of Pebax with 1% nanocellulose



Fig. 5. SEM of Pebax with 3% nanocellulose. Arrows show cellulose nanofibers (white dots)

However, the SEM image of the nanocomposite with 5% cellulose nanofibers showed agglomerated structures on the surface in comparison to the uniform surfaces of other nanocomposites (Fig. 6). This compact agglomeration of cellulose nanofibers showed that cellulose chains had become clumped together. This is been attributed to intermolecular hydrogen bonding and a strong hydrophilic interaction between the cellulosic chains (Bhatnagar and Sain 2005).



Fig. 6. SEM of Pebax with 5% nanocellulose. Arrow indicates the nanocellulose agglomeration

Differential Scanning Calorimetry (DSC) Analysis

The thermal properties of the nanocellulose-reinforced Pebax matrix were determined from DSC thermograms, and their characteristics are collected in Table 4. It was reported that the crystallization enthalpy and temperature (Hc and Tc) of the Pebax copolymer depended on the polyether/polyamide ratio and that wood fibers influenced polyamide crystallization (Sliwa et al. 2012; Kumar et al. 2014). There was no considerable change for crystallization enthalpy and temperature. The crystalline peak temperature (Tc) of nanocomposites was increased minimally by the addition of nanocellulose (Table 4). For the pure Pebax, the exothermic peak occurred at $T_c = 147.39$ °C. These exothermic peaks shifted to a higher temperature of $T_c = 148.76$ °C for nanocomposites with an addition of 3% nanocellulose. This increment was related to the interactions between nanocellulose, polymer chains, and the nucleating agent role of nanocellulose, which increased the crystallization temperature of the Pebax matrix (Chow 2007; Lee et al. 2008; Ziaei Tabari et al. 2012). The glass transition temperatures of samples are reported in Table 4. In principle, the individual components in incompatible polymers occurred as separate phases, which meant that several T_{g} values were measured. With a compatible substance, a homogeneous phase formed and one single glass transition was measured. All of the DSC results revealed one single glass transitions in this study. The T_{g} value of the 3% nanocomposite slightly increased, while the samples with 1% and 5% nanocellulose displayed lower a Tg in comparison to the pure Pebax. Regardless of the composition, the $T_{\rm g}$ decreases could have been related to a plasticizer. Increased concentrations of plasticizer, such as solvent residues (benzyl alcohol), could behave as an unwelcome plasticizer. Plasticizer molecules are relatively small in size as compared to that of polymer host molecules. They can easily penetrate the polymer matrix, causing an interaction between the plasticizer molecule and polymer chain molecules. This may have reduced the cohesive forces operating between the polymer chains, which resulted in an increase in the chain segmental mobility. Easy movements of the polymer chains cause a decrease in the value of T_g (Pradhanl *et al.* 2007). It seems at mixing ratio of 5%, the nanocellulose was coagulated, which negatively affected the thermal stability. The coagulation of CNF in the polymer can be seen in the SEM micrograph (Fig. 6) and mechanical properties (Table 2). The slight increase of T_g in 3% CNF could have been ascribed to the interaction between the filler and the matrix. This phenomenon may have been related to the low molecular mobility of Pebax chains in the interfacial zone as a result of good interaction that causes a decrease in the plasticizing effect of solvent residues (Riesen 1998; Angles and Dufresne 2000; Roohani 2008).

Sample	𝕶µ𝔤 (°C)	T _c (°C)	Enthalpy (ex) (J g-1)
Pebax	38.04	147.39	-24.74
1% CNF	20.07	148.21	-23.31
3% CNF	39.24	148.76	-24.6
5% CNF	36.94	147.16	-20.32

Table 4. Thermal Properties of Nanocomposites

CONCLUSIONS

1. A new nanocomposite made of a bio-sourced thermoplastic elastomer matrix and cellulose nanofiber was prepared by compounding solution casting and melt blending process. The morphology, phase interactions, thermal, and mechanical behavior of the nanocomposites were analyzed using various tests.

2. The FTIR analysis confirmed the presence of Pebax and nanocellulose in nanocomposites and showed that the composition of Pebax could be affected by the content of cellulose nanofiber. The most considerable change in the DSC diagrams was exothermic peaks that shifted to a higher temperature, especially for 3% CNF and a slight increase in the T_g value.

3. Mechanical analysis revealed a remarkable increase in the impact strength and Young's modulus of the nanocomposites, especially in the 3% CNF specimens, which could be related to aspect ratio, nucleation effects, a highly-entangled, web-like structure, high modulus of the cellulose nanofibers, and the strong interaction between the Pebax matrix and nanocellulose. The morphological observation of nanocomposite revealed a fine dispersion of nanofibers in composites up to 3% nanocellulose without agglomeration.

4. Results indicated appropriate effects of nanocellulose for strong interaction and close contact between the nanocellulose and polyamide phase of Pebax polymer. In the end, good properties of nanocellulose as a filler was proved once again even with a non-water-soluble polymer.

ACKNOWLEDGMENTS

The authors thank Nano Novin Polymer Co. (Iran) for the preparation of facilities to produce cellulose nanofibers for this study.

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Article submitted: January 6, 2017; Peer review completed: March 30, 2017; Revised version received and accepted: May 15, 2017; Published: May 23, 2017. DOI: 10.15376/biores.12.3.4972-4985