

Influence of Attapulgites on Cure-Reaction-Induced Phase Separation in Epoxy/Poly(ether sulfone) Blends

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ABSTRACT: The influence of attapulgites (ATTs) on cure-reaction-induced phase separation in diglycidyl ether of bisphenol A/poly(ether sulfone) (PES) blends has been studied with scanning electron microscopy (SEM), transmission electron microscopy (TEM), optical microscopy, time-resolved light scattering, and dynamic mechanical analysis at different ATT and PES concentrations. The SEM results show that the incorporation of a small amount of ATT into the blends can change the final phase morphology markedly and affect the secondary

phase separation. The TEM results show that ATT particles are pinned down by the interfacial tension at the phase interfaces, and this slows the interfacial motion. In addition, the incorporation of a small amount of ATT particles can improve the modulus because of the increased interfacial interaction of the PES-rich and epoxy-rich phases. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 953–959, 2008

Key words: blends; nanocomposites; phase separation

INTRODUCTION

In recent years, nanoscale fillers have been extensively studied because of their large specific surface areas and intrinsic properties. The anisotropy of nanoparticles, such as layered silicates, cubic polyhedral oligomeric silsesquioxane clusters, and rodlike silicates, plays a more important role in the behavior of nanocomposites. Inorganic clay minerals, which have a nanoscale character and low cost, have attracted the attention of many researchers. Montmorillonite (MMT), a common inorganic clay mineral with a layered structure, has been successfully used by many researchers of thermoplastics such as nylon 6,¹ poly(ethylene oxide),² and poly(methyl methacrylate).³ In 2005, Zheng et al.⁴ incorporated organically modified MMT into a poly(ether imide)/epoxy blend. They found that MMT had a dramatic impact on the reaction-induced phase-separation process and the final phase morphology.⁴

Attapulgite (ATT), the rodlike inorganic filler, is a crystalline hydrated magnesium aluminum silicate with a unique three-dimensional structure. Its structural formula is $\text{Si}_8\text{O}_{20}\text{Mg}_5(\text{Al})(\text{OH})_2(\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$, and its ideal structure was studied by Bradley in 1940.⁵ ATT has a fibrous morphology approximately

20 nm in diameter and several micrometers in length. In addition, it has a large surface area, a strong absorptive capacity, which is greater than that of any other natural mineral, and good mechanical strength and thermal stability. These properties make ATT an ideal material for reinforcement. However, ATT, as a polymer reinforcement agent, has not received much more attention in recent years, especially for its use in thermosets. Nutt et al.⁶ proved that epoxy nanocomposites containing ATT have potential for significant improvements in mechanical properties and dimensional stability with temperature changes.⁶

Thermosets, such as epoxy resins, tend to have characteristic low toughness and poor crack resistance. Therefore, in the past 2 decades, much work has been done to toughen these highly crosslinked thermosets with rubber^{7,8} or thermoplastics [e.g., poly(ether imide)^{9,10}].^{9–12} Meanwhile, because the mechanical properties of blends of thermosets and thermoplastics are determined by their final micro-morphologies, much work has been done regarding the kinetics of phase separation and morphology control from both fundamental and applied points of view,^{13–18} and a series of theoretical considerations has been formed.^{11,19,20} However, for cure-reaction-induced phase-separation systems, different phase morphologies are obtained, depending on many complicated factors, such as the curing condition, the composition, and the molecular weights and distribution of thermoplastics.

Both theoretical and experimental studies indicate that some filler particles and fibers have an impor-

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TABLE I
Compositions of the Samples

	A1				A2				A4
	-15	-20	-25	-30	-15	-20	-25	-30	-20
ATT (g)	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.04
DGEBA (g)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
PES (g)	0.15	0.20	0.25	0.30	0.15	0.20	0.25	0.30	0.20

tant influence on the morphology and phase-separation behavior of binary polymer mixtures, especially when the fillers are preferentially wettable to one component of the binary blends. Tanaka et al.²¹ studied the pattern evolution caused by phase separation with glass particles in binary blends,²¹ which proved the hindrance function of glass particles and the wetting effect of one component on the surface of the glass particles. Balazs and coworkers^{22,23} simulated the motion of spherical particles in a phase-separating binary mixture and further showed that, at a low volume fraction, the nanoscale rods in a binary, phase-separating blend can self-assemble into a supermolecular network.²⁴ However, to the best of our knowledge, little attention has been paid to thermoplastic/thermoset blends.

The objective of this study was to investigate the cure-reaction-induced phase separation in ATT/epoxy/poly(ether sulfone) (PES) ternary hybrid nanocomposites and, in particular, to examine the influence of ATT on the whole phase evolution process; this would hopefully give us a better understanding of the mechanism of cure-reaction-induced phase separation in epoxy/PES blends. Therefore, the phase separation of ATT/epoxy/PES blends with different amounts of ATT and PES cured at different temperatures was investigated with time-resolved light scattering (TRLS), optical microscopy (OM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM), and the modulus of the cured blends was measured by dynamic mechanical analysis (DMA). We found that ATT had a dramatic impact on the final phase morphology, and 1–2 wt % ATT could evidently enhance the modulus of the modified epoxy resin.

EXPERIMENTAL

Materials and sample preparation

To improve the dispersion of ATT in the blends, ATT nanocomposites (Attagel 50, Engelhard Co., United States) were modified by the addition of an equivalent amount of γ -methacryloxypropyltrimethoxysilane (KH-570) (China) to a 5 wt % ATT aqueous suspension under a nitrogen atmosphere with vigorous stirring for 6 h. The products were first filtered and washed three times with alcohol and then were dried at 120°C *in vacuo* and ground.

The epoxy oligomer DER331, a low-molecular-weight liquid diglycidyl ether of bisphenol A (DGEBA) with an epoxide equivalent of 182–192, was purchased from Dow Chemical Co. PES (number-average molecular weight = 9600) was supplied by Jilin University (China). The curing agent 4,4'-methylene bis(2,6-dimethylamline) (DIM-DDM) was bought from Aldrich Chemical Co., Inc. (Germany).

A certain amount of ATT was first dispersed in acetone under ultrasonication, the epoxy was then added to the suspension, and it was ultrasonicated again. After the acetone was first vaporized in an oil bath, the sample was placed in a vacuum oven at 120°C for 4 h. After that, PES was melt-blended into the mixture of DGEBA and ATT at 150°C. The mixture was then cooled to 100°C and stirred until a homogeneous solution was obtained. At last, a stoichiometric amount of curing agent DIM-DDM was added, and the mixture was stirred before cooling rapidly to room temperature to avoid further curing. A series of blends were prepared as shown in Table I.

Measurements

A Hitachi H-600 transmission electron microscope (Japan) and a Philips XL 39 scanning electron microscope (Holland) were employed to examine the morphologies of the fractured surfaces (the samples were cured thoroughly and fractured in liquid nitrogen). The phase-separation process during isothermal curing was traced *in situ* on a self-made TRLS apparatus with a controllable hot chamber. The change in the light scattering profiles was recorded at appropriate time intervals. The samples for TRLS observation were melt-pressed films, and the thickness of the films was about 0.06 mm. In the light scattering experiment, information on the phase morphology evolution could be obtained from the systematic change in the curves of the scattering factor versus the scattering light intensity as a function of the time of phase separation, and the most probable phase domain size was $d_m = 2\pi/q_m$, where q_m is the peak scattering vector. The evolving morphologies of the samples were observed *in situ* with an XDS-1B optical microscope with a hot chamber (Chongqing Optical and Electrical Instrument Co., Ltd., China). The modulus of the blends was measured with a Netzsch 242 dynamic mechanical analyzer (Germany).

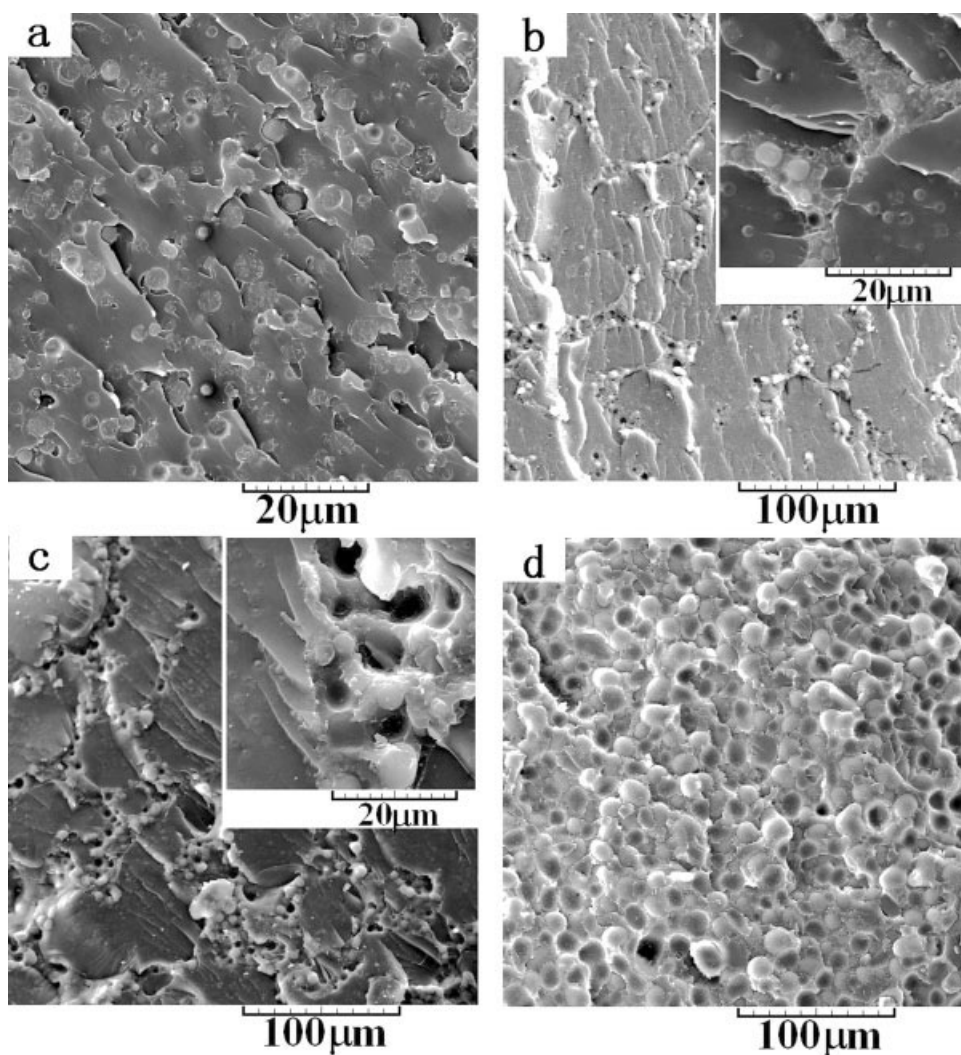


Figure 1 SEM micrographs of (a) A1-15, (b) A1-20, (c) A1-25, and (d) A1-30 cured at 140°C.

RESULTS AND DISCUSSION

Phase morphologies as determined by SEM and TEM

The phase morphologies of blends A1-15, A1-20, A1-25, and A1-30 are shown in Figure 1. The blend with a small amount of PES (A1-15) displays a particle/matrix morphology, in which the PES-rich particles are dispersed in the epoxy-rich matrix. The blends with nearly critical PES concentrations (A1-20 and A1-25) display a networklike phase morphology, whereas the blend with a supercritical PES concentration (A1-30) shows a phase inversion morphology, in which the epoxy-rich particles are dispersed in the PES-rich continuous matrix. It can be concluded that, in comparison with the results of our previous study,²⁵ the incorporation of a small amount of ATT has no dramatic effect on the scope of the critical composition for epoxy/PES blends but diminishes the size of the PES-rich phase greatly, which transforms into a silklike morphology.

Figure 2 presents SEM images of blends containing the same amount of PES (A-20) but different amounts of ATT cured at 140°C. In comparison with the blend without ATT [Fig. 1(a) in ref. 25, PES-15.9/140°C], a networklike phase morphology with a PES-rich silklike phase can be observed in A1-20 and A2-20 [Fig. 2(a,b)]. This shows the character of the dynamic asymmetric system,²⁶ which is similar to the unfilled system with an even larger amount of PES cured at higher temperatures [Fig. 1(d) in ref. 25, PES-18.5/170°C]. The secondary phase separation still occurs in the epoxy-rich phase and the PES-rich phase in A1-20 and A2-20 and is similar to that in the unfilled blends.

However, the phase morphology of A4-20, shown in Figure 2(c), is much different from that of A1-20 and A2-20, in which the PES-rich network has transformed into a particle morphology and the PES-rich particles are not dispersing uniformly, but arrange regularly one by one like a string of beads which keeps the forestall networklike outline. It is difficult to find the secondary structure in the epoxy-rich phase and

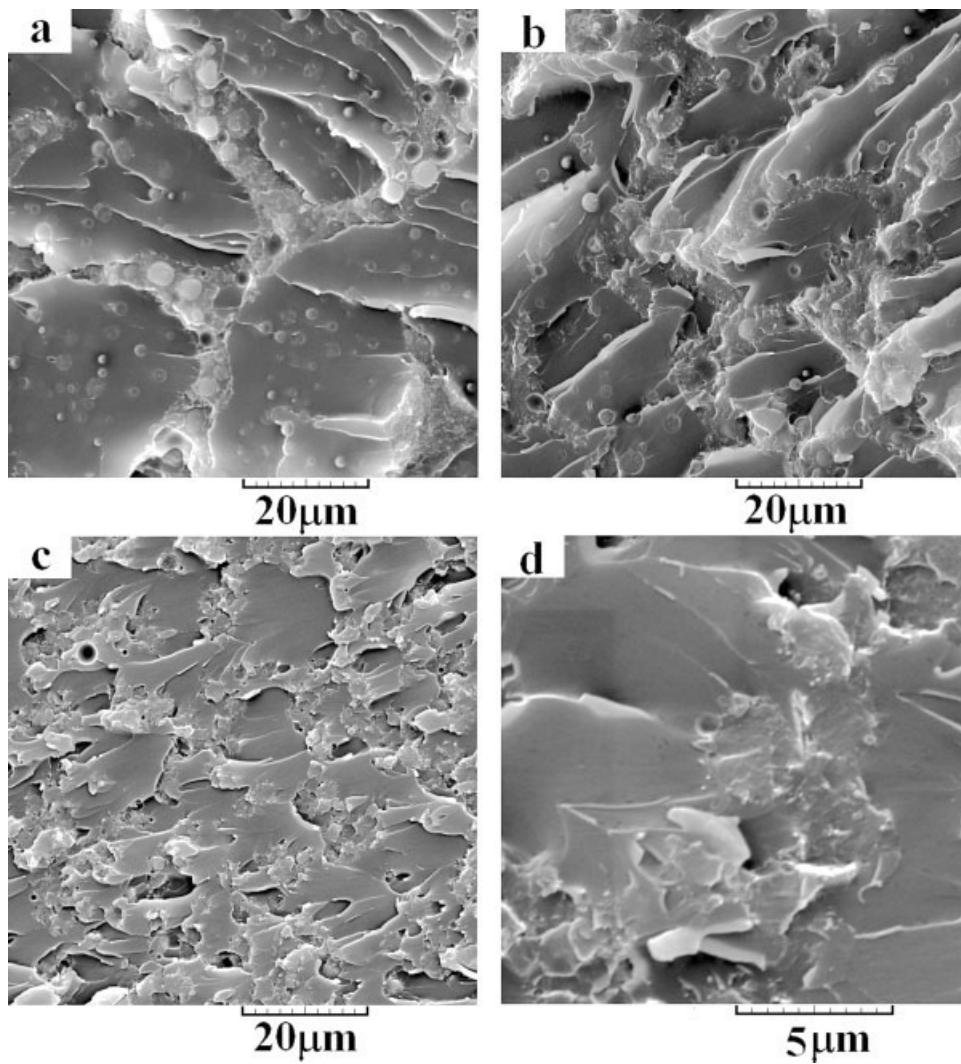


Figure 2 SEM micrographs of (a) A1-20, (b) A2-20, and (c,d) A4-20 cured at 140°C.

the PES-rich phase. Meanwhile, the blends with a higher PES concentration (A-30) show a phase inversion morphology, but the PES-rich particles in

A1-30 are larger than the ones in A2-30. From the aforementioned results, it can be concluded that the incorporation of ATT could block the phase evolu-

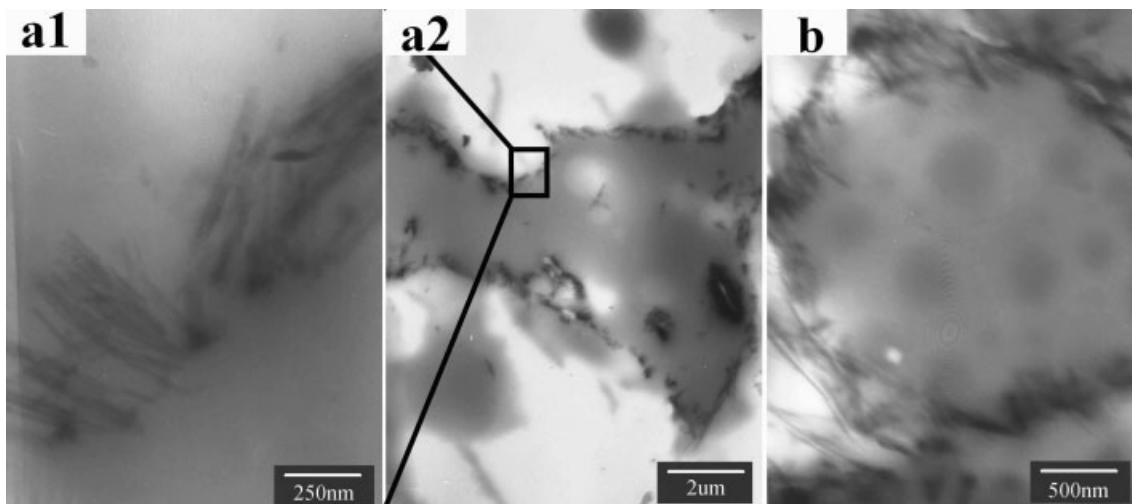


Figure 3 TEM micrographs of the location of ATT: (a1,a2) A2-20 and (b) A4-20 cured at 140°C.

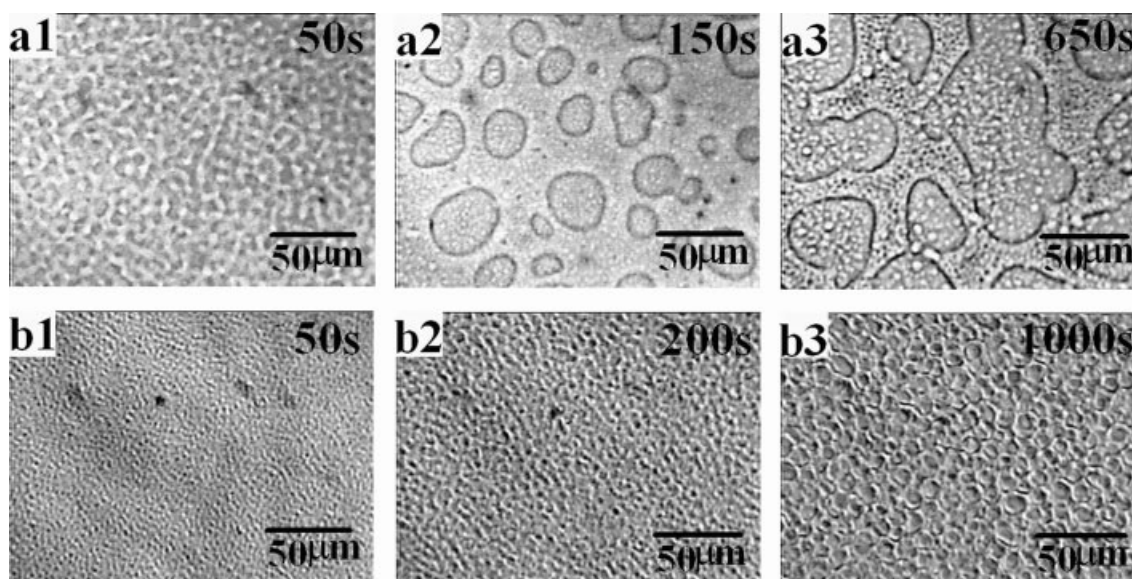


Figure 4 Development of morphologies in (a) A1-20 and (b) A4-20 samples cured at 140°C.

tion and even restrain the occurrence of secondary phase separation.

The TEM micrograph in Figure 3 taken at a higher magnification of the interfaces of the two phases (A2-20 and A4-20) shows that the ATT nanocomposites dispersed in the blends are in the form of individual rods approximately 20 nm in diameter and 500 nm long.⁵ In addition, we notice that most ATT particles are arranged along the interface of the PES-rich and epoxy-rich phases. The particles are probably pinned down by interfacial tension during the phase-coarsening process,^{27,28} even though the ATT particles have been preferentially wetted by the epoxy resin.⁴ Binks^{28,29} suggested that the arrangement of nanoparticles significantly influences the configuration of the interface and mediates the effect of the nanoclay concentration on the modulus and toughness of the composites.

Evolution of the phase morphologies as determined by OM and TRLS

The morphological evolutions of A1-20 and A4-20 blends cured at 140°C have been traced *in situ* by OM and are presented in Figure 4. Obviously, the coarsening process of A1-20 is much faster than that of A4-20 in the early stage of the phase separation; as a result, the secondary phase separation just happens in the former sample, and in comparison with the blends without ATT [Fig. 2(a) in ref. 25, PES-15.9/140°C], the occurrence of the secondary phase separation in A1-20 is much later. Combining these results with the SEM results shown in Figure 2(c), we can suggest that, in A4-20, the silklike phase morphology of the PES-rich phase transforms into dispersed particles in the later stage of the phase evolution. In other words, it is likely to form PES

particles in the later stages of the curing process because of the influence of the ATT particles at the phase interfaces.

The changes in q_m with time with respect to the aforementioned phase evolution process in A-20 are presented in Figure 5. During the curing process of the A1-20 blend, there exists a minimum value in the curve of q_m versus time before the constant value is attained, and this means that the appearance of secondary particles makes the average phase domain size decrease. In the A4-20 blend, q_m does not change any more after reaching a certain value, and this suggests that the secondary phase-separation process is hard to observe in this blend. These results are consistent with the SEM and OM results.

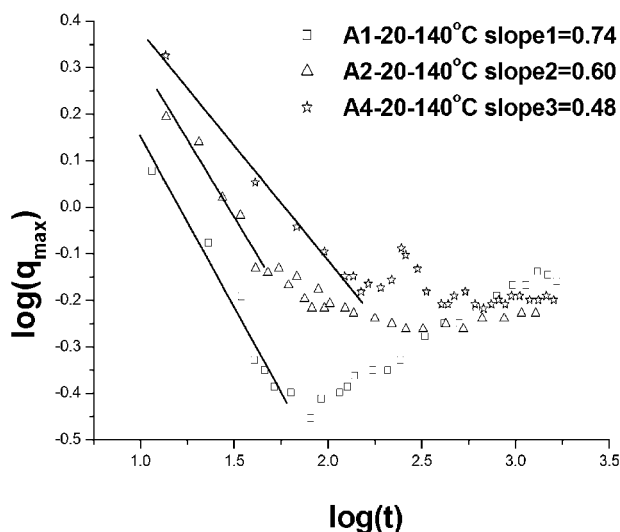


Figure 5 Temporal changes of the peak scattering vector (q_{\max}) versus the time of phase-separation evolution (t) for blends with different contents of ATT.

TABLE II
Slope of $\log q_m$ Versus $\log t$ and Time of the Occurrence of Phase Separation in the Curing Process for Different Compositions and Different Curing Temperatures

		A1-15	A1-20	A1-25	A1-30	A2-20	A4-20
120°C	T_{start} (min)	27.0	26.8	26.9	33.3	21.2	16.8
	Slope	0.49	0.58	0.56	0.17	0.57	0.18
140°C	T_{start} (min)	20.8	14.9	16.4	18.2	12.9	7.1
	Slope	0.50	0.74	0.64	0.46	0.60	0.48
160°C	T_{start} (min)	8.86	9.6	10.0	11.3	8.7	5.0
	Slope	0.52	0.88	0.81	0.28	0.70	0.27

The time of occurrence of phase separation in the curing process and the slope value of $\log q_m$ versus $\log t$ for different curing compositions at different temperatures are shown in Table II. Comparing the time for the occurrence of phase separation in the curing process (T_{start}) values of the blends with the same PES content, we find that, as the concentration of ATT increases, phase separation occurs earlier, and this indicates that the incorporation of ATT decreases the compatibility of epoxy and PES.

For the A1 blends, the slope value of $\log q_m$ versus $\log t$ increases with the curing temperature increasing. Meanwhile, with the same concentration of PES, the slope value of $\log q_m$ versus $\log t$ decreases with the increase in the amount of ATT (0.74 for A1-20, 0.60 for A2-20, and 0.48 for A4-20); all these values are lower than the value of the slope for the unfilled blend,²⁵ being similar to the results in refs. 21–23. It can be concluded from the OM and TRLS results that the ATT particles arranged at the interfaces block the movement of the interfaces, and this makes the coarsening process incomplete and inhibits the occurrence of the secondary phase separation.

Besides, the A1-30 system has a slope value similar to that of the A4-20 blend at the same curing temperature, and this indicates that the ATT particles have a similar effect on the phase morphology

evolution with PES in the phase-separation process, but the amount of ATT particles required is much less than that of PES. It has been noted that a phase-separated structure plays an important role in the toughness and stiffness of the materials, and the bicontinuous phase and inversion phase would provide better properties. Therefore, for toughening purposes, the amount of ATT added to the blend should be appropriate in the blends. Too much ATT will make the PES network break in the late stages of the phase separation (A4-20), and this will affect the mechanical properties of the material.

Mechanical properties

The DMA results in Figure 6(a) show that before postcuring, the modulus of the A2-20 blend is 20% higher than that of the unfilled blend. As shown in Figure 6(b), the tensile strength of the blend with 2 wt % ATT is 10% higher than that of the epoxy/PES blends without ATT. However, these results are not sufficient to indicate whether the increase in stiffness and toughness is provided by the ATT particles themselves or by their arrangement in the interfaces; further investigation is needed to prove this result. Still, from the experimental results, it can be suggested that ATT, as a common inorganic clay

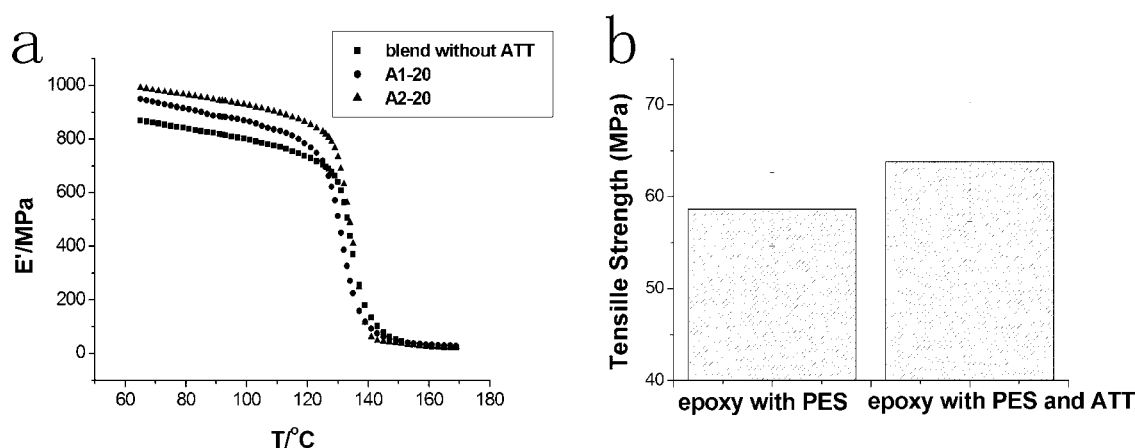


Figure 6 (a) Dynamic mechanical properties for the storage modulus (E') of blends with different amounts of ATT before postcuring in air at a heating rate of 3°C/min and at a constant frequency of 1 Hz and (b) tensile strength at break of different blends.

mineral, is a very promising additive for the modification of epoxy by thermoplastics to improve the stiffness and toughness of the material.

CONCLUSIONS

The influence of ATT on the reaction-induced phase separation of epoxy/PES mixtures has been studied via SEM, TEM, OM, TRLS, and DMA with different compositions. The incorporation of ATT particles does not affect the scope of the critical composition of the epoxy/PES blends but changes the final phase morphology, which has a small phase domain and silklike PES-rich phase. As the amount of ATT in the blends increases to 4 wt %, the occurrence of secondary phase separation is exhibited. The difference from the unfilled blend is attributed to the ATT particles pinning down in the interfaces by interfacial tension, which slows down the interface movements, weakens the coarsening process, and inhibits the occurrence of secondary phase separation. Meanwhile, the arrangement of the ATT particles in the interface area increases the interaction of the two phases and improves the modulus of the material as well. As for applications, ATT could be a very useful additive in epoxy systems modified by thermoplastics.

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