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MORPHOLOGY OF POLY(ETHYLENE OXIDE)/ POLY(VINYL ACETATE) BLENDS

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Abstract—The morphology of poly(ethylene oxide)/poly(vinyl acetate) (PEO/PVAc) blends was examined using small angle X-ray scattering (SAXS) and optical microscopy. The morphological and structural parameters of the blends are dependent on both composition and crystallization conditions. Optical microscopy revealed that blend samples prepared by solution casting crystallized with volume-filling crystals up to a composition of 30/70 wt% PEO/PVAc; at higher PVAc content there was no evidence of crystallization in the temperature range studied. Pure PEO always crystallized with a spherulite-hedrite morphology. The formation of spherulites was relatively favoured at lower crystallization temperatures and by addition of PVAc to PEO. Small angle X-ray intensity profiles were analyzed using a recently developed methodology and it was found that, for a given crystallization temperature, the amorphous and interphase thicknesses increased with increasing PVAc content but that the average crystalline thickness was independent of composition. The morphological and structural properties of the PEO/PVAc blends were attributed to the presence of non-crystallizable material in both the interlamellar and interfibrillar regions.

INTRODUCTION

The crystallization and thermal behavior of poly(ethylene oxide)/poly(vinyl acetate) (PEO/PVAc) blends have been recently studied by Martuscelli *et al.* [1]. It was found that the addition of PVAc to PEO caused a depression in both the spherulitic growth rate and the overall kinetic rate constant. This depression is larger at higher undercooling and at a given crystallization temperature, T_c , increases with increasing PVAc content. It was also noted that samples containing up to about 80 wt% PVAc were completely filled with crystals. A single calorimetric glass relaxation whose temperature changes smoothly with composition was observed. It appears therefore that a single, compatible, amorphous phase is present in PEO/PVAc blends and that this non-crystallizable material is located in the interlamellar and/or interfibrillar regions.

Small angle X-ray scattering (SAXS) and detailed morphological analyses are used in the present study to obtain a more accurate interpretation of the location of the PVAc component and indirectly of the extent of mixing of the two polymers in the amorphous phase. SAXS analysis has been shown to be a valuable tool for investigating the structure and overall morphology of semi-crystalline blends [3-7]. By analyzing such data using model calculations of scattering curves, SAXS studies can provide information on macrostructural parameters such as long period, average lamellar thicknesses of crystalline and amorphous regions and interphase width.

In this study the influence of composition and crystallization temperature on the morphology and

structure of the crystallizable polymer PEO was also investigated.

EXPERIMENTAL

Materials and preparation of blends

The molecular characteristics, sources and codes of the polymers used in this study are listed in Table 1. Before blending, PVAc was purified according to a previously described procedure [1]. Binary blends were prepared by casting 10% (w/v) solutions of preweighed mixtures of PEO and PVAc in chloroform onto petri dishes at room temperature. To ensure complete removal of the solvent, the resulting powders were vacuum dried at 70° for 24 hr. Blend compositions studied were 40/60, 60/40, 70/30, 80/20, 90/10 and 100/0 wt% PEO/PVAc; the blends were examined at crystallization temperatures of 25°, 44° and 52°.

Investigation of morphology

The overall morphology of pure PEO and the PEO/PVAc blends in the form of thin films, obtained by solution casting, was investigated by optical microscopy using a Leitz Ultraphot microscope.

SAXS analysis

To prepare void-free samples, a necessity for small angle X-ray analysis, the dried blends and the pure PEO were compression moulded at 100 psi and 70° using a Carver press. The mould used was specifically designed for the Kratky SAXS apparatus in use here and contained a slot with dimensions of 0.75 × 3.5 cm with a depth of 2 mm. The mould containing the sample was sealed in aluminium foil and placed in a 70° bath for 10 min to allow melting of the sample. It was then rapidly transferred to crystallization baths at either 44 and 52° and maintained at this temperature for 5 and 26 hr, respectively. Previous work [1] has shown that these times are sufficient to ensure complete crystallization of the PEO/PVAc blends.

SAXS studies were carried out using a Kratky camera assuming infinite slit-height geometry. A Kratky Siemens Ag/Cu K_α copper target X-ray tube was used with a Philips

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Norelco generator operating at 40 KV and 20 mA. Data were collected using a Braun one dimensional position-sensitive detector. The raw scattering data were corrected for non-linearity of the detector, noise, and parasitic scattering using version 3 of Vonk's FFSAXS [8] computer program as described below.

Processing of SAXS data

Corrections of the SAXS data were made using the following procedure. Measurements of the scattering intensities of the samples as well as of the parasitic scattering obtained with no sample present, were made by dividing the detector wire into 102 channels. Each channel was calibrated by irradiating the wire uniformly with emissions from a ^{55}Fe source.

To perform quantitative analysis of the scattering arising from lamellar interference, the contribution to the scattering due to thermal density fluctuation within phases and to wide angle scattering (background scattering) must first be removed. In this study the background scattering was assumed constant with respect to the scattering vector s ($s = 2/\lambda \sin \theta$). Desmearing of the scattering curves was performed using the measured slit intensity profile [9]. The desmeared intensities were Lorentz factor corrected [10] by multiplying by s^2 . Guinier [12] has shown that the scattered intensity for an isotropic system can be represented by the following relation:

$$I(s) = \frac{i_e I_0}{p^2} \bar{\eta}^2 V_0 \int_0^\infty \gamma(r) \exp(2\pi i s r) dr \quad (1)$$

where

p = distance from the scattering material to the detector

i_e = Thompson scattering factor

I_0 = incident intensity

V_0 = volume of scattering system

and the three-dimensional correlation function, $\gamma(r)$, can be written as

$$\gamma(r) = \frac{\langle \Delta \eta_i \Delta \eta_k \rangle_r}{\bar{\eta}^2} \quad (2)$$

where $\Delta \eta_i$ is the deviation of the electron density of the i th volume element from the average, $\langle \rangle_r$ represents the average fluctuation over all volume elements separated by r and $\bar{\eta}^2$ is the mean square fluctuation at $r = 0$.

A Fourier transform of Eqn 1 enables one to solve for $\gamma(r)$ in terms of $I(s)$ obtaining

$$\gamma(r) = \frac{\int_0^\infty I(s) \cos(2\pi r s) ds}{\int_0^\infty I(s) ds} \quad (3)$$

The experimentally determined scattering intensity is for a three-dimensional system and must be corrected for comparison with scattering calculated for models containing a one-dimensional lamellar structure. This can be accomplished by multiplying $I(s)$ by s^2 (Lorentz correction).

The one-dimensional correlation function in the x direction is given by

$$\gamma(x) = \frac{\int_0^\infty s^2 I(s) \cos(2\pi x s) ds}{\int_0^\infty s^2 I(s) ds} \quad (4)$$

The general features of the one-dimensional correlation function as obtained from Eqn (4) are shown in Fig. 1a. The first maximum corresponds to the average value of the distance of periodicity. The interphase width, E , is reflected in the curvature of $\gamma(x)$ at the origin. It can be shown that the distance from the origin OR is equal to $E/3$ if

Fig. 1. One-dimensional correlation function, $\gamma(x)$, (solid line), vs correlation distance, x : (a) general features: R is denoted by the vertical line (—) and is at $x = E/3$; P and P' are the points at which the line R intersects the horizontal line (---) at $\gamma_{\min}(x)$ and $1/\gamma_{\min}(x)$ respectively; Q and Q' are the intersection points between the extrapolation of $\gamma(x)$ (·····) and $\gamma_{\min}(x)$ (---). (b) 90/10 wt% PEO/PVAc blend, $T_c = 44^\circ$.

the variation of the electron density in the interphase transition layer is linear (Fig. 2).

According to Vonk and Kortleve [13] a horizontal region in the first minimum of $\gamma(x)$ may be related to the degree of crystallinity, ϕ_s , using the expression:

$$\gamma_{\min}(x) = -\frac{1 - \phi_s}{\phi_s} \quad (5)$$

or

$$\gamma_{\min}(x) = -\frac{\phi_s}{1 - \phi_s} \quad (6)$$

where Eqn (5) applies when $\phi_s > 0.5$ and Eqn (6) applies when $\phi_s < 0.5$.

In Figure 1a the slope of the linear region in γ beyond $x = E$ and the lines PQ and P'Q', at the values

Fig. 2. Electron density profile of a lamella with transition layers; ρ_c and ρ_a are the electron densities of the crystalline and amorphous phases respectively.

$\gamma(x) = \gamma_{\min}(x)$ and $\gamma(x) = (\gamma_{\min}(x))^{-1}$ respectively, can be used to find the total average thicknesses of the amorphous and crystalline layers $\langle t_a \rangle_n$ and $\langle t_c \rangle_n$ using the relations

$$PQ = \langle t_a \rangle_n - \frac{\langle E \rangle}{3(1 - \phi_s)}; \quad P'Q' = \langle t_c \rangle_n - \frac{\langle E \rangle}{3\phi_s} \quad (7)$$

These relations are valid only for a one dimensional structure with n alternating parallel crystalline and amorphous lamellae. The average crystalline thickness $\langle C \rangle_n$ and the average amorphous thickness $\langle A \rangle_n$ can now be easily obtained using the relations (Fig. 2)

$$\langle C \rangle_n = \langle t_c \rangle_n - \langle E \rangle_n \quad (8)$$

$$\langle A \rangle_n = \langle t_a \rangle_n - \langle E \rangle_n \quad (9)$$

where E is the interphase width.

The model used in the present work to describe the scattering from a lamellar structure is the lamellar pseudo two-phase structure discussed by Vonk [11]. A lamellar pseudo two-phase structure is defined as consisting of alternating parallel crystalline and amorphous lamellae connected by transition layers which are placed in stacks large enough not to perturb the small angle X-ray scattering. The profile of electron density for the model is shown in Fig. 2. The variation of the electron density is assumed to be linear. As reported by Vonk [11] the density profile of the lamellae can be considered as the convolution of the profile of a true two phase structure of crystallinity ϕ_s with a "pseudo top-hat" function of width E .

The above description is qualitatively consistent with (for example) the experimental curve for the 90/10 wt% PEO/PVAc blend shown in Fig. 1b.

RESULTS AND DISCUSSION

Morphology

PEO may crystallize from the melt in a spherulitic, hedritic or intermediate spherulitic-hedritic morphology depending on crystallization conditions and molecular weight [14, 15]. The principal features of these morphologies are summarized in Refs 16 and 17.

A complete study of the influence of molecular mass and crystallization conditions on the molecular superstructure of PEO has been reported by Mandelkern [14]. For a given molecular mass, the formation of hedritic crystals was favoured by decreasing the undercooling. In particular the morphological maps presented in Ref. 14 predict an intermediate spherulitic-hedritic morphology for PEO samples having a molecular weight of 20,000 daltons and crystallized at temperatures ranging from room temperature to 52°, conditions similar to those used in the present study.

Optical micrographs of thin films of pure PEO are shown in Fig. 3. It can be seen that the PEO

used in this study crystallizes with an intermediate spherulitic-hedritic morphology similar that described by Mandelkern [14]. It should be noted that PEO crystallizes with a morphology in which spherulites are predominant when the samples are not isothermally crystallized. Figure 3a shows Maltese crosses and fibrous crystals radiating from a central point, characteristics of spherulites, together with

Fig. 3. Light micrographs of thin films of pure PEO; (a) T_c = room temperature; (b) T_c = 44°; (c) T_c = 52°.

Fig. 4. Light micrographs of thin films of 80/20 wt% PEO/PVAc (a) $T_c = 44^\circ$; (b), (c) $T_c = 52^\circ$.

concentric rings indicating step-like growth of the structure, characteristic of hedrites. As the crystallization temperature is increased (Figs 3b and 3c) the formation of PEO crystals in which hedrites predominate is favoured. The Maltese cross birefringence pattern is lost and step growth is shown clearly by the presence of hexagonally shaped cracks on the film surface. It should be noted that some fibrils radiating from central points are still present. The addition of PVAc to PEO appears to favour the spherulitic morphology (Figs 4 and 5). In fact, for blends containing 20 wt% PVAc, the hedritic character is clearly observed only for the sample crystallized at 52° (Figs 4b and c). In this sample the concentric arrangement is retained and the Maltese cross birefringence is eliminated if the film is rotated 90° under the microscope. For blends containing 60 wt% or more PVAc, the PEO always crystallizes with an almost complete spherulitic morphology independent of crystallization temperature (Fig. 5c). The crystals in these blends become more heavily dendritic in character, and their interfibrillar regions appear to

increase in size. Another interesting feature is that the blend samples are always completely volume filled with the PEO crystalline superstructure truncated by impingement. There is no evidence that the non-crystallizable component segregates in large domains in intraspherulitic regions or in interspherulitic contact zones exceeding the dimensions corresponding to the resolving power of the technique used. This result and the fact that the spherulites in blends containing high wt% PVAc are more open and coarse, suggest that in these blends PVAc is present only in interfibrillar and interlamellar regions of PEO crystals. This hypothesis is confirmed by the SAXS analysis presented in the following section.

SAXS results

Lorentz corrected desmeared patterns for the 90/10 wt% PEO/PVAc blends crystallized at 44° and 52° are shown in Figs 6 and 7 respectively. Using Bragg's law, long periods, L , calculated from the peak positions were obtained for all samples. The

Fig. 5. Light micrographs of thin films of PEO/PVAc blends (a) PEO/PVAc 60/40 wt%, $T_c = 52^\circ$; (b) PEO/PVAc 60/40 wt%, $T_c = 44^\circ$; (c) PEO/PVAc 40/60 wt%, $T_c = 44^\circ$.

Fig. 6. Lorentz corrected desmeared intensity vs s for the 90/10 wt% PEO/PVAc blend crystallized at $T_c = 44^\circ$.

values of L as a function of composition for the two crystallization temperatures investigated are plotted in Fig. 8. As shown in this figure for blends crystallized at 52° , L increases markedly with increasing PVAc content. For blends crystallized at 44° , a minimum corresponding to 80/20 wt% PEO/PVAc is shown. The occurrence of this minimum may be explained by the fact that the crystallization for pure PEO and for 90/10 wt% PEO/PVAc began when the sample started to cool—at a temperature higher than 44° . The position of the first maximum in the one dimensional correlation function calculated as discussed above is also shown in Fig. 8 and good agreement with the values of the long period is observed. It should be noted that, for 70/30 and 60/40 wt% blends crystallized at 44° , the correlation functions were so diffuse that no peak was observed.

In the present experiments no well defined horizontal region could be observed in the first minimum of the one dimensional correlation function (Fig. 1b). In fact, as shown in Fig. 1b, the wings of the first maximum overlap part of the minimum and hence the apparent value of $\gamma_{\min}(x)$ is too high and cannot be used in Eqns 5, 6 and 7. This obstacle can be

Fig. 7. Lorentz corrected desmeared intensity vs s for the 90/10 wt% PEO/PVAc blend crystallized at $T_c = 52^\circ$.

Fig. 8. Long distance periodicity, P (Å) vs blend composition: $\circ, \bullet$ Long period from Bragg's law; $\square, \blacksquare$ Correlation function peak position.

overcome by substituting the crystallinity, ϕ_s , obtained by DSC, in Eqns 5 and 6. Thus a theoretical value of $\gamma_{\min}(x)$ was used to obtain the lines PQ and P'Q' in Fig. 1b instead of the experimentally determined value. When using this procedure, it is assumed that all amorphous material is located in the interlamellar regions and that the densities of the PEO crystalline and amorphous phases and those of PVAc are the same.

Using the relations described in the previous section, the average size of the crystalline $\langle C \rangle_n$ and amorphous $\langle A \rangle_n$ regions and of the transition layer $\langle E \rangle_n$ are obtained and are shown in Figs 9–11. These parameters depend on T_c and composition.

The average crystalline thicknesses $\langle C \rangle_n$ are within experimental error for the sample crystallized at 52° with no dependence on PVAc content (Fig. 9). For the samples crystallized at 44° , $\langle C \rangle_n$ decreases upon addition of 10 wt% PVAc to PEO; further addition of PVAc does not significantly modify the value of $\langle C \rangle_n$.

The average interlamellar amorphous thickness, $\langle A \rangle_n$, for a given T_c , increases monotonically with

Fig. 9. Average crystal thickness, $\langle C \rangle_n$, vs blend composition.

Fig. 10. Average amorphous interlamellar thickness, $\langle A \rangle_n$, vs composition.

increasing wt% PVAc (Fig. 10); on the other hand for a given composition, $\langle A \rangle_n$ is greater for the higher crystallization temperature investigated. In addition, the average interphase thickness increases with increasing wt% PVAc (Fig. 11). It is interesting to note that there is no dependence of the interface thickness on T_c .

According to the model used, the increase of the long period, L , with composition is due to the increase in the interlamellar amorphous phase and the interphase thicknesses and is believed to be caused by the inclusion of some of the PVAc between crystalline lamellae in both the interlamellar amorphous regions and interphase zones.

If all the PVAc added to PEO were in the interlamellar regions ($A + E$), the values of the long period of the PEO crystallized from the blend, L_{calc} could be predicted by the following relation, assuming volume additivity

$$L_{\text{calc}} = \frac{L_0}{V_2} \quad (10)$$

Fig. 11. Average interphase thickness, $\langle E \rangle_n$, vs composition

Table 1. Characteristics of polymers used in the present investigation

Polymer	Source and trade name	Molecular mass
Poly(ethylene oxide) (PEO)	PEO 2 (Fluka AG)	$\bar{M}_n = 20,000^*$
Poly(vinyl acetate) (PVAc)	PVAc K40 (Montedison)	$\bar{M}_n = 64,000^\dagger$

*Determined by measuring the intrinsic viscosity in water at 30° using the equation [5]: $[\eta](dl/g) = 1.25 \times 10^{-4}(\bar{M}_n^{0.78})$.

†Determined by measuring the intrinsic viscosity in acetone at 25° using the equation [6]: $[\eta](dl/g) = 2.14 \times 10^{-5}(\bar{M}_n^{0.68})$.

where V_2 is the volume fraction of the crystallizable material in the blend and L_0 is the long period of the pure PEO obtained experimentally. The above relation is valid when a one-dimensional model of alternating crystalline and amorphous lamellae is considered. As shown in Table 2, the calculated values, L_{calc} , are always higher than the experimentally determined values, L , indicating that PVAc is not present between the lamellae.

In considering these results and the observation that for any composition and T_c studied the PEO crystalline superstructures are volume filling, it can be deduced that some PVAc is present in the interfibrillar regions; as the PVAc content in the blend increases, the amount of PVAc in the interfibrillar regions increases. This is confirmed by the increase in coarsening of the spherulite fibrils observed in blends containing a high wt% PVAc.

To study the morphology of semicrystalline blends, the Keith and Padden rejection or δ parameter [2] has been often used. δ is defined as D/G , where D is the diffusion rate of the non-crystallizable component in the melt and G is the spherulitic growth rate of the crystallizable polymer. δ , which has units of length, is related to the location of the non-crystallizable component. Qualitatively a value of δ smaller than the interlamellar region implies that the non-crystallizable polymer is trapped between the crystalline lamellae. If δ is larger than the interlamellar amorphous regions but smaller than the interfibrillar regions, the amorphous material is present mainly in interfibrillar spherulitic regions. For very high δ values, the non-crystallizable material segregates in interspherulitic regions. Assuming that D is dependent only on temperature, δ is inversely proportional to the spherulitic growth rate at a given temperature.

In the case of the PEO/PVAc blends, G was found to decrease with increasing PVAc content. The morphologies of PEO/PVAc blends observed using SAXS and light microscopy can now be interpreted in terms of the δ parameter: because of the relatively high

Table 2. Comparison of the long period, L_{calc} , calculated by assuming all the PVAc to be interlamellar, with L , obtained applying Bragg's law to experimental data for samples crystallized at 52°

Composition	L_{calc}	L
PEO 100%	354	354
PEO/PVAc 90/10	393	359
PEO/PVAc 80/20	442	363
PEO/PVAc 70/30	505	390
PEO/PVAc 60/40	590	440

value of G , at low PVAc content δ is smaller than the interlamellar region where PVAc is essentially found. With increasing PVAc content, the growth rate decreases causing an increase in δ . A blend composition exists (most likely between 30 and 40% wt% PVAc) for which δ equals the length of the interlamellar regions. At this composition the amorphous material also begins to segregate in the interfibrillar regions.

It should be noted that δ is dependent also on possible specific interactions existing between the two polymers. In particular, favourable specific interactions between the two components should increase the T_g of the system and hence decrease both D and G .

CONCLUSION

Analyses of PEO/PVAc blends using light microscopy and SAXS appear to be consistent with the model of a pseudo-lamellar structure consisting of crystalline lamellae separated by amorphous and transition regions containing PEO and PVAc. On the other hand the coarsening of the PEO spherulites, observed especially for blends with greater wt% PVAc and the low values of long periods obtained experimentally compared with calculated values, indicate that some of the non-crystallizable material is also present in interfibrillar regions. For blends containing high wt% PVAc, the relatively low spherulitic growth rate could be responsible for such an interfibrillar segregation of PVAc, in agreement with the Keith and Padden rejection parameter (δ).

In conclusion, this work has shown that the use of the one dimensional correlation function in the analysis of small angle X-ray patterns in conjunction with a detailed study using light microscopy is a simple method that can provide information on the overall morphology of polymeric blends containing

a semicrystalline component and an amorphous component.

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