PREPARATION AND PROPERTIES OF PLA NANOCOMPOSITES WITH INORGANIC NANOFILLERS AND CELLULOSE FIBRES

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Abstract
Polylactide (PLA) nanocomposites containing inorganic nanofillers, either 3 wt.% montmorillonite (MMT) or 5 wt.% nano-sizes calcium carbonate (NCC), and 15 wt.% cellulose fibres were prepared and studied. Good dispersion of nanoparticles in the PLA matrix was obtained. X-ray analysis and TEM examination evidenced that exfoliation of MMT was achieved. Dynamic mechanical response, thermal and mechanical properties, and also thermal stability of the composite materials were investigated with various methods. All the fillers, especially MMT, enhanced cold crystallization of PLA matrix, possibly by augmenting nucleation.

1 Introduction

Polylactide (PLA), a biodegradable polymer derived from agricultural products containing starch, draws a growing attention because of his strength and stiffness. However, the enhancement of thermal stability, mechanical and barrier properties of polymeric materials, including PLA, can be achieved [1-7] by mixing with other polymers or various types of fillers like calcium carbonate [1,10], montmorillonite [1,2], calcium phosphate [8,9]. Composites of PLA with cellulose fibres (CF) are fully biodegradable and renewable systems which can offer several advantages for both processing and mechanical behaviour [11].
The present communication is aimed at analysing the effect of addition of CF on the properties of PLA nanocomposites with nanofillers of different type and surface characteristics such as organically modified montmorillonite (MMT) and modified precipitated calcium carbonate (NCC). PLA reinforced with nanoparticles (PLA/MMT, PLA/NCC), cellulose fibres (PLA/CF), as well as ternary composites with both CF and nanoparticles (PLA/MMT/CF, PLA/NCC/CF) have been prepared by melt mixing and analysed by various techniques.

2 Experimental Part

2.1 Materials

The study utilized polylactide (PLA) 2002D produced by NatureWorks (USA) with D-lactide content of 2.5%, Mw=114 000 g/mol, Mw/Mn= 1.3, density of 1.24 g/cm^3. The glass

transition temperature (T_g) and melting point (T_m) determined by differential scanning calorimetry (DSC) were 58 and 152°C, respectively.
Two types of nanofillers were used to prepare nanocomposites. Nano-sized precipitated calcium carbonate, Socal U_1S_2, denoted here as NCC was supplied by Solvay Chemicals (Austria). The surface of particles, with an average single grain size 80 nm, was modified with 3 wt. % of stearic acid. Montmorillonite Cloisite 30B organo-modified with methyl-bis(2-hydroxyethyl) tallowalkyl ammonium cations (MMT) was provided by Southern Clay Products (Gonzales, TX).
The cellulose fibres (CF, Technocel® 500-1), with length of 500 μm and an average transversal size 20 μm, were obtained from CFF GMBH & Co.KG (Germany).

2.2 Nanocomposite preparation

All the materials: PLA, NCC, MMT and CF were thoroughly dried in a vacuum oven at 100, 120, 107, 105 °C, respectively, for 4, 12, 16, 12 hrs, respectively, to reduce the moisture content.
PLA composites with 5 wt. % of NCC and with 3 wt.% of MMT were obtained by melt mixing method in an internal mixer Brabender at 180-190°C at the constant rotation speed of 50 rpm for 10 and 15 min., respectively. In a second step 15 wt.% of CF was added and the mixing process was continued at 170°C for 10 min. PLA composites with 5 wt.% of NCC, 3 wt.% of MMT, 15 wt.% CF were also prepared. Neat PLA was processed in similar way to have a reference material. Melt processing was carried out in a dry nitrogen atmosphere to prevent thermooxidative degradation of the PLA.

2.3 Testing Methods

1 mm and 0.5 mm thick films were prepared by compression molding at 180°C for 3 min followed by quenching to room temperature between aluminum blocks. The thermal behavior of nanocomposites was analysed by a DSC technique at a heating/cooling rate of 10°C/min using TA Instruments DSC 2920. Specimens were heated to 180°C, annealed for 3 min., cooled to room temperature and again heated to 200°C. Thermogravimetric studies (TGA) were carried out at a heating rate of 20°C/min in air and in nitrogen atmosphere using Thermogravimetric Analyzer TA Instruments 2950. Dynamic mechanical properties were studied by Dynamic Mechanical Thermal Analyser Mk III (DMTA Rheometrics Mk III) in dual cantilever bending mode at the frequency of 1 Hz, in the temperature range from –120°C to 120°C and the heating rate of 2°C/min on specimens with dimensions of 30×10×1 mm^3 cut out from 1 mm thick films. The structure of the materials was examined under a scanning electron microscope (SEM) JOEL LV5500. The clay exfoliation was studied by means of wide angle X-ray scattering (WAXS) and transmission electron microscopy (TEM) of 70 nm thick ultrathin sections using TEM TESLA BS 500 operating at 90 kV. Uniaxial tensile drawing was performed on Linkam Minitester 200N TST350 at 25 and 35°C at a strain rate of 5%/min. Oar shaped specimens for tensile tests, with sizes conforming to ASTM D 638 type IV, were cut out from 0.5 mm thick films.

3 Results and Discussion

TEM examination (Fig. 1) and WAXS diffractograms (Fig. 2) demonstrated that MMT was well exfoliated in PLA matrix after melt processing.

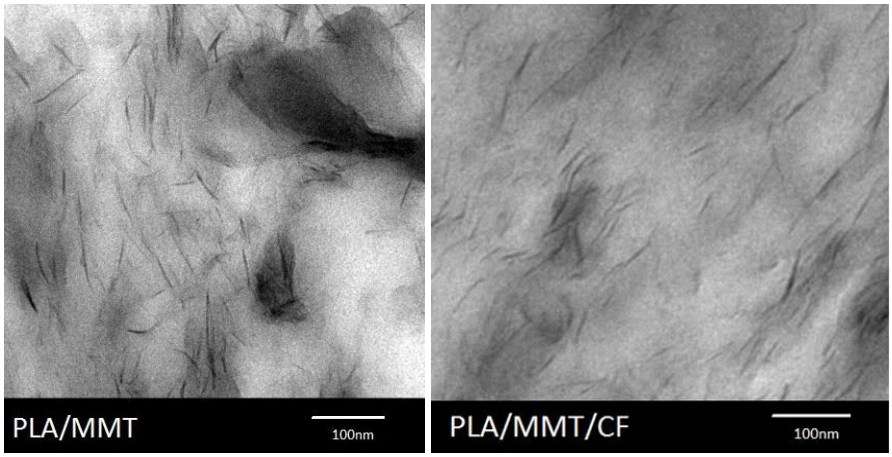

Figure 1. TEM micrographs of PLA/MMT and PLA/MMT/CF.

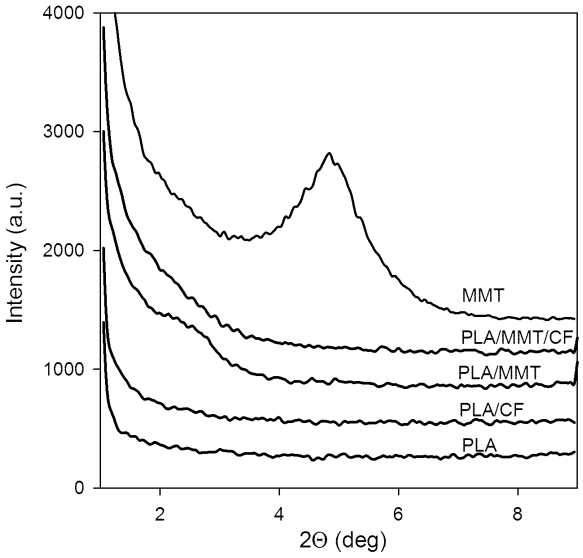

Figure 2. WAXS diffractograms of PLA based nanocomposites with MMT and CF.

SEM studies of cryo-fracture surface of the PLA/NCC/CF (Fig. 3) evidenced that dispersion of NCC in PLA matrix was almost homogeneous, with limited formation of agglomerates of nanoparticles. The same applies for PLA/NCC nanocomposite. SEM examination confirmed also good dispersion of MMT in PLA/MMT and PLA/MMT/CF.

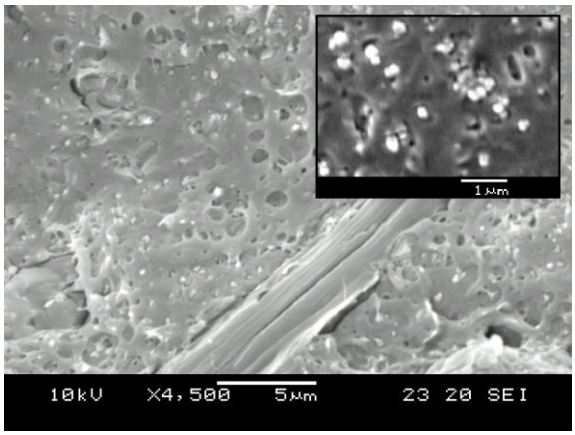

Figure 3. SEM micrograph of PLA/NCC/CF.

Thermograms of the materials studied recorded during the second heating are collected in Fig. 4. It appears that all the fillers enhanced the cold crystallization of PLA, which was reflected in a decrease of the cold crystallization peak temperature (T_{cc}) up to of about 15°C and in an increase of the crystallization enthalpy, as compared to that of neat PLA, possibly due their nucleating activity. The strongest effect was observed in PLA/MMT nanocomposite. Glass transition temperature (T_g) of all the materials was practically the same, 58-59°C. DMTA measurements confirmed only slight changes in T_g; temperature of the loss modulus E" was in the range of 57-59°C. It has to be added that during the first heating in the DSC the enthalpy of crystallization was usually equal to the melting enthalpy evidencing that the films were amorphous prior to the heating in the DSC.

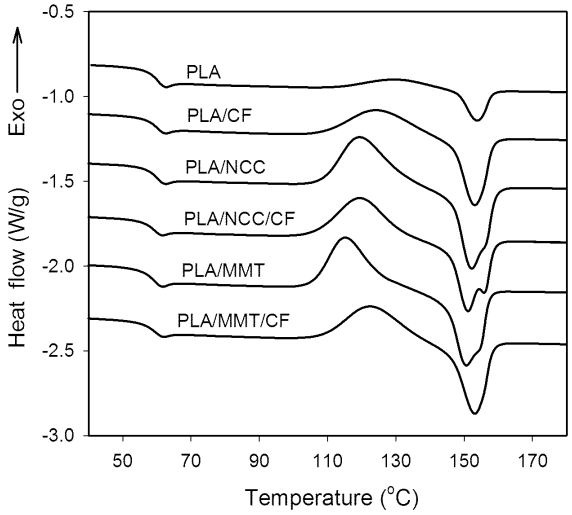

Figure 4. Second DSC heating thermograms for PLA and the composite materials.

Temperatures of maximum rate of weight loss (T_d) during TGA experiments are listed in Table 1. NCC decreases whereas MMT improves the thermal stability of the materials.

	T_d (°C)	
Sample code	**In Air**	**In Nitrogen**
PLA	355	352
PLA/CF	360	359
PLA/NCC	333	346
PLA/NCC/CF	344	338
PLA/MMT	379	378
PLA/MMT/CF	370	364

Table 1. Temperatures of maximum rate of weight loss (T_d) measured during TGA experiments.

Results of mechanical tests performed at 25 and 35°C are summarized in Table 2. It appears that at 25°C the yield stress decreased in PLA/NCC as compared to neat PLA whereas all the materials with CF fractured before yielding. At 35 °C the decreased yield stress was observed in all composites, especially those with CF. Only PLA/NCC exhibited elongation at break comparable with that of neat PLA, at 25°C and also at 35°C. DMTA measurements showed that the presence of CF improved the storage modulus E' of the composite materials.

Sample code	T (°C)	σ_y (MPa)	σ_b (MPa)	ε_b (m/m)
PLA	25	49.9	45.9	0.21
PLA/CF	25	-	46.0	0.05
PLA/NCC	25	43.5	42.5	0.24
PLA/NCC/CF	25	-	44.8	0.05
PLA/MMT	25	49.5	46.7	0.07
PLA/MMT/CF	25	-	41.8	0.04
PLA	35	44.8	40.2	0.34
PLA/CF	35	32.7	32.4	0.05
PLA/NCC	35	40.4	35.8	0.37
PLA/NCC/CF	35	35.6	32.7	0.05
PLA/MMT	35	43.1	39.5	0.07
PLA/MMT/CF	35	27.5	26.5	0.03

Table 2. Comparison of mechanical properties: yield stress (σ_Y), stress at break (σ_b) and strain at break (ε_b) of neat PLA and composite materials.

4 Conclusions

PLA/NCC, PLA/MMT, PLA/CF, PLA/NCC/CF and PLA/MMT/CF composites were prepared and examined. In the nanocomposite materials good dispersion of fillers was obtained. MMT was well exfoliated in PLA matrix after melt processing. The fillers caused a decrease of cold crystallization temperature and increased the crystallization enthalpy of PLA, possibly due to their nucleating activity. The addition of the fillers did not result in a marked change in T_g. The presence of MMT elevated temperature of maximum rate of weight loss in both PLA/MMT and PLA/MMT/CF nanocomposites. The mechanical properties depended on composition. The presence of CF caused early fracture before yielding at 25°C. At 35°C a decrease in the yield stress was observed in all the composite materials as compared to neat PLA. Only PLA/NCC exhibited the elongation at break comparable to that of neat PLA.

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