

Polyamide 6-Organoclay-Impact Modifier Nanocomposites

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ABSTRACT

In this study, polyamide 6, organically modified montmorillonite, and ethylene/glycidyl methacrylate (E-GMA) and ethylene/butyl acrylate/maleic anhydride (E-BA-MAH) terpolymers acting as impact modifiers for polyamide were melt blended in a co-rotating twin screw extruder to investigate the effects of component concentrations on the final properties of ternary nanocomposites. The morphology, in terms of XRD and SEM analysis, melt flow characteristics and tensile properties of the produced composites were investigated. XRD patterns showed that the interlayer spacing of the organoclay Cloisite® 25A increased in polyamide 6-montmorillonite binary nanocomposites as well as in ternary systems. In the presence of elastomer, the MFI of both unfilled polyamide 6 and ternary nanocomposites decreased owing to the high viscosity of elastomer.

Tensile strength of the ternary systems resembled the tensile strength of binary blends of elastomers and polyamide 6. It can be concluded that effect of elastomer is more dominant than the effect of organoclay.

Keywords: polyamide 6, polymer nanocomposites, impact modification, organoclay

INTRODUCTION

Polymer-clay nanocomposites are a class of particulate-filled composites. The reinforcement material is a layered silicate, which is in the form of sheets with thickness of one to few nanometers and length of hundreds to thousands of nanometers. They show several advantages over typical composites in terms of mechanical, thermal, physical and barrier properties owing to the high aspect ratio of the reinforcement material [1].

Toyota researchers obtained polyamide 6-clay nanocomposites by in-situ polymerization of ϵ -caprolactam in the interlayer gallery region of organoclay [2-4]. Vaia et al suggested that nanocomposites can be obtained by direct polymer melt intercalation and can be combined with conventional polymer processing techniques where polymer chains diffuse into the space between the clay layers or galleries [5-7]. In the processing equipment like extrusion and injection molding, the agglomerates of nanoclays are broken down due to the external forces from the polymer melt and the diffusion of macromolecules into the gaps.

Polymer melt applies an external force on clay agglomerates and this force depends on the shear rate, melt

viscosity of the polymer matrix, surface area of clay, and surface tension between the polymer melt and clay interface. On the other hand, the diffusion of macromolecules depends on melt temperature and chain structure of polymer, extrusion time, interlayer spacing of the clay and also type and concentration of surfactant modifiers at the clay surface [6-9].

This study is conducted to see the effects of addition of an elastomeric material on polyamide-6 organoclay nanocomposites. Polyamide 6 has reactive functionalities through amine and carboxyl end groups that are capable of reacting to form graft moieties with the elastomers used. The ethylene-based elastomers have glycidyl methacrylate (GMA), butyl acrylate (BA), and maleic anhydride (MAH) functional groups. GMA contains epoxide functionality, capable of reacting with both the acid and amine end groups of polyamide 6 [10]. The anhydrides can react only with the amine ends of polyamide 6 chains [11]. In addition to these reactions, reactions may take place between the terminal amino groups of polyamide 6 and ester groups of butyl acrylate [12].

In this study, the effects of elastomer type and concentration on the properties of ternary nanocomposites composed of polyamide-6, organically modified montmorillonite, and ethylene/glycidyl methacrylate (E-GMA) and ethylene/butyl acrylate/maleic anhydride (E-BA-MAH) reactive terpolymers acting as impact modifiers for polyamide are investigated.

XRD analysis was used for examining the interlayer distance of organoclay layers. The fractured surfaces were etched in hot xylene and examined using a scanning electron microscope (SEM) to explain the mechanism of deformation and toughening. The mechanical behavior of modified nanocomposites was evaluated in terms of tensile properties, tensile strength, Young's modulus, and toughness. Flow characteristics were studied by Melt Flow Index measurements.

EXPERIMENTAL

The polymer matrix, polyamide 6 (Teklamid) was purchased from Polyone Company. Two different types of elastomeric materials; Lotader AX 8840, ethylene-glycidyl methacrylate (E-GMA) and Lotader 2210, ethylene-butyl acrylate-maleic anhydride (E-BA-MAH) used in this study were purchased from Arkema Chemicals. Cloisite® 25A, a layered silicate, modified by dimethyl, hydrogenated tallow, 2-ethylhexyl quaternary ammonium ion, was purchased from Southern Clay Products. According to supplier's data, modifier concentration and original d-spacing are 95 meq/100 and 18.6 Å, respectively. Organically treated montmorillonite (2 wt %), elastomer (5 wt %) and polyamide-6 (93 wt %) nanocomposites

were prepared by melt compounding in a Thermoprism TSE 16 TC, co-rotating, intermeshing twin-screw extruder (D = 16 mm, L = 384 mm) at a screw speed of 250 rpm and a feed rate of 25 g/min. The temperature profile of the barrel was 220-240-240-240-240 °C from hopper to the die. Prior to compounding, polyamide-6, organically modified montmorillonite and elastomer were dried under vacuum at 80 °C for 24 h. Dry pellets of polyamide-6 and elastomers were manually blended inside the main feeder and fed from the main port. The organoclay particles, inside the second feeder, were fed to the extruder simultaneously from the main feed port. The pellets obtained were dried and fed to the extruder from the main feeder and extruded again. Dry extruded pellets were injection molded (Microinjector, Daga Instruments) using a nozzle temperature of 235 °C and mold temperature of 30 °C. After injection molding, the samples were immediately sealed in polyethylene bags and stored in desiccators for at least 24 h prior to any testing.

Tensile tests were performed according to ASTM D 638 on injection molded specimens. All mechanical tests were performed at 23 °C. Tensile properties reported represent the average of the results on at least five samples. Toughness values of the samples were measured by calculating the area under the stress-strain curves.

X-ray diffraction (XRD) patterns were obtained by a Phillips PW-3710 diffractometer equipped with CuK α X-ray radiation, operating at 40 kV and 55 mA. The diffraction patterns were collected between angles (2 θ) of 1° to 10° at a scanning rate and step size of 3°/min and 0.02°, respectively. The fracture surfaces of the materials obtained by impact testing were examined by a low voltage Scanning Electron Microscope (JEOL JSM-6400). Melt flow index (MFI) measurements were carried out according to ASTM D1238-79 using an Omega Melt Flow Indexer. Conditions of temperature and load were selected as 235°C and 2.16 kg, respectively.

RESULTS AND DISCUSSION

Table 1 shows the d-spacing of organoclay in powder form and polyamide 6 based nanocomposites with/without elastomers. Polyamide 6 showed no peak in the 2 θ =1-10° interval. The interlayer spacing of the organoclay Cloisite®25A increased more in binary polyamide 6-montmorillonite nanocomposites, than in ternary systems. This increase indicates that the basal spacing has been expanded owing to the intercalation of polyamide 6 and elastomers into the organoclay galleries.

The MFI results of the materials prepared by using different elastomers and various organoclays are given in Table 2. MFI of polyamide decreases (viscosity increases) upon addition of elastomer, owing to the high viscosity of elastomers and the possible reactions between elastomers and polyamide 6. However, the addition of clay on this blend does not significantly change the MFI, since the amount of clay in the structure is low. It is known that as

polymer melt viscosity increases, the shear applied to the clay agglomerates increases as higher stress is transferred which may facilitate separation of clay platelets. However, according to Table 2, as melt viscosity of the processed nanocomposites increases, basal spacing of the organoclay decreases. This may be due to the higher molecular weight of the elastomers in comparison to polyamide 6, which makes penetration of the polymer more difficult into the interlayer spacing.

As observed in Figure 1, tensile strength decreases with elastomer addition. The effects of GMA and MAH reactive groups on tensile strength are nearly the same. An increase in strength with the addition of organoclay is obtained due to the high aspect ratio of montmorillonite, which provides high contact surface area between the filler and the polymer matrix.

In ternary nanocomposites with elastomers, it is observed that the tensile strength and modulus of the samples are lower than the tensile strength and modulus of polyamide 6/organoclay nanocomposite. Thus, it can be concluded that the effect of elastomeric material is more dominant than the effect of montmorillonite.

Table 1. XRD data of the nanocomposites

	d-spacing (Å)
Cloisite®25A in powder form	18.6
Polyamide 6 + 2 wt % Cloisite®25A	58.1
Polyamide 6 + 2 wt % Cloisite®25A + 5 wt % E-BA-MAH	46.1
Polyamide 6 + 2 wt % Cloisite®25A + 5 wt % E-GMA	32.0

Table 2. Melt Flow Index data of the samples

MFI (g / 10 min)	No Clay	2% Cloisite® 25A
Polyamide 6	34.2 ± 0.9	35.3 ± 2.9
Polyamide 6 + 5% E-BA-MAH Blend	19.8 ± 0.5	21.3 ± 0.2
Polyamide 6 + 5% E-GMA Blend	24.4 ± 0.4	17.2 ± 0.1

As seen in Figure 2, Young's modulus of polyamide-6 increases in the presence of both elastomers and montmorillonite. Since the organoclay has a higher modulus than polyamide-6 matrix, modulus increases with organoclay addition. The possibility of the modulus improvements in the presence of elastomeric material is due to the interaction of polyamide-6 and reactive elastomers.

The Young's modulus of the ternary systems is lower in comparison to the Young's modulus of nanocomposites without

the elastomers. The organic modifier in the clay facilitates dispersion of clay by weakening the interlayer adhesion and promoting the compatibility with the polymer chains via strong polar interactions. However, the molecular weight of the elastomers are higher in comparison to polyamide 6, which makes penetration of the polymer more difficult into the interlayer spacing. X-ray measurements also support this phenomenon.

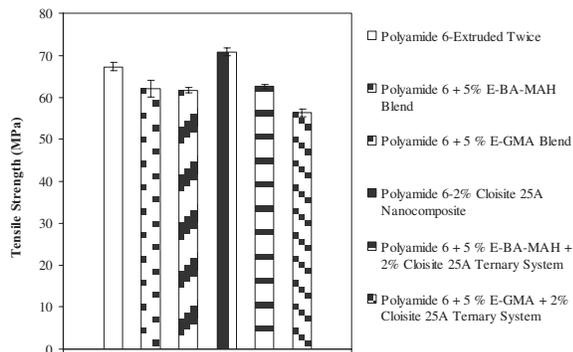


Figure 1. Tensile strength of the nanocomposites

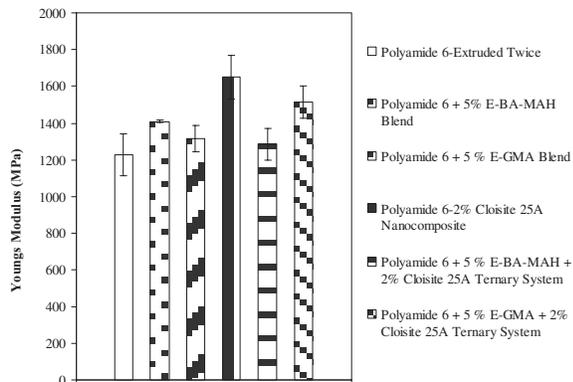


Figure 2. Young's Modulus of the nanocomposites

Toughness of the processed blends, nanocomposites and ternary systems were measured by calculating the area under stress-strain curves. The toughness values of the processed samples can be seen in Figure 3. At 5 % elastomer content, toughness remains nearly the same for elastomers Lotader 8840 and Lotader 2210, because of the low amount of elastomer. Incorporating montmorillonite to the system increases toughness except for the ternary system with E-GMA. It is seen that toughness in both polyamide 6/organoclay nanocomposites or in ternary systems, is directly related to the interlayer spacing

measured from X-ray analysis. As interlayer spacing of clay increases, toughness increases.

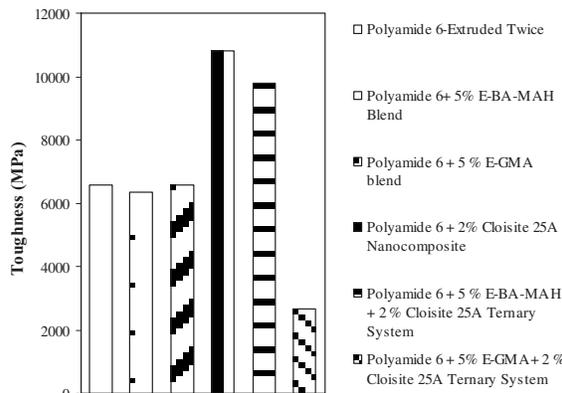


Figure 3. Toughness of the nanocomposites

CONCLUSIONS

XRD patterns of the nanocomposites showed that the interlayer spacing of the organoclay Cloisite® 25A powder increases when the powder is incorporated into polyamide 6 and polyamide 6/elastomer blend matrices.

In ternary systems composed of polyamide-6, organoclay and elastomeric material, tensile strength decreases in the presence of elastomer. The tensile strength and Young's modulus of polyamide 6 increase with the addition of organoclay. In nanocomposites with elastomers, since the tensile strength and modulus of the samples are lower than the tensile strength and modulus of polyamide 6/organoclay nanocomposite, it can be concluded that effect of elastomeric material is more dominant than the effect of montmorillonite.

At 5 % elastomer content, toughness of the binary blends remains nearly the same when compared to pure polyamide 6. Incorporating montmorillonite to the system increases the toughness in samples containing 2 % Cloisite® 25A except for the nanocomposite with 2 % Cloisite® 25A and 5 % E-GMA. It is seen that toughness in nanocomposite systems without elastomer is directly related to the interlayer spacing measured by XRD. As interlayer spacing of clay increases, toughness increases.

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