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Thermal Stability, Mechanical Properties and Solvent Resistance of PP/clay Nanocomposites Prepared by Melt Blending

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Abstract: In this research, the melt blending technique was used to prepare various polypropylene (PP) based nanocomposites. A commercial organoclay (denoted 15A) served as filler for PP matrix and the polypropylene grafted maleic anhydride (PP-g-MA) was used as compatibilizer. The morphology of the nanocomposites was studied using X-ray diffraction (XRD). XRD results showed that these nanocomposites are best described as intercalated systems. PP/Clay nanocomposites showed good thermal stability in the TGA analysis. By introducing about 3% clay in the nanocomposites, the onset temperature of the degradation increased by 22°C over that of the pure PP/PP-g-MA blend. Mechanical testing showed that the polypropylene nanocomposites had an enhanced Young's modulus, hardness and slightly decreased tensile strength with increasing clay loading as compared the pure PP/PP-g-MA blend. The solvent resistance of PP/Clay nanocomposites is slightly decreased with increasing clay loading.

Key words: Polypropylene (PP), nanocomposites, organoclay, compatibilizer, thermal stability, intercalated

INTRODUCTION

It is believed that the presence of only a small amount of clay can greatly improve many properties of polymers, if nanodispersion of clay in the matrix is realized (Alexander and Dubois, 2000). Polymer/clay nanocomposites have been a great interest since the research at the Toyota company found that polyamide-6-clay nanocomposites gave greatly enhanced mechanical properties, along with a large increase in the heat distortion temperature, at only 5% clay loading (Usuki *et al.*, 1993; Tang *et al.*, 2003). Generally, there are five ways to make nanocomposites: solution method, in situ intercalation polymerization, melt blending, template synthesis and sol-gel, which melt blending is favored in industry (Alexander and Dubois, 2000).

The clay is highly organophilic, which means that it must generally be organically-modified by treatment some organophilic agents, in order to obtain nanocomposites with polymers (Liang *et al.*, 2004; Hai *et al.*, 2004).

Polypropylene is the most widely used polyolefine polymers, but, because of their non-polar backbones, it is a challenge to make nanocomposites of PP by melt blending with organically modified clay. In most instances, maleicanhydride grafted PP was used as a compatibilizer (Wang *et al.*, 2000; Zhang *et al.*, 2005;

Kawasumi *et al.*, 1997; Kato *et al.*, 1997; Liu and Wu, 2001; Hasegava *et al.*, 1998) to permit the formation of the nanocomposites.

Recent works have shown that polypropylene nanocomposites could be formed by direct melt blending polymer with an oligomerically-modified clay (Su *et al.*, 2004a, b, c). Typically, the oligomerically modified clays contain 25% inorganic clay and 75% oligomer but a variation in the oligomer content can lead to more advantageous behaviour on some properties. The disadvantage of using this oligomeric surfactant containing lauryl acrylate is its ability to plasticize the polymer (Zhang *et al.*, 2005, 2006a, b).

In the present research, we compare the PP/Clay nanocomposites with the pure PP/PP-g-MA blend prepared through the melt blending method by using maleic anhydride grafted PP (PP-g-MA) as a compatibilizer, in terms of their morphology, thermal stability, mechanical properties and solvent resistant.

MATERIALS AND METHODS

Materials: The materials used in this study were clay, polypropylene and compatibilizer (MA grafted PP). The clay (Southern Clay Products, Inc., Gonzales, Texas, USA) was cloisite 15A which is a natural montmorillonite

modified with a quaternary ammonium salt which is shown in Fig. 1. Modifier is 2M2HT (dimethyl, dihydrogenate-dtallow, quaternary ammonium, where HT is hydrogenated tallow (65% C18, 30% C16, 5% C14, anion: chloride). In this clay, concentration is 125 meq/100g clay and (%) moisture is <2% and (%) weight loss on ignition is 43%. Polypropylene (P10800, MFI = 8.5 g 10 min at 190°C) was acquired from Bandare Emam petrochemical complex (Bandare Emam, Iran) and PP-g-MA (MFI = 5 g 10 min at 230°C, MA content = 0.5-0.7 wt. %) was obtained from the Kimia Javid Sepahan company (Iran).

Preparation of PP/clay nanocomposites: All nanocomposites were prepared using melt blending in a Brabender plasticorder at 70 rpm and 175°C for 10 min; the calculated amount of PP, PP-g-MA and clay (Table 1) was put into the Brabender mixer at the same time. After 10 min of blending, the mixture was removed from the chamber and allowed to cool to room temperature. Then, the samples were transferred to a laboratory press and compression molded into 150×150×5 mm plates. The pressing process had five steps: First step was preheating 155°C for 4 min, second step was pressing at 5 bar for 50 sec, third step was pressing at 10 bar for 80 sec, fourth step was pressing at 20 bar for 100 sec and fifth step was pressing at 25 bar for 100 sec (cooling). The composition of the nanocomposites is given in Table 1.

Methodology: Dispersibility of the organoclay in the polymer matrix was evaluated by XRD. XRD patterns were recorded by a Philips xpert X-ray generator with Cu Kα radiation at 40 kV and 40 mA. The diffractograms were

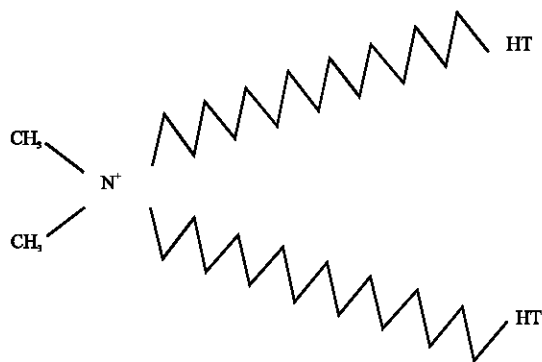


Fig. 1: Structure of the quaternary ammonium salt

Table 1: Composition of PP/Clay nanocomposites

Sample	PP (wt. %)	PP-g-MA (wt. %)	Clay (wt. %)
PP1	85	15	0
PP2	82	15	3
PP3	80	15	5
PP4	78	15	7
PP5	95	0	5

scanned in 2θ ranges from 1 to 10° at a rate of 2.4° min. The basal spacing of the silicate layers, d, was calculated according to Bragg's Eq. $\lambda = 2d \sin \theta$.

Thermogravimetric analysis, TGA, was carried out on a Chan TG131 unit under argon at a scan rate of 20°C per minute from room temperature to 600°C at 15 mgr scale. Temperatures are reproducible to ±0.01°C.

Tensile properties (Youn's modulus and tensile strength) were measured according to ASTM D638 using instron 4411 tensile test machine at a strain rate 50 mm min⁻¹. The shore hardness was measured according to ASTM D2240-95 by using a Shore-A hardness instrument (Zwick). All measurements were taken three times and the result values were averaged.

The solvent resistance of PP/Clay nanocomposites was measured as follows: The samples with similar shape (20×10×2 mm³) maintained at about 25°C for 43 h. The percentage of the change in mass was calculated by using the below formula:

$$\text{Change in mass (\%)} = [(M - M_0) / M_0] \times 100$$

Where:

M₀ = Represents the dried weight of the specimen and

M = The weight of the specimen after immersion.

RESULTS AND DISCUSSION

Characterization of the clay and its nanocomposites by XRD: X-ray diffraction (XRD) technique was employed to assess the dispersibility of nanoclay in the nanocomposites. According to the dispersion status of layered clays in the polymeric matrix, three types of composites can be classified: (1) conventional macrocomposites, (2) partially exfoliated composites, including intercalated clays and (3) fully exfoliated nanocomposites. The XRD patterns of the cloisite 15A, PP3 and PP5 are shown in Fig. 2. As seen, the characteristic (001) plane diffraction peak of cloisite 15A is around 2θ = 7.25°, while the peak of PP3 is shifted to lower angles compared with cloisite 15A (2θ = 5.3°), this indicates that the molecules of PP-g-MA are intercalated into the layered silicates of clay, expanding the basal spacing of organoclay. The strong hydrogen bonding between the maleic anhydride group and the oxygen group of the silicate as well as the shear force exerted on organoclay during melt blending can produce the driving force necessary for the intercalation. The interlayer spacing of the clay as well as its compatibility with polymer are increased, so the clay galleries could easily be intercalated with PP. The peak of PP5, is around 2θ = 7°. It is clear that, the d spacing of PP5 is nearly the same as that of the cloisite 15A. It indicates that the PP5 has

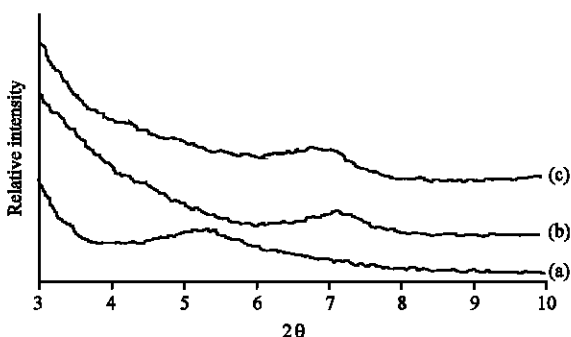


Fig. 2: X-ray diffraction pattern for (a) Cloisite 15A; (b) PP5; (c) PP3

deintercalated the morphology, which may result from immiscibility between PP and organoclay because PP does not include any polar group in its backbone. This observation clearly indicates that the PP-g-MA plays a compatibilizing role, as expected, by interacting sufficiently with cloisite 15A and the PP matrix. Similar behaviour has been seen previously (Chiu *et al.*, 2004).

TGA characterization of nanocomposites: The thermal stability of polymer/clay nanocomposites is usually studied by thermogravimetric analysis (TGA). One of the parameters that is of interest from the TGA curves is the onset of the degradation, which is usually taken as the temperature at which 10% degradation occurs ($T_{0.1}$). The data are tabulated in Table 2 and shown graphically in Fig. 3.

As shown in Fig. 3 and Table 2, PP nanocomposites show enhanced thermal stability. The onset temperature increases by 22°C at 3% clay loading, while at higher clay loading, 5 and 7%, the onset temperature of the nanocomposites are 13 and 14.5°C higher than that of the pure PP/PP-g-MA blend. Similar behaviour has been seen previously (Zhang *et al.*, 2005, 2006a, b; Jang *et al.*, 2005; Zhang *et al.*, 2004). This enhancement of the thermal stability indicates that the PP/PP-g-MA/15A nanocomposites were not simple blends but that PP/PP-g-MA molecularly compounded with 15A. Comparison of PP3 and PP5 (without PP-g-MA) indicates that the simultaneous presence of PP-g-MA and clay in the PP matrix could induce a positive effect on the thermal stability of PP, but this effect is negligible because the thermal stability of the PP and PP-g-MA are identical. This observation has been seen previously (Chiu *et al.*, 2004). The enhanced thermal stability of the polymer/clay nanocomposites is attributed to the lower permeability of oxygen and the diffusibility of the degradation products from the bulk of the polymer caused by the exfoliated clay in the composites (Ma *et al.*, 2001; Kodgire *et al.*, 2001; Manias *et al.*, 2000; Ahmadi *et al.*, 2004).

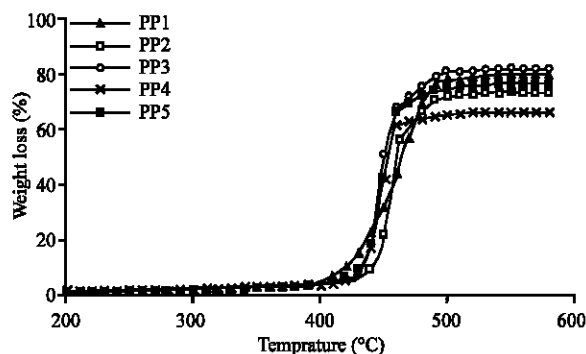


Fig. 3: The TGA curves for PP/Clay nanocomposites and pure PP/PP-g-MA blend

Table 2: TGA data, in argon, for PP/Clay nanocomposites

Sample	PP1	PP2	PP3	PP4	PP5
$T_{0.1}$ (°C)	420	442	433	434.5	433

Table 3: Mechanical properties of PP/Clay nanocomposites and pure PP/PP-g-MA blend

Sample	PP1	PP2	PP3	PP4	PP5
Tensile strength (MPa)	33.98	33.92	31.64	31.69	37.12
Young's modulus (MPa)	1360	1350	1369.29	1505	1565.67
Hardness	70	71	71	73	71

Mechanical properties: The mechanical properties of the nanocomposites, such as tensile strength, Young's modulus and shore hardness, have been evaluated and the data are presented in Table 3.

In PP/Clay nanocomposites, the tensile strength is slightly decreased as compared the pure PP/PP-g-MA blend, while Young's modulus is increased with increasing clay loading. These observations have been seen previously (Zhang *et al.*, 2005, 2006a, b; Jang *et al.*, 2005). The reduction in tensile strength with increasing clay loading can be attributed to the inevitable aggregation of the silicate layers in high clay content. The enhancement of the Young's modulus can be described to resistance exerted by clay layers against plastic deformation of the polymer. In addition, the stretching resistance of polymer chains with an extended conformation in the gallery also contributed to the modulus enhancement. The less tensile strength for PP3 than PP5 can be attributed to the plasticizing effect of PP-g-MA. The shore hardness of PP/Clay nanocomposites increases with increase in clay content. The uniformity distributed intercalated platelets improved the stiffness of nanocomposites. The presence of these stiff clay platelets and entanglement of polymer chains made the PP nanocomposites harder.

Solvent resistance property of PP/Clay nanocomposites:

Figure 4 shows the results of the solvent resistance of PP/Clay nanocomposites with different clay content in pure toluene after 43 h at 25°C. Polypropylene is not

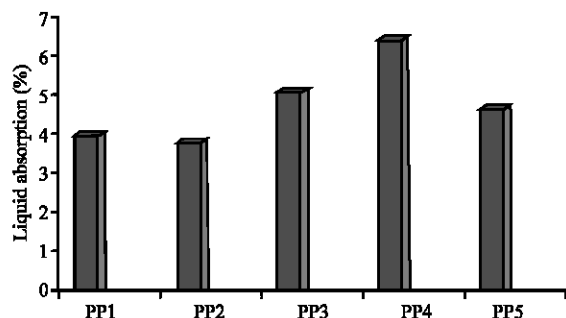


Fig. 4: Solvent resistance of PP/Clay nanocomposites with different clay content in pure toluene after 43 h at 25°C

dissolved in toluene, but it absorbs toluene and swells. As the clay loading is increased, the absorption values of toluene in PP/Clay nanocomposites are slightly increased compared with the pure PP/PP-g-MA blend, except for the nanocomposite with 3% clay. This phenomenon can be attributed to the inevitable aggregation of silicate layers with increasing clay loading. The solvent resistance of PP3 is lower in relative to PP5, because PP5 doesn't have clay.

CONCLUSIONS

In this study, we successfully prepared PP/Clay nanocomposites by melt blending the polypropylene with organoclay (denoted cloisite 15A) and PP-g-MA. XRD results showed that these nanocomposites are best described as intercalated systems. PP/Clay nanocomposites showed good thermal stability in TGA analysis. TGA analysis showed that, by introducing about 3% clay in the nanocomposites, the onset temperature of the degradation increased by 22°C over that of the pure PP/PP-g-MA blend. Mechanical testing showed that the polypropylene nanocomposites had an enhanced Young's modulus, hardness and slightly decreased tensile strength with increasing clay loading compared with the pure PP/PP-g-MA blend. The nanocomposites hadn't superior solvent resistance when compared to that of the pure PP/PP-g-MA blend and the absorption values of toluene in PP/Clay nanocomposites were slightly increased, as the clay loading was increased.

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