SEMI INTERPENETRATING NETWORK DERIVED FROM POLYLACTIC ACID/POLYURETHANE BLEND AND REINFORCED WITH CELLULOSE NANOCRYSTALS

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Abstract

The current work aims to prepare and characterize bionanocomposites based on cellulose nanocrystals and semi interpenetrating networks prepared from PLA and PU. Nanocrystals were dispersed in PU phase with an innovative, novel method called as co-solvent assisted surfactant-less method. The characterization of the materials was done by tensile testing, differential scanning calorimetry and thermogravimetric analysis. The results were progressive and supported the premise that SIPNs are a viable option to prepare mechanically enhanced hybrid matrix that can impart improved mechanical properties to nanocomposites. Additionally, the dispersion method produced excellent dispersion of nanocrystals in the polyol phase, which was successfully transferred to the nanocomposite.

1. Introduction

Slowly and steadily, the focus of academic and industrial research is shifting towards a more sustainable bio-based economy, with the one major aim: to reduce the carbon footprint. In the field of polymeric materials, due to the identical reason, the field of bio-composites has gained unprecedented attention in last few years. Bio-composites are now looked upon as a well-intentioned alternative to petroleum based materials due to their environment friendly nature. Apart from being eco-friendly, biocomposites are also economical. They offer numerous opportunities. The potential applications of bio-composites include high value products that can be used as packaging materials, automotive materials, coatings, adhesives, membranes and many more. Although, promising developments have been made in the field of bio-composites but further research is required to bring them at par with petroleum based composites [1].

Poly lactic acid (PLA) is one of the most common biopolymers, as it holds a discrete advantage that it can be commercially produced from cornstarch. Additionally, it has excellent mechanical properties with elastic modulus as high as 4 GPa and tensile strength of 63 MPa [2]. It is one of the most popular bio based polymer to prepare bio-based composites and impressive results have been published, comprising PLA based biocomposites are processed by commercial viable methods [3]–[5]. However,

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PLA lacks a very particular desirable characteristic of commodity plastics: good toughness. It is extremely brittle with less than 4 % elongation to break. It also has low heat distortion temperature which makes it unsuitable for use in regions known for prolonged and hot summers. Various attempts have been made to improve the properties of PLA such as plasticization [6], blending [7] and rubber (elastomer) toughening [8]. This work focuses on a rather different approach to improve properties of PLA, which is to create a crosslinked co-continuous network with another polymer and reinforcing it with cellulose nanocrystals (CNCs).

Cellulose based nano-reinforcements have gained unprecedented attention in past decade, again due to their relevance to bio-based economy. Apart from being bio-based, they have excellent mechanical properties, with elastic modulus between 100-160 GPa, making them ideal candidate for reinforcing polymers. Good dispersion of nanocellulose in polymer matrix remains one of the key desirable in a nanocomposite study. CNCs, a specific kind of nanocellulose, are used in this research. They have rod shape morphology with length of 100-160 nm and diameter of 3-20 nm. They are usually obtained by acid hydrolysis of cellulose and are known for their high surface area and exceptional mechanical properties [9].

Inter penetrating networks (IPNs) in polymer is defined as “Polymer comprising two or more networks that are at least partially interlaced on a molecular scale but not covalently bonded to each other and cannot be separated unless chemical bonds are broken” [10]. They provide a specific advantage that a hybrid cross-linked matrix can be created for composites; the hybrid matrix has properties of both polymers. They are known to improve properties such as impact resistance, abrasion resistance, and mechanical properties [11]. According to our best knowledge, IPNs and SIPNs have rarely been used for bionanocomposites and might give an interesting alternative to improve the properties of promising polymers, such as PLA.

In this work, semi-IPNs (SIPNs) based on PLA and polyurethane (PU) were created and reinforced with CNCs, which were dispersed in polyol and subsequently into SIPN matrix with the help of a novel method. The mechanical and thermal properties of CNC reinforced SIPNs based on PLA and PU are reported and discussed. The nanocomposites were characterized by tensile testing, dynamic mechanical analysis and differential scanning calorimetry. Scanning electron microscopy was used for analysis of morphology. The results are promising with indication that synthesizing interpenetrating network and reinforcing with CNC can be an advantageous step towards commercialization of biocomposites.

2. Materials

PLA (pellets) was kindly supplied by Futerro (Escanaffles, Belgium). The melt flow index of PLA was 8g/10 minutes.

Jagropol 400, a castor oil based polyol (CO-polyol), was provided by Jayant agro-organic, Mumbai. The reported average functionality and viscosity was 3 and 700 -1100 mPa.s, respectively.

Freeze dried cellulose nanocrystals (2012-FPL-CNC-043) were kindly supplied by USDA Forest Product Laboratory US Forest Service (Madison, USA).

Lupranate M20S, 4, 4’-diphenylmethane diisocyanate (MDI), was procured from BASF SE (Ludwigshafen, Germany). The isocyanate content was 32% and viscosity was 250 mPa.s.

1,4 Dioxane (99.5 % purity, Merck KGaA) was purchased from VWR, Sweden.

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3. Methods

3.1. CNC dispersion in CO-polyol

A novel method is reported in which CNC dispersion can be transferred from water to CO-polyol. It was designed considering the phase diagram of ternary liquids with partial miscibility [12]. In brief, a mixture was prepared by mixing 10 grams of CO-polyol and 100 grams of 3 wt. % CNC dispersion in water with the help of ultra turrax homogenizer. The mixture was heated at 75 °C and stirred simultaneously with the help of star shaped magnet. Gradually, evaporating water was replaced by CO-polyol with the help of dioxane solvent (as it is solvent for both water and CO-polyol). With the addition of dioxane, the mixture became fairly transparent. 50 grams of CO-polyol and 100 gram of dioxane was eventually added. No cloud point was observed, which was used as indicator for stability of system. The emulsion was heated for 3 hours to remove the volatiles and kept in vacuum at 70 °C for 24 hours to remove any remaining volatiles. This method is mentioned as CASL method in future text.

3.2. Preparation of SIPNs and nanocomposite

SIPNs and the nanocomposite were prepared by solution casting. A 5 wt. % PLA solution was prepared by dissolving PLA pellets in dioxane overnight. The precalculated amount of CO-polyol (CNC dispersed CO-polyol for nanocomposites) and isocyanate was added to the PLA solution, stirred and casted on Teflon mould. The formulation of Neat PLA and PU, SIPN and SIPN reinforced nanocomposites are provided in Table 1. The solutions in Teflon mould were dried under vacuum for 12 hours to obtain thin films of around 150 µm, which were further processed by compression molding at pressure of 1-2 MPa in order to remove residual solvent and warpage. To remove any remaining traces of solvent, the films were further annealed under vacuum at the temperature of of 75 +/- 5 °C for 24 hours. Before any testing, they were kept in controlled environment at room temperature (23 ± 2 °C) and 55 ± 5 % relative humidity for at least 48 hours. PU films were prepared in similar way except for compression molding as thermosets cannot be reprocessed, once they are crosslinked. In the future texts, the samples are named according to following convention: SIPN 7030 represents sample with 70 wt. % PLA and 30 wt. % PU.

Table 1. Formulations (expressed as proportion out of 100) of samples of neat PLA and PU, SIPNs, and SIPNs reinforced with CNCs (1wt%). The isocyanate/hydroxyl ratio was kept constant at 0.8 and PLA PU ratio 7030, which was decided after optimization experiment discussed in section 4.1.

	Sample name			
Materials	Neat PLA film	SIPN film	SIPN (1) CNC film	Neat PU film
PLA	5	4.9	5	0.0
CO-Polyol	0	1.26	0	19.3
CO-Polyol (5 wt%)CNC	0	0	1.36	0.0
Isocyanate	0	0.84	0.86	12.8
Dioxane	95	93	92.8	67.9

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Total	100	100	100	100

3.3. Characterization

CNC dispersion in CO-polyol was studied using an optical microscopy. The images were gathered by Nikon Eclipse LV100N POL optical microscope (Tokyo, Japan) with software NIS-Elements D 4.30.02.

The morphology of SIPN materials were studied by Field-emission scanning electron microscopy (FESEM) Zeiss Ultra Plus (Oberkochen, Germany). The samples were fractured in liquid nitrogen and mounted vertically on a clamp. Solvent etching was also done in order to remove PLA and get depth contrast.

Shimadzu AG-X universal testing machine (Kyoto, Japan) was used to measure tensile properties of rectangular strips (70mm x 5mm). A load cell of 1 kN and crosshead speed of 3 mm/min was used. The gauge length was kept fixed at 20 mm. Minimum 7 readings were recorded from each sample.

Mettler Toledo DSC 822e equipment (Schwerzenbach, Switzerland) was used for differential scanning calorimetry. 6-10 mg of samples in aluminum pans were cooled to -70 °C and heated to 200 °C and cooled down again at -70 °C. This was done in order to remove thermal history. Finally, a scan was conducted from -70 ° to 200 °C, which was recorded and analyzed.

Netzsch STA 449 F3 TG-DTA/DSC analyzer (Selb, Germany) was used for thermometric gravimetric analysis. 10 mg of sample was heated in tungsten furnace at 10 °C/min till 700 °C and the weight loss and DTG curves were recorded.

4. Results and Discussion

4.1. Determination of matrix composition

In order to determine the optimum concentration of PU in PLA, an optimization experiment was conducted with concentration of PLA, CO-polyol and isocyanate as independent variable and tensile properties as response variable. PLA was kept as major component in order to preserve the ecofriendly nature of matrix, In brief, samples were prepared with polymer concentration (PLA: PU) of 80:20, 70:30 with isocyanate hydroxyl ratio of 0.6 and 0.8. The tensile results analysis indicated that the PLA: PU ratio with 70:30 and isocyanate hydroxyl ratio of 0.8 displayed optimized properties (results not shown here). It was decided that the same combination will be reinforced with CNCs, and it will be henceforth referred to as SIPN.

4.2. Dispersion of CNC

Figure 1 presents the optical microscopy images presenting results from CASL method. Figure 1 (a) represents the image for CNC CO-polyol mixture that was dispersed with the help of sonication (2 hours, probe sonicator) as a reference. It clearly reveals the inability of sonication to disperse CNC in viscous liquid. On the other hand, images from CASL method (Figure 1, (b) and (c)) provides us conclusive proof that CNCs are well dispersed in CO-polyol and thus the efficiency of method was established.

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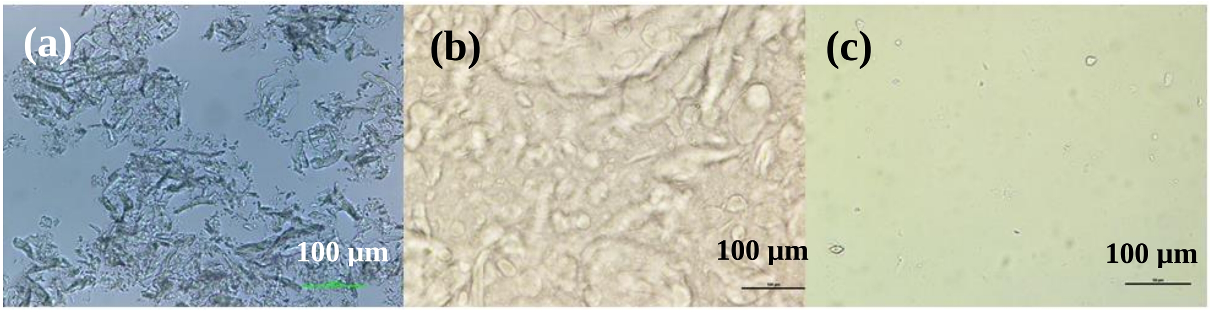

Figure 1. Optical microscopy images corroborating the effectiveness of co-solvent assisted surfactant less method: (a) CNC in polyol after sonication (2 hours); agglomerates are visible indicating ineffectiveness of sonication, (b) CNC in CO-polyol after removal of water from dispersion prepared by CASL method, (c). CNC in CO-polyol after vacuum evaporation of dispersion from CASL method.

4.3. Microstructure

FESEM images confirmed that the SIPNs have the co-continuous morphology as presented in Figure 2, which represents the SIPN sample in liquid nitrogen and followed by etching in dioxane. The PU network can be observed. This co-continuous network is one of the inherent requirement of SIPNs, and the reason of their superior mechanical properties as the system act as self-reinforced system [13].

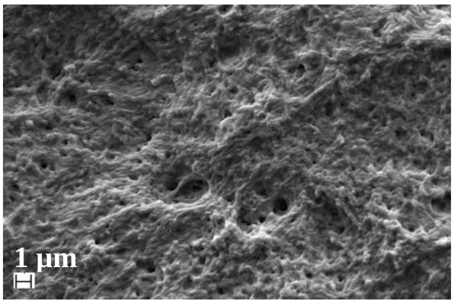

Figure 2. Microstructure of SIPN from fractured samples etched in dioxane; the interpenetrating PU network can be easily observed.

4.4. Mechanical properties

Figure 3 provides stress-strain curves of neat PLA, PU, SIPN and SIPN nanocomposite. The results are assuring that creating the interpenetrating nework even with highly elastomeric polymer such as PU at considerably high concentration (30 wt. %), gives notable properties. The elastic modulus of PU is 1.3 MPa and that of SIPN is 911 GPa. It is one of the major advantage of co-continuous morphology, that it acts as self-reinforced system [13]. Additionally, reinforcing SIPN (1 wt. %) with CNC improves its modulus to 1.4 GPa. However, the desired elongation (ductility) is again absent. Nevertheless, we were able to create a hybrid material with comparable property to original PLA. The main advantage of this material is that it is thermally enhanced as explained in next section.

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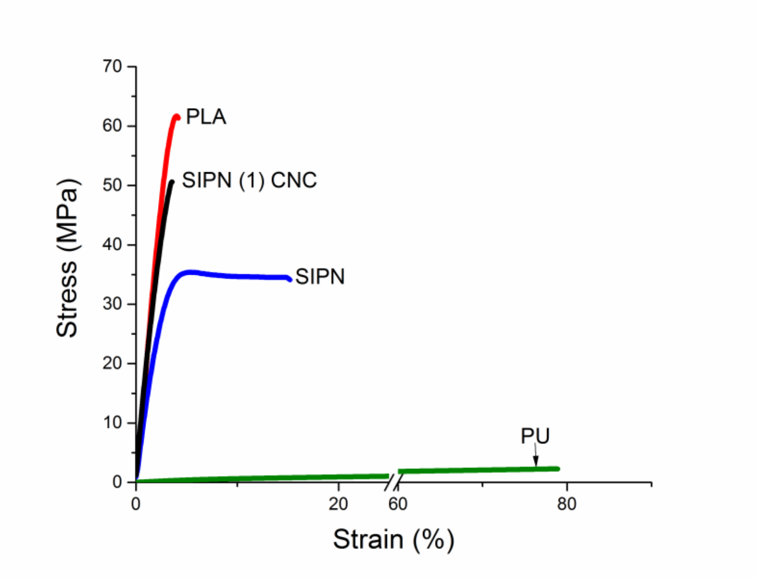

Figure 3. Stress-strain curves of neat PLA and PU, their SIPN and the SIPN reinforced with CNC. Making PU network in the PLA results in improved toughness with marginal decrease in modulus and the CNC reinforced SIPN further improve the modulus.

4.5. Thermal properties

One of the most interesting finding in this study was the thermal properties of SIPNs. Table 2 presents the glass transition temperatures (T_g) of samples measured with the help of DSC. It can be observed that PU has very low T_g when comparing to PLA. However, their mixture in 30:70 ratio apparently have higher Tg than PLA (and PU). The results are an anomaly to “law of mixtures” and definitely beneficial to us as PLA has comparatively lower T_g from commercial polymers. The increase appear to be more prominent in CNC reinforced samples.

Table 2. Values of Tg obtained from DSC curves for PLA, SIPN, SIPN based nanocomposite and PU.

Sample	Glass transition temperature (Tg) ℃
PLA	49.9
SIPN	51.6
SIPN (1) CNC	56.4
PU	5

The damping properties were evaluated from DMA results. It has been reported that area under tan delta curve can be used to characterize damping characteristics: larger the area under curve better the damping [14]. The magnitude of areas under the tan delta curves for PLA, SIPN and SIPN based nanocomposites were 6.7, 9.2 and 7.2. The results indicate that creating SIPNs lead to vibration resistant materials, as area under curve is increasing. SIPNs, when reinforced with CNCs, the area is again decreasing, but yet greater than PLA. A reason behind this observation might be increase in amorphous content due to incorporation of PU.

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Degradation behavior was studied with the help of TGA/DTG curves. The PLA displayed a steep degradation and PU exhibited a three-step degradation, and degradation of SIPN and SIPN based nanocomposites follows an intermediate pattern (curves not shown here). The quantitative analysis of TGA results are presented in Table 3. It provides the amount of sample (in percentage) decomposed between 0 °C and 400 °C. PLA was almost completely decomposed (98.3%), while SIPN and CNC reinforced SIPN decomposed 84.3 % and 82.4 %, indicating they are thermally superior materials when compared to PLA. Once again, the explanation behind this is PU network in hybrid matrix, which has higher stability (56.6 % decomposition below 400 °C); the end result is superimposed properties.

Table 3. Amount of sample decomposed between 0 and 400 °C as calculated from DTG curves.

Sample	% Decomposition (0-400 ℃)
PLA	98.3
SIPN	84.3
SIPN (1) CNC	82.4
PU	56.6

5. Conclusion

This study concludes with establishing the relevance of creating interpenetrating network in polymers and using them as hybrid matrix for bionanocomposites. SIPNs based on PLA and PU were prepared and reinforced with CNCs (1 wt%). The materials mechanical and thermal properties were evaluated. The hybrid material (SIPN-CNC) was thermally advanced. The results indicate that SIPNs offer advantages over corresponding polymers and quite possibly be a viable option as matrix for bio based materials, which suffer from inferior properties from petroleum based materials. Additionally, CNC were dispersed with a novel method and benefits of CNCs as reinforcements were established. Finally, it is worth mentioning that the bionanocomposites prepared in this study are 90% bio-based.

Further work can be conducted with the purpose to improve the loss in ductility in CNC reinforced IPNs; possibly by using chain extenders or by decreasing crosslink density.

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