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COMPARATIVE STUDY OF THE EFFECTS OF CELLULOSE NANOWHISKERS AND MICROCRYSTALLINE CELLULOSE ADDITION AS REINFORCEMENT IN FLEXIBLE FILMS BASED ON BIOPOLYMER BLENDS

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Abstract

The objective of this study is to compare the effects of the addition of cellulose nanowhiskers and microcrystalline cellulose on properties of flexible films based on biodegradable polymer blends. Composite films containing 1 wt. % of microcrystalline cellulose and 1-2 wt. % of cellulose nanowhiskers were prepared by melt extrusion, using a twin screw extruder machine and blown extrusion process. The effects of the addition of cellulose nanowhiskers and microcrystalline cellulose on mechanical and thermal properties of biocomposite films were investigated by tensile tests, XRD, TG, DSC and FE-SEM analysis and the correlation between properties was discussed.

Introduction

Since the advent of the food can in the 19th century, protection, hygiene, product quality and convenience have been major drivers of food technology and packaging innovation. In recent years, there has been a rising demand for packaging that offers both ease of use and high quality food to consumers with busy lifestyles. Currently, the materials used for food packaging consist of a variety of petroleum-derived plastic polymers, metal, glass, paper, and board, or combinations thereof. These materials and polymer used in various combinations to prepare materials with unique properties which efficiently ensure safety and quality of food products from processing and manufacturing through handling and storage and, finally, to consumer use [1- 3]. The use of plastics in packaging has increased worldwide. The packaging industry is the largest user of plastics; more than 90 % of flexible packaging is made of plastics and only 17 % of rigid packaging [4]. Flexible packaging is widely used instead of rigid and semi-rigid packaging because of its flexible characteristics like low weight, durability, cost effectiveness, attractiveness and its easiness to be shaped [3-5]. Flexible packaging is in general not recyclable, practically non-degradable, consequently not selectively collected and as such, it ends up in the main stream of municipal household waste to be dumped into a landfill, representing a serious global environmental problem. Therefore, the use of bio-based materials to develop biodegradable films can be an important alternative to minimize the quantities of plastic waste material disposed of to landfill throughout the world. The recent preoccupation with environment makes the using of biodegradables material instead the commons polymers in the production of flexible and other packaging for food or agro products a sustainable perfect choice. Its renewable nature and natural origin are capable to transform the packaging industry and society habits.

Among commercial biodegradable plastics, poly(lactic acid) (PLA), a class of crystalline biodegradable thermoplastic polymer with relatively high melting point and excellent mechanical properties, and poly (butylene adipate-co-terepthalate) (PBAT), an aliphatic-aromatic copolyester are among the most promising materials to be considered as environmentally friendly high performance biodegradable plastics. Recently PLA has been highlighted because of its availability from renewable resources such as corn and sugar beets [6-8]. PLA is a biodegradable polyester with good biocompatibility and physical properties, such as high mechanical strength, and shows a number of interesting properties including biodegradability, high strength and high modulus [9, 10]. PLA is considered a relatively brittle material, thus it needs to be plasticized to produce flexible packaging films by cast film extrusion or blown film extrusion [10, 11]. PBAT has gained research and industry attention due to good processability in extrusion lines LDPE; besides PBAT begins to degrade after only few days in soil and enzymatic environments in contrast to petroleum derived polymers, such as polypropylene, polyethylene, that takes hundreds or even thousands of years to degrade [9,10]. The PBAT is considered a good candidate for the toughening of PLA due to its high toughness and biodegradability and no indication of environmental risk (ecotoxicity) when are introduced into composting processes [12, 13]. The combination of these two materials in a blend (PBAT/PLA), aims to bring the best characteristics for a biodegradable material, therefore aliphatic polyesters are the most promising biodegradable materials because they are readily susceptible to biological attack [12, 13]. Unfortunately, PBAT/PLA blends yet have poor properties for application in flexible food packaging field, related to performance, such as its limited mechanical properties and cost. Several composites have been developed by adding reinforcing compounds to polymers to enhance the thermal, mechanical and barrier properties. The use of fillers from natural resources at nanoscale and microscale level as reinforcements to biodegradable polymer and polymer blends may open new possibilities for improving not only the properties but also the cost-price-efficiency [5, 14, 15].

The incorporation of cellulose nanowhiskers and microcrystalline cellulose is being large studied because its abundance in nature, low density, relative high strength and stiffness, renewable nature and biodegradability [15-17]. The incorporation of nanoparticles as a filler in a polymeric matrix can produce a composite with better properties than a compound made with micro particles instead. The great differential of nanoparticles are their higher surface/volume ratio, the smaller the particle is greater the ratio. This technology can even change the visual properties of some material, like the color of gold [15-17].The target of this study was to produce flexible film composites based on biodegradable PBAT/PLA blends reinforced with cellulose nanowhiskers and microcrystalline cellulose and to compare the properties of reinforced PBAT/PLA flexible film with neat PLA/PBAT blend flexible film.

Experimental

Materials

The materials used in this study to prepare the polymeric matrix were Poly Lactic Acid (PLA), Poly Butylene Adipate Terephtalate (PBAT) and as fillers commercial Microcrystalline Cellulose (MCC, Avicel PH- 101, FMC BioPolymer, USA) and Cellulose Nanowhiskers.

Preparation of Cellulose Nanowhiskers

Cellulose nanocrystals were produced from commercial microcrystalline cellulose (MCC, Avicel PH- 101, FMC BioPolymer, USA). The MCC was treated by acid hydrolysis in a concentrated sulfuric acid solution (64 wt% sulfuric acid in water). The ratio of MCC to acid solution was 1-8.75 g/ml. The treatment was performed at 45 °C and under strong stirring. The selection of the initial conditions was based on the work of Dong [16] and subsequently optimized for this system [17].After treatment, the hydrolyzed cellulose (HC) was washed 4–5 times, separating the crystals from the solution by centrifuge (12,000 rpm, 10 min) after each washing. The final aqueous suspension was freeze-dried (lyophilized) to avoid re-agglomeration of the cellulose crystals.

Preparation of blend and composite

PLA and PBAT pellets and the nanoclay were dried at 60 ± 2 ºC for 4 h to reduce its moisture content to less than 2 %. The PBAT/PLA blend (80 %/ 30% based on wt. %) and PBAT/PLA reinforced with 1 % (wt. %) of cellulose microcrystalline (PBAT/PLA/ Micro) and 1-2 % (wt. %) of cellulose nanowhiskers (PBAT/PLA/Nano1 and PBAT/PLA/Nano2, respectively) were processed by extrusion using a twin screw extruder Haake Rheomix with 16 mm and L/D = 25 rate from Thermo Scientific. The temperature profile was 95/ 118/ 125/ 135/ 135/ 135 ºC. Screw speed was 50 rpm. The extrudates coming out of the extruder were cooled down for a better dimensional stability, pelletized by a pelletizer, dried again at 60 ± 2 ºC for 4 h and fed into extrusion blown film, single screw machine with 25 mm diameter, Carnevalli, and specimens test samples were obtained.

Analyses

Tensile tests: Tensile specimens were obtained in the way of process and in longitudinal way from the films samples in order to evaluate the mechanical behavior and tested using an INSTRON Universal Testing Machine, model 5564 according to ASTM D 882-91 standard at 25ºC and a loading rate of 10mm/min. Six replicates were made of each sample and the average values were reported.

X Rays Diffraction (XRD): XRD patterns were recorded on a Simens - D5000 diffractometer operated at 40 kV and 40 mA, with CuKα radiation (λ= 15.4 Å).

Thermogravimetric analysis (TG): In this study the tests were made in a Mettler Toledo TGA module "TGA/SDTA851e".

Differential Scanning Calorimetry (DSC): (DSC) analyses were carried out using a Mettler Toledo DSC 822e from 25 to 250°C at a heating rate of 10 °C/min under nitrogen atmosphere (50 ml/min).

Field Emission Scanning Electron Microscopy (FE-SEM): FE-SEM of cryofractured samples under liquid nitrogen were carried out using a JEOL-JSM-6701 F, microscope with an accelerating voltage of 1-30 kV, using EDS Thermo-Scientific mod. Noran System Six software, in carbon sputtered samples.

Results and Discussion

Tensile tests results:

Figure 1 shows the diagram stress (MPa) X strain (mm/mm) for PBAT/PLA blend and its composites, PBAT/PLA/Micro 1%, PBAT/PLA/Nano 1% and PBAT/PLA/Nano 2 %,. From of this Figure it is possible observe that the stress increases linearly with strain, due to cellulose Nanowhiskers addition. The addition of Microcrystalline Cellulose in PBAT/PLA blend initially causes an increase in strength followed by a pronounced reduction, as well as a reduction in strain properties.

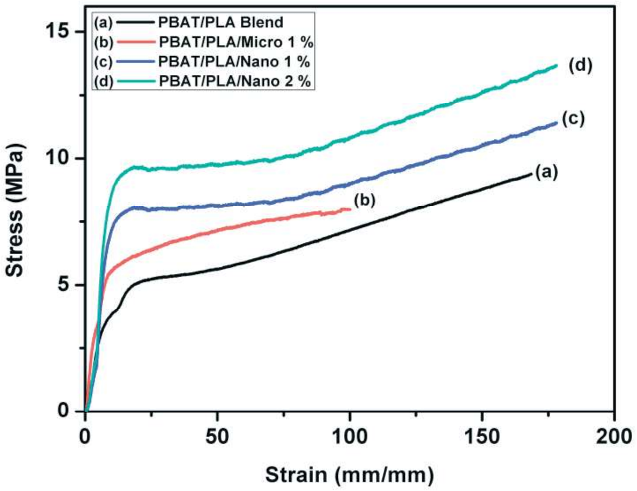

Figure 1. Diagram stress (MPa) X strain (mm/mm) for PBAT/PLA blend and its composites.

Table I presents the results of tensile tests of PBAT/PLA blend and its composites. The results presented shows the average values calculated from the data obtained in tests for five test specimens. From Table I it can be seen increase of the tensile strength at break, elongation at break and Young modulus properties of blend due to nanowhiskers addition. The addition of microcrystalline cellulose in PBAT/PLA blend led to a reduction of its tensile properties.

Table 1. Tensile test results of PBAT/PLA blend and its composites.

Sample	Tensile strength at break (MPa)	Elongation at break (%)	Young's modulus (MPa)
PBAT/PLA Blend	9.6 ± 0.4	370 ± 27	45 ± 3.6
PBAT/PLA/Micro 1 %	7.9 ± 0.3	279 ± 23	38 ± 2.8
PBAT/PLA/Nano 1 %	12.1 ± 0.3	460 ± 32	73 ± 4.2
PBAT/PLA/Nano 2 %	14.5 ± 0.2	478 ± 39	98 ± 7.3

X Rays Diffraction (XRD) analysis results:

The XRD patterns of PBAT/PLA blend and its composites are shown in Figure 2. As can be seen in Figure 2, the XRD spectrum of PBAT/PLA blend showed three prominents 2θ peak at around 9.5º; 28.5º and 29.5º, which has reduced of intensity due to nanowhiskers addition, and practically disappears upon microcrystalline cellulose addition.

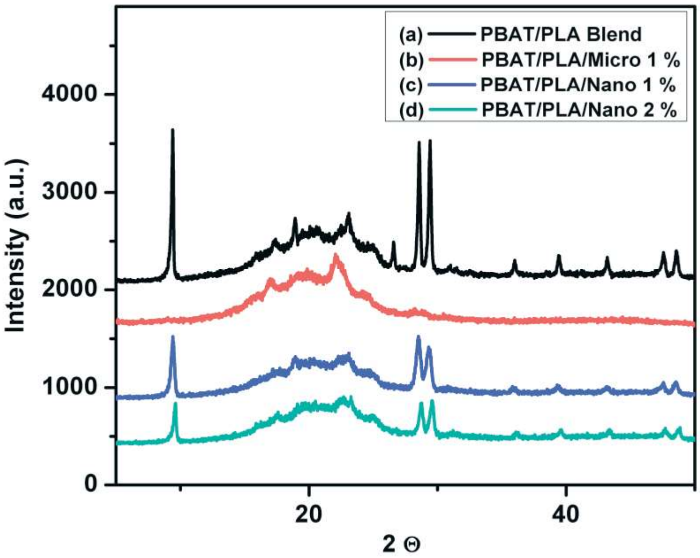

Figure 2. XRD diffraction patterns for the PBAT/PLA blend and its composites.

Thermogravimetric analysis (TG) results:

Figure 3 shows the TG (Figure 3a) and DTG (Figure 3b) thermograms of PBAT/PLA blend and its composites. TG of the composites showed a great difference in weight loss and in the onset temperature when compared with the neat blend. As can be seen in Table I the onset temperature of PBAT/PLA blend increased due to microcrystalline cellulose and nanowhiskers addition.

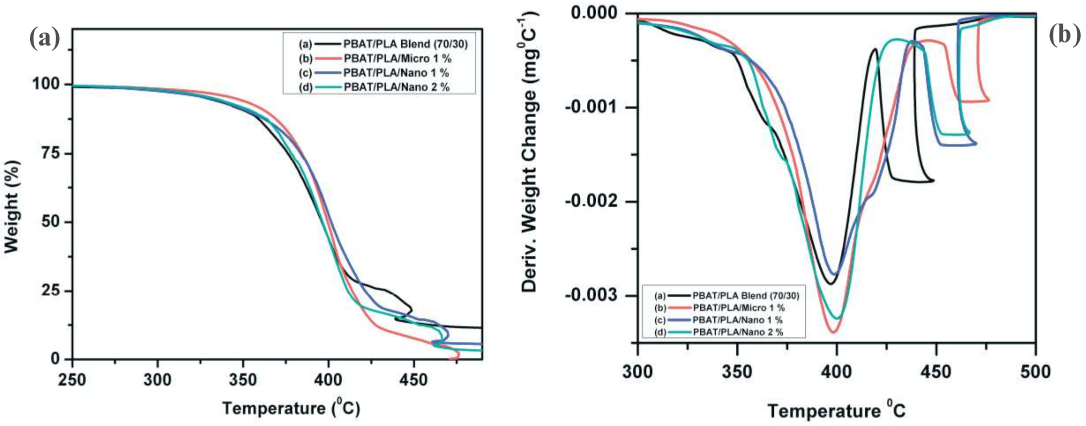

Figure 3. TG (3a) and DTG (3b) thermograms of PBAT/PLA blend and its composites.

Table II. Decomposition temperature and weight loss of PBAT/PLA Blend and its composites

Flexible Films	T_{onset} (°C)	T_{max} (°C)	Weight Loss (%)
PBAT/PLA Blend	341.1	405.9	87.4
PBAT/PLA/Micro [(a)]	365.7	410.3	99.1
PBAT/PLA/Nano 1[(b)]	346.8	415.7	93.7
PBAT/PLA/Nano 2 [(c)]	367.8	409.6	95.5

[(a)]PBAT/PLA/Microcrystalline cellulose; [(b)] PBAT/PLA/Nanowhiskers 1 %; [(c)] PBAT/PLA/Nanowhiskers 2 %

Differential Scanning Calorimetry (DSC) analysis results:

The results of DSC are exposed in Table II and they show no difference in the melting temperature of the neat blend when compared to the nanocomposites films but when compared to its composites. From Table II, it could be inferred that compared with the PBAT/PLA blend the endothermic melting enthalpy of PBAT/PLA blend increased considerably due to microcrystalline cellulose and nanowhiskers addition. The increases in the melting enthalpy can be attributed to the increase in crystallinity of PBAT/PLA composite.

Table II. DSC analysis results of PBAT/PLA Blend and PBAT/PLA Composite Flexible Films

Flexible Films	Melting Temperature (T_m, °C)	Melting Enthalpy (ΔH_m,Jg^{-1})
PBAT/PLA Blend	154.78	4.5
PBAT/PLA/Micro 1[(a)]	153.83	5.6
PBAT/PLA/Nano 1[(b)]	154.34	7.6
PBAT/PLA/Nano 2[(c)]	154.98	9.5

[(a)]PBAT/PLA/Microcrystalline cellulose 1 %; [(b)]PBAT/PLA/Nanowhiskers 1 %; [(c)]PBAT/PLA/Nanowhiskers 2 %

Field Emission Scanning Electron Microscopy (FE-SEM) analysis results:

FE-SEM micrographs of cryofractured surfaces of the PBAT/PLA blend and composite specimens were studied to understand the failure mechanisms and also study possible interaction between different components. FE-SEM micrographs of PBAT/PLA blend and its composites in different magnifications are showed in Figure 4. Figure (4a) is an overview of PBAT/PLA blend showing a uniform dispersion of in the PBAT matrix. Micrographs surface of PBAT/PLA/Micro with 3.000 X and 6.000 X of magnifications are showed in Figures (4b) and (4c), respectively. It can be seen in these figures a homogeneous distribution of microcrystalline particles, but with several large aggregates of the particles in the surface of the blend. Further in Figures (4b) and (4b) large number of holes in the PBAT/PLA blend are visible where microcrystalline particles have been located before the fracture.

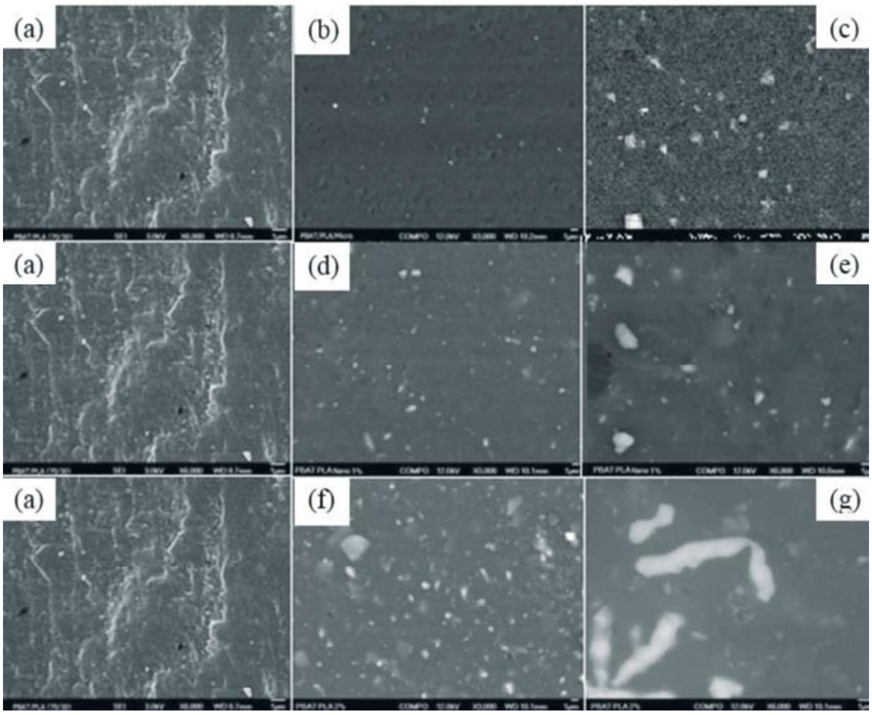

Figure 4. FE-SEM micrographs of PBAT/PLA blend (6.000 X) (4a), and its composites: PBAT/PLA/Micro (3.000 X) (4b), (6.000 X) (4c); PBAT/PLA/Nano 1 % (3.000 X) (4d), (6.000 X) (4e); PBAT/PLA/Nano 2 % (3.000 X) (4f), (6.000 X) (4g).

Cellulose nanowhiskers addition in blend led to a homogeneous distribution of nanoparticles, and reduced occurrence of the large aggregates and holes in the PBAT/PLA blend, Figures (4d-4g). These result suggests good adhesion between nanowhiskers cellulose and PBAT/PLA blend matrix, when compared with cellulose microcrystalline addition, which could play an important role in improving the mechanical performance of the resulting nanocomposite.

Conclusion

Results showed gains in tensile strength at break, elongation at break and Young modulus properties of blend due to nanowhiskers addition. The addition of microcrystalline cellulose in PBAT/PLA blend led to a reduction of its tensile properties. These result suggests good adhesion between nanowhiskers cellulose and PBAT/PLA blend matrix, when compared with cellulose microcrystalline addition, which may have played an important role in improving the mechanical performance of the resulting nanocomposite.

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