

PREPARATION AND CHARACTERIZATION OF PLA NANOCOMPOSITES WITH NANOCELLULOSE FILLED PVAC

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Abstract

PLA composites with nanocellulose filled poly(vinyl acetate) (PVAc/NC), were prepared by mixing aqueous PVAc emulsion with NC suspension and melt blending with PLA. The nanocomposites were analysed by SEM, AFM, TGA, DMTA and tensile mechanical tests, and the properties were compared with those of PLA/NC composites. Functionalization of PLA and NC by glycidyl methacrylate (GMA) was also applied to improve the nanofibre dispersion and interfacial interactions in the composites. PLA/PVAc/NC composites showed better dispersion of nanofibres into the polyester matrix, good thermal stability and higher tensile modulus and strength, as compared to PLA/NC.

1 Introduction

Cellulose nanofibres (NC) and nanowhiskers derived from renewable biomass have attracted much interest as an alternative to micro-sized reinforcements in composite materials [1-9]. Homogeneous dispersion of cellulose nanoparticles in polymer matrices is difficult to achieve by means of traditional melt processing techniques owing to the high tendency of NC to form aggregates, as a consequence of the interactions between hydroxyl groups and high surface area of cellulose nanoparticles [10, 11]. Proper dispersion and distribution of nanoparticles in the polymer matrix, as well as in the processing solvent, are the prerequisite for creating polymer nanocomposites that can display notable improvement of physical and mechanical properties [12]. In order to increase the dispersion of cellulose nanoparticles in non-aqueous polymer solution or suspension, several strategies have been adopted including the use of surfactants [13] and chemical modification on the particle surface [4, 14-18]. However, the surface functionalization can reduce or even suppress the interactions between the nanoparticles, limiting their reinforcing effect. It has been reported for cellulose acetate butyrate composites containing cellulose nanowhiskers that native nanocellulose has a superior reinforcing capability as compared to silylated ones [15].

Since it is difficult to disperse uniformly NC in a non-polar medium, the processing of cellulose nanocomposites was initially limited to solvent casting [3-7, 19]. Recently, melt compounding methods have been developed [8, 9, 20]. To avoid the nanoparticle aggregation, Jonoobi *et al* [21] mixed NC with a small amount of PLA in acetone/chloroform mixture and

then prepared composites by melt-mixing the dried mixture with PLA in extruder. In the present paper, we report on the preparation and characterization of PLA/NC and PLA/PVAc/NC nanocomposites prepared by mixing PVAc emulsion and NC suspension (PVAc/NC), followed by melt blending with PLA in internal mixer. Owing to the miscibility of PVAc with PLA over all the composition range and the biodegradability of their blends [22], PLA/PVAc/NC nanocomposites are expected to give rise to biodegradable systems with tuneable properties depending on the composition.

2 Materials and testing methods

2.1 Materials

Poly lactide (PLA) was supplied by NatureWorks (Polymer 3051D, specific gravity= 1.25, MFR = 10-25 g/10 min (210°C/2.16Kg), melt temperature = 150–165 °C, glass transition temperature = 55-65 °C). Microcrystalline cellulose, vinyl acetate (purity >99%), glycidyl methacrylate (GMA) (purity >97%) and di-benzoyl peroxide (DBPO) were purchased from Sigma Aldrich, Italy.

Cellulose nanofibres were prepared by the acid hydrolysis of commercial microcrystalline cellulose. NC was functionalized with GMA (NC-GMA) by following the procedure reported by Stenstad *et al.* [23]. Grafting was confirmed by FT-IR analysis and grafting percentage (63%) and grafting efficiency (41%) were calculated based on weight gain. The GMA grafted PLA (PLA-GMA) was prepared in toluene by grafting GMA in the presence of free radical initiator (DBPO).

2.2 Processing of nanocomposites

Nanocomposites were prepared following two different routes: (i) NC was first dispersed in PLA by solvent casting (organic) (masterbatch 1), then melt mixed with PLA; (ii) NC was dispersed in PVAc emulsion (aqueous) (masterbatch 2) followed by melt mixing with PLA.

Masterbatch 1: NC (or NC-GMA) aqueous suspension (0.4 g NC in 400 ml water) was solvent-exchanged to acetone by a series of centrifuging and re-dispersing steps, then different mixtures of PLA and nanofibres were prepared by mixing the nanofibres suspension with PLA dissolved in acetone-chloroform mixture. Similarly, a masterbatch for PLA-g-GMA film with nanocellulose was prepared. The masterbatches were poured on flat plate, then after solvent evaporation, were dried at 60°C under vacuum for 10 hours.

Composites	Compositions (wt.%)	Sample code
PLA/NC	99/1	NC1
PLA/NC	97/3	NC3
PLA/NC	95/5	NC5
PLA/PLA-g-GMA/NC	94/3/3	PLA-GMA3
PLA/NC-GMA	97/3	NC-GMA3
PLA/PVAc/NC	95/4/1	NC*1
PLA/PVAc/NC	80/17/3	NC*3
PLA/PVAc/NC	66/28/6	NC*6

Table 1. List of examined composites with their code

Masterbatch 2: NC aqueous suspension was mixed with previously prepared PVAc aqueous emulsion at 40 °C. The masterbatches were poured on a flat plate, dried and immersed in

water to remove water extractable components. Finally, the materials were dried at 60°C under vacuum for 10 hours.

PLA nanocomposites were prepared by the addition of masterbatch 1 or masterbatch 2 into required amount of bulk PLA in Brabender Plasti-corder internal mixer at 170 °C for 5 min setting the rotor speed at 60 rpm. The prepared samples are enlisted with their code in Table 1.

2.3 Analytical techniques

The morphology of nanocellulose was characterized by transmission electron microscopy with a Philips TEM CM12 (Netherlands). A drop of dilute aqueous suspension of nanocellulose was put on a carbon coated Cu grid, then dried under vacuum and stained with Ruthenium vapours. TEM images were obtained at an acceleration voltage of 120 KV. The morphology of the nanocellulose fibres was also studied by Atomic Force Microscopy (AFM) in a 5500 Scanning Probe Microscopy (Agilent Technologies) operating in the contact mode in air. Samples were prepared by dispersing 1 mg of nanofibres in 20 mL of distilled water in an ultrasonic bath at room temperature for 30 min. A droplet of the solution was cast onto a microscope slide and dried in vacuum oven at 70 °C for 1 hour. The morphology of the dispersed nanofibres was analysed by AFM; the diameter distribution was measured by a semi-automatic software (UTHSCSA Image Tool) from AFM images. Scanning Electron Microscopy (SEM) analysis was carried out on the cryogenically fractured surface of composites samples. The sample surfaces were sputter coated with gold in an Edward Sputter Coater and analysed by JEOL JSM-5600LV SEM microscope.

Thermogravimetric analysis (TGA) of PLA, NC and composites was carried out in a TGA Q500 TA Instruments analyser. The samples (6-15 mg) were heated from 50 to 600 °C at 5 or 10 °C min⁻¹ under both nitrogen and air. The change of weight loss percent and its derivative (DTG) were recorded as a function of temperature. A differential scanning calorimeter, Perkin-Elmer Pyris Diamond DSC, was also employed to study the phase transition behaviour of various samples, using a heating/cooling rate of 10 °C/min.

Tensile mechanical tests were performed on dumb-bell shaped specimens (8 mm² cross section, 2 mm thickness, 35 mm gauge length) at room temperature by using an Instron machine model 4505 operating at a cross-head speed of 10 mm/min, according to ASTM D638 test method.

3 Results and discussion

3.1. Characterization of nanocellulose

Fig. 1a shows a TEM micrograph of a dilute suspension of NC obtained from microcrystalline cellulose. It can be seen that the nanocellulose rods appear mostly separated, accompanied by the presence of agglomerates. The particle size distribution was found to be almost wide, but the majority of the sizes belonged to the nanometric range. In the case of cellulose fibres, it has been reported that the sulfuric acid hydrolysis usually cleaves the amorphous region of microfibrils longitudinally, resulting in a diameter reduction from micron to nanometres [6]. In AFM analysis data were recorded using both amplitude image and height image mode. Fig. 1b shows the amplitude image of a suspension of NC prepared by sulfuric acid hydrolysis. It can be noticed that the suspension contains particles and rods in the nano dimension. Fig. 2 shows the diameter distribution of cellulose nanofibres. The average diameter was found to be 23.6 ± 7.3 nm.

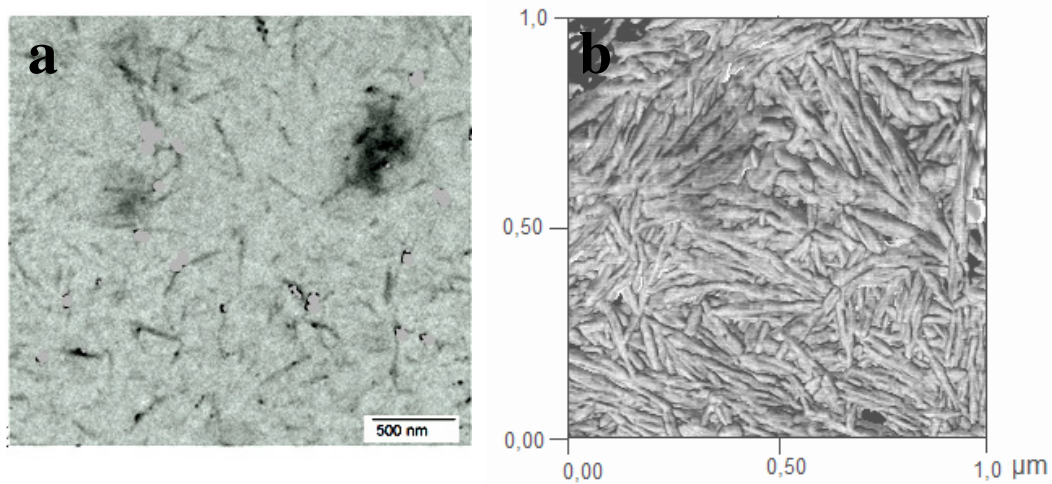


Figure 1. (a) TEM and (b) AFM images of nanocellulose isolated from microcrystalline cellulose

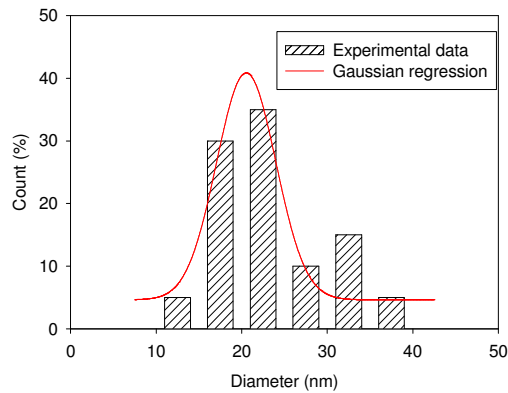


Figure 2. Distribution of diameter of nanocellulose isolated from microcrystalline cellulose

3.2 Morphology of nanocomposites

Fig. 3 shows the SEM images of fractured surface of the PLA nanocomposites with different NC content.

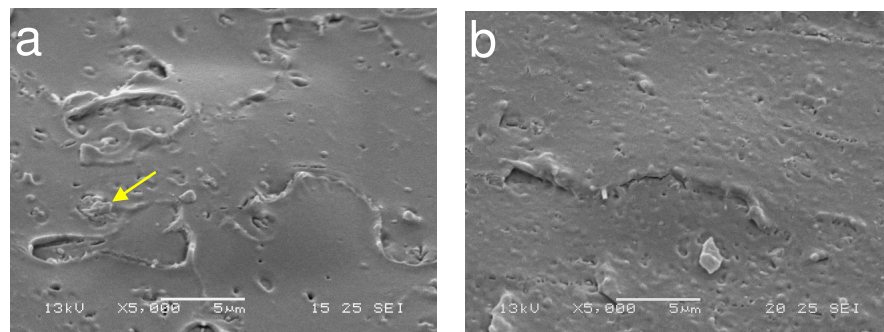


Figure 3. Scanning electron micrographs of (a) PLA/NC and (b) PLA/PVAc/NC (NC content, 3 wt.%)

The dispersion of nanocellulose into PLA and the fractured surface morphology of the nanocomposites were examined by SEM microscopy. In the case of NC1 and NC3, it can be

seen that the cellulose nanoparticles are homogeneously dispersed inside the PLA matrix with limited formation of agglomerates. These agglomerates increased as NC content increased. Better dispersion of nanofibres into PLA was found in the case of nanocomposites containing either functionalized components (PLA-GMA3 and NC-GMA3) or nanocellulose dispersed in PVAc (NC*3, prepared in aqueous media) as compared to NC3.

3.3 Thermogravimetric analysis

Fig. 4 shows the TGA curves of PLA, NC, PLA/NC 99:1, PVAc and PLA/PVAc/NC 95:4:1 analyzed at 10 °C min⁻¹ in nitrogen. In Fig. 4, it is seen that nanocomposite of PLA with NC displayed higher thermal stability than NC. It is also seen that PLA nanocomposite (NC*1) in presence of PVAc displayed higher thermal stability than NC1. PVAc started to degrade at 218 °C on the other hand PLA undergoes thermal degradation above 200 °C by hydrolysis, lactide reformation, oxidative main chain scission, and inter or intramolecular transesterification reactions [24].

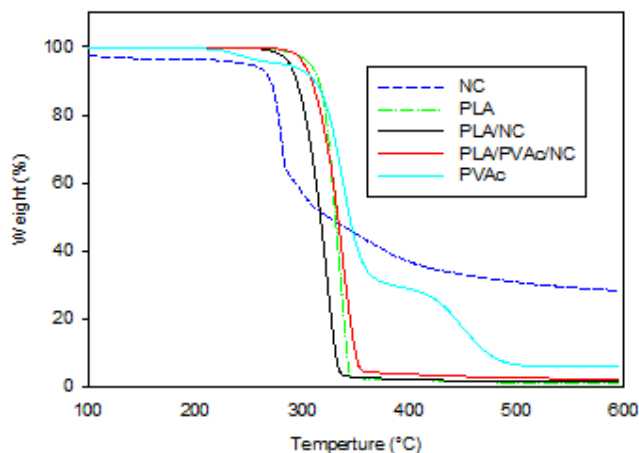


Figure 4. TGA curves of PLA, PVAc, NC and their nanocomposites

The cellulose nanocrystals also exhibited a thermal behaviour markedly different from that of the original cellulose. The typical decomposition of original cellulose showed an onset temperature above 350 °C. The cellulose nanocrystals, on the other hand, showed a gradual thermal decomposition that started at a lower temperature, around 150 °C; they lost nearly 40 wt.% of their mass in the range of 150-300 °C. Similar behaviour was reported by Lu *et al* for nanocellulose samples [25]. They mentioned that higher thermal conductivity of cellulose nanocrystals might be ascribed to smaller phonon scattering in the bundle of crystallized cellulose chains in the cellulose nanocrystals than in the amorphous random chains of cellulose.

3.4 Mechanical properties

The results of tensile mechanical tests on PLA and nanocomposites are reported in Table 2. It is seen that the addition of cellulose nanofibres into PLA increased the elastic modulus of nanocomposites due to the higher modulus of NC [26]. The elastic modulus of NC3 and NC5 samples did not show further improvement with increasing the NC content. This is probably, due to agglomeration of NC at higher content, as it was observed by SEM analysis. Although, the elastic modulus of NC1, NC3 and NC5 samples was increased by addition of NC, no

improvement was found in tensile strength. Higher values of elastic modulus and tensile strength of nanocomposites were found for samples prepared from masterbatch 2 procedure. It must also be noticed that the functionalization of components contributes to a significant increase of both elastic modulus and tensile strength. For the same concentration of NC (3 wt.%) the highest values of tensile parameters were recorded for PLA/PVAc/NC system. This could be attributed to a better dispersion of NC in PVAc followed by mixing with PLA. A further increase of NC content in PLA/PVAc/NC nanocomposite (NC*6) did not involve an increase of the elastic modulus, which is probably due to the occurrence of large agglomeration phenomena at higher NC concentration.

Sample	Modulus (MPa)	Strength (MPa)	Elongation at break (%)
PLA	2188 ± 348	48.08 ± 1.62	4.04 ± 0.77
NC1	2425 ± 168	48.82 ± 2.65	3.45 ± 0.14
NC3	2240 ± 69	47.83 ± 0.59	2.86 ± 0.32
NC5	2331 ± 270	46.07 ± 1.30	3.56 ± 0.28
PLA-GMA3	2417 ± 84	53.69 ± 2.19	3.66 ± 0.28
NC-GMA3	2547 ± 122	52.35 ± 1.77	2.91 ± 0.32
NC*1	2545 ± 61	54.28 ± 2.04	2.91 ± 0.06
NC*3	2621 ± 80	55.09 ± 0.99	2.36 ± 0.05
NC*6	2367 ± 135	53.91 ± 2.45	2.86 ± 0.21

Table 2. Tensile properties of PLA and its nanocomposites

4 Conclusions

The effect of different processing strategies of PLA/NC nanocomposites on the phase dispersion of NC, as well as on the thermal and mechanical properties of these systems was investigated by varying the nanocellulose content. For improving the dispersion of NC into PLA matrix, different approaches such as functionalization of PLA and NC by glycidyl methacrylate or inclusion of NC in PVAc (PVAc/NC) were applied. Better dispersion of nanofibres was found for PLA nanocomposites containing PLA or NC functionalized with GMA or PVAc/NC system. Higher tensile modulus and strength were found for PLA nanocomposites with PVAc/NC. These composites also exhibited improved thermal stability as compared to plain NC and PLA components.

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