

Morphology and Properties of Nylon 6 and High Density Polyethylene Blends in Presence of Nanoclay and PE-g-MA

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ABSTRACT: In this study, we report the synergistic effect of nanoclay and maleic anhydride grafted polyethylene (PE-g-MA) on the morphology and properties of (80/20 w/w) nylon 6/high density polyethylene (HDPE) blend. Polymer blend nanocomposites containing nanoclay with and without compatibilizer (PE-g-MA) were prepared by melt mixing, and their morphologies and structures were examined with scanning electron microscopy (SEM) and wide angle X-ray diffractometer (WAXD) study. The size of phase-separated domains decreased considerably with increasing content of nanoclay and PE-g-MA. WAXD study and transmission electron microscopy (TEM) revealed the presence of exfoliated clay platelets in nylon 6 matrix, as well as, at the interface of the (80/20 w/w) nylon 6/HDPE blend–clay

nanocomposites. Addition of PE-g-MA in the blend–clay nanocomposites enhanced the exfoliation of clays in nylon 6 matrix and especially at the interface. Thus, exfoliated clay platelets in nylon 6 matrix effectively restricted the coalescence of dispersed HDPE domains while PE-g-MA improved the adhesion between the phases at the interface. The use of compatibilizer and nanoclay in polymer blends may lead to a high performance material which combines the advantages of compatibilized polymer blends and the merits of polymer nanocomposites. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1801–1811, 2012

Key words: nanocomposites; compatibilization; clay; coalescence; intercalation

INTRODUCTION

Polymer blending has become a convenient route for the development of new polymeric materials over the past several decades. However, most polymers are immiscible due to the unfavorable enthalpy of mixing. High density polyethylene (HDPE) and nylon 6 blends are interesting from an industrial point of view because they represent an economic and versatile method to modify the basic properties of polymers, combining the thermo mechanical properties of nylon 6 with the easy process ability of HDPE. On the other hand, HDPE has low permeability to water vapor, while nylon 6 has low oxygen permeability. Therefore, blends of HDPE and nylon 6 could provide good barrier to both water and oxygen. Unfortunately they are incompatible due to the different polarity and crystalline structure. Blends of incompatible polymers are usually characterized by low dispersion between phases, high interfacial

tension and poor adhesion, which result low mechanical properties in the blends. To improve the miscibility in immiscible polymer blends, block or graft copolymers have been employed as compatibilizers that reduce the dispersed domain sizes by increasing the interfacial adhesion and lowering the interfacial tension in blends.^{1–6}

Recently, several research groups^{7–19} showed the role of nanoclay as compatibilizer in immiscible polymer blends. For instance, Voulgaris et al.⁷ reported a decrease in dispersed domain sizes in (25/75 w/w) polystyrene (PS)/poly(ethyl methacrylate) (PEMA) blend in presence of organoclay. They explained it in terms of emulsification effects of excessive surfactants in organoclay. Hong et al.⁸ showed a decrease in the domain sizes in poly(butylene terephthalate) (PBT)/HDPE blend as long as the clays were dispersed in the PBT matrix. The presence of clay changed the viscosity ratio of the polymers and suppressed the coalescence of dispersed domains in the blend. Gelfer et al.⁹ reported that preferential location of nanoclay in poly(methyl methacrylate) (PMMA) phase increased the viscosity of PMMA in (50/50 w/w) PS/PMMA blend that lowered the dispersed PS domain sizes. Wang et al.¹⁰ reported that intercalation of both the polypropylene (PP) and PS chains inside the same clay galleries greatly reduced the PS domain sizes in

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(70/30 w/w) PP/PS blends. They assumed that these cointercalated polymer chains played the role of compatibilizer, similar to that of a block copolymer. Sinha Ray et al.^{11,12} reported improved miscibility between polycarbonate (PC) and PMMA in PC/PMMA blends in presence of organoclay. They also reported that location of intercalated clay silicate layers selectively at the interface decreased the interfacial tension and dispersed domain sizes in PP/PS blend system.¹³ Khatua et al.¹⁴ have reported that selective dispersion of exfoliated clay platelets in nylon 6 phase decreased the average domain sizes of dispersed ethylene propylene rubber (EPR) phase in (80/20 w/w) nylon 6/EPR blends. The exfoliated clay silicate layers in the matrix phase could prevent the coalescence of dispersed EPR domains during mixing. Yoon et al.¹⁵ showed that selective dispersion of clays in acrylonitrile butadiene styrene (ABS) phase decreased the viscosity ratio of PP and ABS polymers in (70/30 w/w) ABS/PP blend that reduced the dispersed droplet sizes of PP in the blend. Li et al.¹⁶ reported that selective localization of exfoliated clays in nylon 6 phase increased the viscosity of nylon 6 that restricted the coalescence of dispersed poly(phenylene oxide) (PPO) droplets in (50/50 w/w) PPO/nylon 6 blend. Gcwabaza et al.¹⁷ showed that intercalation of both the PP and poly(butylene succinate) (PBS) chains into the same silicate layers at the interface and change in viscosity ratio of the polymers resulted in a homogeneous dispersion of PBS domains in (70/30 w/w) PP/PBS blends with various amount of clay (0.5–5 wt %). Mehta et al.¹⁸ reported a decrease in dispersed EPR domain sizes in (70/30 w/w) PP/EPR blends with various amount of clay, intercalated in the PP phase. They explained it in terms of increase melt viscosity of matrix PP phase by the clay that lowered the viscosity ratio during melt mixing. Kelnar et al.¹⁹ showed that presence of 5 wt % nanoclay in (90/10 w/w) polyamide 6 (PA6)/PS blend resulted in a finer distribution of PS particles and better interfacial adhesion between the polymers. Fillipone et al.²⁰ studied the effect of organoclay on the morphology of (75/25 w/w) HDPE/PA6 blends. Organoclay located exclusively inside the more hydrophilic PA phase during the melt compounding; giving a phase separated elongated organoclay-rich PA6 domains in HDPE matrix. They showed that the filled minor phase eventually merged once the extruded pellets were melted again, giving rise to a cocontinuous microstructure. Fang et al.²¹ investigated the influence of organoclay on the morphology of PA6/HDPE/organo-bentonite clay and PA6/HDPE-grafted-acrylic acid (PEAA)/organoclay nanocomposites, prepared via melt processing. The majority of the organoclay platelets were concentrated in the PA6 phase and in the interfacial region between PA6

and HDPE (PEAA). The organoclay platelets played the role of coupling species between the two polymers, increasing the interaction of the two phases in certain extent.

In summary, literature reports on the use of block/graft-copolymers or nanoclay as compatibilizer in various immiscible polymer blends. However, reports^{22–24} on the combined effect of nanoclay and graft copolymer on morphology and properties of immiscible polymer blends are relatively rare, that provides the scope for further investigations. Thus, the objective of our work was to study the combined effect of a reactive compatibilizer (PE-g-MA) and nanoclay (cloisite 20A) on the morphology and properties of immiscible polymer blend, consisting of (80/20 w/w) nylon 6/HDPE with reference to the properties of the blends in absence and presence of only nanoclay and PE-g-MA. The rationale behind choosing cloisite 20A was that nylon 6 is well-known to exfoliate cloisite 20A,^{25,26} whereas HDPE chains intercalate the organic silicate layers.²⁷ Thus, in (80/20 w/w) nylon 6/HDPE blend–clay nanocomposites, the clay could selectively be dispersed in the matrix phase (nylon 6) of the blend because of its favorable interaction with nylon 6. Again, in (20/80 w/w) nylon 6/HDPE blend, clay could selectively be dispersed in the dispersed phase where HDPE become the matrix phase. Thus, the morphology and properties of the nylon 6/HDPE blend, as affected by the location of the clay, can be studied in details by considering these two compositions of the blend.

EXPERIMENTAL

Materials details

Commercial grade nylon6 (Aegis[®] H100MP) was obtained from Honeywell-Plastics. HDPE (M5018L) was obtained from Haldia Petrochemicals, Haldia, India. Maleic anhydride grafted polyethylene (PE-g-MA, A-C[®] 575P) was purchased from Honeywell-Plastics, USA. Cloisite 20A, a modified montmorillonite, was supplied by Southern Clay Pdt. It is a montmorillonite modified with dimethyl dihydrogenated tallow ammonium to increase the layer spacing (d) of Na⁺-montmorillonite. The cation exchange capacity (CEC) of cloisite 20A is 95 mequiv/100g of the clay. Hereafter, cloisite 20A is referred to as the clay.

Preparation of the blends

Blends of nylon 6 and HDPE were prepared at two different compositions [80/20 and 20/80 w/w] with various amounts (0–5 phr (parts per hundred resin)] of PE-g-MA and (or) clay by melt mixing in an

internal mixer (Brabender; S. C. Dey and Co., Kolkata, India) at 250°C and 60 rpm for 20 min. To avoid moisture induced thermal degradation, all polymers and the clay were dried in a vacuum oven at 80°C for 36 h before the melt mixing. Finally, the blends were compression molded in a hot press at 250°C for 20 min under constant pressure (20 MPa) for morphological analysis. Mechanical properties of the blends were investigated with the injection molded samples.

CHARACTERIZATION

Morphological study

The phase morphology of the nylon 6/HDPE blends was studied with scanning electron microscope (FESEM, Carl Zeiss-SUPRA™ 40 and VEGA II LSU, TESCAN, Czech Republic), operated at an accelerating voltage of 5 kV. The specimens were kept in liquid nitrogen for ~ 30 s and then broken inside liquid nitrogen. The fractured surface of the samples was coated with a thin layer of gold to avoid electrical charging, and scanning electron microscopy (SEM) images were taken on the fracture surface.

The number-average (D_n) domain diameter was obtained with an Image analyzer (Scion Corp.). The cross-sectional area (A_i) of each domain in the FESEM micrograph was measured and then converted into the diameter (D_i) of a circle having the same cross-sectional area by using the equations:

$$D_i = 2(A_i/\pi)^{\frac{1}{2}}, \quad (1)$$

$$D_n = \sum N_i D_i / \sum N_i, \quad (2)$$

where, N is the number of dispersed domains in the Fesem micrograph.

X-ray diffraction study

The d -spacing of the layer structure of the pure clay, as well as, that in nylon 6/HDPE blends was examined by using a wide angle X-ray diffractometer, (WAXD, Ultima-III, Rigaku Corp., Japan) with nickel-filtered CuK α line ($\lambda = 0.15404$ nm), operated at 40 kV and 100 mA, at a scanning rate of 0.5°/min. The sample-to-detector distance was 400 mm.

TEM analysis

The location of the clay platelets in nylon 6/HDPE blend–clay nanocomposites, without and with PE-g-MA, was studied by transmission electron microscopy (HRTEM: JEM-2100, JEOL, Japan), operating at an accelerating voltage of 200 kV. The samples were ultra-microtomed at cryogenic condition with a thickness of 60~ 80 nm. Since the clay has much higher

electron density than neat polymers, it appeared dark in TEM images.

Mechanical properties

Thermomechanical properties (storage modulus) of the injection molded blends were measured in tension film mode at a constant vibration frequency of 1 Hz, a temperature range of 40–130°C, and a heating rate of 5°C/min in a nitrogen atmosphere by using a dynamic mechanical analyzer (DMA 2980 model, TA Instruments Inc.). The dimension of the specimen was 30 × 6.40 × 0.45 mm³. Tensile measurements were carried out using a universal tensile testing machine (Hounsfield HS 10KS, UK) at room temperature with an extension speed of 5 mm/min and an initial gauge length of 35 mm. Injection molded dumb-bell shaped samples (64 mm × 12.7 mm × 3.2 mm) were used for tensile testing, allowing at least 24 h after molding to relax the stresses induced during cooling. The results reported were the averages of five samples for each composite. Impact test data were obtained with an IZOD Impact testing machine according to ASTM 256 with notched samples.

Thermo gravimetric analysis (TGA)

The thermal stability (temperatures correspond to initial degradation, 50 wt % degradation, and maximum weight loss) of the blends without and with the clay and (or) PE-g-MA was investigated with thermo gravimetric analysis (TGA-209F, from NETZSCH, Germany). The sample was heated in air atmosphere from room temperature to 600°C at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Morphology study

The SEM images of (80/20 w/w) nylon 6/HDPE blend with various amounts (0–6 phr) of clay are shown in Figure 1. As observed, in the pure blend [Fig. 1(a)], the HDPE phase dispersed as larger spherical domains ($D_n \approx 4.26$ μm) in nylon 6 matrix. Due to the high interfacial tension between the two immiscible polymers, the spherical morphology is the most thermodynamically favored. This will limit the product of the surface tension times the surface area, because a spherical particle has the minimal surface area, of all shapes. The spherical domains thus minimize their surface area to volume ratio and hence limit the free energy of the blend by minimizing the surface energy at the continuous matrix/dispersed droplet interface.²⁸ In addition, the microvoids surrounding the HDPE droplets indicated

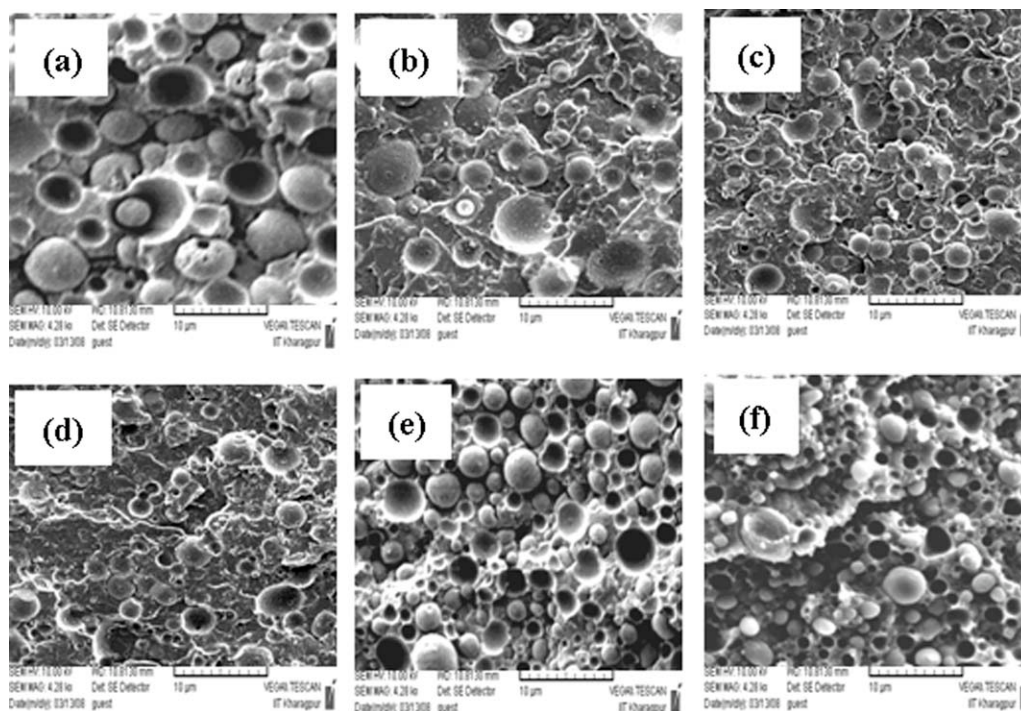


Figure 1 SEM images of (80/20 w/w) nylon 6/HDPE blend (a), and the blend with: (b) 1 phr PE-g-MA, (c) 4 phr PE-g-MA, (d) 5 phr PE-g-MA, (e) 1 phr clay, and (f) 3 phr clay. All the images were taken at same magnification ($\times 428,000$), with a scale bar of 10 μm .

weak interfacial adhesion between nylon 6 and HDPE due to the immiscible nature of the polymers. Since the bulk properties of a polymer blend strongly depend on the quality of the interface, its modification using compatibilizing agent is generally required to get better final performances by promoting enhanced adhesion between the phases, low interfacial tension and more uniform and finer dispersion of the minor phase. Addition of small amount (1 phr) of PE-g-MA in the blend reduced the domain size ($D_n \approx 3.72 \mu\text{m}$) of dispersed HDPE phases [Fig. 1(b)]. With increasing amount of PE-g-MA, the dispersed domain size was decreased gradually [Fig. 1(c,d)]. Addition of 1 phr of clay in (80/20 w/w) nylon 6/HDPE blend [Fig. 1(e)] reduced drastically the dispersed HDPE domain sizes ($D_n \approx 2.32 \mu\text{m}$). The reduced domain sizes in (80/20 w/w) nylon 6/HDPE blends by the addition of clay could be explained with the following assumptions. The clay acted as nucleating agent at the initial stage of phase separation, resulting in formation of lots of nucleation sites. Second, selective location of the clay platelets in the matrix phase (nylon 6) might have increased the melt viscosity of the matrix phase to an extent and thus lowered the ratio of disperse/matrix (η_d/η_m) phases depending on the clay loading. Third, the exfoliated clay platelets in the matrix phase could act as barrier that prevented the coalescence of dispersed domains. Thus, the mobility of the domains was suppressed and the domain sizes

of the blends were reduced. The decreasing nature of D_n of HDPE in the blend by the addition of clay was comparable with the D_n of the blend with various amounts of PE-g-MA. However, for a particular loading (phr), the decrease in D_n of the blend was much prominent with clay, compared with that of PE-g-MA.

Interestingly, addition of both PE-g-MA and clay in the blend greatly reduced the D_n of the dispersed HDPE domains (Fig. 2). For instance, the D_n of the (80/20 w/w) nylon 6/HDPE blend with the combination of clay (0.5 phr) and PE-g-MA (0.5 phr) was 1.74 μm , which is smaller than the D_n of the blend with 3 phr PE-g-MA ($D_n \approx 2.28 \mu\text{m}$), and comparable with the D_n ($\approx 1.64 \mu\text{m}$) of the blend containing 3 phr of clay. These results indicated that the extent of mixing between the polymer phases increased significantly when both the clay and PE-g-MA were present in the system. This improvement in compatibility in presence of both the clay and PE-g-MA was due to the following reasons: (i) the clay platelets presented in the matrix phase acted as physical barrier that prevented the coalescence of the dispersed domains; (ii) presence of PE-g-MA at the interface increased the adhesion between the polymer phases and thereby lowered the interfacial tension.

It was found that the amount of clay and PE-g-MA in the mixture (phr) had a profound effect in decreasing D_n of the blend. For instance, combination of 2 phr clay and 1 phr PE-g-MA showed a

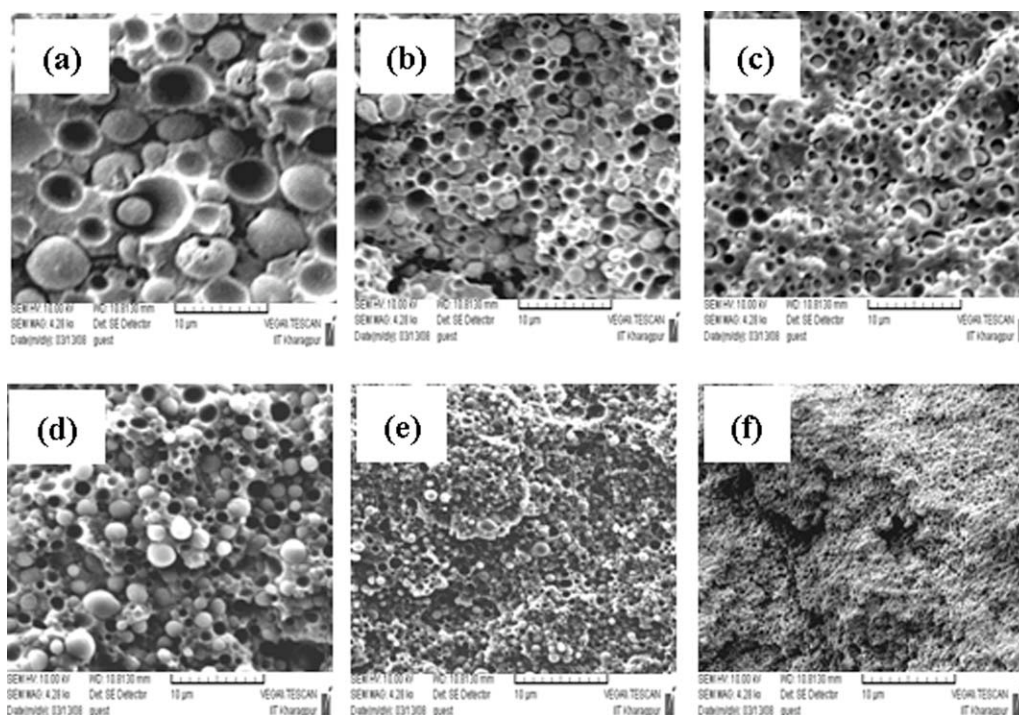


Figure 2 SEM images of (80/20 w/w) nylon6/HDPE blend (a), and the blend with: (b) 0.5 phr PE-g-MA/0.5 phr clay, (c) 2.5 phr PE-g-MA/0.5 phr clay, (d) 2 phr PE-g-MA/1 phr clay, (e) 1.5 phr clay/1.5 phr PE-g-MA, (f) 2 phr clay/1 phr PE-g-MA. All the images were taken at same magnification ($\times 428,000$), with a scale bar of 10 μm .

significant reduction in D_n ($\approx 0.46 \mu\text{m}$) of HDPE than that of 1 phr clay and 2 phr PE-g-MA in the blend ($D_n \approx 2.14 \mu\text{m}$). This indicated that presence of higher amount of clay in the mixture (PE-g-MA and clay) was more effective in reducing D_n of the blend. PE-g-MA is well known to exfoliate the clay.²⁹ At lower clay loading, clay layers were mostly exfoliated at the interphase (in PE-g-MA) of the blend and a minor amount of the clay in the nylon 6 matrix. However, discernible amount of the clay would also be found in the HDPE phase, as PE-g-MA promotes exfoliation of clays in HDPE.³⁰ In presence of higher loading of clay compared with PE-g-MA, the clay layers were mostly located in nylon 6 matrix, thereby increasing the matrix viscosity and a fraction of clay layers were exfoliated at the interphase and HDPE phase of the blend. Thus, with increasing amount of clay content in the mixture, the morphology of (80/20 w/w) nylon 6/HDPE blend became finer and uniform than that with lower clay content though the total amount of PE-g-MA and clay remain same. With increasing amount of PE-g-MA, the extent of exfoliated clay platelets at the interphase was increased. Again, PE-g-MA acts as a compatibilizer for exfoliation of the clay in HDPE phase.³⁰ Thus, at higher loading of PE-g-MA in the mixture (PE-g-MA and clay), discernible amount of clay might have exfoliated inside the HDPE domains that increased the viscosity ratio of disperse/matrix (η_d/η_m) phases. Furthermore, incorporation of 1.5

phr clay and 1.5 phr PE-g-MA showed finer and uniform distributions of HDPE domains ($D_n \approx 1.16 \mu\text{m}$) in (80/20 w/w) nylon 6/HDPE blend. These results indicated that a (50/50 w/w) mixture of PE-g-MA and clay could effectively reduce the D_n of HDPE in (80/20 w/w) nylon 6/HDPE blend than that of using PE-g-MA only. Thus, presence of both PE-g-MA and clay in the blend played a synergistic effect where PE-g-MA improved the interfacial adhesion between nylon 6 and HDPE, and the barrier effect of exfoliated/intercalated clay platelets in the matrix phase prevented the coalescence of dispersed domains during melt mixing.

On the basis of SEM images, the reduction in D_n of the (80/20 w/w) nylon 6/HDPE blend with the loading (phr) of PE-g-MA, clay and a (50 : 50 w/w) combination of the two is shown in Figure 3. A sharp decrease in D_n of the blend with PE-g-MA, as well as, with the clay was evident at lower loading and then a slow but gradual decrease in D_n of the blend was observed. The decrease in D_n of the dispersed HDPE phase with various amounts of the clay was very similar to the (80/20 w/w) nylon6/HDPE blend with various amounts of PE-g-MA as reactive compatibilizer. However, the decrease in D_n of HDPE was much prominent with addition of clay rather than that with PE-g-MA. Interestingly, addition of both the clay and PE-g-MA in (50 : 50) combination lowered the D_n of the blend to a greater extent than that of using only PE-g-MA or

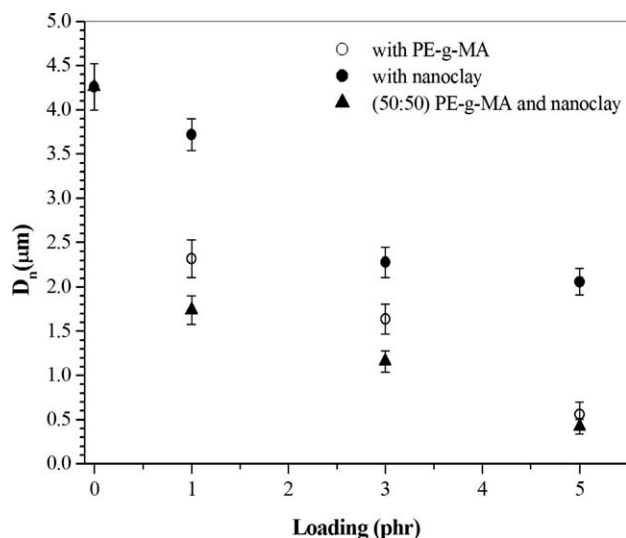


Figure 3 Plot of D_n versus loading (phr) of clay and PE-g-MA in (80/20 w/w) nylon6/HDPE blend.

clay at similar loading (total phr of the clay and PE-g-MA).

Figure 4 represents the SEM micrograph of the fractured surface of (20/80 w/w) nylon 6/HDPE blend, showing the nylon 6 phase dispersed in the HDPE matrix. The nylon 6 particles appeared as spherical domains ($D_n \approx 3.76 \mu\text{m}$) due to weak interfacial adhesion between the two phases. On addition of small amount (2 phr) of PE-g-MA, the average

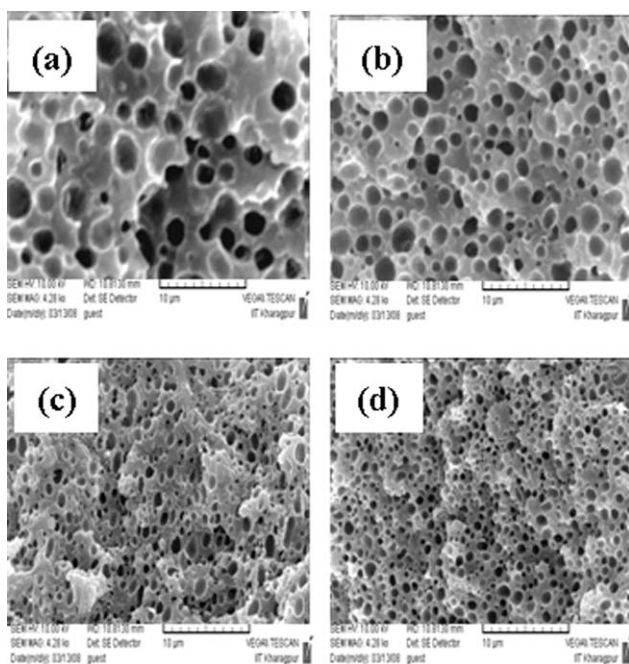


Figure 4 SEM images of (20/80 w/w) nylon 6/HDPE blend (a), and the blend with: (b) 2 phr PE-g-MA, (c) 4 phr PE-g-MA, and (d) 6 phr PE-g-MA. All the images were taken at same magnification ($\times 428,000$), with a scale bar of $10 \mu\text{m}$.

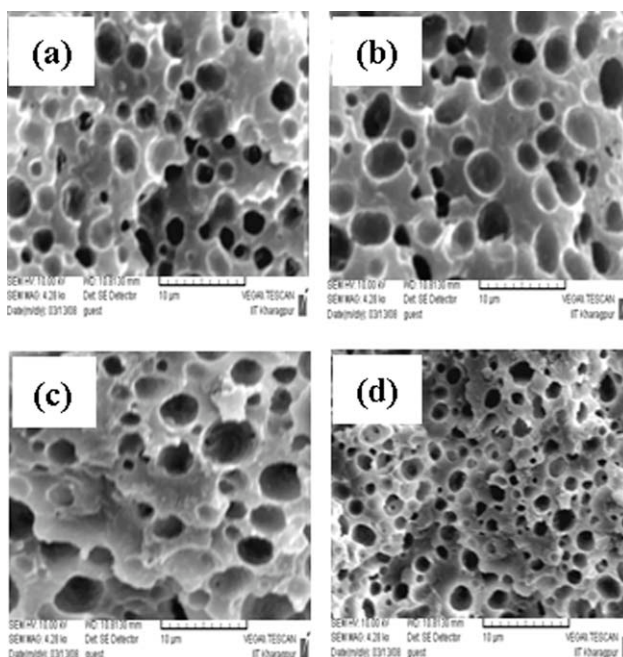


Figure 5 SEM images of (20/80 w/w) nylon6/HDPE blend (a), and the blend with: (b) 2 phr clay, (c) 4 phr clay and, (d) 6 phr clay. All the images were taken at same magnification ($\times 428,000$), with a scale bar of $10 \mu\text{m}$.

dispersed domain size ($D_n \approx 2.48 \mu\text{m}$) in the blend was decreased. However, addition of 2 phr of clay increased the average dispersed domain size ($D_n \approx 4.84 \mu\text{m}$) due to preferable dispersion of the clay in nylon 6 domains (Fig. 5). Addition of 6 phr clay to (20/80 w/w) nylon 6/HDPE blend led to a reduction in the domain size ($D_n \approx 2.78 \mu\text{m}$) of the nylon 6 phases. This suggested that at higher clay loading few clay layers were located in the HDPE matrix, which suppressed the coalescence and the agglomeration of nylon 6 phases.

On addition of both PE-g-MA and clay in (20/80 w/w) nylon 6/HDPE blend the average dispersed domain size ($D_n \approx 3.76 \mu\text{m}$) was increased and the spherical shape of the domains shifted to more irregular shapes (Fig. 6). In presence of 1 phr PE-g-MA and 3 phr clay the dispersed nylon 6 domain size was increased ($D_n \approx 4.14 \mu\text{m}$) compared with the pure blend and was comparable with that ($D_n \approx 4.28 \mu\text{m}$) of (20/80 w/w) nylon 6/HDPE blend with 4 phr clay. Presence of 2 phr PE-g-MA and 2 phr clay marginally decreased the dispersed domain size ($D_n \approx 3.40 \mu\text{m}$) compared with the pure blend. We assumed that in presence of small amount of clay and PE-g-MA together, the synergistic effect was not operating. Indeed, the effects of PE-g-MA and clay in reverse composition (20/80 w/w) of the blend were partially neutralized. This could be rationalized considering that PE-g-MA not only formed PE-g-nylon 6 copolymers granting the compatibilization of the (20/80 w/w) nylon 6/HDPE blend but also the

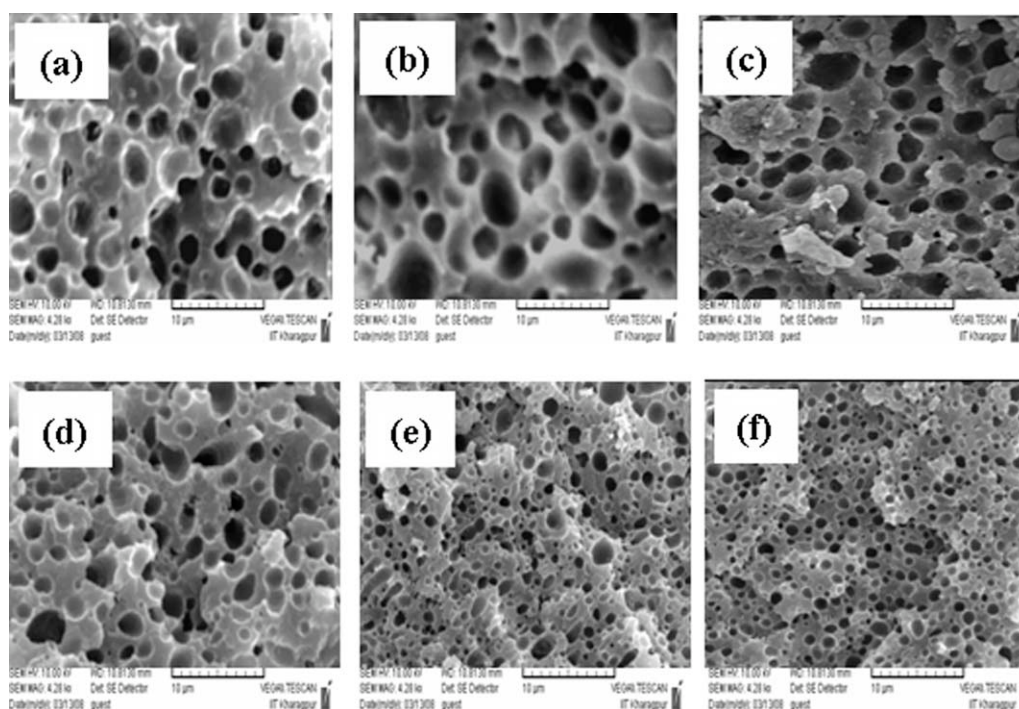


Figure 6 SEM images of (20/80 w/w) nylon 6/HDPE blend (a), and the blend with: (b) 1 phr PE-g-MA/3 phr clay, (c) 2 phr PE-g-MA/2 phr clay, (d) 3 phr PE-g-MA/1 phr clay, (e) 5 phr clay/1 phr PE-g-MA, (f) 5 phr clay/2 phr PE-g-MA. All the images were taken at same magnification ($\times 428,000$), with a scale bar of 10 μm .

interactions with the clay led to exfoliation of the clay layers in nylon 6 domains. In presence of higher amount of clay (5 phr), the domain sizes of nylon 6 phases decreased gradually with increasing amount of PE-g-MA. In any case, the morphology of all (20/

80 w/w) nylon 6/HDPE/PE-g-MA/organoclay composites studied in this work was coarser than that of the (20/80 w/w) nylon 6/HDPE blend with only PE-g-MA or clay.

To investigate the role of clay in decreasing the D_n of HDPE in (80/20 w/w) nylon 6/HDPE blend, we considered the morphology of the clay in neat polymers as well as that in the blend. Figure 7 shows the WAXD profiles of the clay itself and its nanocomposites with nylon 6, HDPE and nylon 6/HDPE blends. The clay itself exhibited the characteristic peak at a 2θ of 3.54° correspond to the d -spacing of 2.49 nm. The shifting of the clay peak position to lower 2θ region (2.82°) in HDPE/clay (1 phr) nanocomposites indicated the intercalation of HDPE chains inside the clay galleries with a d -spacing of 3.13 nm. Whereas, absence of any clay peak in nylon 6/clay (1 phr) and PE-g-MA/clay (1 phr) nanocomposites indicated the exfoliation of clays in nylon 6 matrix^{25,26} and PE-g-MA matrix,²⁹ consistent with the previous reports. Interestingly, absence of clay characteristic peaks in (80/20 w/w) nylon 6/HDPE blends with 1 phr clay, without and with PE-g-MA, indicated the exfoliation of the clay layers in nylon 6 phase. However, in (20/80 w/w) nylon 6/HDPE blend with 5 phr of clay, a broad peak was observed at lower region ($2\theta \approx 2.66^\circ$) which indicated the intercalation of clays ($d_{001} \approx 3.32$ nm) in the blend. We assumed that, at higher clay loading (5 phr), along with the exfoliation of clays in nylon 6 phase,

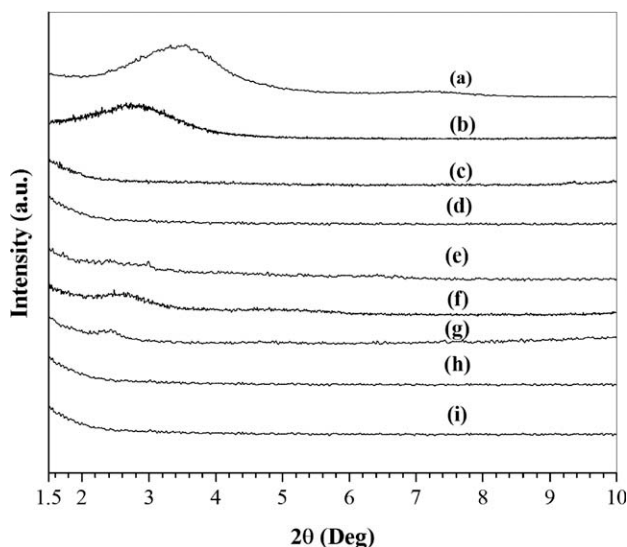


Figure 7 WAXD plots for (a) Cloisite 20A, (b) HDPE/clay 1 phr, (c) nylon 6/1 phr clay, (d) PE-g-MA/1 phr clay, (e) (20/80 w/w) nylon 6/HDPE/1 phr clay/1 phr PE-g-MA, (f) (20/80 w/w) nylon 6/HDPE/5 phr clay, (g) (20/80 w/w) nylon 6/HDPE/5 phr clay/1 phr PE-g-MA, (h) (80/20 w/w) nylon 6/HDPE/1 phr clay, (i) (80/20 w/w) nylon 6/HDPE/1 phr clay/1 phr PE-g-MA.

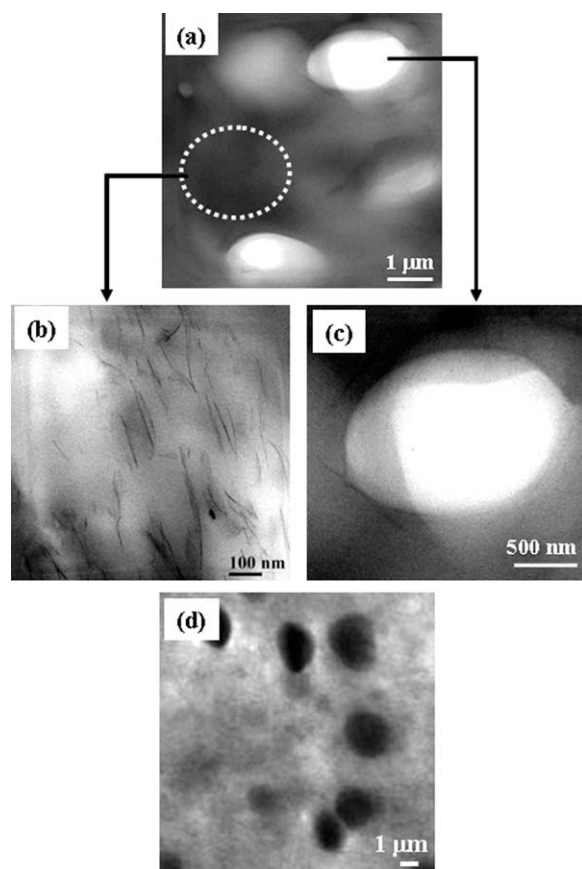


Figure 8 TEM images of (80/20 w/w) nylon 6/HDPE blend with clay (1 phr) at different magnifications: (a) low magnification, (b) nylon 6 matrix at higher magnification, (c) HDPE domains at higher magnification, (d) (20/80 w/w) nylon 6/HDPE blend with clay (1 phr) at low magnifications.

discernible amount of clays were also intercalated in HDPE phase of the blend. Thus, clays might have exfoliated in the nylon 6 domains and intercalated in HDPE matrix of (20/80 w/w) nylon 6/HDPE blend–clay (5 phr) nanocomposites. In presence of small amount of PE-g-MA and clay together in the blend, no characteristic peak of the clay was observed. Whereas in presence of higher amount (5 phr) of clay and small amount (1 phr) of PE-g-MA together, a small hump of the clay was observed in the blend.

This could be explained by considering the exfoliation of clay either in PE-g-MA phase²⁹ or nylon 6 domain at lower clay loading in (20/80 w/w) nylon 6/HDPE blend.

Figure 8 represents the TEM images of the nylon 6/HDPE blends with 1 phr clay at two different compositions. As observed [Fig. 8(a)], in (80/20 w/w) nylon 6/HDPE blend–clay nanocomposites, HDPE phase dispersed as domains with average domain diameter of $\approx 2.24 \mu\text{m}$, which is in good agreement with the D_n value calculated from the SEM image ($D_n \approx 2.32 \mu\text{m}$). The nylon 6 matrix appeared as dark region due to the presence of clay in nylon 6 phase. The TEM images at higher magnification clearly indicated the exfoliation of the clay silicate layers in the nylon 6 matrix [Fig. 8(b)], and absence of the clay layers inside the HDPE domains [Fig. 8(c)]. This was due to the difference in polarity of the polymers (nylon 6 and HDPE) where the organo-clay preferentially dispersed in the polar polymer (nylon 6). Thus, the exfoliated clays in the matrix phase played the role of barrier that prevented the coalescence of the dispersed HDPE domains during melt mixing. However, in the reverse composition (20/80 w/w nylon 6/HDPE) of the blend, the clay layers were selectively located inside the nylon 6 dispersed phase [Fig. 8(d)]. Thus, absence of the clay layers in the HDPE matrix failed to prevent the coalescence of the dispersed nylon 6 domains in (20/80 w/w) nylon 6/HDPE blend–clay system.

Mechanical properties

Table I illustrates the tensile properties of (80/20 w/w) nylon 6/HDPE blends and its nanocomposites. Presence of very small amount of PE-g-MA increased the tensile strength and modulus of the blend, but in the presence of higher amount of PE-g-MA the tensile strength and modulus of the blend were decreased. The low modulus of PE-g-MA was believed to be responsible for the observed trends. Addition of clay in (80/20 w/w) nylon 6/HDPE blend increased the tensile strength and modulus and the increment of tensile strength was much

TABLE I
Mechanical Properties of (80/20 w/w) Nylon 6/HDPE Blends with Various Amounts of PE-g-MA and Nanoclay

Sample details	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
(80/20 w/w) nylon 6/HDPE	24.5 \pm 1.5	13.4 \pm 1.2	2.26 \pm 0.5
(80/20 w/w) nylon 6/HDPE/0.5phr PE-g-MA	24.8 \pm 1.3	14.5 \pm 1.2	2.17 \pm 0.4
(80/20 w/w) nylon 6/HDPE/3phr PE-g-MA	23.1 \pm 1.5	21.2 \pm 1.3	1.83 \pm 0.5
(80/20 w/w) nylon 6/HDPE/0.5phr clay	29.6 \pm 1.2	11.8 \pm 1.3	2.82 \pm 0.5
(80/20 w/w) nylon 6/HDPE/3phr clay	25.2 \pm 1.5	8.7 \pm 1.2	3.12 \pm 0.3
(80/20 w/w) nylon 6/HDPE/0.5phr PE-g-MA/0.5phr clay	32.8 \pm 1.5	13.6 \pm 1.5	2.98 \pm 0.5
(80/20 w/w) nylon 6/HDPE/2.5phr PE-g-MA/0.5phr clay	30.4 \pm 1.5	19.3 \pm 1.3	2.75 \pm 0.5
(80/20 w/w) nylon 6/HDPE/1phr PE-g-MA/2phr clay	34.7 \pm 1.6	14.3 \pm 1.2	3.85 \pm 0.5

TABLE II
Mechanical Properties of (20/80 w/w) Nylon6/HDPE Blends with PE-g-MA and (or) Nanoclay

Sample details	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
(20/80 w/w) nylon 6/HDPE	22.1 ± 1.4	12 ± 0.4	1.78 ± 0.5
(20/80 w/w) nylon 6/HDPE/1phr PE-g-MA	20.4 ± 1.3	15 ± 0.5	1.07 ± 0.3
(20/80 w/w) nylon 6/HDPE/1phr clay	26.4 ± 1.2	10 ± 0.4	2.38 ± 0.2
(20/80 w/w) nylon6/HDPE/1phr clay/1phr PE-g-MA	29.2 ± 1.6	13.5 ± 0.6	2.04 ± 0.5

higher than that of adding small amount of PE-g-MA in the blend. This was due to the reinforcing effect of rigid inorganic clays. Addition of both PE-g-MA and clay remarkably improved the tensile strength and modulus of the pure blend system. This remarkable improvement could be attributed to compatibilizing effect of PE-g-MA with better dispersion and exfoliation of clay silicates in the matrix phase of the blend. Furthermore, addition of clay in the (80/20 w/w) nylon 6/HDPE blend decreased the elongation at break while presence of small amount of PE-g-MA increased the elongation at break compared with the pure blend system. Presence of both the PE-g-MA and clay showed higher elongation at break in the blend than that of using only clay in the blend.

The mechanical properties of (20/80 w/w) nylon6/HDPE blends without and with PE-g-MA and (or) clay are shown in Table II. As observed, presence of 1 phr PE-g-MA improved the elongation property, but lowered the tensile strength and tensile modulus of the blend. However, addition of 1 phr clay significantly improved the tensile strength and tensile modulus of the blend, with slight lowering in the elongation property. Interestingly, addition of both the PE-g-MA and clay (1 phr each) improved the tensile and elongation properties of the blend. This might be due to the presence of PE-g-MA at the interface of the blend which enhanced the phase adhesion between the constituent polymers, and hence the elongation property of the blend.

Impact properties

Table III demonstrates the effect of PE-g-MA and clay on the impact strength of (80/20 w/w) nylon 6/HDPE blend. It can be seen that addition of clay into (80/20 w/w) nylon 6/HDPE blend drastically decreased its impact strength. The reduction in impact strength could be attributed to the immobilization of macromolecular chains by the clay particles, which limited the ability to adapt to the deformation and make the material more brittle. In addition each silicate layer or aggregates of silicate layers was the site of stress concentration and could act as a micro crack initiator. On contrary, addition of small amount of PE-g-MA remarkably increased the impact strength of the blend. Addition of both the clay and PE-g-MA increased the impact strength of the (80/20 w/w) nylon 6/HDPE blend than that of the pure blend. The impact strength of (80/20 w/w) nylon 6/HDPE blend containing 3 phr clay was much less than that of (80/20 w/w) nylon 6/HDPE blends containing 0.5 phr clay and 0.5 phr PE-g-MA, though the blends had almost similar domain diameter. This could be attributed to the improved interfacial adhesion between nylon 6, HDPE and clay silicates, resulting from the formation of PE-g-nylon 6 copolymer. Furthermore, the impact strength of (80/20 w/w) nylon 6/HDPE blend with 1 phr PE-g-MA was less than that of (80/20 w/w) nylon 6/HDPE blend with both the PE-g-MA and clay (0.5 phr each). We assumed that presence of exfoliated clay platelets in PE-g-MA made the interface of the blend stronger than that without any clay. In absence of PE-g-MA, the impact strength of

TABLE III
Impact Properties of (80/20 and 20/80 w/w) Nylon 6/HDPE Blends with Various Amount of PE-g-MA and (or) Clay

Sample details	Impact strength (KJ/m ²)
(80/20w/w) nylon6/HDPE	7.47 ± 0.4
(80/20w/w) nylon6/HDPE/0.5 phr PE-g-MA	7.95 ± 0.5
(80/20w/w) nylon6/HDPE/1 phr PE-g-MA	8.50 ± 1.4
(80/20w/w) nylon6/HDPE/3 phr PE-g-MA	10.20 ± 0.2
(80/20w/w) nylon6/HDPE/0.5 phr clay	6.67 ± 0.5
(80/20w/w) nylon6/HDPE/1 phr clay	6.06 ± 0.5
(80/20w/w) nylon6/HDPE/3 phr clay	4.50 ± 0.3
(80/20w/w) nylon6/HDPE/0.5 phr PE-g-MA/0.5 phr clay	8.30 ± 0.5
(80/20w/w) nylon6/HDPE/2.5 phr PE-g-MA/0.5 phr clay	14.40 ± 0.6
(80/20w/w) nylon6/HDPE/2 phr PE-g-MA/1 phr clay	12.60 ± 0.4
(80/20w/w) nylon6/HDPE/1.5 phr PE-g-MA/1.5 phr clay	11.50 ± 0.5
(80/20w/w) nylon6/HDPE/0.5 phr PE-g-MA/2.5 phr clay	10.20 ± 0.6

the (80/20 w/w) nylon 6/HDPE blend did not increase even when 3 phr of the clay was added to the blend. This clearly indicates that the clay does not improve the interfacial adhesion between nylon 6 and HDPE phases, whereas PE-g-MA does.

Dynamic mechanical analysis

Storage modulus (Fig. 9) of the (80/20 w/w) nylon 6/HDPE blend was decreased with the addition of PE-g-MA due to lower modulus of PE-g-MA. However, in lower temperature range, the storage modulus of (80/20 w/w) nylon 6/HDPE blend in presence of both 1 phr clay and 1 phr PE-g-MA increased remarkably than that of pure blend and the blend with 1 phr PE-g-MA. With increasing temperature, due to plasticizing effect of PE-g-MA, the storage modulus of (80/20 w/w) nylon 6/HDPE blend containing both 1 phr clay and 1 phr PE-g-MA was decreased than that of (80/20 w/w) nylon 6/HDPE blend. The storage modulus of the blend with 1 phr clay was significantly higher than the blends containing PE-g-MA or, a combination of PE-g-MA and clay. This was due to the exfoliation of the clay silicates selectively in the nylon 6 matrix of the (80/20 w/w) nylon 6/HDPE blend in absence of PE-g-MA. The large surface area of the exfoliated silicates layers reduced the mobility of the nylon 6 chains close to the silicate layers that increased the modulus of nylon 6 phase. Okamoto et al.^{31,32} has already reported much higher increment in storage modulus for nylon 6 in presence of clay.

Thermal stability

Figure 10 displays the TGA curves of (80/20 w/w) nylon 6/HDPE blends and its nanocomposites. It

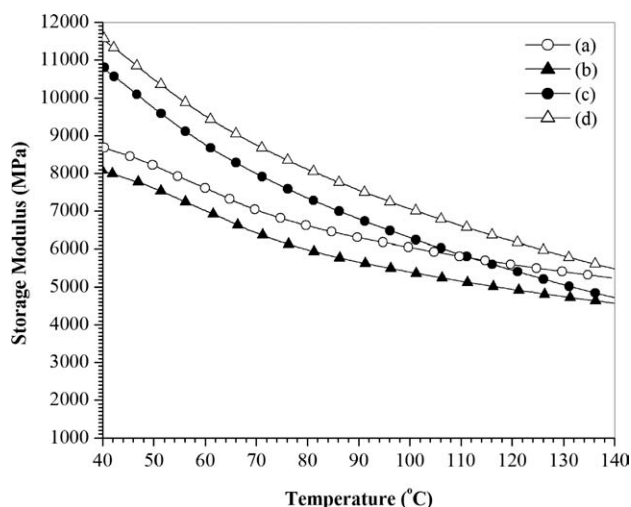


Figure 9 Storage modulus of (20/80 w/w) nylon 6/HDPE blend (a), and the blend with (b) 1 phr PE-g-MA; (c) combination of 1 phr PE-g-MA/1 phr clay; and (d) 1 phr clay.

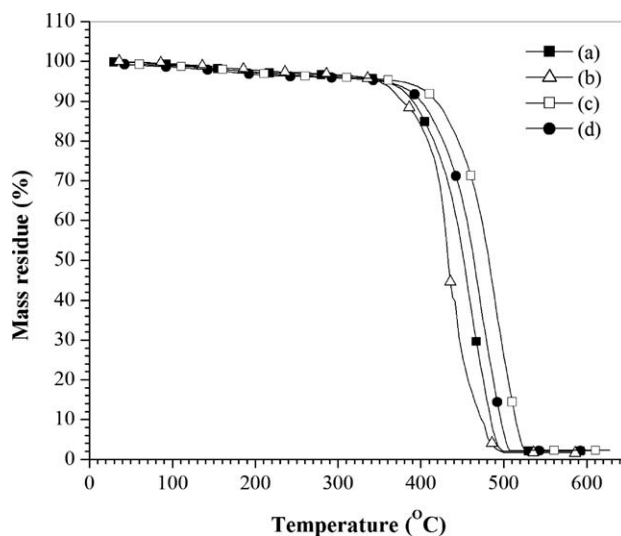


Figure 10 TGA scans for (80/20 w/w) nylon 6/HDPE blend (a), and the blend with (b) 1 phr PE-g-MA; (c) 1 phr clay; and (d) combination of 1 phr PE-g-MA/1 phr clay.

can be seen that all samples displayed single-step degradation process. The onset decomposition temperature for (80/20 w/w) nylon 6/HDPE blend with 1 phr PE-g-MA was observed at lower temperature than that of the pure blend. The initial decomposition temperature of (80/20 w/w) nylon 6/HDPE blend in presence of both PE-g-MA and clay (1 phr each) was lower than that of (80/20 w/w) nylon 6/HDPE blend with 1 phr clay. The degradation of PE-g-MA was probably responsible for this observation. Furthermore, (80/20 w/w) nylon 6/HDPE blend with both PE-g-MA and clay (1 phr each) exhibited higher decomposition temperature than that of pure blend and the blend with 1 phr PE-g-MA, indicating enhancement of thermal stability due to better dispersion of clay layers in the polymer matrix. The dispersed clay silicate layers in the polymer matrix could be more effective in hindering diffusion of volatile decomposition products within the nanocomposites. Moreover, the thermal stability of (80/20 w/w) nylon 6/HDPE blend with 1 phr PE-g-MA and 3 phr clay was higher than that of (80/20/3/1 w/w) and (80/20/1/1 w/w) nylon 6/HDPE/PE-g-MA/clay systems (not shown in figure).

CONCLUSIONS

The morphology and properties of the (80/20 w/w) nylon 6/HDPE blends in presence of clay and PE-g-MA were studied. The average domain size (D_n) of dispersed HDPE phase was decreased when small amount (1 phr) of clay or PE-g-MA was added in the blend. WAXD and TEM studies revealed exfoliation of clay platelets selectively in nylon 6 matrix of the blend-clay nanocomposites. However, in (20/80 w/w) nylon 6/HDPE blend, the same effect of clay

was not observed when HDPE became the matrix phase and clays were selectively dispersed in nylon 6 domains. Addition of small amount of clay increased the D_n of the dispersed nylon 6 phase in (20/80 w/w) nylon 6/HDPE blend. Whereas small amount of PE-g-MA significantly lowered the D_n of the dispersed phase in (20/80 w/w) nylon 6/HDPE blend. This observation led us to conclude that presence of exfoliated clay platelets in the matrix phase restricted the coalescence of dispersed domains during melt-blending that led to finer dispersion of HDPE domains in the blend–clay nanocomposites. A combination of both the clay and PE-g-MA greatly reduced the D_n of HDPE than that obtained by using the individuals at same loading in the blend. Presence of PE-g-MA at the interface of the blend improved the phase adhesion in the blend–clay nanocomposites and favored exfoliation of clays at the interface. Thus, the synergy between the clay and PE-g-MA favored the formation of small domains in the blend with improved mechanical strength and elongation property. It was shown that excellent morphology and a satisfactory balanced between toughness and stiffness could be obtained by optimizing the loading of PE-g-MA and clay in nylon 6/HDPE blend.

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