

Studies on Nylon-6/EVOH/Clay Ternary Composites

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Nylon-6 (Ny-6)/EVOH blends are interesting host multiphase systems for incorporation of low clay contents. The Ny-6/EVOH blend is a unique system, which tends to chemically react during melt-mixing, affecting thermal, morphological and mechanical properties of the ternary systems containing clay. The addition of clay seems to interrupt the chemical reaction between the host polymers at certain compositions, leading to lower blending torque levels when clay is added. A competition between Ny-6 and EVOH regarding the intercalation process takes place. Ny-6 seems to lead to exfoliated structure, whereas EVOH forms intercalated structure, as revealed from XRD and TEM analyses, owing to thermodynamic considerations and preferential localization of the clay in Ny-6. Hence, the ternary systems have combined intercalated and delaminated morphology or complete exfoliated morphology depending on blend composition and clay content. Selective extraction experiments (gel content) indicate the formation of chemical reaction between the Ny-6 and EVOH, and give an indirect indication of the polymer content residing in the galleries. The thermal properties of the polymers were found to be affected by the occurrence of chemical reaction, the level of intercalation and exfoliation and plasticizing effect of the low molecular weight onium ions treating the clay. Of special interest is the increased storage modulus attained upon the addition of only 1.5 wt% clay. POLYM. COMPOS., 27:15–23, 2006. © 2005 Society of Plastics Engineers

INTRODUCTION

Nanocomposite materials consisting of organic polymers and inorganic clay have recently evoked intense research interests owing to their unique characteristics [1]. From the point of view of obtaining improved physical/mechanical properties of nanocomposites, exfoliation is preferred to

intercalation. In general, intercalation is observed when the polymer matrix and the clay have intermediate interaction levels, while exfoliation is observed when the polymer and the clay have strong attractive interactions. Hence, as in the preparation of immiscible polymer blends, compatibility between the polymer and clay is desired [2].

Multiphase polymer blends have been of great importance in the development of new synthetic materials. However, polymer blends usually result in heterogeneous, two, or multiphase materials exhibiting poor properties. Although the limited components miscibility is sometimes used to improve specific properties, generally immiscibility of the polymers hinders utilization of their blends. The general challenge of polymer blending is to overcome the low entropy of mixing and unfavorable enthalpy of mixing typical of most high molecular weight polymers. The achievement of compatibilization, whether by addition of a third component (i.e., compatibilizer) or by in situ chemical reactions between the blend's components (reactive blending) has played an important role in the development of polymer blends [3]. Ethylene vinyl alcohol (EVOH) copolymers appear to have the potential of forming compatible or even miscible blends in the amorphous state with a variety of polymers containing functional groups such as esters, methacrylates, acetoxys, ethers, and the like [4]. The technological incentive toward nylon/EVOH blends is in packaging applications. Polyamides are engineering semicrystalline thermoplastics having low permeability for CO₂, while EVOH copolymers are semicrystalline materials showing excellent oxygen barrier properties in their dry state [5].

Nanocomposites based on organoclays and homopolymers have been extensively investigated; however, nanocomposites based on organoclays dispersed in immiscible polymer blends are relatively rare although novel materials, which combine the properties of polymer blends and nanometric clays, can be visualized. It is expected that such materials will differ in the level of clay dispersion (e.g., the extent of exfoliation/intercalation of layered silicates) and the blend phase morphology (e.g., the average size of phase-separated domains) compared with single polymer/clay

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nanocomposites. Surprisingly, in spite of the potential of ternary nanocomposites, very few studies have dealt with this subject [6–11]. A study on PA-6 (polyamide-6)/PP nanocomposites containing 4 wt% clay has revealed a rather limited enhancement of the blend's mechanical properties. This was attributed to two main factors: the lack of interaction between the treated clay and PP and the incompatibility of the matrix polymers. However, it was shown that the mechanical properties of the PA-6/PP blends could be enhanced by using a suitable compatibilizer, such as maleated polypropylene [3]. The former study [12] regarding Ny-6 and EVOH blends revealed that this system is uniquely highly interacting owing to chemical reactions between the EVOH hydroxyl groups and Ny-6 carboxyl terminal groups, leading to chain extension by high-temperature melt-blending.

This study focuses on the interrelations between Nylon6/EVOH/clay composites and their characteristics, i.e., intercalation and exfoliation levels, thermal, and dynamic mechanical behavior.

EXPERIMENTAL

Materials

The EVOH used is a commercial product, containing 32 mol% ethylene, of Kuraray, Japan. The Nylon-6 (Ny-6) used, PB145 grade, is a commercial product obtained from Polyram, Israel. Copolyamide 6/6.9 (Ny-6/6.9) is a random copolymer of 51% $\text{HN}-(\text{CH}_2)_5-\text{CO}$ and 49% $\text{HN}-(\text{CH}_2)_6-\text{NH}-\text{CO}-(\text{CH}_2)_7-\text{CO}$, obtained from EMS, Switzerland. Nylon-11 (Ny-11, Rilsan B) is obtained from Atofina, France. The treated-clay used (Nanomer-1.30TC, organo-montmorillonite with an unspecified treatment) was obtained from Nanocor, Illinois. It is claimed to be designed for ease of dispersion into Ny-6 to form nanocomposites. The thermal stability of the organic treatment relevant to the mixing conditions was confirmed by TGA tests (not shown here).

Preparation of Blends

Prior to melt blending, the polymers were ground into powder, which was dried in vacuum at 80°C, for 15 h. The EVOH, nylon, and clay components were dry-blended at selected ratios, and subsequently, melt-mixed at 250°C in a Brabender plastograph, equipped with a 50 cm³ cell, at 20 rpm for 50 min. Neat polymers and each individual polymer containing the same clay amounts as in the ternary composite were also melt-mixed. All the resulting blends were compression molded at 250°C and 980 MPa into 3-mm-thick plaques for characterization.

Characterization

Nonextractable content was determined by dimethylformamide (DMF) extraction for EVOH, Ny-6, Ny-6/6.9 and

Ny-11, or by *m*-cresol extraction for EVOH and Ny-6. The thermal behavior of the blends was studied by differential scanning calorimetry measurements (DSC). A Mettler DSC 30 system, under an inert nitrogen atmosphere, at a heating rate of 10°C/min was used. Samples were heated to a temperature above their melting point, cooled at the same rate, and subsequently, reheated. The melting behavior of the blends was determined from the second heating runs. The enthalpy values are normalized to the relative polymers' content. Dynamic mechanical properties of the compression molded specimens were measured using a dynamic mechanical thermal analysis system (DMTA, Perkin-Elmer Series 7), in the three-point bending mode. The system was operated at 1 Hz, under nitrogen atmosphere, at a heating rate of 3°C/min. The structure of the composites was examined by a Philips X'PERT system X-ray diffraction (XRD), with a Cu K α radiation source operated at 40 kV, 40 mA, and a scanning rate of 0.5°/min. A Philips CM120 transmission electron microscope (TEM), operated at 120 kV, was used to observe the level of clay dispersion used. The images were taken at a nominal under focus of 4–7 nm, where any amplitude contrast is enhanced with phase contrast. Images were recorded digitally by a Gatan 791 MultiScan CCD camera, using the Digital Micrograph 3.1 software package. The ultrathin sections were prepared at –30°C, with a Reichert ULTRACUT E ultramicrotome, using a glass knife.

RESULTS AND DISCUSSION

Brabender Compounding

Diagrams of mixing torque vs. time for neat Ny-6, EVOH and their 50/50 blends with and without clay are presented in Fig. 1. The neat EVOH torque decreases with time owing to a gradual thermal degradation at the 250°C processing temperature, and becomes practically constant after 30 min of mixing. The Ny-6 torque level is constant with mixing time. As for the 50/50 Ny-6/EVOH blend, the torque level is higher than those of each of the neat constituent polymers, and significantly increases with mixing time. A similar trend is obtained for a 75/25 Ny-6/EVOH blend (not shown here). Literature reports on EVOH/nylon blends processed in an extruder, characterized by short residence times (several minutes), describe the formation of intermolecular hydrogen bonds between the amide and hydroxyl groups of Ny-6 and EVOH, respectively [4, 5]. Indeed, at the short mixing times, formation of hydrogen bonds may be dominating; however, for the longer mixing times (up to 45 min), another mechanism is dominating leading to the significantly increasing torque level seen already after about 20 min of mixing. It is interesting to note that although EVOH undergoes reduction in melt viscosity, i.e., scission reactions, the torque of the 50/50 Ny-6/EVOH blend significantly increases. Hence, a chemical reaction between polar groups of the constituent polymers may be taking

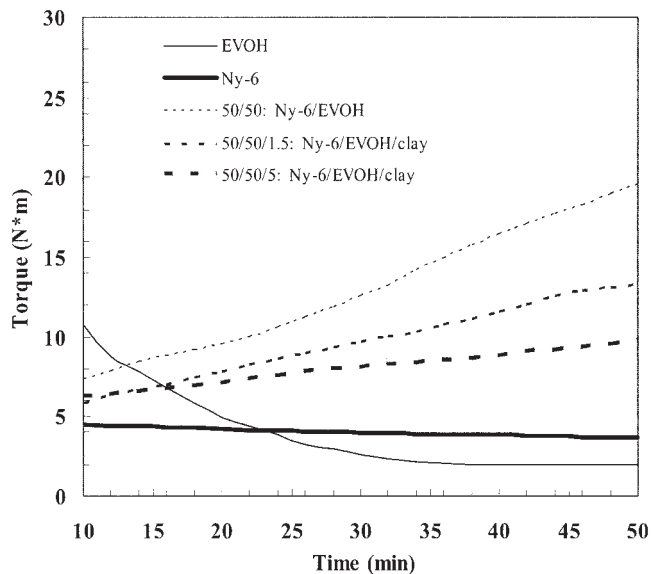


FIG. 1. Brabender plastograms of neat EVOH, Ny-6, 50/50 Ny-6/EVOH, 50/50/1.5 and 50/50/5 Ny-6/EVOH/clay, at 250°C and 20 rpm.

place, in addition to the formation of hydrogen bonds, as was recently suggested [12]. Most probably, chemical reactions have taken place between EVOH hydroxyl groups and carboxyl terminal groups of Ny-6.

The mixing torque of reference samples, namely, individual polymers with clay, shows that the addition of 1.5 or 5 wt% clay to Ny-6 does not significantly affect the mixing torque (Fig. 2). EVOH containing 1.5 wt% clay shows constant torque with mixing time; however, when 5 wt% clay is added to EVOH, a marked torque upturn occurs reaching high torque values. In a previous study of EVOH/clay, the torque upturn was attributed to the clay fracturing

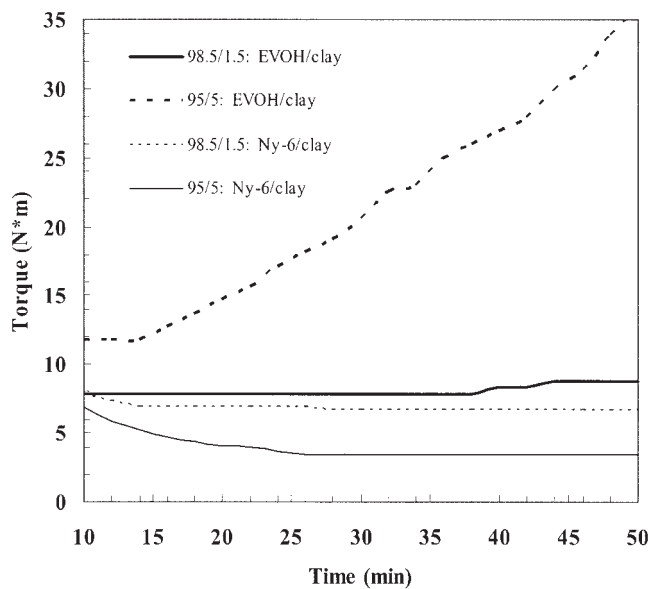


FIG. 2. Brabender plastograms of neat 98.5/1.5 and 95/5 Ny-6/clay and 98.5/1.5 and 95/5 EVOH/clay, at 250°C and 20 rpm.

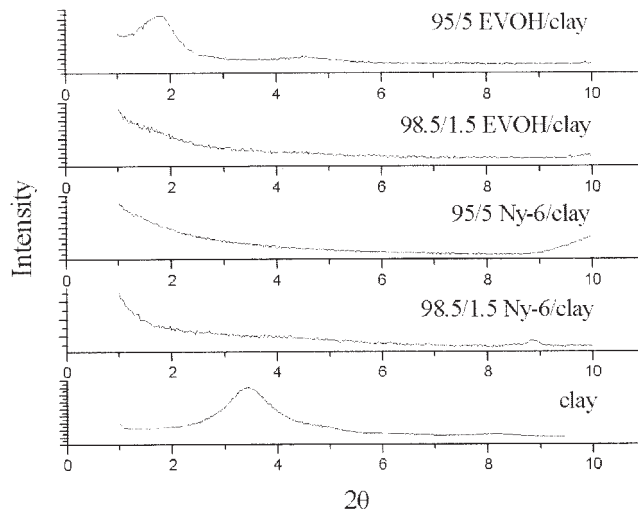


FIG. 3. XRD patterns of neat clay, 98.5/1.5 and 95/5 Ny-6/clay and 98.5/1.5 and 95/5 EVOH/clay Brabender cell mixing, at 250°C for 50 min.

processes, formation of new platelet surfaces, and thus, increasing interaction levels with the EVOH matrix [13].

Surprisingly, the addition of clay to the 50/50 Ny-6/EVOH blend resulted in lower torque levels, becoming more pronounced for the higher clay amount (Fig. 1), though still, the torque increases with mixing time. The latter behavior may be interpreted by understanding the competition between several controlling mechanisms, i.e., intercalation, exfoliation, preferential localization of the clay in one of the polymers, and occurrence of chemical reactions between EVOH and Ny-6. It is suggested that owing to intercalation processes, which occur after several minutes of mixing, less EVOH and Ny-6 chains are available outside the galleries for chemical interaction to take place, leading to lower torque levels (viscosity), compared with the torque level of the system without clay, i.e., 50/50 Ny-6/EVOH blend (Fig. 1). Although after longer mixing times, fracturing processes and delamination are taking place (as is verified by XRD and TEM), leading to new availability of the neat polymers outside the galleries, there might not be sufficient time for chemical reaction between them to occur during melt mixing. Moreover, according to XRD and TEM results, it seems that more clay fraction is intercalated and surrounded by Ny-6 rather than by EVOH, hence, the torque increase is expected to be less significant, as seen in Fig. 2 for the neat polymers in the presence of the clay.

XRD

The clay morphology and its level of dispersion were studied by two complementary methods namely, XRD and TEM, which were found supportive. Figure 3 shows XRD patterns of the individual polymers containing 1.5 and 5 wt% clay. The XRD patterns of EVOH containing 1.5 wt% clay do not show a characteristic basal reflection, which is

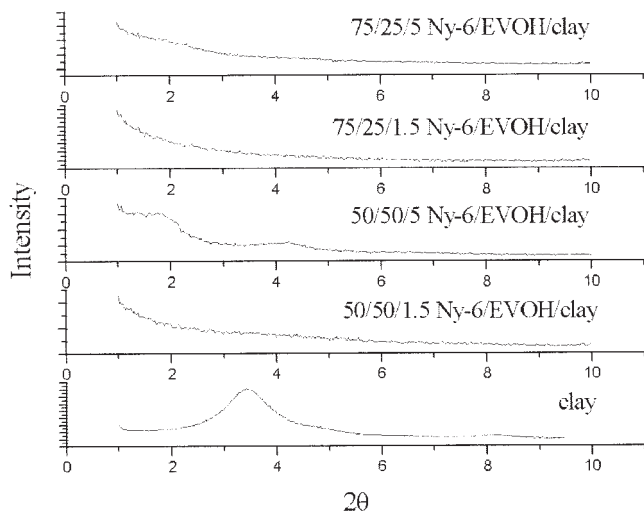


FIG. 4. XRD patterns of neat clay, 50/50/1.5 and 50/50/5 Ny-6/EVOH/clay and 75/25/1.5 and 75/25/5 Ny-6/EVOH/clay Brabender cell mixing, at 250°C for 50 min.

indicative of an exfoliated clay structure. When 5 wt% clay is incorporated in EVOH, also an intercalated structure is obtained with a characteristic peak at $2\theta = 1.8^\circ$ ($d_{(001)} = 48.5 \text{ \AA}$). For Ny-6, an exfoliated structure with no characteristic peaks is obtained irrespective of the clay content. Although both polymers (Ny-6 and EVOH) are polar in nature, their tendency to intercalate/exfoliate is different. According to Lee and Han [2] two factors should be considered, namely, very strong intermolecular attractive interactions (hydrogen bonds) between the hydroxyl groups in EVOH and those existing upon the clay surface, and melt viscosity. Both may have an important role on the dispersability and the exfoliation of clay aggregates for compatible polymer/clay systems. As the viscosity is considered, according to the Brabender data, EVOH melt viscosity is higher than that of Ny-6 during the first 20 min of mixing. Intercalation processes are known to take place in the beginning of melt mixing [14]; therefore, this may explain the higher tendency of clay in the presence of Ny-6, having lower viscosity than EVOH, to undergo advanced intercalation and eventually exfoliation.

As clay is added to the 50/50 Ny-6/EVOH blend (Fig. 4), a competition between EVOH and Ny-6 regarding intercalation is taking place. When 1.5 wt% clay is added to the blend, a complete exfoliated structure is obtained. However, when 5 wt% clay is added, there is a shoulder-like peak at $2\theta = 1.8^\circ$, similar to the location of the peak seen when 5 wt% clay is added to EVOH (Fig. 4). The peak is, however, broader and lower in intensity suggesting more exfoliated fraction compared to the case of only EVOH with 5 wt% clay. This implies that in the 50/50/5 Ny-6/EVOH/clay system, more Ny-6 chains are intercalated than EVOH chains. The clay may be preferentially located in the Ny-6 phase. This is also supported by the result that addition of clay to the 75/25 Ny-6/EVOH blend, where Ny-6 is the major component, leads to an exfoliated structure irrespec-

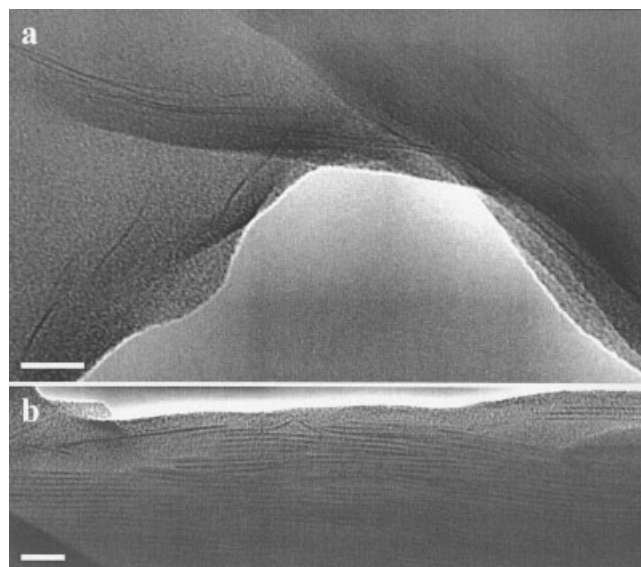


FIG. 5. TEM micrographs of 95/5 EVOH/clay Brabender cell mixing, at 250°C for 50 min (bar = 20 nm).

tive of clay content, i.e., 1.5 or 5 wt% (lack of basal reflections, Fig. 4). Hence, the lower the EVOH content in the blend, the higher the delamination level achieved. This is in agreement with Ellis's study [15] on PA-6/EVOH nanocomposites, who found that increasing the content of EVOH in the blend (75 compared to 50 wt%) induces intercalation, instead of exfoliation owing to thermodynamic considerations.

TEM

TEM was studied on selected samples so as to verify and complement the X-ray results. Reference samples of each polymer containing 5 wt% clay were initially examined. Figure 5 displays the intercalated compound of EVOH containing 5 wt% clay. The dark lines are the silicate layers separated by about 2 nm, in agreement with the d-spacing observed by XRD. The shoulder-like peak observed in the XRD pattern implies that there are clay populations of higher gallery heights, or even exfoliated platelets, as can be seen in the lower left-side of Fig. 5a. The length of the platelets ranges from 20 nm to several hundred nanometers. In TEM micrographs of composites containing delaminated clay, individual silicate layers embedded in the polymer matrix are observed.

A TEM micrograph of Ny-6 containing 5 wt% clay is shown in Fig. 6. Well-dispersed individual silicate layers of 1 nm in thickness embedded in the Ny-6 matrix are observed in agreement with the X-ray patterns depicted in Fig. 3 (no characteristic peak is observed). In all presented sample regions (Fig. 6a–d), the silicate layers seem to be shorter than 50 nm, implying that the platelets were severely fractured during melt-mixing under the high shear field. The ternary system containing 5 wt% clay, 50/50/5 Ny-6/EVOH/clay, shows a combined morphology of intercalation

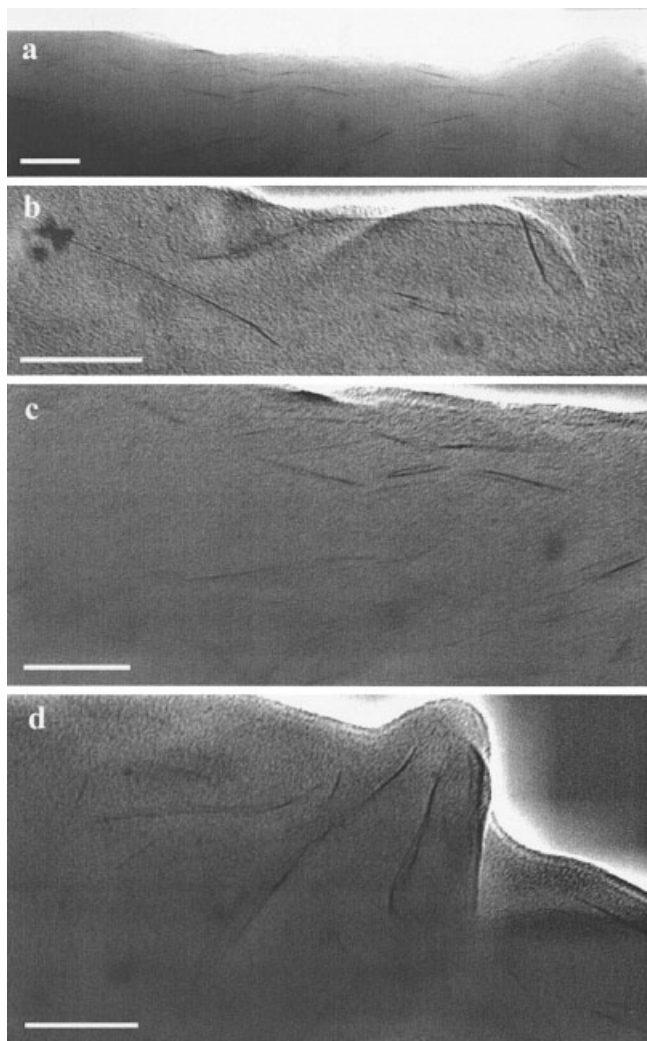


FIG. 6. TEM micrographs of 95/5 Ny-6/clay Brabender cell mixing, at 250°C for 50 min (bar = 50 nm).

and delamination (Fig. 7). Figure 7a shows mostly intercalated clay, which seems similar to the morphology seen for the reference EVOH/clay composite, with gallery heights of about 2 nm. However, there are other regions exhibiting higher gallery heights and less ordered structures (Fig. 7b). Even completely exfoliated morphology is seen in other areas (Fig. 7c and d), as was seen for the reference sample of Ny-6 containing clay. However, when only 1.5 wt% clay was added, an exfoliated structure was obtained, in agreement with the X-ray results (Fig. 8). The platelets length is about 50–150 nm, and their average thickness is few nanometers, thus leading to high aspect ratios, which is a key for achieving efficient matrix reinforcement.

The TEM results suggest that exfoliation requires an optimal clay content. Increasing the clay content above a critical level induces coalescence of the clay platelets, leading to mixed intercalation and exfoliation, instead of complete exfoliation, as in the case of 50/50/5 Ny-6/EVOH/clay.

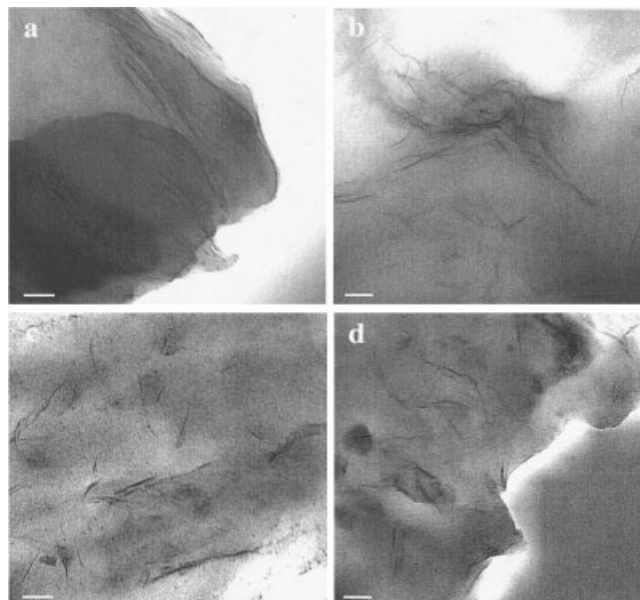


FIG. 7. TEM micrographs of 50/50/5 Ny-6/EVOH/clay Brabender cell mixing, at 250°C for 50 min (bar = 50 nm).

Solvent Extraction (“Unextractable” Content)

To examine the occurrence of chemical reactions between EVOH and Ny-6 and the level of intercalation, dimethylformamide (DMF) selective extraction experiments were performed, and the results are listed in Table 1.

DMF is a solvent for neat EVOH and nonsolvent for Ny-6 (Ny-6 absorbs some DMF, about 2.5 wt%). If no chemical reaction between EVOH and Ny-6 has occurred, DMF is expected to completely extract EVOH from its blends with Ny-6. However, only a few weight percent were extracted from both the 50/50 and the 75/25 Ny-6/EVOH blends. This implies that Ny-6 reacts with EVOH, hindering its extraction by DMF. To further study the effect of clay content in a blend, reference samples of each polymer with clay were also examined. EVOH containing 1.5 wt% clay was almost completely dissolved (5 wt% EVOH unextracted). However, when 5 wt% clay was incorporated in EVOH, ~55 wt% unextractables were obtained. These results may be related to both the levels of intercalation and exfoliation. In the former case (EVOH containing 1.5 wt% clay), where EVOH was completely dissolved, an exfoliated structure was obtained according to XRD and TEM results. In the latter case (EVOH containing 5 wt% clay), the unextracted material is probably the intercalated fraction. Hence, extraction experiments may provide a complementary indication regarding the composite morphology and corroborate the XRD results. As expected, addition of clay to Ny-6 did not cause any extraction in DMF. In the ternary systems, only low amounts of EVOH were extracted, and even less for the higher clay content. Interestingly, for the 50/50/5 Ny-6/EVOH/clay blend, the blend has even gained some weight. The combination of high interaction level of Ny-6 with EVOH accompanied by chemical reactions be-

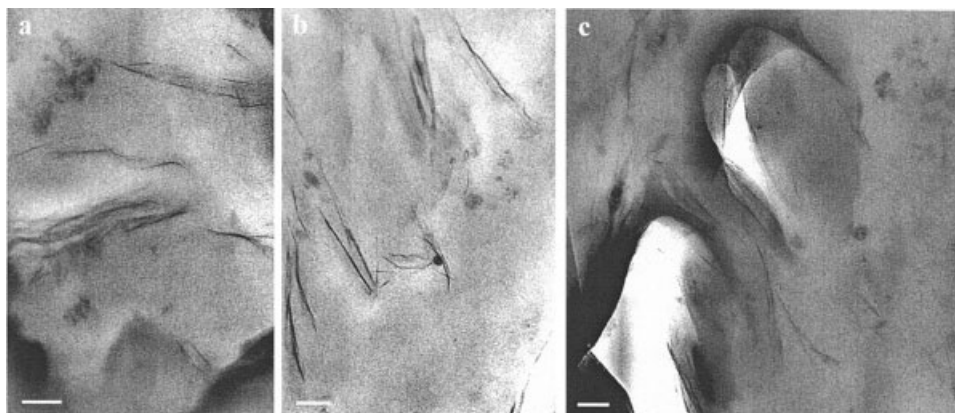


FIG. 8. TEM micrographs of 50/50/1.5 Ny-6/EVOH/clay Brabender cell mixing, at 250°C for 50 min (bar = 50 nm).

tween them and EVOH intercalation leads to less EVOH chains available for extraction.

DSC

The thermal characteristics of EVOH, Ny-6, and their blends, are summarized in Table 2. The melting endotherms of Ny-6 and EVOH appear individually in their blend thermograms. They may represent crystals of the two individual polymers and probably also as block copolymers owing to the chain extension reaction between Ny-6 and EVOH, as suggested in a former study [12]. The melting temperature and degree of crystallinity of both polymers significantly decrease in the blends compared to the neat polymers. EVOH melting endotherm is even absent in the Ny-6 rich blend (75/25 Ny-6/EVOH). Two effects may be considered: formation of hydrogen bonds and chemical reaction between the two polymers resulting in a copolymer consisting of EVOH and Ny-6 blocks. When EVOH serves as a major component, it rapidly crystallizes owing to the strong self-associated hydrogen bonds occurring between adjacent hydroxyl groups, thus, dominant compared to the intermolec-

ular hydrogen bonds between Ny-6 and EVOH. In EVOH rich blends, the small amount of Ny-6 does not practically disturb the fast EVOH crystallization, in agreement with Nir et al. [4]. However, when Ny-6 constitutes the major phase, the amide group content is higher than the amount of available hydroxyl groups. Therefore, the probability of forming intermolecular hydrogen bonding is high, and thus, sharply reduces the EVOH crystallinity and increases its content in the amorphous miscible blend phase. In addition, for high Ny-6 contents, more carboxyl terminal groups are available for chemical reaction with hydroxyl groups of EVOH. The resulting block copolymer does crystallize due to the large blocks, however, at a lower level than the corresponding homopolymers, thus, contributing to the reduction of T_m of both, Ny-6 and EVOH crystals. Conversely, Ny-6 crystallizes at all blend compositions. However, the interruption to Ny-6 crystallization process is less significant for the 75/25 compared to the 50/50 Ny-6/EVOH

TABLE 1. Summary of extraction experiments in DMF.

Sample	Material extracted ^a (%)
Neat EVOH	-98
Neat Ny-6	2.5
98.5/1.5 EVOH/1.30TC	-96
95/5 EVOH/1.30TC	-43
98.5/1.5 Ny-6/1.30TC	-0.5
95/5 Ny-6/1.30TC	2
50/50 Ny-6/EVOH	-4
50/50/1.5 Ny-6/EVOH/1.30TC	-6
50/50/5 Ny-6/EVOH/1.30TC	11
75/25 Ny-6/EVOH	-6
75/25/1.5 Ny-6/EVOH/1.30TC	-8
75/25/5 Ny-6/EVOH/1.30TC	-2

^a Negative values represent weight loss, while positive values represent weight gain.

TABLE 2. DSC thermal properties of Nylon-6/EVOH/1.30TC blends.

Sample	T_c (°C)	2nd heating	
		T_m (°C)	ΔH_m (mJ/g)
Ny-6	185	220	72
EVOH	148	174	56
98.5/1.5 EVOH/1.30TC	151	180	79
95/5 EVOH/1.30TC	119	158	45
98.5/1.5 Ny-6/1.30TC	189	220	86
95/5 Ny-6/1.30TC	186	213	54
50/50 Ny-6/EVOH	130	204	22
	157	156	4
50/50/1.5	164	209	27
Ny-6/EVOH/1.30TC	133	163	12
50/50/5	165	210	31
Ny-6/EVOH/1.30TC	140	169	11
75/25 Ny-6/EVOH	173	215	40
	-	-	-
75/25/1.5	174	215	45
Ny-6/EVOH/1.30TC	-	-	-
75/25/5	173	216	44
Ny-6/EVOH/1.30TC	-	-	-

blends. Presumably, as Ny-6 content increases, more Ny-6 chains are chemically unbound to EVOH, and thus, available for crystallization. The crystallization temperatures of both polymers significantly decrease in the 50/50 Ny-6/EVOH blend, and only a single crystallization peak was observed for the 75/25 Ny-6/EVOH blend.

The effect of clay on the crystallization behavior of each polymer has been studied prior to dealing with the effect of clay on the crystallization behavior of the polymers in the ternary blend. The addition of 1.5 wt% clay to EVOH or to Ny-6 resulted in a higher degree of crystallization compared to the level without clay, without actually affecting the crystallites quality, as seen in the enthalpy values and melting temperatures, respectively. Apparently, the clay acts as a nucleating agent. However, when 5 wt% clay was added to each polymer, the degree of crystallization was lower than that without clay, and the crystallites quality was damaged (Table 2). Owing to the high interaction level between each polymer and the clay, the crystallization process is interrupted at the higher clay contents. Moreover, when EVOH is the matrix polymer, a fraction of the EVOH chains remains intercalated, and thus, cannot crystallize, which further lowers the crystallization level.

As for the thermal properties of the ternary systems, when clay is added to the 50/50 Ny-6/EVOH blend, the interruption to crystallization of the blend's components is less pronounced than in the absence of clay; hence, the degree of crystallinity, melting, and crystallization temperatures are higher. Apparently, the clay presence interrupts the occurrence of chemical reaction between EVOH and Ny-6, and therefore, more neat polymers are available to form crystallites. The clay presence does not significantly affect the thermal properties of the polymers when present in the 75/25 Ny-6/EVOH blend. When Ny-6 is the major component, "excess" carboxyl groups are available for interaction with EVOH, thus, the clay does not interrupt the occurrence of chemical reaction.

DMTA

Loss and storage moduli of EVOH and Ny-6 were examined. The loss modulus of EVOH and Ny-6 exhibit the following peaks: β -transitions at -30 and -67°C , respectively, and α -transitions at 48 and 10°C , respectively (Fig. 9). The neat polymers exhibit adjacent α -transitions. Owing to the strong interaction level between Ny-6 and EVOH, a single α -transition seems to result for the Ny-6/EVOH blends. The blends' loss modulus peak appears between these of the two neat polymers (Figs. 9 and 10). The glassy storage modulus values for the 50/50 Ny-6/EVOH blend are between those of the neat polymers, and for the 75/25 Ny-6/EVOH blend, the modulus is even higher than that of the neat polymers (Figs. 11 and 12, respectively). Although at this composition (75/25 Ny-6/EVOH blend), the degree of crystallinity decreases, and its modulus level is higher than in the case of 50/50 Ny-6/EVOH blend. In addition, as a result of less interruption to the occurrence of chemical

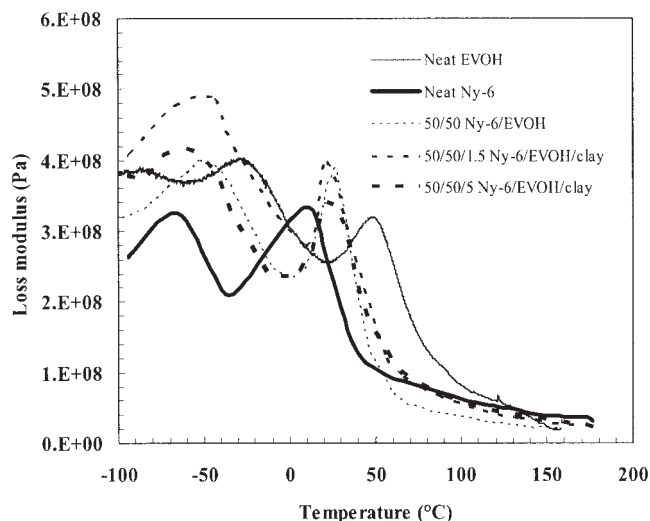


FIG. 9. E'' (loss modulus) of neat EVOH, Ny-6, 50/50 Ny-6/EVOH, 50/50/1.5 and 50/50/5 Ny-6/EVOH/clay Brabender cell mixing, at 250°C and 20 rpm for 50 min.

reaction between Ny-6 and EVOH at the 75/25 composition, higher polymers' densities may result in, leading to the modulus increase.

The addition of 1.5 wt% clay to the neat polymers (98.5/1.5 Ny-6/clay or EVOH/clay) leads to a modulus increase (Table 3) for both polymers owing to the high modulus of the clay and its high interaction level with the polymers. Another factor contributing to the modulus increase is the achievement of exfoliated clay structure. However, for an increased amount of clay (5 vs. 1.5 wt%), the modulus decreases, and in the case of EVOH, to a value even lower than that of neat EVOH. The modulus decrease can be a result of a lower degree of crystallinity of the polymers in the clay presence (Table 2) and to a plasticizing

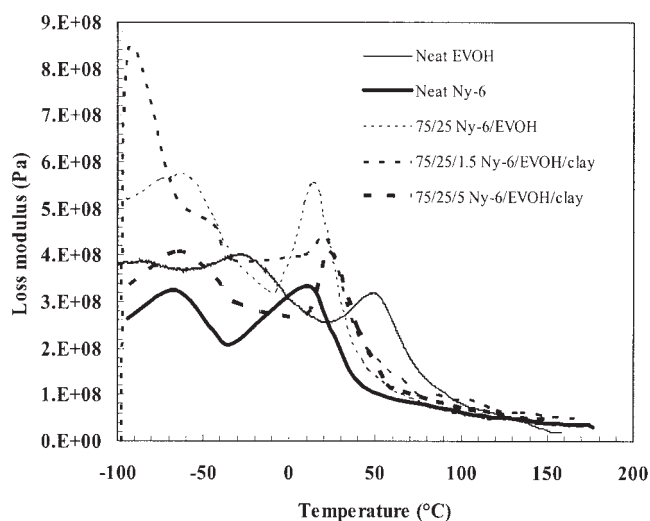


FIG. 10. E'' (loss modulus) of neat EVOH, Ny-6, 75/25 Ny-6/EVOH, 75/25/1.5 and 75/25/5 Ny-6/EVOH/clay Brabender cell mixing, at 250°C and 20 rpm for 50 min.

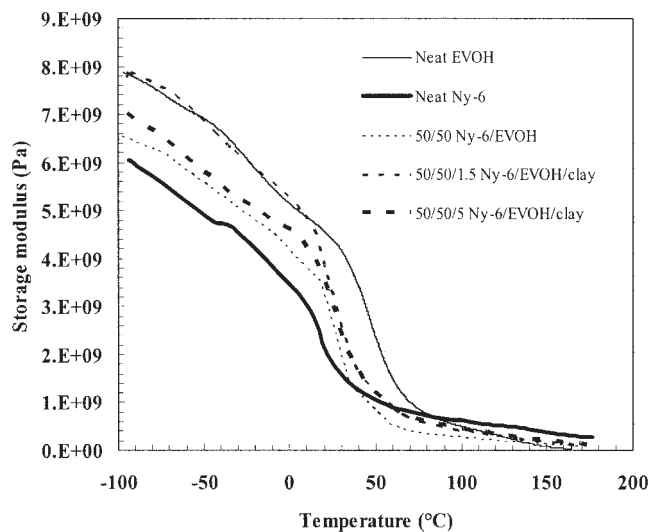


FIG. 11. E' (storage modulus) of neat EVOH, Ny-6, 50/50 Ny-6/EVOH, 50/50/1.5 and 50/50/5 Ny-6/EVOH/clay Brabender cell mixing, at 250°C and 20 rpm for 50 min.

effect of the organic low molecular weight clay-treating compound. In the case of EVOH, the modulus decline is more significant than that of the composite with Ny-6, which can be a result of intercalated compared to exfoliated clay structure in these two cases, respectively. The glass transition temperature of the polymers increases with the addition of clay to each of the neat polymers, but increases more significantly for the lower clay contents. This may be a result of an adverse plasticizing effect of the organo-onium ions treating the clay at the high clay contents.

As for the modulus of the ternary blends containing 50/50 Ny-6/EVOH with 1.5 or 5 wt% clay, a similar tendency is seen, namely a modulus increase by addition of low clay content, and subsequently, a modulus decrease for the

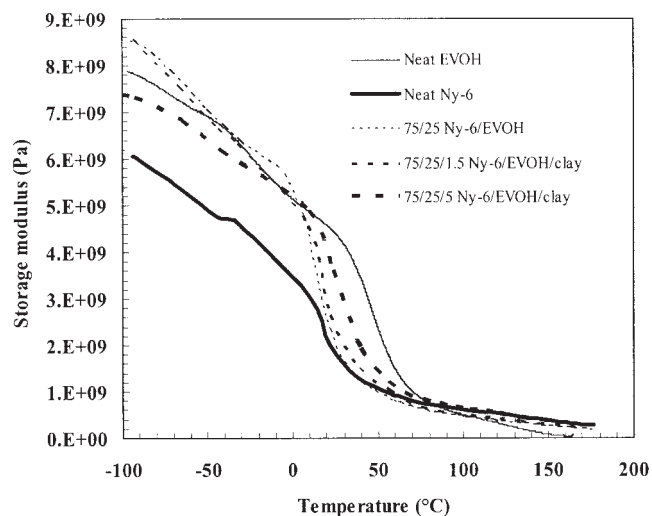


FIG. 12. E' (storage modulus) of neat EVOH, Ny-6, 75/25 Ny-6/EVOH, 75/25/1.5 and 75/25/5 Ny-6/EVOH/clay Brabender cell mixing, at 250°C and 20 rpm for 50 min.

TABLE 3. Dynamic mechanical properties of Nylon-6/EVOH/1.30TC blends.

Sample	T_g (°C)	Storage modulus at -100°C (Pa)
Neat EVOH	48	8.0E + 09
Neat Ny-6	10	6.0E + 09
EVOH + 1.5% 1.30TC	55	1.1E + 10
EVOH + 5% 1.30TC	51	6.4E + 09
Ny-6 + 1.5% 1.30TC	15	8.3E + 09
Ny-6 + 5% 1.30TC	11	7.0E + 09
50/50 Ny6/EVOH	25	6.5E + 09
50/50/1.5 Ny6/EVOH/1.30TC	25	7.8E + 09
50/50/5 Ny6/EVOH/1.30TC	24	7.0E + 09
75/25 Ny6/EVOH	14	8.5E + 09
75/25/1.5 Ny6/EVOH/1.30TC	22	8.6E + 09
75/25/5 Ny6/EVOH/1.30TC	23	7.4E + 09

higher clay amount; however, it is still higher than without clay, i.e., the 50/50 Ny-6/EVOH blend. When a 75/25 Ny-6/EVOH composition is used, the modulus increases when 1.5 wt% clay is added; however, it decreases for 5 wt% clay to a value lower than that without clay (75/25 Ny-6/EVOH blend). In this case, probably the effect of plasticizing owing to exfoliation, which exposes the organo-onium ions, is more significant than the reinforcing effect of the clay. In the ternary systems, at both polymer blend compositions, the single T_g (as determined by DMTA) is constant or increases with the clay content (for 50/50 and 75/25 Ny-6/EVOH, respectively), in contrast to the clay effect on the T_g of the individual polymers, i.e., lowering the glass transition temperature (Table 3).

In summary, best reinforcement is attained by the addition of an optimal content of clay undergoing exfoliation, thus, leading to minimum interruption to the occurrence of chemical reaction between Ny-6 and EVOH, less interruption to the polymers' crystallization process, and introduction of low content organo-onium ions having an undesirable plasticizing effect.

CONCLUSIONS

- Optimal clay content is required to attain significant reinforcement.
- There is a competition between clay reinforcing effect and clay interruption to the occurrence of chemical reaction between the polymers. The balance between these two mechanisms determines the composites thermal and mechanical properties.
- The high interaction level between the polar polymers and the clay leads to advanced intercalation, and sometimes, exfoliated structures for the ternary systems.
- Solvent extraction experiments provide some insight regarding the content of bound unextract polymer inside the galleries.

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