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Effects of entrapment on spherulite morphology and growth kinetics in poly(ethylene oxide)/epoxy networks

Yin Ping Huang, E.M. Woo*

Department of Chemical Engineering, National Cheng Kung University, Tainan 701-01, Taiwan, ROC

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Abstract

Poly(ethylene oxide) (PEO) is known to be miscible with diglycidylether bisphenol-A (DGEBA)/4,4′-diamino diphenylsulfone (DDS) epoxy system before and after cure. As PEO starts to crystallize in the miscible mixtures (either uncured liquid or cured network), entrapment and interactions between the species can play an important role on the growth kinetic and lamellar/spherulitic morphology. Thermal analysis, growth kinetics analysis, and morphology characterization were performed on a PEO-epoxy system, and the results were found to be useful in providing critical interpretation. In general, entrapment between the growing species and epoxy/DDS was found to be more extensive in the uncured system. In addition, the interactions between the species are different before and after cure. The interactions between PEO and epoxy/DDS become less in the cured networks. The morphology and growth kinetics of the PEO crystals was in turn affected by the contents and chemical structures (functional group, molecular weight, crosslink, etc.) of the amorphous diluents (i.e. epoxy/DDS). The morphology of PEO in the cured PEO/epoxy system is quite similar to that observed in the neat PEO. This study attempted to offer a molecular microscopic view on commonly observed depression of growth kinetics of semicrystalline polymers in the presence of a diluent (an amorphous polymer or other non-crystallizing species) © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene oxide); 4,4′-Diamino diphenylsulfone; Epoxy

1. Introduction

Poly(ethylene oxide) (PEO), owing to a relatively simple structure and capability of packing into crystals to form a semicrystalline polymer, is widely studied as a model system. Miscibility of PEO with poly(methyl methacrylate) (PMMA) have been widely documented [1–7]. PEO contains an ether (–O–) group in the main chain while PMMA possesses a carboxyl (–COO–) group in its pendant position. Other than the well known miscibility in the classical PEO/PMMA system that has been extensively documented, PEO is immiscible with most other methacrylic polymers, such as poly(propyl methacrylate), poly(butyl methacrylate), poly(cyclohexyl methacrylate), etc., or with any of polyacrylates. Our earlier investigations pointed out that there might be likely a window of acrylic structures within which PEO may be miscible with certain other acrylic-type polymers. As a result, it has been recently discovered that PEO is miscible with two other methacrylate polymers: poly(phenyl methacrylate) and poly(benzyl methacrylate) [8,9]. In the cases of miscible PEO/PMMA PEO/PBzMA, or PEO/PPhMA, there are no strong specific interactions. Nevertheless, PEO is also known to form a homogeneous mixture with other polymers through specific interactions. PEO is known to be miscible with a few polymers that contain groups capable of forming intermolecular hydrogen bondings with PEO. Examples include miscible blends of PEO with phenoxy [10], poly(acrylic acid) [11], poly(methacrylic acid) [12], etc. More recently, PEO has been proven to form a miscible blend with poly(vinyl phenol), a polymer containing an –OH group on its pendant phenyl [13].

In addition, issues of miscibility and phase behavior of PEO in crosslinked thermosetting polymers, such as epoxy or phenolic systems, have been of interests. Upon co-curing, PEO is miscible with a crosslinked diglycidylether bisphenol-A (DGEBA) epoxy cured with an aromatic amine, 4,4′-diamino diphenylsulfone (DDS) by forming interpenetrating network with crosslinked epoxy [14]. Guo et al. reported immiscibility in an cured PEO/epoxy system; however, the DGEBA epoxy in their study was cured with an aliphatic amine (tetraethylenepentamine, TEPA) [15]. In addition, PEO has also been reported to be miscible with thermosetting novolac resins [13,16].

* Corresponding author. Tel.: +886-6-275-7575, ext. 6270, fax: +886-6-234-4496.

E-mail address: emwoo@mail.ncku.edu.tw (E.M. Woo).

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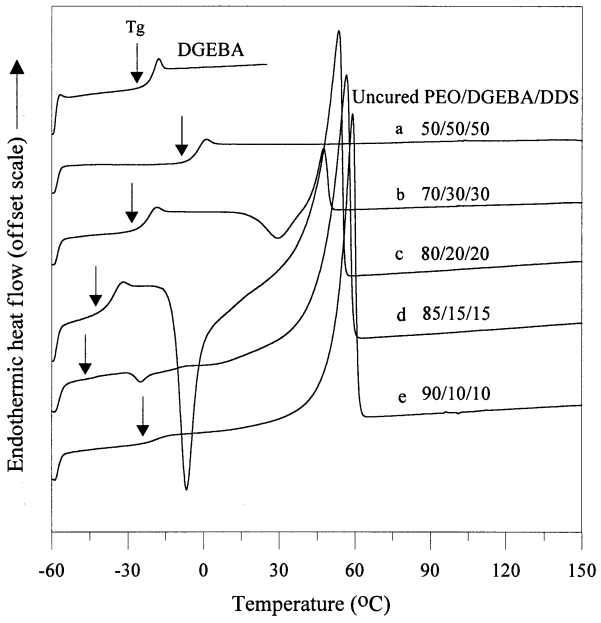

Fig. 1. DSC thermograms revealing only one apparent T_g in all uncured mixtures: (a) 50/50/50, (b) 70/30/30, (c) 80/20/20, (d) 85/15/15, and (e) 90/10/10 (in wt. ratios).

Extensive hydrogen bonding or other specific interactions between the ether (–O–) of PEO and –OH of the epoxy chains can be expected to help ensure a uniform distribution of linear PEO chains in the crosslinked networks. Epoxy resins undergo significant chemical reactions in transforming from an uncured liquid mixture to a finally crosslinked network. Interactions between the PEO and epoxy molecules are thus different depending on the state of curing. PEO crystallization is always critical in understanding the phase behavior and morphology. The objective of this study was to investigate PEO growth kinetics and morphology as influenced by the state of cure in a crosslinking system. Interactions (between PEO and epoxy) and molecular weights of epoxy both change dramatically as a result of cure. Extents of entrapment of molecular species between the growing lamellae (or fibrilla) are thus varying with the state of cure. Influences on the morphology, growth kinetics of PEO, and effect on the thermal behavior of the blends (uncured PEO/epoxy mixtures and cured networks) were the main focus of this study.

2. Experimental

2.1. Materials and sample preparation

PEO was obtained from a specialty polymer supplier (Alderich) with $M_v = 2 \times 10^5$ g/mol, $T_g = -60$°C, $MP =$ 6267°C (manufacturer's data), and it was used as-received. DGEBA was obtained from Fluka with an epoxide equivalent weight of 178 g (or a degree of polymerization, $n = 0.04$). The epoxy or epoxy/PEO mixtures were crosslinked (cured) with DDS was supplied by Ciba-Geigy as HT-976, which has an H-equivalent weight of 62 g.

PEO/DGEBA mixtures were first prepared by solution-blending using dichloromethane (CH_2Cl_2). The solvent in the liquid mixtures was first vaporized under a hood at a controlled temperature, followed by final solvent removal in a vacuum oven for 72 h at 60–70°C. After drying off the solvent, DDS was introduced into PEO/epoxy mixtures in a mold kept at 120°C. The PEO/epoxy/DDS mixtures were then melt-mixed thoroughly until they appeared homogeneous. The PEO/epoxy/DDS mixtures were then cured at designated curing temperatures for a fixed time. Both uncured mixtures and cured solids were examined.

2.2. Apparatus

The glass transition temperatures and other thermal transitions of neat polymers and their blends were measured with a differential scanning calorimeter (Perkin-Elmer DSC-7) equipped with a mechanical intracooler and a computer for data acquisition/analysis. Sub-ambient DSC runs (temperatures lower than −50°C) were cooled with a liquid nitrogen tank and helium gas purge. All T_g measurements were made at a scan rate of 20°C/min, and T_g was taken as the onset of the transition (change of the specific heat) in the DSC thermograms.

A polarized-light optical microscope (Nikon Optiphot-2, POL) was used for examining preliminary phase structure. The blends were cast as thin films on glass slides, dried properly in a temperature-controlled oven before they were examined using the optical microscope. For comparison, samples for optical examination were prepared using the same solvents and casting temperature as those used in preparing the thermal analysis samples. Furthermore, to evaluate effects of miscibility on crystallization, the spherulitic growth rates of neat PEO in comparison to PEO in the PEO/epoxy networks were estimated using the polarized-light optical microscope (POM) equipped with CCD television camera. The spherulitic growth rate studies were investigated by placing samples on a heating stage (Linkam THMS-600 with TP-92 temperature programmer). Thin cast-films were sandwiched between two glass slides and first melted on a hot stage at 85–90°C for 5 min, and then transferred to another hot stage at a pre-determined T_c as quickly as possible. Growth of spherulites was monitored on screen and recorded on a cassette, which could be played back for re-examination. The video pictures could also be temporarily frozen for measuring the growth rate. A micrometer was used to calibrate the magnification of the video pictures. At low temperatures, the crystallization/growth rates were relatively slow, and the spherulites were measured by taking the camera photos at periodic times. Good agreement was found between these two methods (camera-shot photos vs. video recording). At high growth rates, however, only video recording/play-back was used for more accurately monitoring the dynamic changes.

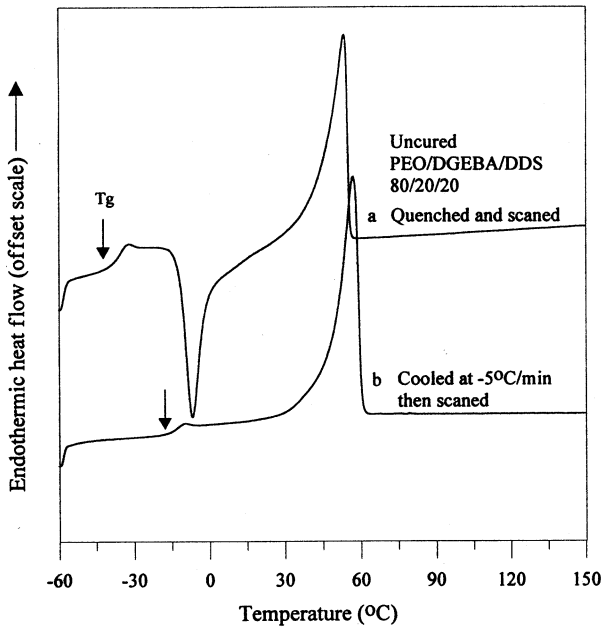

Fig. 2. T_g and T_m comparisons for uncured mixture of 80/20/20 (PEO/DGEBA/DDS) subjected to two different thermal treatments: (a) quenched then scanned, (b) cooled slowly at −5°C/min then scanned to reveal T_g.

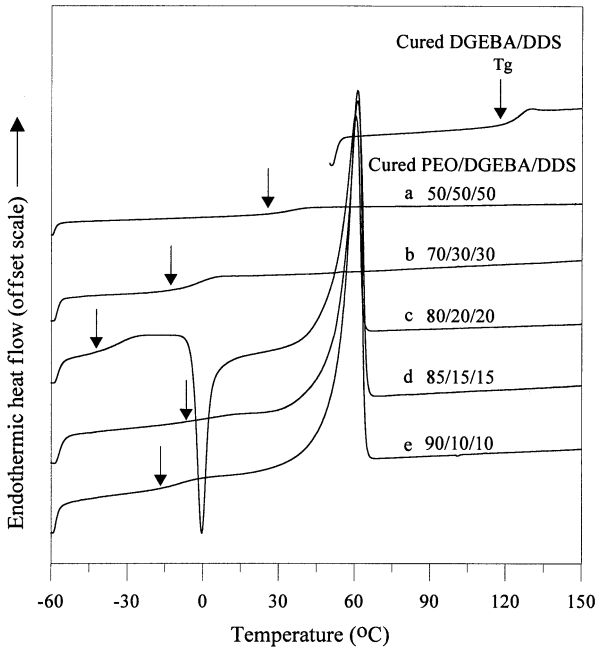

Fig. 3. DSC analysis result for the cured PEO/DGEBA/DDS networks: (a) 50/50/50, (b) 70/30/30, (c) 80/20/20, (d) 85/15/15, and (e) 90/10/10 (wt. ratios).

3. Results and discussion

3.1. Glass transitions of PEO-epoxy mixtures

The PEO/DGEBA/DDS mixtures and cured networks have been proven to be miscible as reported in the literature [14]. Phase morphology of all uncured PEO/DGEBA/DDS mixtures or their cured networks used in this study was again examined using POM. No discernible domains were found, and all samples appeared to be optically clear as far as the maximum magnification could tell. Their glass transitions and thermal behavior were investigated. DSC analysis was performed on the samples to reveal their glass transition behavior. For a uniform thermal history in all samples, the thermograms are the results of second runs after quenching from temperatures just above T_g. Fig. 1 shows DSC thermograms revealing only one apparent T_g in all uncured mixtures. The PEO/DGEBA/DDS compositions examined were (a) 50/50/50, (b) 70/30/30, (c) 80/20/20, (d) 85/15/15, and (e) 90/10/10 (in wt. ratios). All thermograms clearly show that there is only one T_g for each composition, and that the only T_g is composition-dependent. By applying the conventional T_g criterion for determining phase miscibility, the uncured PEO/epoxy mixtures are apparently homogeneous showing only one phase. The neat PEO possesses a low T_g of −60°C. Expectedly, at increasing PEO content in the mixtures, T_g should be decreasing. This is indeed the observed trend as long as the crystallinity of PEO in the PEO/epoxy mixtures could be suppressed by fast-quenching, e.g. for Cases a–d in Fig. 1. The suppression of PEO crystallinity is evidenced by appearance of a significant crystallization exotherm following the T_g transition in the mixture during scanning. At a high PEO content, e.g. Case (e) of Fig. 1, the decreasing trend in T_g of the mixtures is reversed. T_g of the 90/10/10 (PEO/DGEBA/DDS) mixture is −22°C, while that of the 80/20/20 (PEO/DGEBA/DDS) mixture is lower at −45°C. It must be noted that the 90/10/10 (PEO/DGEBA/DDS) mixture does not show evidence of suppressed PEO crystallinity upon quenching. It suggests that a significant percentage of PEO remained in distinct crystalline domains in the 90/10/10 (PEO/DGEBA/DDS) mixture and did not dissolve into the mixture at all. This might lead to a much lower actual content of PEO in the amorphous region of the 90/10/10 (PEO/DGEBA/DDS) mixture, leading to an apparently higher T_g than what would be expected from the apparent composition. We will provide further evidence in later sections.

Fig. 2 shows the T_g and T_m comparisons as revealed in the DSC thermograms for samples of uncured mixture of 80/20/20 (PEO/DGEBA/DDS) that have been subjected to two different thermal treatments: (a) quenched then scanned, (b) cooled slowly at −5°C/min then scanned to reveal T_g. The PEO crystallinity in the mixture of 80/20/20 (PEO/DGEBA/DDS) could be suppressed as long as a fast-quenching (from above the melt to below T_g) was imposed prior to DSC scanning. The quenched mixture (with all PEO remaining in the amorphous region) exhibited a T_g of about −45°C. However, the slow-cooled mixture (cooled at −5°C/min from above the melt) allowed growth of segregated PEO crystalline domains, which led to a much reduced PEO content in the amorphous region of the mixture. The observed T_g is about −20°C for the slow-cooled mixture. This comparison demonstrates the effect of unsuppressed

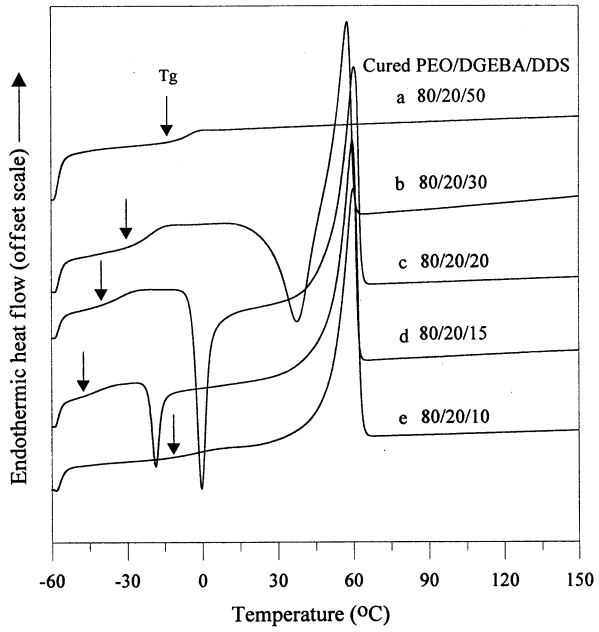

Fig. 4. DSC analysis result for the cured PEO/DGEBA/DDS networks: (a) 80/20/50, (b) 80/20/30, (c) 80/20/20, (d) 80/20/15, and (e) 80/20/10.

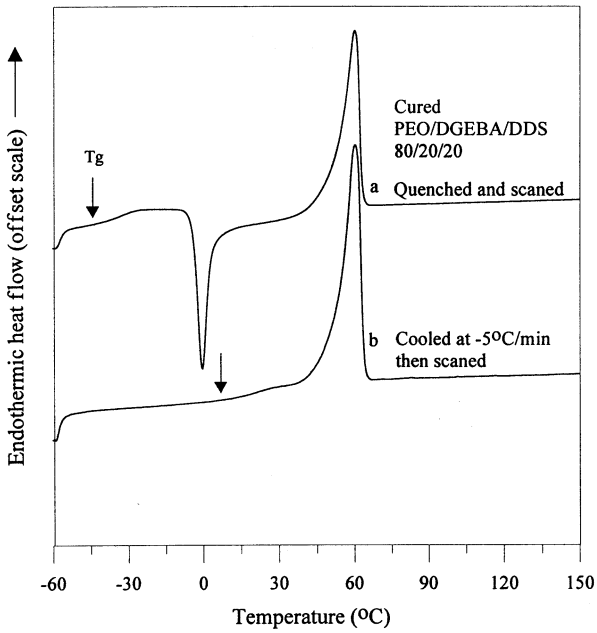

Fig. 5. T_g and T_m comparisons for cured PEO/DGEBA/DDS (80/20/20) samples subjected to two different thermal treatments: (a) quenched then scanned, (b) cooled slowly at −5°C/min then scanned to reveal T_g.

crystallinity on the glass transition behavior of blends or polymer mixtures. Evidently, the quenching and suppression of crystallinity in the PEO/DGEBA/DDS (80/20/20) mixture led to intimately mixing on a molecular scale between the PEO chains and epoxy/DDS molecules. In addition, specific interactions may be expected owing to extensive sites available for H-bondings between the ether group of PEO and the hydroxyl or amine groups in epoxy/DDS. Growth of PEO in the uncured mixture may lead to a more evident extent of entrapment of epoxy/DDS species within the PEO lamellar bundles. In addition, the figure also shows that the T_m of PEO in the quenched PEO/DGEBA/DDS mixture is significantly lower than that in the slow-cooled sample. This fact suggests a more severe disruption of PEO lamellae in the quenched sample.

Glass transition behavior of the cured PEO/epoxy networks (177°C, 4 h) was next examined. Fig. 3 shows DSC analysis result for the cured PEO/DGEBA/DDS networks. The compositions examined were (a) 50/50/50, (b) 70/30/30, (c) 80/20/20, (d) 85/15/15, and (e) 90/10/10. All thermograms clearly show that there is only one T_g for each composition of cured PEO/epoxy networks, and that the only T_g is composition-dependent. By applying the conventional T_g criterion for determining phase miscibility, the cured PEO/epoxy mixtures are apparently homogeneous. It suggests that if one disregards the crystalline domains, the linear PEO chains distribute evenly throughout the crosslinked epoxy network. Again, if a significant percentage of PEO remains in distinct crystalline domains in the cured 90/10/10 (PEO/DGEBA/DDS) network (DSC Trace-e), it leads to a much lower actual content of PEO in the amorphous region of the 90/10/10 (PEO/DGEBA/DDS) network. The cure network exhibits a higher T_g than what would be expected from the apparent composition.

The previous figure shows that T_g of the cured PEO/epoxy networks decreases with increasing PEO contents. Similarly, a decrease in the crosslinking density also leads to a lower T_g. Fig. 4 shows the DSC analysis result for the cured PEO/DGEBA/DDS networks, whose compositions (in decreasing contents of DDS) were: (a) 80/20/50, (b) 80/20/30, (c) 80/20/20, (d) 80/20/15, and (e) 80/20/10. All thermograms show that there is only one T_g for each composition of cured PEO/epoxy networks, and that the only T_g decreases with lowering the DDS content. Again, the result suggests that the linear PEO chains distribute evenly throughout the cross-linked epoxy network for all compositions investigated here.

Again, suppression of PEO crystallinity and entrapment of epoxy within the growing PEO lamellar bundles were investigated by comparing the thermal transitions. Fig. 5 shows the T_g and T_m comparisons as revealed in the DSC thermograms for cured PEO/DGEBA/DDS (80/20/20) samples that have been subjected to two different thermal treatments: (a) quenched then scanned, (b) cooled slowly at −5°C/min then scanned to reveal T_g. The PEO crystallinity in the cured PEO/DGEBA/DDS network could be effectively suppressed as long as a fast-quench scheme (from above the melt to below T_g) was imposed prior to DSC scanning. The quenching led to all PEO remaining in the amorphous region and the sample exhibited a T_g of about −45°C. However, the slow-cooled sample (cooled at −5°C/min from above the melt) allowed growth of segregated PEO crystalline domains. The observed T_g is about 0°C for the slow-cooled sample. Again, it demonstrates the

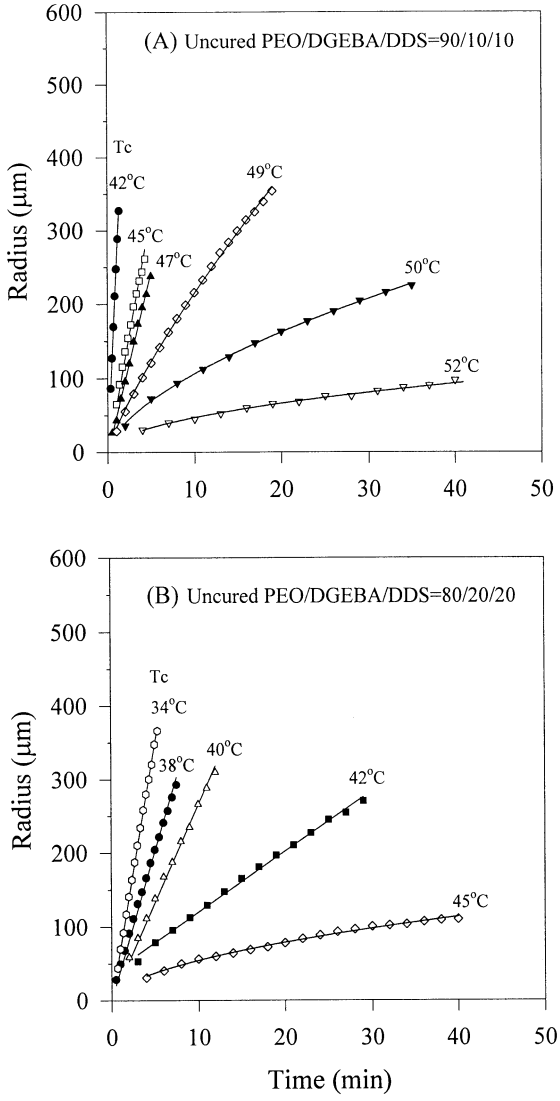

Fig. 6. Spherulite growth rates measured for uncured PEO/DGEBA/DDS mixtures: (A) 90/10/10, and (B) 80/20/20, as a function of time.

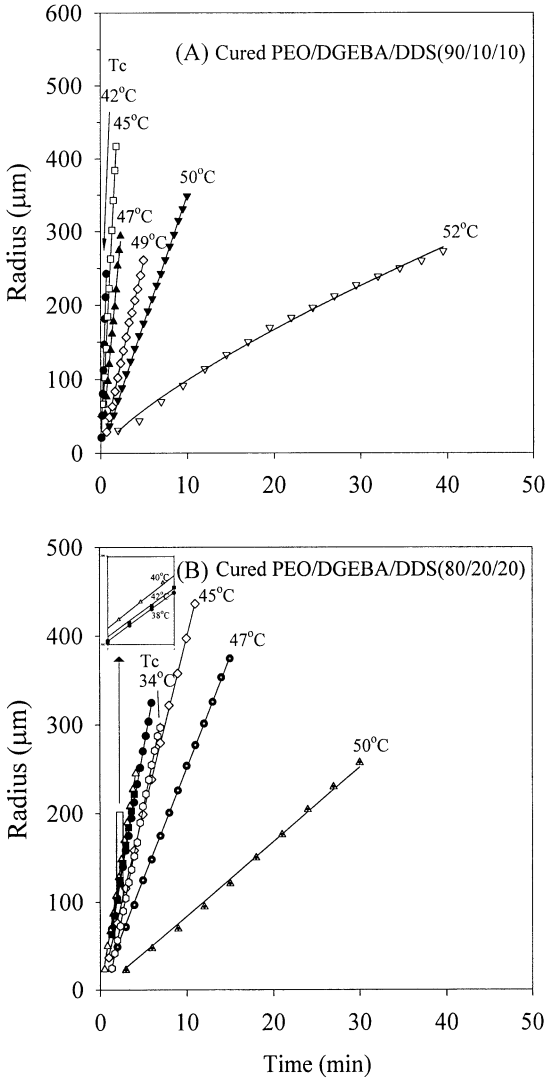

Fig. 7. Growth rates measured for cured PEO/DGEBA/DDS: (A) 90/10/10 and (B) 80/20/20, as a function of time.

effect of unsuppressed crystallinity on the glass transition behavior. In addition, the figure also shows that T_m of PEO in the quenched PEO/DGEBA/DDS is comparable with that in the slow-cooled sample. This is different from the observation in the case of uncured PEO/DGEBA/DDS mixture (Fig. 2), in which the T_m differed more significantly between the quenched and slow-cooled samples. This suggests that entrapment and disruption of PEO lamellae may be comparatively less in the cured PEO/epoxy system than that in the uncured PEO/DGEBA/DDS mixture. More data and interpretation will be offered in later sections.

3.2. Spherulitic growth in uncured vs. cured networks

Spherulitic growth and morphology for all mixture compositions were observed at isothermal temperatures in the range 42–52°C. The growth rate was measured for the neat PEO and PEO/epoxy mixtures. All compositions showed a growth pattern that was dependent on the temperature and compositions. For brevity, micrographs are not shown, but the growth rates were plotted as a function of time. Fig. 6A and B shows the growth rates measured for: (A) uncured PEO/DGEBA/DDS (90/10/10) and (B) 80/20/20 mixtures as a function of time. Both exhibited a similar growth pattern that the growth is quite linear with respect to time at the lower temperature range, but becomes nonlinear at higher temperature range.

The growth patterns in the cured networks were then examined within a range of temperature. Fig. 7A and B shows the growth rates measured for: (A) cured PEO/DGEBA/DDS (90/10/10), and (B) 80/20/20 mixtures as a function of time. The temperature of observation is as indicated directly on the curves. The cured PEO/epoxy network exhibited a growth pattern that is comparatively more linear with respect to time than the uncured counterpart, suggesting a possibility that interactions between PEO and the

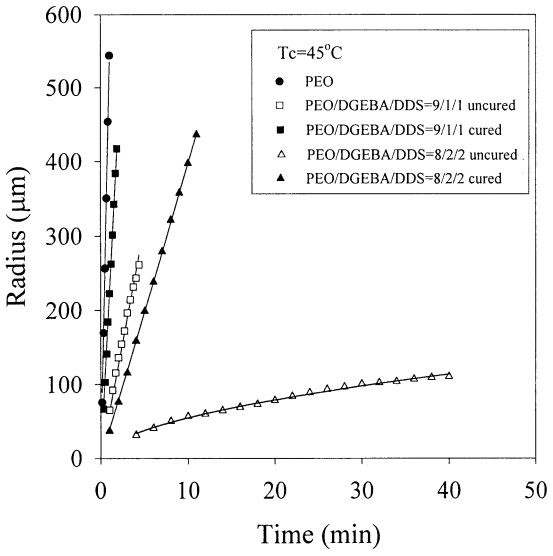

Fig. 8. Dimension of PEO spherulites as a function of time for uncured PEO/DGEBA/DDS and cured counterparts of three different compositions: 100/0/0 (i.e. neat PEO), 90/10/10, and 80/20/20.

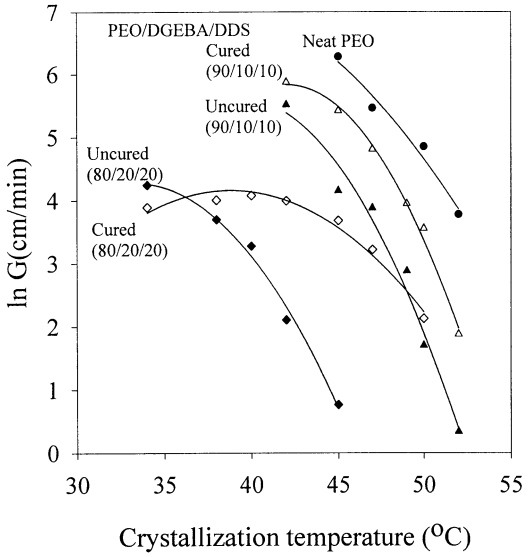

Fig. 9. Growth rates (in natural logarithm scale) as functions of temperature of crystallization for PEO spherulites in the uncured PEO/DGEBA/DDS and cured counterparts of three different compositions: 100/0/0 (i.e. neat PEO), 90/10/10, and 80/20/20.

epoxy molecules might be different between the uncured mixtures and cured networks.

It is evident that the slope (growth rate) of the curves becomes lower upon increasing the epoxy/DDS content, indicating a reduction in growth rates on introducing miscible amorphous epoxy/DDS component to the crystallizing PEO polymer. For an overall comparison showing the effects of composition and the cure state on the PEO growth. A fixed temperature was chosen as an example of comparison. The radius of PEO spherulites was plotted as a function of time of crystallization (at 45°C) for each of the compositions. Fig. 8 shows the radius of the PEO spherulites as a function of time for uncured PEO/DGEBA/DDS and cured counterparts of three compositions: 100/0/0 (i.e. neat PEO), 90/10/10, and 80/20/20. Two distinct features are observed in the figure. Firstly, the growth rates for the cured system are faster and more linear than for the uncured counterparts. Secondly, the growth rates decrease with increasing contents of epoxy/DDS in the uncured mixtures or in the cured networks. The linear dependence of the growth rates in cured PEO/epoxy networks implies that the epoxy was more completely rejected from the crosslinked miscible PEO/epoxy networks. By comparison, rejection of epoxy molecules from the uncured mixtures was less likely or less completely owing to stronger interactions between the PEO and epoxy/DDS molecules. The stronger interactions and greater entrapment of the epoxy/DDS molecules between the growing fibrils or lamellae of the PEO spherulites apparently led to slower growth rates.

Fig. 9 shows the growth rates (in natural logarithm scale) as functions of temperature of crystallization for PEO spherulites in the uncured PEO/DGEBA/DDS and cured counterparts of three different compositions: 100/0/0 (i.e. neat PEO), 90/10/10, and 80/20/20. Apparently, the PEO growth rate in the cured system is faster than that in the uncured counterparts when compared at the same temperature of crystallization.

3.3. Growth kinetics analysis

Lauritzen-Hoffman theory [17,18] is often used to analyze the experimental results of crystal growth of semicrystalline polymers. Lauritzen-Hoffman equation commonly is expressed as following:

$$G = G_0 \, exp\left(\frac{-\Delta F^*}{RT_c}\right) \exp\left(\frac{-\Delta\phi^*}{K_B T_c}\right). \tag{1}$$

This theory has been extended to describing the crystallization kinetics in semicrystalline/amorphous blend systems [19–23]. For a polymer (2)-diluent (1) system, it is modified as [24]:

$$G = v_2 G_0 \, exp\left(\frac{-\Delta F^*}{RT_c}\right) \exp\left(\frac{-\Delta\phi^*}{K_B T_c}\right), \tag{2}$$

where v_2 is the PEO volume fraction, G_0 a pre-exponential factor assumed to be constant or proportional to T_c, K_B the Boltzman constant, ΔF^* the activation energy for the transport of the crystal and $\Delta\phi^*$ is the free energy required to form a nucleus of critical size. In Eq. (2), the terms in the exponent are related as:

$$\Delta F^* = \frac{U^* T_c}{T_c - T_\infty}, \tag{3}$$

$$\frac{-\Delta\phi^*}{K_B T_c} = \frac{K_g}{f T_c \Delta T} + \frac{2\sigma T_m^{eq} \ln v_2}{b_0 \Delta H_f \Delta T}, \tag{4}$$

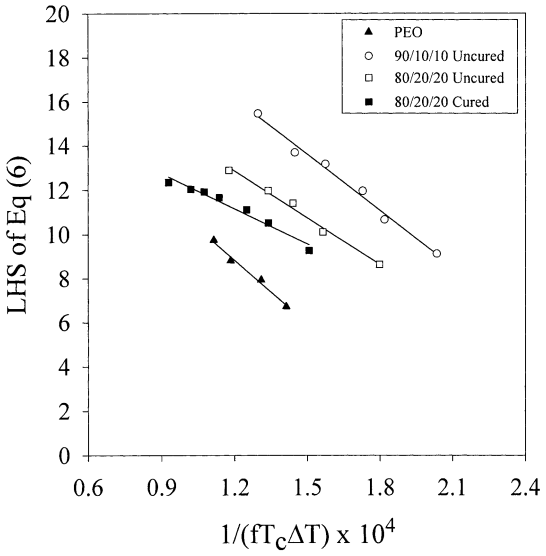

Fig. 10. Plots of LHS of Eq. (6) vs. $[1/T_c(\Delta T)f]$ for the cured samples and the uncured PEO/DGEBA/DDS systems of several compositions.

K_g is the nucleation factor depending on the regimes in which the growth falls into:

$$K_g = \frac{Zb_0\sigma\sigma_e T_m^{eq}}{K_B \Delta H_f}, \quad (5)$$

where $Z = 4$ (Regime I, III) and $Z = 1$ (Regime II). ΔH_f is the enthalpy of fusion per unit volume of the crystalline component (PEO). By taking logarithm on both sides of Eq. (2), one is able to extract the values of critical kinetic parameters from the graphic method. After taking logarithm and proper re-arrangement, the following expression can be defined:

$$\ln G - \ln v_2 + \frac{U^*}{R(T_c - T_\infty)} - \frac{0.2T_m^{eq}\ln v_2}{\Delta T} = \ln G_0 - \frac{K_g}{fT_c\Delta T}, \quad (6)$$

$\Delta T = T_m - T_c$ is the degree of supercooling, and f is a correction factor accounting for the change of melting enthalpy with temperature and is given by $f = 2T_c/(T_m + T_c)$, where T_m is the equilibrium melting temperature. For this system, ΔT is greater than 17.5 K, therefore $Z = 4$ (Regime-III) is assumed. $U^* = 4120$ cal/mol and $T_\alpha = T_g - 51.6$ K, according to Williams-Landel-Ferry (WLF) [25] was used in plotting. The following values were also used [26]: $\sigma = 0.1b_0\Delta H_f$, $b_0 = 4.65 \times 10^{-8}$ cm, $K_B = 1.380 \times 10^{-23}$ J/K (Boltzman constant).

By plotting the left-hand-side (LHS) term vs. right term of Eq. (6) [i.e. LHS vs.$1/(T_c\Delta Tf)$], it led to an intercept = $\ln G_0$, slope = K_g. Fig. 10 shows plots of LHS of Eq. (6) vs. $[1/T_c(\Delta T)f]$ for the cured samples in comparison with uncured PEO/DGEBA/DDS systems of several compositions. The plots yielded the values of K_g (slope) and G_0 (intercept), which in turn were used to calculate the other parameters associated with the PEO spherulites grown in the cured vs. uncured systems.

Relevant results of calculations are listed in Table 1. Earlier, it has been reported that for the neat PEO, Regime-III crystallization starts from $\Delta T = 17.5$°C and continues up to a higher value of supercooling [28]. In addition, the K_g values obtained from the slope of the straight lines are also given. By using b_0 (molecular thickness) = 4.65×10^{-8} cm, $\Delta H_f = 2.13 \times 10^9$ erg/cm^3 $(= 2.13 \times 10^2$ J/cm$^3)$ according to the literature [26,27], the values of $\sigma\sigma_e$ and σ_e for the neat PEO or the uncured vs. cured PEO/epoxy systems could be calculated (values shown in Table 1). In this study, the values of ΔT are all greater than 17.5°C, which suggest that spherulitic crystallization may take place only in Regime-III. A comparison of the surface free energy for the uncured and cured systems also revealed that entrapment of epoxy within the growing PEO lamellar bundles might be widely different between the two states of cure (uncured vs. cured states). The value for the neat PEO ($\sigma\sigma_e = 451.8$ erg^2/cm^4) in this study is higher than the earlier reported literature value (e.g. $\sigma\sigma_e = 274$ erg^2/cm^4 in Ref. [28]). Nevertheless, slightly different approaches have been used in extracting the values. We then compare the surface energy values obtained for the different cure states/compositions in the systems examined in this study. The values of σ_e are more comparable between the neat PEO and PEO/DGEBA/DDS (90/10/10) mixture but that for the PEO/DGEBA/DDS (80/20/20) mixture is significantly lower. This may be quite expected because quenching of the PEO/DGEBA/DDS (90/10/10) mixture did not lead to suppression of PEO crystallinity, while significant suppression of PEO crystallinity was observed in the PEO/DGEBA/

Table 1
Kinetic values of G_0, K_g and σ_e for PEO crystallization in uncured vs. cured PEO/DGEBA/DDS systems

	T_g (K)	T_m (K)	G_0 (cm/sec)	K_g (K^2)	$\sigma\sigma_e$ (erg^2/cm^4)	σ_e (erg/cm^2)
Uncured PEO/DGEBA/DDS						
Neat PEO	206	347.53	1.61×10^7	9.64×10^4	451.8	45.61
PEO/DGEBA/DDS 90/10/10	254.06	340.48	1.24×10^9	8.44×10^4	395.5	39.9
PEO/DGEBA/DDS 80/20/20	232.93	335.98	2.36×10^7	7.02×10^4	329.0	33.2
Cured PEO/DGEBA/DDS						
PEO/DGEBA/DDS 80/20/20	232.92	344.16	5.82×10^5	5.26×10^4	246.3	24.9

DDS (80/20/20) mixture. Entrapment and disruption of PEO lamellae is more severe in the uncured PEO/DGEBA/DDS (80/20/20) mixture than the uncured PEO/DGEBA/DDS (90/10/10). Similar trend was also observed for the cured PEO/DGEBA/DDS system. The extent of disruption of PEO lamellae varies depending on the compositions in the cured network and it is more evident in the cured PEO/DGEBA/DDS (80/20/20) mixture than the cured PEO/DGEBA/DDS (90/10/10). The result and its trend of variation in lamellar surface energy are in agreement with the thermal analysis characterization discussed earlier. Guo et al. [16] have also reported a similar trend of variation of σ_e in a PEO/novolac system (cured with an aliphatic hexamine).

3.4. Spherulite morphology for the cured vs. uncured systems

Changes in interactions in the PEO/epoxy mixtures were found to influence the kinetics as well as morphology of the PEO spherulites. Fig. 11(A)–(C) shows comparison of PEO spherulitic morphology (grown at same condition of 42°C) in the PEO/DGEBA/DDS mixtures prior to and after curing (A, B respectively). For comparison purposes, Fig. 11(C) shows the typical neat PEO spherulites grown at 42°C. The spherulites were more spread out or plane-stretched when cast as films in comparison to the actual dimensions of PEO spherulites grown in bulk. Apparently, the state of mixing between PEO and epoxy can be influenced by the extent of entrapment of epoxy/DDS molecules within the PEO lamellar bundles. Prior to cure, interactions between the PEO and epoxy/DDS molecules (especially the hydrogen bonding between PEO and DDS) are extensive and intimate on the molecular levels. Interlamellar entrapment is significant as the PEO molecules are being packed into spherulites grown in the PEO/DGEBA/DDS mixtures. The growth rate of PEO spherulites is slowed down owing to significant entrapment. In addition, Graph-A shows that the number of lamellar branches is more limited but each of the lamellar bundles is significantly coarsened to a feather-like pattern. By comparison, in a cured network of PEO/epoxy, the cured epoxy network is less likely to remain entrapped between the lamellar bundles of a growing PEO spherulite. The size of the PEO spherulites in uncured PEO/DGEBA/DDS is smaller than that in the cured PEO/DGEBA/DDS (Graph-A). In addition, the DDS (containing $-NH_2$) and DGEBA (containing epoxide and –OH) molecules already react into a network containing only the hydroxyl (–OH) group. The interactions between PEO and epoxy/DDS become less in the cured networks. Graph-B shows that the morphology of PEO in the cured PEO/epoxy system is dramatically different from that seen in the uncured PEO/DGEBA/DDS system but is quite similar to that observed in the neat PEO (Fig. 11(C)). The morphology result fully supports the calculated values of the spherulite kinetics.

Interestingly, Goldenfeld et al. [29–31] also reported a dendritic crystal (somewhat similar to the feather-like spherulite reported here) and they attributed that peculiar (dendritic) morphology to the effect of diffusion-control during crystallization. For the PEO-epoxy system, the feather-like growth of the PEO spherulites appeared at higher temperatures for a specific PEO/epoxy/DDS composition (e.g. 80/20/20). For the uncured system, all PEO/epoxy/DDS blend compositions developed a feather-like morphology (at temperatures nearer T_m, i.e. Regime-I), but a regular spherulite at lower temperatures. Feather-like PEO crystal in the uncured PEO/epoxy/DDS mixtures occurred in later stage during which diffusion control may be in act. This is in agreement with the Goldenfeld et al.'s mechanism that the dendritic features are a combined effect of the diffusion of the crystallizing material to the growth front and the uncrystallizable (amorphous) materials from the front. The mechanism leading to the feather-like morphology of the PEO spherulites in the uncured PEO/epoxy/DDS mixtures may comply with the Goldenfeld et al.'s mechanism. However, the feather-like morphology was not seen in the cured (crosslinked) PEO/epoxy/DDS system or neat PEO. More interestingly, with the absence of DDS, ie., the uncured PEO/DGEBA did not develop a feather-like morphology. This fact suggests that specific interactions between PEO (–O– group) and DDS ($-NH_2$) might be responsible for the peculiar morphology in addition to the diffusion control. Therefore, the mechanism of dendritic features according to Goldenfeld et al. [29–31] is interesting, but we feel that entrapment caused by the strong specific interactions is more active in the uncured PEO/epoxy/DDS system, and it helps in developing a feather-like PEO crystal morphology. Future work using infrared spectroscopy to probe interrelationships between interactions before/after curing and development of feather-like morphology is on going and will be reported later.

4. Conclusion

This study has offered a molecular microscopic view on commonly observed depression of growth kinetics of semicrystalline polymers in the presence of a diluent (an amorphous polymer or other non-crystallizing species). PEO is miscible with DGEBA/DDS epoxy system (in the amorphous domains) before and after cure. As PEO starts to crystallize in the miscible mixtures (either uncured liquid or cured network), entrapment and interactions between the species play an important role on growth kinetic and lamellar/spherulitic morphology. Thermal analysis, growth kinetics analysis, and morphology characterization were performed and the results are in good agreement in providing critical interpretation. Thermal analysis was performed on the quenched and slow-cooled samples of the same compositions for both uncured and cured systems. For samples of PEO-rich compositions (90/10/10 or 85/15/15), fast-quench could not suppress the PEO crystallinity. For

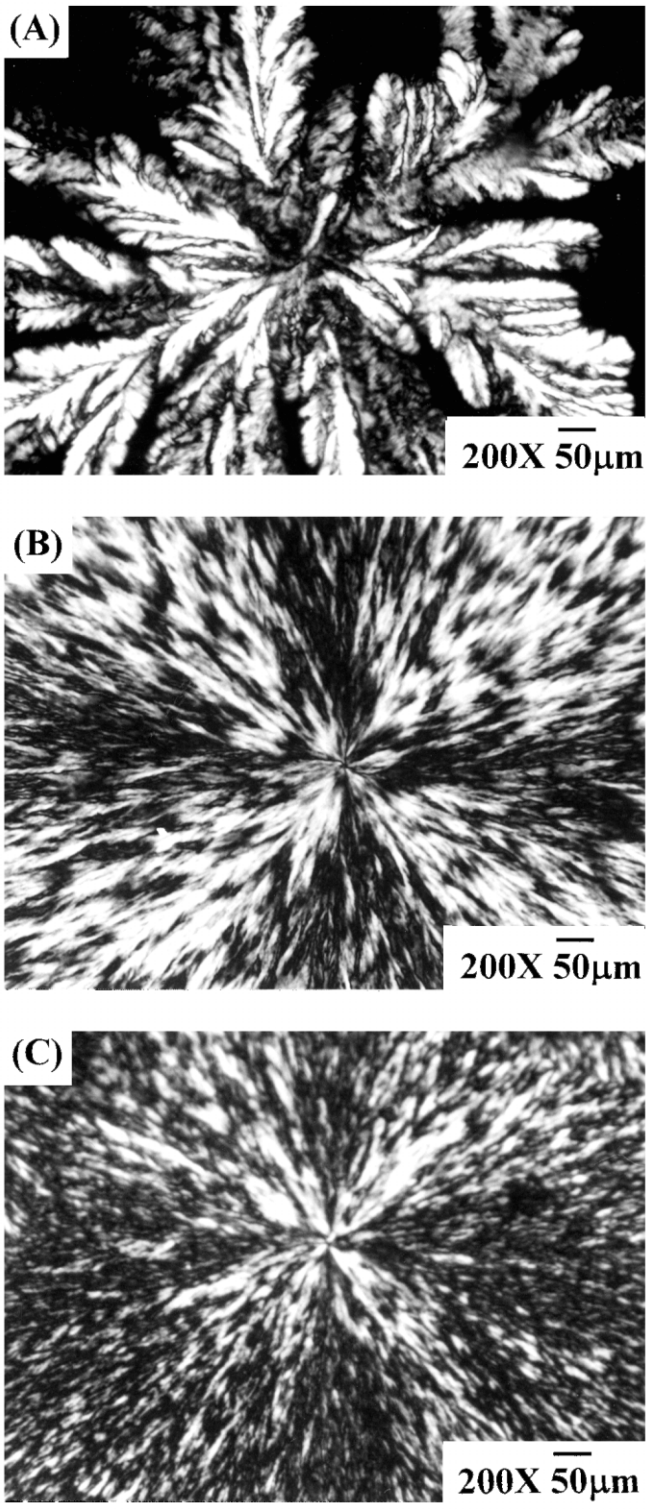

Fig. 11. PEO spherulitic morphology in (A) uncured PEO/DGEBA/DDS (80/20/20), (B) cured sample, and (C) neat PEO.

compositions of increasing epoxy contents (e.g. 80/20/20 or 80/20/30). The quenched and slow-cooled samples exhibited significantly different T_g and/or T_m, suggesting that the apparent mixture compositions and actual compositions in the amorphous domains were different depending on extents of the formation of PEO crystalline domains. The morphology and growth kinetics of the PEO crystals was in turn affected by the contents and chemical structures (functional group, molecular weight, crosslink, etc.) of the amorphous diluents (ie., epoxy/DDS).

In general, entrapment between the growing species and epoxy/DDS was found to be more extensive in the uncured

system. Suppression of PEO crystallinity and entrapment of epoxy within the growing PEO lamellar bundles were much less in the PEO/DGEBA/DDS) mixtures of PEO-rich compositions (e.g. 90/10/10). However, at increasing content of DGEBA/DDS in the mixtures (e.g. 80/20/20), the PEO crystallinity could be more readily suppressed upon quenching from above the melt. As PEO started to crystallize from the mixtures, the entrapment of the epoxy species in the growing PEO lamellae/fibrilla caused a significant slow-down of the kinetics. In addition, the morphology characterization revealed that the number of fibrillar branches is reduced but each of the bundles is more coarsened, leading to a feather-like growth. By comparison, in a cured network of PEO/epoxy, the cured epoxy network is less likely to remain entrapped between the fibrillar bundles of a growing PEO spherulite. This is quite easily conceivable if one considers the fact that a crosslinked network is inter-connected and is less likely to become entrapped with the PEO lamellae/fibrillae. In addition, the interactions between the species are different before and after cure. The interactions between PEO and epoxy/DDS become less in the cured networks. Future work using infrared spectroscopy (FTIR) to probe interrelationships between interactions before/after curing and development of feather-like morphology is on going and will be reported later.

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