

THERMAL PROPERTIES OF POLYPROPYLENE NANOCOMPOSITES WITH ORGANOCCLAY AND DISCARDED BOND PAPER

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Abstract

This work concerns the study of the effect of discarded bond paper on the thermal behavior of the polypropylene/organophilic clay nanocomposite. A brown polycationic bentonite from state of Paraíba, Brazil, was treated industrially with sodium carbonate to transform it into a bentonite which swells in water and then treated with ammonium chloride hexadecyltrimethylammonium to turn it into a swellable organoclay in organic liquids. Polypropylene with 3 % polypropylene graft compatibilizer (PP-g-AM) was mixed with 1 % and 2 % by weight of discarded bond paper and with 1%, 2% e 5 % by weight of organophilic clay using a twin-screw extruder. The specimens were prepared by the injection process. The nanocomposite specimens were characterized by XRD, SEM, and thermal analysis (ATG and DSC). The nanocomposites showed improved thermal properties compared with the polymer without filler.

Introduction

There has been increasing interest in preservation of the environment and sustainability of resources. So, the use of natural fibers is receiving renewed attention as an alternative to inorganic counterparts in materials technology. Particular consideration has been paid to cellulose fibers, which are the most abundant biomass resource on Earth [1].

The utilize of natural cellulosic fibers in composites have attracted the attention of researchers, manufactures and user agencies due to the consequence of exploitation of non-renewable resources and management of agro-industrial wastes leading to environmental and ecological balances. Certainly, natural cellulosic fibers are rapidly emerging as novel low cost materials for several industrial applications [2].

Natural fiber reinforced polymer composites have various applications, such as use in automotive industry, furniture, packaging and building construction fields. The main constituent of natural fiber is cellulose, which contains a huge number of polar hydroxyl groups that would lead to a highly hydrophilic property of fiber and a very poor interface between the natural fiber and polymer matrix. Compared with synthetic fibers, the advantages of using natural fiber in

composites are their low specific gravity, cheaper, renewability, biodegradability, and environmentally friendly [3-4].

Polymeric nanocomposites have attracted substantial scientific interest and developments over the last two decades with an enormous market opportunity especially for the automotives and packaging industries. It was based on layered silicates, principally montmorillonites (nanoclays), are the most commonly utilized reinforcing additives in thermoplastic polymers due to their nanoscale features giving rise to unique and superior combination of properties achievable at low loading, normally 1-5 %, compared to around 30-40 % in conventional polymer composites [5].

Polymer nanocomposites are polymers that have been reinforced with little quantities of nano-sized particles (nanofillers). These materials represent a radical alternative to conventional filled polymers. In contrast to conventional composites, where the reinforcement is on the order of micrometres, polymer nanocomposites are exemplified by discrete constituents on the order of a few nanometres. An important class of nanofillers involves nanoclays belonging to the smectite group, such as montmorillonite. Montmorillonite belongs to the family of 2:1 layered silicates. Its structure involves layers about one nanometer thick, each of which consists of two tetrahedral silica sheets fused to an edge-shared octahedral sheet of aluminium/magnesium oxide/hydroxide. To produce nanocomposite materials with best properties and performance, these nanoclays must be intercalated with the polymer matrix and also totally exfoliated [6].

The study of polymer organoclay nanocomposite due to its superior properties compared with pristine polymer has attracted main research and commercial interests. The inclusion of small concentrations of nanoparticles in polymers (< 5 wt. %) can have a significant impact on material properties. The increase in mechanical properties such as tensile strength and modulus, solvent resistance barrier properties and flame retardant are a couple of selected examples of the advantages provided by this new class of materials. But, to fully use this increase, it is necessary to achieve a relatively uniform dispersion of the clay nanoparticles within the polymeric host matrix [7-8].

During nanocomposites preparation by melt compounding initially an intercalation process of the polymer macromolecules into the interlayer spaces occurs and finally clay mineral exfoliation in the polymer matrix. This process is diffused control and requires a balance between shear rate and residence time to reach complete exfoliation. However, these requirements have some drawbacks, since polymer degradation can also take place [9].

Polypropylene/montmorillonite (PP–MMT) is one of the most frequently utilized nanocomposites to obtain property improvements produced in different forms and applications by means of a range of manufacturing processes at a relatively low cost. There is ample evidence that PP–MMT formed by melting processing is the most preferred method to produce nanocomposites for commercial use. The improvement on final properties usually depends on the degree of exfoliation, delamination, and clay dispersion [10].

A great extent of exfoliation is even more difficult to achieve in polypropylene (PP) than in other, more polar polymers. Nanocomposites cannot be prepared successfully from PP and an organophilic silicate (OMMT), a compatibilizer agent, usually a functionalized polymer like

maleated PP (MAPP), must also be added to the composite. The structure of PP/silicate composites is complicated even in the presence of a compatibilizer agent containing several structural entities in varying amounts [11-12].

Polypropylene clay nanocomposites are usually prepared by melt-blending, with organoclays and compatibilizers such as maleic anhydride (PP-g-MA). Compatibilizers are really required due to the huge polarity difference between the polyolefin matrix and the clay. PP-g-MA allows wetting of the clay surface by hydrogen-bond interactions between the anhydride functions and the oxygen atoms at the surface of the silicate layers. Normally, the morphology of clay/PP nanocomposite is a mixed intercalated/exfoliated structure [13-15]. The objective of this work is to obtain a polypropylene nanocomposite with using Brazilian clay and used bond paper for increasing thermal properties of this nanocomposite.

Materials and Methods

Isotactic polypropylene (iPP) with a melt flow index of 2.2 dg min⁻¹ (230 °C/2.16 Kg), was purchased from Braskem S.A., Brazil. An organophilic bentonite prepared with a commercial sodium bentonite (Chocolate Clay) from the state of Paraiba, Brazil, was used in this work. Four kilograms of discarded bond paper were collected and fragmented and placed in a plastic container with 40 liters of water. After 24 hours, this material was stirred with a mixer for 30 minutes at maximum speed of 2.800 rpm. After stirring the pulp was placed in a fabric bag and placed in a centrifuge to 2.300 rpm to facilitate drying. After centrifugation the paper pulp was passed on a 50 mesh sieve to reduce the size of the paper and then dried at 60 °C for 72 hours. The organophilic clay and the paper with Irganox B215 FF (a blend of 0.2% of antioxidant and 0.4%, a thermal stabilizer) were manually mixed with coupling agent maleic anhydride (PP-g-MA), in a 3 wt % concentration to improve the clay adhesion to the polymer matrix.

A Mapplan Coperion twin screw extruder was used with a temperature range of 180 to 205 °C and 800 rpm rotation. A Battenfeld TM 750/210 injection was used to manufacture the specimens for tensile strength. The temperature injection was 190°C, and the mold temperature was 60°C. For X-ray diffraction (XRD) was used the Diffractometer PANalytical X'Pert PRO, using Cu K α radiation. Scanning electron microscopy was performed with an FEG FEI Inspect F50 instrument. The Balzers SCD 050 Sputter Coater was used to cover the samples with Au.

The melt and crystallization characteristics of the nanocomposites were studied with a Mettler Toledo DSC822^c differential scanning calorimeter (DSC). The specimens were subjected to temperatures of 25-280 °C at a heating rate of 10 °C min⁻¹ in a nitrogen atmosphere. Melting enthalpy value for 100% crystalline PP is 209 kJ kg⁻¹. To study the nanocomposite mass loss, the Mettler Toledo SDTA851^c thermogravimetric analysis was used. The specimens were submitted to temperatures of 25 to 650 °C at a heating rate of 10 °C min⁻¹ in an inert nitrogen atmosphere (N₂ flow 50 mL min⁻¹) and an oxygen atmosphere (O₂ flow 50 mL min⁻¹).

The nanocomposites identification is presented in Table I.

Table I. Identification specimens

Specimen	Identification
PP	Polypropylene, pristine
PP AM	Polypropylene with PP-g-MA
PPA 1%	Polypropylene with 1 % in weight of organophilic clay
PPA 2 %	Polypropylene with 2 % in weight of organophilic clay
PPC 1%	Polypropylene with 1 % in weight of cellulose
PPC 2%	Polypropylene with 2 % in weight of cellulose
PPAC 1%	Polypropylene with 1 % in weight of organophilic clay and 1 % in weight of cellulose
PPAC 2%	Polypropylene with 2 % in weight of organophilic clay and 2 % in weight of cellulose

Results and Discussion

Figure 1 shows the X-ray diffraction patterns of the nanocomposites with “organophilic clay”. Table II presents the basal spacing values that were obtained for the “chocolate” clay and the nanocomposites.

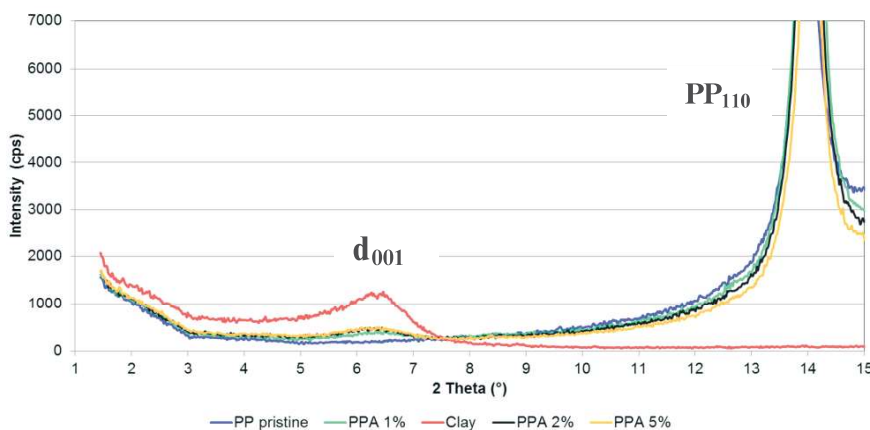


Figure 1. X-ray diffraction patterns of nanocomposite with organophilic clay.

Table II. Values of basal spacing obtained from the curves in the Figure 1

Specimens	d_{001} (Å)
Organophilic clay	13.70
PPA 1 %	13.87
PPA 2 %	14.28
PPA 5 %	14.11

Samples of the nanocomposites (PPA 1 %, PPA 2 % and PPA 5 %) clay peaks have suffered slight increase in the values of the interplanar distances. It was observed that there was an accentuated decrease in peak intensity for the organophilic clay nanocomposites because these peaks practically disappeared. This reduction in intensity of the main peak clay in relation to

nanocomposites suggest a disorganization of the clay lamellae, indicating a probably formation of exfoliated nanocomposites structures.

According Yadong et al. (2014) [16] intensity and the reduction in peak broadening indicate that the stacked plates becomes more disordered and partial exfoliation of the clay occurs. These results suggest that the dispersion of the clay plates within the polypropylene matrix is significantly increased in the presence of PP-g-MA.

Figures 2 and 3 show two micrographs of nanocomposite PPA 1 % and PPAC 1%, respectively. With SEM it was possible to observe the homogeneous distribution of the clay and cellulose fibers added to the polymer matrix.

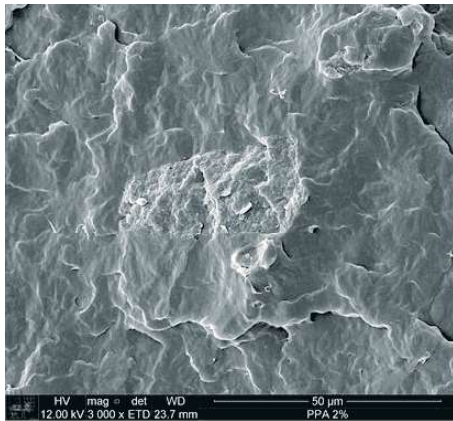


Figure 2. SEM– PPA 1 % scale 50 μm

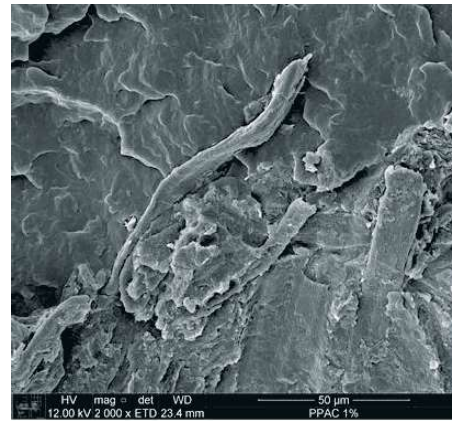


Figure 3. SEM– PPAC 1 % scale 50 μm

Table III shows the small changes in the crystallization temperature of PP pristine in relation to the nanocomposites with organoclay clay and cellulose; the difference of temperature in 3 °C in the nanocomposites is not significant. Table IV shows small changes in the melting temperatures of the nanocomposites of organophilic clay and cellulose. There was a temperature change of 2 °C in the nanocomposites in relation PP Pristine. Table V are presented the crystallinity values for the nanocomposites from DSC curves. The additions of nanoparticles in semi-crystalline polymers, in general, not affect significantly the crystallinity of the nanocomposite materials. It has been proposed, however, that these particles produce a large number of nucleating sites and in turn reduce the size of resulting spherulites [17].

Table III. Crystallization temperatures for the nanocomposites from DSC curves.

<i>Sample</i>	<i>Temperature (°C)</i>
PP pristine	125
PPAM	126
PPA 1 %	128
PPA 2 %	128
PPA 5 %	128
PPC 1 %	127
PPC 2 %	128
PPAC 1 %	128
PPAC 2 %	128

Table IV. Melt temperatures for the nanocomposites from DSC curves.

<i>Sample</i>	<i>Temperature (°C)</i>
PP pristine	175
PPAM	176
PPA 1 %	178
PPA 2 %	176
PPA 5 %	176
PPC 1 %	177
PPC 2 %	175
PPAC 1 %	176
PPAC 2 %	176

Table V. Crystallinity values (%) for the nanocomposites from DSC curves.

<i>Sample</i>	<i>Crystallinity (%)</i>
PP pristine	45
PPAM	48
PPA 1 %	44
PPA 2 %	44
PPA 5 %	44
PPC 1 %	46
PPC 2 %	47
PPAC 1 %	47
PPAC 2 %	46

Figure 4 shows the TG decomposition curves in an inert atmosphere (N_2) for the hybrid nanocomposites with organoclay and cellulose. The thermal stability is the same for the nanocomposites with clay. For PP pristine and PPAM, the decomposition temperature was smaller in relation to nanocomposites, demonstrating that the clay and cellulose promoted enhanced, improving the thermal stability of the hybrid nanocomposites.

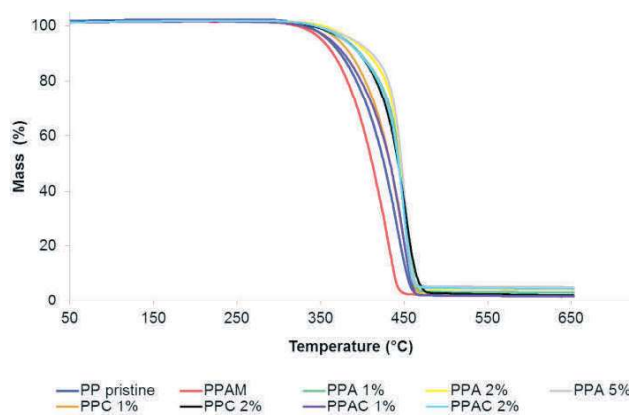


Figure 4. TG curves in a nitrogen atmosphere at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

Figure 5 show the TG decomposition curves are presented in a reactive atmosphere (O_2) for the hybrid nanocomposites with organoclay and cellulose. In an oxidizing atmosphere, the samples with PP pristine, PPAM, hybrid nanocomposites with clay and cellulose decompose into similar profiles.

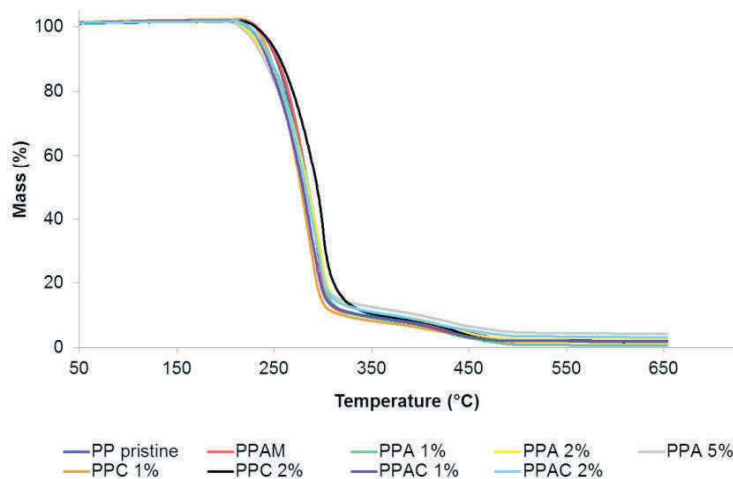


Figure 5. TG curves in a oxygen atmosphere at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

Conclusions

There was probably formation of nanocomposites exfoliated clay as demonstrated in the test X-ray diffraction. The SEM showed homogeneous distribution of the clay added to the polymer matrix. There were no significant changes in the thermal analysis by DSC for the hybrid nanocomposites of clay and cellulose. TG analysis the clay and cellulose promoted enhanced, improving the thermal stability of the hybrid nanocomposites in relation PP pristine.

Acknowledgments

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