Influence of Nanoclay and Coupling Agent on the Physical and Mechanical Properties of Polypropylene/Bagasse Nanocomposite

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ABSTRACT: In this work, the effects of nanoclay (1–4 wt %) and coupling agent (2 and 4 wt %) loading on the physical and mechanical properties of nanocomposites are investigated. Composites based on polypropylene (PP), bagasse flour, and nanoclay (montmorillonite type) was made by melt compounding and then compression molding. When 1–3 wt % nanoclay was added, the tensile properties increased significantly, but then decreased slightly as the nanoclay content increased to 4%. The impact strength was 6% lower by the addition of 1 wt % nanoclay, it was decreased further when the nanoclay content increased from 1 to 4%. Finally,

INTRODUCTION

Nanotechnology is a very promising field for industrial applications. The real revolution in nanomaterial applications, however, is expected to involve widely used bulk products. One of the first applications of nanotechnology was the production of nanofillers for the improvement of the mechanical properties of polymers.¹ The interest in producing composite materials with nanosized filler or reinforcement, i.e., nanocomposites, has grown tremendously in recent years.² Nanocomposites are a relatively new generation of composite materials where at least one of the constituent phases has one dimension of less than 100 nm.³ This new family of composites has attracted much attention because of their remarkable improvements in material properties when compared with those of the virgin/ unfilled polymer or conventional micro- and macrocomposites.4-7

Polymer based nanocomposites represent a new class of reinforced polymers containing small quantities (1–5 wt %) of nanoparticles like carbon nanotubes and nanofibers, TiO_2 , nanoclay, etc. to improve the

the water absorption of PP/bagasse composites was lowered with the increase in nanoclay content. Additionally, the coupling agent, 4 wt % MAPP, improved the mechanical and physical properties of the composites more than the 2 wt % MAPP. From these results, we can conclude that addition of nanoclay enables to achieve better physical and mechanical properties in conventional composites. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1386–1390, 2009

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materials properties.^{7–10} The small size of the reinforcement leads to an enormous surface area and thereby to increased interaction with the polymer matrix on molecular level, leading to materials with new properties. These improvements included high moduli^{11,12}; increased tensile strength¹³ and thermal stability^{10,14}; decreased gas permeability,¹⁵ improved flammability propeties¹⁶ and decrease in water absorbance¹⁷; and increased biodegradability of biodegradable polymers.¹⁸

The main nanofillers used today are carbon nanotubes (synthetic) and nanoclay (natural product). Synthetic carbon nanotubes are very expensive. Nanoclays (layered silicates), in contrast, are especially interesting for bulk applications because they are relatively inexpensive, commercially available, exhibiting a layered morphology with high aspect ratio, large specific surface areas and they cause an improvement in the mechanical properties of polymers.¹⁹ Commonly used nanoclays include montmorillonite, hectorite, and saponite, all of which belong to the same general family of 2 : 1 layered or phyllosilicates (Fig. 1).18 The combination of clays and functional polymers interacting at the atomic level constitutes the basis for preparing an important class of inorganic-organic nanostructured materials. Polymer-layered silicate nanocomposites containing low levels of exfoliated clays such as montmorillonite

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Figure 1 Schematically illustration of three different types of thermodynamically achievable polymer/layered silicate nanocomposites.¹⁸ [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and vermiculite have a structure consisting of platelets with at least one dimension in the nanometre range (Fig. 1). The platelet aspect ratio exceeds 300, giving rise to a high degree of polymer-clay surface interaction which results in barrier and mechanical properties that are far superior to those of the base material.²⁰

Polypropylene (PP) is particularly interesting because of its low cost and good mechanical properties. This polymer has a wide range of applications such as packaging, fibers, automobile industry, nondurable goods and in building construction.^{21–23} PP has been used in conventional composites for a long time and shows better mechanical properties with even low amounts of filler.¹ However, very few efforts have been made to improve the properties of PP/wood composites with nanoclay.^{11,12,18} The objectives of this work are the following: (1) to prepare PP/bagasse composites containing nanoclay (montmorillonite type) and (2) to study the effect of different nanoclay and coupling agent contents on physical and mechanical properties.

EXPERIMENTAL

Materials

The bagasse used as reinforcement was directly obtained from local sugar cane mill, after being processed to extract sugar and liquor. This "as received" material was dried at 95°C for 24 h and then was chopped and sieved. Bagasse pieces of 4– 6 cm in length were ground with a Thomas-Wiley miller to pass through a 50-mesh screen, and then were dried again and stored in sealed plastic bags before compounding.

Virgin PP, with the trade name Poliran P10800, was obtained from Bandar Imam Petrochemical Company, Iran. Its melt flow index was 7–10 g/ 10 min at 190°C and 2.16 kg as measured by ASTM D 1238-04.²⁴ The coupling agent, maleated polypropylene (MAPP) was obtained from Eastman Chemical Products, Epolene G-3003TM has an acid number of 8, and a molecular weight of 103,500. Nanoclay (montmorillonite type) was a product of Southern Clay Products: Cloisite Na+ (for which the negative charges of its layers are compensated with Na+ ions). Montmorillonite is classified as magnesium aluminum silicate which has a sheet morphology, and can be used to make a new class of clay/polymer nanocomposites.

Compounding and sample preparation

The compounding process used included two steps. First PP and nanoclay was kneaded in a Haake rotor mixer for 10 min. The bagasse flour and MAPP was then added and blended for an additional 20 min. The compounding temperature was 170°C and the



Figure 2 Effect of nanoclay and MAPP content on tensile stress yield.

rotation speed was 60 rpm. The composites were compression-molded to produce the samples according to ASTM standard. Typical molding conditions were: press temperature 170°C, pressure during heating 3 MPa, heating time 15 min and cooling time 15 min.

The mass ratio of fiber to PP was controlled at 30/ 70 for all blends. The effects of two variable factors, namely the nanoclay and MAPP contents, on the composite properties were examined. The concentration was varied from 0 to 4% for nanoclay and 2 and 4% for MAPP, based on the total weight of PP and fiber.

Mechanical properties

After molding, test specimens were conditioned at $23 \pm 2^{\circ}$ C, $50 \pm 5\%$ RH for at least 40 h according to ASTM D 618-99.²⁵ The mechanical behavior of the nanocomposites was characterized via tensile test in accordance with ASTM D 638-99.²⁵ Strength measurements of samples were conducted using an Instron testing machine (Model 1186). The crosshead speed during the tension testing was 1.5 mm/min. The Charpy impact strength was measured with impact pendulum tester (Model TMI, No. 43-01) according to ASTM D 256-97 with unnotched samples at room temperature.²⁶ Each value obtained represented the average of six samples.

Water absorption

The water absorption test was performed based on ASTM D 570-98.²⁷ Each composition of samples was cut into rectangular shapes of $50 \times 10 \times 1.0 \text{ mm}^3$ (length × wide × thickness). The sample was oven dried at 50°C for 24 h to a constant weight (W_0). The specimens were immersed in distilled water for 24 h at a temperature 23 ± 1°C. Then, the excess water on the surface was wiped off by blotting paper and specimens were weighed using an analytical balance with 0.1 mg precision (W_t). The amount of water

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absorbed (M_t) was determined by using the following equation.

$$M_t(\%) = (W_t - W_0)/W_0 \times 100 \tag{1}$$

where W_t and W_0 , are the weights of the specimen before and after immersion in water, respectively.

RESULTS AND DISCUSSION

Tensile properties

The tensile properties of PP/bagasse composites containing different contents of clay are presented in Figures 2 and 3. From the curves of Figure 2 it is evident that moderate increase in tensile yield occurred upon filling the polymer matrix with nanoclay, indicating a reinforcing effect. The 1 and 2 wt % samples (with 2 wt % MAPP) showed the maximum increment by 8 and 11%, respectively. The phenomenon was stronger for using 4 wt % MAPP. Similar behavior can be observed in Figure 3, where the significant increase in tensile modulus is plotted versus nanoclay content. The differences in strength improvement with respect to MAPP concentration are very prominent at the highest nanoclay content. These results confirm the strong interaction between the PP matrix and Cloisite Na+. Similar results have been reported by Sinha Ray and Okamoto28 who studied the properties of polymer/layered silicate nanocomposites. Their data show that the tensile modulus of a polymeric material has been shown to be remarkably improved when nanocomposites are formed with layered silicates.

Izod impact strength

Figure 4 represents the dependence of the unnotched Izod impact with various nanoclay contents. It is seen that unlike tensile properties, the impact strength of the composites is generally decreased with increasing nanoclay content. This is



Figure 3 Effect of nanoclay and MAPP content on tensile modulus.

consistent with the results reported by most authors.^{3,4,19} The presence of nanoclay particles in the PP matrix provides points of stress concentrations, thus providing sites for crack initiation. Another reason for decrease in impact strength may be the stiffening of polymer chains. For high impact properties, in fact, a slightly weaker adhesion between fiber and polymer is desirable, as it would result in a higher degradation of impact energy, supporting the so-called fiber pull-out.^{29,30} It should be noted that for specific applications, the impact strength can be increased by using impact modifiers or by using natural fibers having higher microfibril angle.^{31–35}

Water absorption

Figure 5 shows the values of the water absorption for the composites, which vary depending upon the nanoclay loading. Polymers do slightly absorb moisture, indicating that moisture is absorbed by the wood component in the composite. Weight gain upon exposure to water after 24 h decreased as the percentage of MAPP and nanoclay increased for all composites tested, the weight gains for all specimens were less than 3.5%. According to Das et al.,³⁶ initially, water saturates the cell wall (via porous tubular and lumens) of the bagasse fiber, and next water occupies void spaces. Because composite voids and the lumens of bagasse fibers were filled with nanoclay, this prevents the penetration of water by the so-called capillary action into the deeper parts of composite. This may suggest that the water absorption was occurred in the surface layer. On the other hand, the use of 4 wt % MAPP leads to better interaction and decreases in the water sorption and slow moisture penetration in the composite systems.

CONCLUSIONS

The experimental results of our study indicate the tensile modulus and yield of PP/bagasse composites



Figure 4 Effect of nanoclay and MAPP content on unnotched impact strength.



Figure 5 Effect of nanoclay and MAPP content on water absorption (24 h).

increased about 26 and 15%, respectively, with addition of 3 wt % nanoclay, but then decreased slightly as the nanoclay content increased to 4%. The impact strength was lowered 6% by the addition of 1 wt % nanoclay, it was lowered further when the nanoclay content increased from 1 to 4 wt %. The water absorption of composites was lowered with the increase in nanoclay content. Additionally, the coupling agent, 4 wt % MAPP, improved the mechanical and physical properties of the composites more than the 2 wt % MAPP. From these results, we can conclude that the addition of nanoclay increases not only the tensile strength of PP/bagasse composite, but also improves its water absorption property. As a consequence, it is possible to conclude that nanoclay enables to achieve better physical and mechanical properties than conventional composites.

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