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Reverse exfoliation in a polymer nanocomposite by blending with a miscible polymer

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Abstract

An investigation of the permeability to methanol of blends of a PA-6 nanocomposite and ethylene-vinyl alcohol copolymers (EVOH), containing approximately 32 mol% ethylene, has been conducted. Blends were prepared by melt compounding and permeation measurements were performed by gravimetric uptake methods. The nanocomposite polyamide exhibited significantly reduced permeability compared to the unmodified polymer. The blends exhibited permeability that was non-linear with blend composition. The nanoscale filler in a blend containing up to 50 wt% EVOH remained fully exfoliated, however, in a blend containing 75 wt% of EVOH there was little or no exfoliation and the blend had a measured permeability lower than that of either of the pure components. Electron microscopy and X-ray analysis has indicated a reversal of exfoliation of the nanocomposite filler particles to be responsible.

Keywords: Nanocomposites; Blends; Miscibility

1. Introduction

Modification of polymers using nanoscale (1×10^{-9} m) filler particles that are characterized by a high surface area to thickness aspect ratio, has assumed increased attention recently. The filler particles are typically approximately 1 nm thick with lateral dimensions of the order 200–1000 nm. This interest was spurred initially by reports of significant mechanical property improvements in PA-6 [1] that was reinforced with filler particles, derived from naturally occurring Smectite clays. These polymer nanocomposites usually display significant improvements in modulus and heat deflection temperature at relatively low levels (2–8 wt% filler particles) of filler inclusion. Polymer nanocomposites have also been shown to possess good flammability resistance [2] and enhanced barrier performance to diffusing species when compared to the unmodified polymers. Consequently, there has been considerable experimental [1–4] and theoretical [5] interest in these materials for many different polymers.

An essential step in fabricating the polymer nanocomposite requires 'exfoliation' of the layered platelets to produce a random distribution. For polyamides this can be done with naturally occurring smectite clays by treating the latter with organophilic materials such as the quaternary ammonium salt of octadecylamine, ODA. The treated clay may be added to monomer before the polymerization stage or added directly to polymer in a melt mixing process.

Ethylene-vinyl alcohol copolymers, EVOH, are widely used as barrier polymers. A nanocomposite EVOH would be expected to provide even better barrier performance, however, complete exfoliation of a suitable nanoscale filler in EVOH, to the same degree as that commonly observed for polyamide nanocomposites, is currently not possible [6–8]. The latter reported studies indicated that the nanocomposite filler maintains significant structural order when examined by X-ray analysis, which is usually interpreted as incomplete exfoliation.

There has been notable interest in blends of polyamides and EVOH copolymers [9–14], however, there is no clear correlation of how phase behavior is influenced by vinyl alcohol content of the EVOH and the amide content of the polyamide. Several studies [12–14], however, have concluded that PA-6 and EVOH copolymers containing approximately 29 mol% ethylene form miscible blends. Accordingly, in this study, the blending of a nanocomposite PA-6 with a miscible EVOH polymer containing approximately 32 mol% ethylene has been explored as a route to

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form EVOH nanocomposites that may not be attainable using conventional procedures. In this paper, it will be shown that this is possible for certain blend compositions. Conversely, the rather unusual phenomenon of what appears to be the reversal of the exfoliation of the nanoscale particles back into layered aggregates in a PA-6 nanocomposite/EVOH blend has been found to occur when there is an excess of the antagonistic EVOH in the blend.

2. Experimental

2.1. Materials

The unmodified PA-6 is a general purpose resin and was obtained from Honeywell as Capron 8208. The PA-6 nanocomposite (PA-6 N) was obtained from Unitika Ltd and is a reactor grade nanocomposite containing approximately 4 wt% of a synthetic phillosilicate nanocomposite filler of proprietary composition. The EVOH resins were obtained from Evalca Corp. as F101A and J102B. Both contain approximately 32 mol% ethylene, however, the J102B has microstructural differences that lead to an overall slightly lower level of crystallinity, as measured by heat of fusion in differential scanning calorimetry (DSC) (68 J/g), compared to the F101A (76 J/g). The latter also has a slightly higher melting point 184 °C compared to 182 °C for the J102B.

2.2. Processing

Unless noted otherwise, all polymers were melt processed using a DSM Research Mini-Extruder (co-rotating twin screw extruder) and Mini-Injection Molder. Dried polymers (4–4.5 g total mass) were melt processed for 2 min at 240 °C and injection molded using a DSM Minimolder, operating with compressed air at 90 psi, into coupons with approximate dimensions $12 \times 60 \times 2\ \mathrm{mm}^3$. When compared to conventional injection molding, the molding conditions are moderate with relatively low shear forces applied during mold filling.

2.3. Analytical procedures

Permeability measurements were performed according to procedures described in the literature [15] using simple gravimetric techniques. Molded dry coupons of the polymers were placed in an excess ($500\ \mathrm{cm}^3$) of methanol at ambient temperature (25 °C). Liquid uptake was recorded gravimetrically using a closed weighing bottle and a balance capable of measuring to an accuracy of 10^{-5} g. Samples were carefully dried using paper prior to weighing and exposure to humidity was minimized. The average thickness of the coupons was recorded before immersion in the fuel.

The permeability coefficient P, of a material is given by Eq. (1):

$$P = DS \tag{1}$$

where D, is the diffusion coefficient and S, is the equilibrium solubility of permeant in the polymer. The latter quantity is measured as the saturation uptake (g/g). Assuming that diffusion obeys Fick's first law, the determination of D and hence P by simple liquid sorption techniques is well approximated by Eq. (2) [16]

$$M_t/M_\infty = 4(Dt/\pi h^2)^{0.5} \tag{2}$$

where h, the thickness of the coupon. Thus by measuring the increase of mass (M_t) as a function of time (t) and plotting this as M_t/M_∞ versus $(t/h^2)^{1/2}$ a straight line of slope $4\,(D/\pi)^{1/2}$ is obtained, from which D may be determined. The treatment of data in this manner is valid only for the early stages of sorption and although less exacting than other methods of determining P it does provide a meaningful comparison of behavior. Only single determinations of P were made.

DSC was performed using a Perkin–Elmer, Series 7, calorimeter at a heating rate of 10 °C/min. The melting point, T_m, is reported as the maximum of the melting endotherm. X-ray diffraction was performed using a Siemens D500 diffractometer using narrow slits. Data of relative intensity were recorded as a function of 2θ.

Transmission electron microscopy (TEM) samples were prepared using a diamond knife on a Reichert-Jung Ultracut E microtome equipped with a FC 4E cryo unit at a set temperature of − 60 °C. The TEM samples were obtained as 90 nm thick sections. TEM was performed using a Phillips 430T microscope operated at an accelerating voltage of 300 kV.

3. Results and discussion

A quantitative summary of the permeability parameters of methanol in PA-6, the PA-6 nanocomposite, the EVOH copolymers and their blends is shown in Table 1. The results confirm that the lower level of crystallinity in the J102B copolymer leads to an approximate 50% increase in the permeability coefficient when compared to the F101A. The increase appears to originate from both the increased solubility of the diffusing species and the significantly higher diffusion coefficient in the J102B. The raw data from the two EVOH copolymers is also shown in Fig. 1.

Additionally, the information shown in Fig. 2 shows the procedure to determine D and the effectiveness of the nanocomposite filler on the reduction of the diffusion coefficient for PA-6. The lines drawn in Fig. 2 represent best straight line fit to the data. The equilibrium methanol solubility is reduced in the nanocomposite compared to an unmodified PA-6, however, the lower permeability is caused primarily by the reduction of D. Although most of the reduced permeability is ascribed to the presence of the

Table 1
Summary of measured values of *D* and *P* and sorption of methanol in pure polymers and EVOH/PA-6 nanocomposite blends

Material	Diffusion coefficient ($\times 10^{-13}$ m^2/s)	Sorption coefficient (g/g)	Permeability coefficient ($\times 10^{-14}$ m^2/s)
J102B/PA-6 N 25/75	1.59	0.123	1.96
F101A/PA-6 N 25/75	1.59	0.125	1.99
J102B/PA-6 N 50/50	3.317	0.158	5.25
F101A/PA-6 N 50/50	1.59	0.146	2.33
J102B/PA-6 N 75/25	7.09	0.179	12.67
F101A/PA-6 N 75/25	5.02	0.161	8.10
Capron 8202	17.66	0.154	27.19
PA-6 N	1.59	0.113	1.80
J102B	2.826	0.178	5.03
F101A	2.0	0.159	3.3

platy filler, the crystal habit of the PA-6, as revealed by X-ray diffraction, was also shown to be influenced by the presence of the particles. This observation is in agreement with previous findings [17], however, it is unlikely to have a profound influence on permeability.

Attempts to fabricate an EVOH nanocomposite, using the same ODA treated smectite clays that are known to produce fully exfoliated nanocomposite polyamides, were unsuccessful [6]. Although these results are not reported here in detail, there was no discernable effect on permeability and TEM and X-ray analysis revealed a non-exfoliated morphology.

There have been a number of studies [12–16] on polyamide/EVOH blends that indicate the formation of compatible mixtures with beneficial barrier properties. Moreover, blends of PA-6 and EVOH with 29 mol% ethylene content have been determined to be miscible [16]. Both thermal analysis and TEM on the blends prepared here have confirmed the formation of miscible blends of the PA-6 nanocomposite and both EVOH polymers. The permeability of the blends containing 25 wt% of the respective EVOH were rather insensitive to the EVOH copolymer used. As the EVOH content of the blends increased not only did the blends containing the J102B copolymer exhibit inferior barrier properties when compared to the equivalent F101 EVOH blend, but also at high EVOH contents (75 wt%) the blends were even more permeable than their pure constituents. The data is also shown in Table 1 and a pictorial summary of this is shown as Fig. 3.

Fig. 4 shows the raw data of the measured weight changes for blends of PA-6 N and the J102B copolymer compared to their pure constituents. The data indicate some deviation from case one diffusion, which was a feature of all

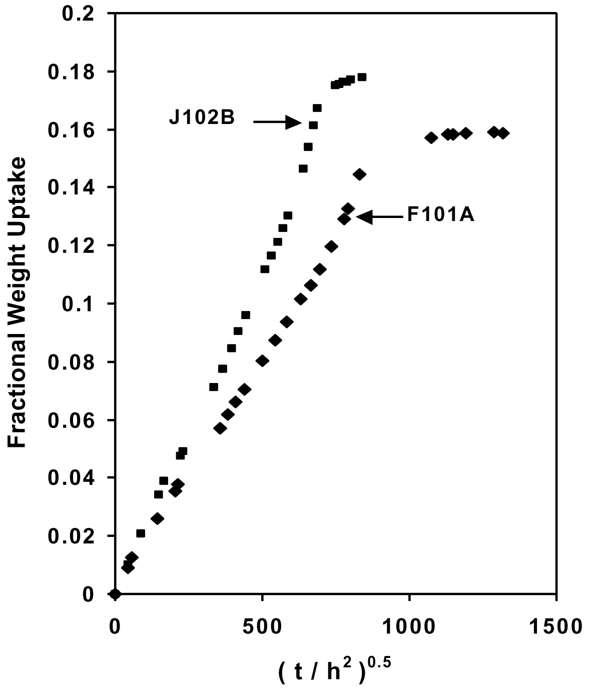

Fig. 1. Weight uptake of methanol in EVOH copolymers.

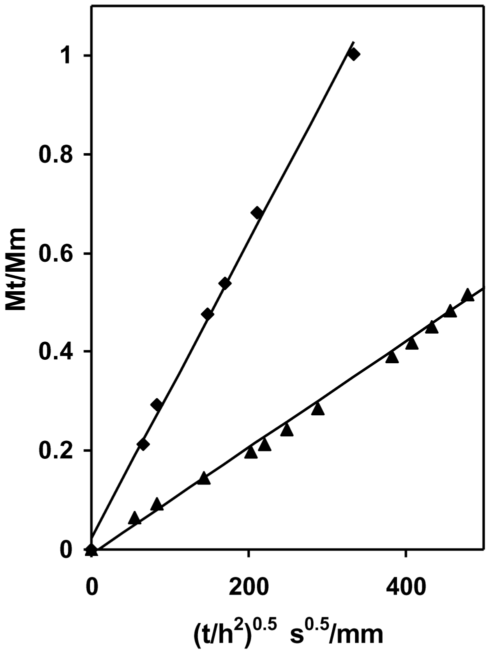

Fig. 2. Comparison of the determination of the diffusion coefficient of methanol in PA-6 (◆)and PA-6 N (▲).

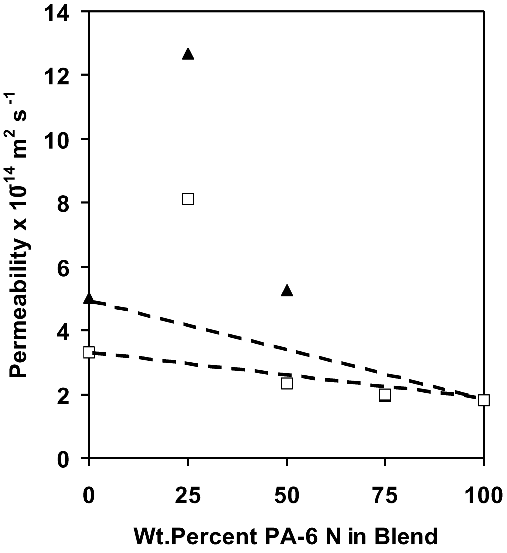

Fig. 3. Influence of Blend composition on the permeability of EVOH/PA-6 N blends (▲ J102B; □ F101A).

the blends investigated. This may be the result of plasticization of the polymers by the diffusing species and the associated decrease in T_g to a temperature below that of the test temperature [18]. There are additional factors that may be responsible for these observations that are discussed below.

In general, the morphological features of miscible binary crystalline blends are complex. Although the blends exist as one phase (miscible) in the melt, segregation of the two polymers during crystallization can occur by different mechanisms to produce different morphologies [19]. Thermal analysis of the crystallized blends indicates two clear melting regimes consistent with the formation of pure crystals of each polymer. This may have a significant influence on transport properties, however, currently nothing is known about the morphology of crystallized polyamide/EVOH blends. There may also be some chemical reactivity between the constituents at the blending temperature, however, DSC revealed no significant changes in crystallinity that would account for the observations noted above. Crystallinity changes would have a significant effect on permeability, however, none were observed. Measured heats of fusion indicated linear additivity. For example the blend containing 75 wt% J102 B had a measured heat of fusion of 50 J/g for this component that is consistent with a value of 68 J/g measured for the pure polymer. Similarly, the heat of fusion of the PA-6 N in a blend containing 50 wt% of the nanocomposite was approximately half (33 J/g) of that for the pure polymer.

The measured values of solubility in Table 1 also support a non-morphological basis for the observed increases in permeability in the blends containing high quantities of EVOH. The latter conclusion is also supported by measurements [12] of oxygen permeability in PA-6/EVOH blends, which showed linear additivity with blend composition. This would be compromised if significant changes in the degree of crystallinity had occurred.

Secondly, and more importantly, there is evidence that the increasing presence of the EVOH in the blend induces a coalescence of the nanoparticulate, i.e. a reverse exfoliation process appears to be taking place. This may be the result of a straightforward reversal of the thermodynamic processes that were in place to produce exfoliation in PA-6 in the first place. Alternatively, the effect may be morphological in origin, produced during the crystallization of the two blend constituents. The latter corresponds to a phase segregation process during crystallization, however, based on the evidence presented below, the former appears the most likely.

The TEM micrographs of some of the various blends are shown in Fig. 5. First, the micrographs indicate a uniform continuous matrix consistent with the miscible nature of the blends. More interestingly, the micrographs provide visual confirmation of the development of an organized nanoparticulate morphology as the EVOH content increases. The PA-6N exfoliated nanocomposite exhibited a random straw-like pattern of particles. As the EVOH content of the blend increased the development of layered platelets,

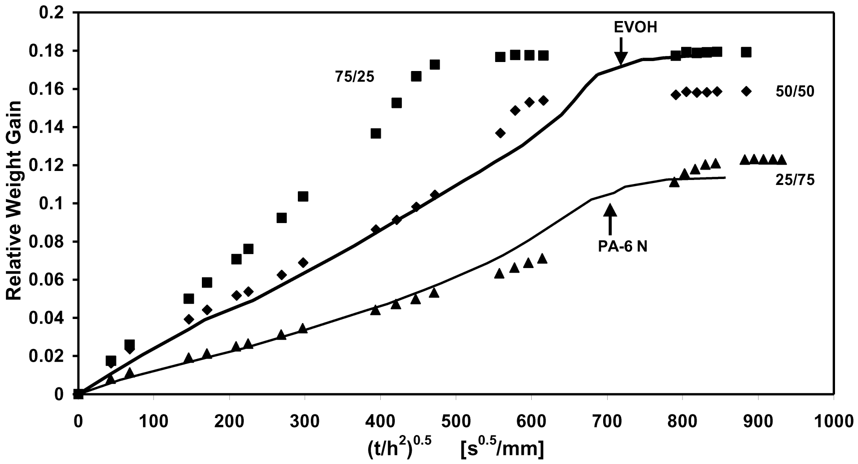

Fig. 4. Relative weight gain in methanol of blends of J102B EVOH and PA-6N. Pure polymers solid lines are also shown.

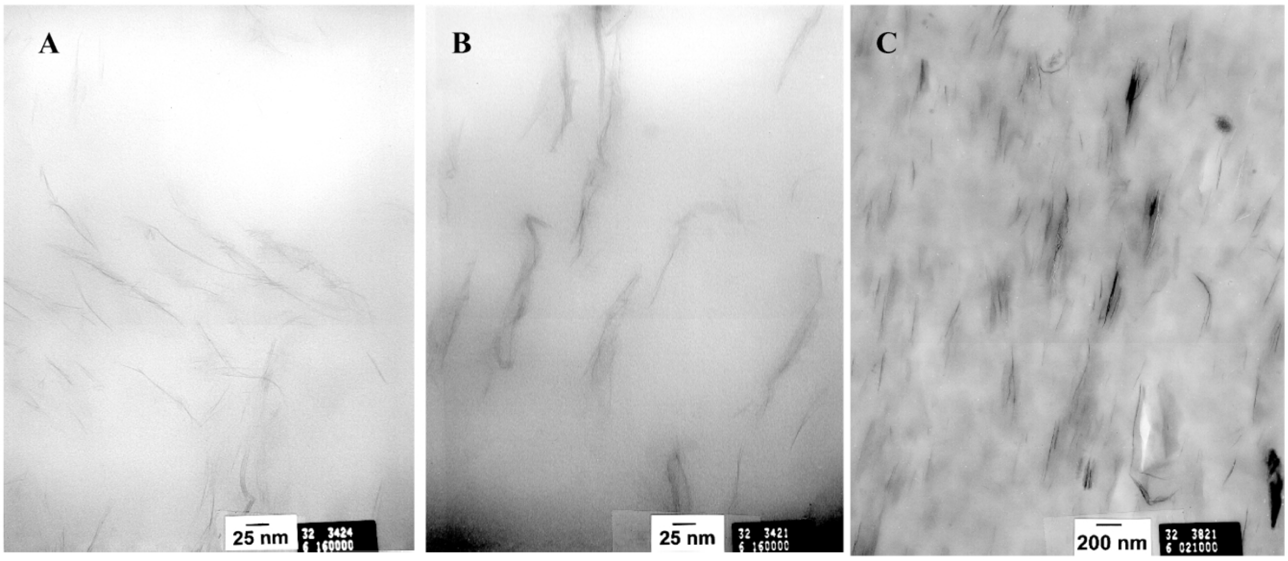

Fig. 5. TEM of blends of EVOH polymer (F101A) and PA-6 N; (A—25/75; B—50/50; C—75/25).

i.e. aggregates, appeared. The pure PA-6 nanocomposites provided a TEM micrograph showing complete exfoliation similar to that presented (A) for the 25 wt% EVOH blend in Fig. 5. Additionally, X-ray analysis of the blends, shown in Fig. 6, also shows the development of order at low angles in the blends as the EVOH content increases.

The fully exfoliated PA-6N has no diffraction peaks at low angles associated with incomplete exfoliation. The peaks at high angles ($2\theta = 20-22$) are associated with the crystalline habits of the polymers [8,17]. The main peak at $2\theta = 21.8$ is associated with the excess PA-6 in the blend and is consistent with findings that the γ form predominates in PA-6 nanocomposites [17,20]. The predominance of the peak at approximately $2\theta = 20$ is associated with the EVOH [8]. The development of a peak at low angle ($2\theta \approx 4$) in the X-ray scattering, as the EVOH content in the blend increases, indicates the progressive development of layered structures in the blend at high EVOH levels even though the overall nanocomposite filler content in the blend is actually decreasing.

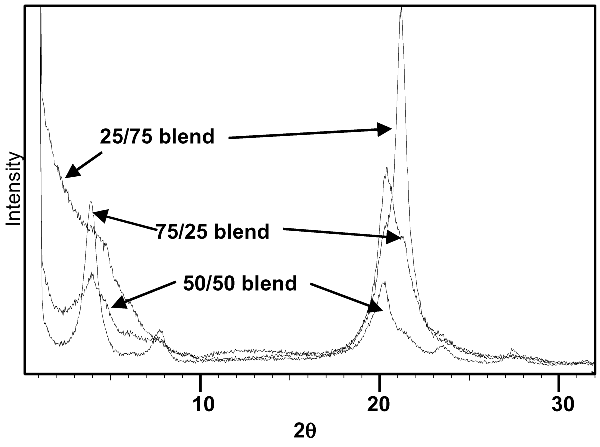

Fig. 6. X-ray diffraction of blends of EVOH copolymer (J102B) and PA-6 N.

The main consequence of these changes from the perspective of transport properties is that the PA-6 nanocomposite component in 25/75 PA-6 N/EVOH blend begins to behave like pure PA-6 upon exposure to methanol. Indeed, the permeability coefficients for blends containing 75 wt% EVOH are approximately the weighted arithmetic average of the pure unmodified components (see Table 1), a result that would be expected if significant exfoliation was lacking. The permeability coefficients of the 50/50 blends are not affected to the same extent. The blend containing the F101 EVOH maintains elevated barrier resistance to methanol, which suggests a rather sharp transition to reverse exfoliation between 50 and 75 wt% EVOH.

4. Conclusions

Blending of a nanocomposite PA-6 with miscible polymers has been explored as a route to form nanocomposites that may not be attainable using conventional procedures. A nanocomposite PA-6, containing only 4 wt% of a synthetic nanoparticulate, was found to offer an approximate 10-fold reduction in the diffusion coefficient of methanol, when compared to an unmodified nylon 6. The permeability to methanol of the latter nanocomposite was also reduced by 33% over that measured for an EVOH copolymer. Blends of PA-6 nanocomposite and EVOH copolymers were found to produce miscible blends that maintained complete exfoliation of the nanoparticulate at moderate levels (up to 50 wt%) of EVOH inclusion; however, at high levels (75 wt%) of EVOH content, the nanoparticulate was found to become ineffective as a barrier to transport and the permeability of the blends was severely reduced.

Both TEM and X-ray methods indicate this was caused by the apparent reverse exfoliation of the platelets back into layered aggregates. This is the first published report noting this behavior, however, it remains to be seen if it is more universal. Not surprisingly, studies in our laboratory on miscible polyamide blends, where the treated clay exfoliates in both polymers have also shown complete exfoliation in the blends.

Characterization of nanocomposites remains an analytical challenge. TEM and X-ray diffraction continue to be the two principal techniques for qualifying the degree of exfoliation or 'dispersion' of the nanoparticulates. TEM is a superior method but unfortunately is only a local analytical tool; i.e. only a small portion is sampled. The information presented here supports the proposal that the determination of transport properties of polymer nanocomposites is a simple and an effective method to characterize exfoliation on a large scale that can be used to supplement these two main characterization methods.

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