Phase Separation, Cure Kinetics, and Morphology of Epoxy/Poly(vinyl acetate) Blends

M. G. Prolongo,[1] C. Arribas,[1] C. Salom,[1] R. M. Masegosa[2]

[1]Dpt. Materiales y Producción Aeroespacial, E. T. S. I. Aeronáuticos, Universidad Politécnica Madrid, Spain
[2]Dpt. Física y Química Aplicadas a la Técnica Aeronáutica, E. U. I. T. Aeronáutica,
Universidad Politécnica Madrid, Spain

ABSTRACT: Epoxy based on diglycidyl ether of bisphenol A + 4,4′diaminodiphenylsulfone blended with poly(vinyl acetate) (PVAc) was investigated through differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA) and environmental scanning electron microscopy (ESEM). The influence of PVAc content on reaction induced phase separation, cure kinetics, morphology and dynamic-mechanical properties of cured blends at 180°C is reported. Epoxy/PVAc blends (5, 10 and 15 wt % of PVAc content) are initially miscible but phase separate upon curing. DMTA α-relaxations of cured blends agree with T_g results by DSC. The conversion-time data revealed the cure reaction was slower in the blends than in the neat system, although the autocatalytic cure mechanism was not affected by the addition of PVAc. ESEM showed the cured epoxy/PVAc blends had different morphologies as a function of PVAc content: an inversion in morphology took place for blends containing 15 wt % PVAc. The changes in the blend morphology with PVAc content had a clear effect on the DMTA behavior. Inverted morphology blends had low storage modulus values and a high capability to dissipate energy at temperatures higher than the PVAc glass-transition temperature, in contrast to the behavior of neat epoxy and blends with a low PVAc content. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1507–1516, 2007

Key words: thermoplastic; thermoset; phase separation; morphology; glass transition

INTRODUCTION

Epoxy thermosetting polymers are widely used as adhesives, encapsulants, and matrices for composite materials. In their applications epoxy thermosets are usually modified, incorporating a rubber or a thermoplastic polymer in order to improve their toughness.[1–4] Most of the recent studies have investigated an initially homogeneous mixture consisting of a thermoplastic dissolved in an epoxy precursor: the epoxy monomer and the curing agent. On curing, the initially miscible blends phase separate, giving rise to different morphologies as a function of the thermoplastic content. The final properties of the cured system depend on the curing conditions and the thermoplastic content.[1,5–24]

Most epoxy/thermoplastic blends reported in the literature have used high-performance engineering thermoplastics[5–14] like poly(ether sulfone),[6] polycarbonate,[8] or poly(ether imide),[7,11] which have high glass-transition temperatures (T_g) and under certain curing schedules have generated an adequate morphology for improving mechanical properties, mainly toughness.

In a previous work[24] we reported a differential scanning calorimetry (DSC) study of an epoxy thermosetting polymer modified with poly(vinyl acetate) (PVAc), which is a ductile thermoplastic with a moderate T_g of approximately 44°C. That preliminary study revealed that the epoxy precursor, diglycidyl ether of bisphenol A plus 4,4′-diaminodiphenylsulfone (DGEBA + DDS), blended with 10 wt % PVAc, formed a homogeneous solution that phase-separated upon curing at 180°C, the T_g, and conversion data upon curing this blend were reported. In this system it was feasible to follow the induced reaction phase separation through T_g monitoring because the glass transition of PVAc was much lower than the T_g of the epoxy network. Moreover, it was reported[17] that another epoxy precursor blended with PVAc showed reaction-induced phase separation that led to improvement in toughness.

The main aim of the present work was to examine the influence of PVAc content on the cure kinetics and on phase separation upon curing epoxy (DGEBA+DDS)/PVAc blends containing different PVAc contents (0, 5, 10, or 15 wt %) as well as to characterize the materials generated. Specifically, we report
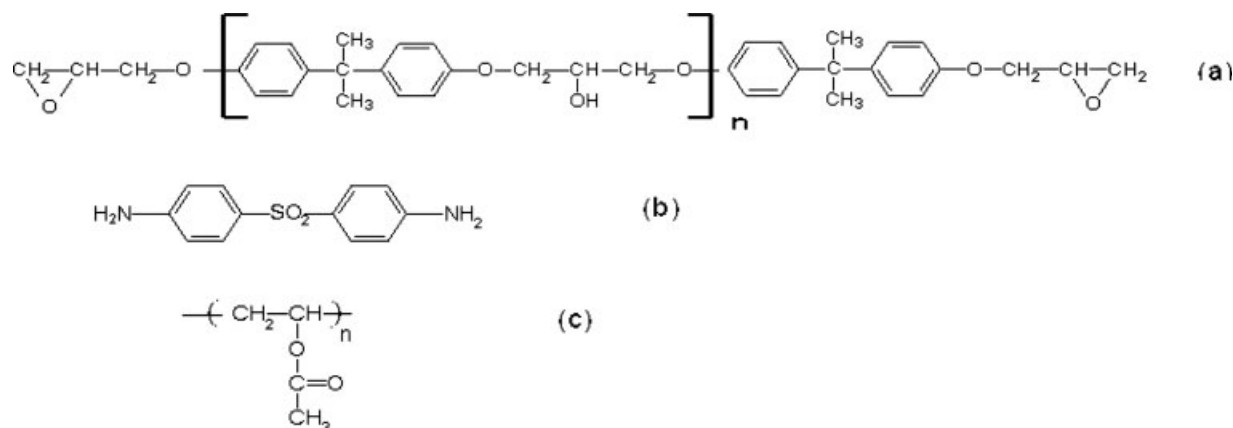
Figure 1 Chemical structures of (a) epoxy DGEBA prepolymer, (b) DDS, and (c) PVAc.

the evolution of glass transitions and conversion on the cure process and the morphology and dynamic-mechanical properties of the cured materials.

EXPERIMENTAL

Materials and blend preparation

The epoxy prepolymer was based on diglycidyl ether of bisphenol A supplied by Uneco S. A. (Barcelona, Spain) under the commercial name Araldit F. The number-average molecular mass, M_n, was 380 g/mol, which was determined by chemical titration of the end groups. The curing agent was 4,4′-diaminodiphenylsulfone (DDS) manufactured by Sigma-Aldrich Chemical Co. (Madrid, Spain) (98 wt %). Poly(vinyl acetate) (PVAc) with an M_n of 8.6×10^4 g/mol and a polydispersity of index 1.9 was purchased from Polysciences Inc. (Eppelheim, Germany). Acetone Panreac QP (Barcelona, Spain) (0.3 wt % water content) was used as a solvent. Frekote from Loctite (Madrid, Spain) was employed as a mold release product. The chemical structures of the three components are shown in Figure 1.

The epoxy prepolymer and DDS were always used with a stoichiometric ratio of amino-hydrogen to epoxy. The epoxy/PVAc blends were obtained by mixing appropriate amounts of their respective solutions in acetone. Three blend compositions with different percentages of PVAc (5, 10, or 15 wt %) were prepared in addition to the neat epoxy (0 wt % PVAc). These solutions were cast onto aluminum pans for differential scanning calorimetry (DSC). The acetone was carefully eliminated by degassing under vacuum at 40°C for approximately 20 h. This schedule assured the removal of the solvent without a significant curing reaction. To obtain specimens for dynamic mechanical thermal analysis (DMTA) measurement, the reactive solutions were cast onto aluminum molds previously treated with Frekote. The

blends were cured at $T_c = 180°C$ for 3 h under atmospheric pressure; afterward, acetone was eliminated by degassing under vacuum at 80°C for about 3–4 h. Specimens (2 × 10 × 30 mm) were cut from the cured panels.

DSC measurements

A Mettler Toledo model 821e differential scanning calorimeter was used to measure glass-transition temperatures and heats of reaction. All measurements were done at a heating rate of 20°C/min under a nitrogen atmosphere. The instrument was calibrated with indium and zinc. Samples of 10–20 mg were used.

The samples were cured in an air oven at 180°C for various intervals so that different degrees of cure were achieved. Then the samples were rapidly cooled by taking the pans out of the oven and placing them in an 18°C environment. Afterward, they were scanned in the DSC (from −50°C to 360°C). T_g values were taken at the midpoint of the heat capacity change.

DMTA measurements

Dynamic mechanical thermal analysis of cured samples was performed in dual cantilever bending mode using a DMTA V Rheometric Scientific instrument. All measurements were done at a frequency of 1 Hz, producing a 1% bending deformation, with the temperature increasing from −40°C to 240°C at a heating rate of 2°C/min. The maxima of the tan δ temperature plots were determined in order to identify the α-relaxations associated with the glass transitions. Three specimens of each blend composition were scanned.

ESEM measurements

Environmental scanning electron microscopy was used to study the morphology of the cured samples.
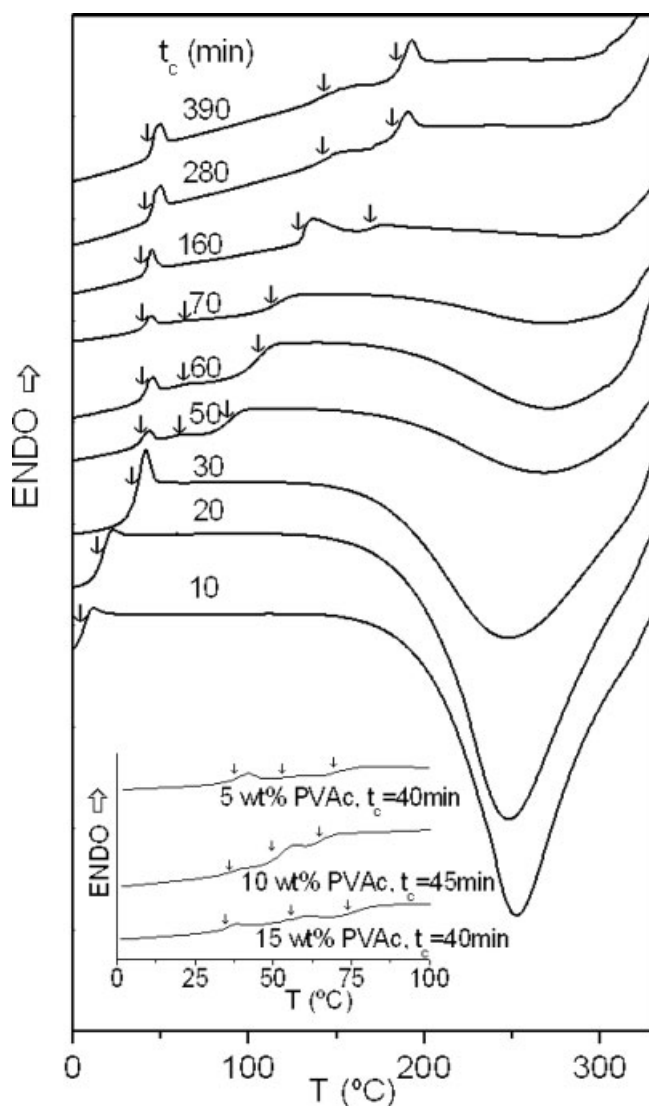
Figure 2 DSC thermograms for epoxy/PVAc blends containing 15 wt % PVAc obtained after curing at $T_c = 180°C$ for different curing time (min). The inset shows the thermograms at the beginning of phase separation for blends with different compositions cured at $T_c = 180°C$.

Because of the nonconducting nature of the specimens, the environmental SEM mode was selected. A Phillips XL30 instrument was used with a beam energy of 20 kV, that did not severely damage the samples. The water vapor pressure was 0.6–0.7 Torr, corresponding to a relative humidity of approximately 5%.

RESULTS AND DISCUSSION

DSC study: glass-transition temperatures

Blends of epoxy (DGEBA+DDS) and PVAc containing 5, 10, or 15 wt % PVAc were scanned in the DSC after being cured at 180°C for different times (t_c) in order to determine the glass transitions and the re-

sidual heats of reaction. Figure 2 shows some of the thermograms obtained for blends containing 15 wt % PVAc. The steps in the heat flow were related to the T_g values of the phases in the samples, which were followed by a broad exothermal peak that corresponded to the curing reaction heat.

In the first stages of the reaction ($t_c \leq 30$ min), the presence of a single T_g indicated a unique miscible phase, whereas for samples cured for longer times ($t_c \geq 40$ min), three glass transitions were detected. The two main T_g values were designated as T_{g1}, the lowest, and T_{g2}, the highest, and the third one, localized in between, was designated as T_{g3}. The detection of these T_g values was coincident with the appearance of opacity in the blends, confirming that phase separation had taken place during the curing reaction. The thermograms for blends having 5 and 10 wt % PVAc showed similar patterns, that is, a single T_g could be identified when t_c was less than 30 min; however, the intermediate T_{g3} only appeared in the range of $40 < t_c < 60$ min, and finally for $t_c \geq 60$ min, only two glass transitions (T_{g1} and T_{g2}) were noticeable. The occurrence of three glass transitions is illustrated in the inset of Figure 2, which shows the DSC scan amplification (0°C–100°C) for blends containing 5, 10, and 15 wt % PVAc that were cured 40–45 min at 180°C. In contrast, the neat epoxy showed a single T_g over the entire curing process that increased with curing time.[24]

To clearly illustrate the evolution of the glass transitions as the cure progressed, T_g versus time results are displayed in Figure 3. The data for neat epoxy and some of the data for the epoxy/PVAc blend with 10 wt % PVAc were previously reported.[24] As can be seen, at a t_c from 0 to 30 min, the system showed miscibility, presenting a single T_g that continuously increased with time. All compositions were phase-separated after being cured for $t_c > 30$ min, and at the beginning of the phase separation, three T_g values (T_{g1}, T_{g2}, and T_{g3}) were detected. The lowest T_g (T_{g1}) was very close to that of pure PVAc; therefore, it could be assigned to a phase essentially composed of PVAc. The highest T_g (T_{g2}) increased with reaction time and after 3 h reached the final value (~183°C), which was very close to the final T_g value reached for neat epoxy, so this phase should be composed basically of cured epoxy. The intermediate T_g (T_{g3}), detected at the beginning of the phase separation ($40 < t_c < 70$ min), revealed the presence of a phase that evolved and disappeared as the cure progressed. The detection of the three T_gs when the phase separation was first observed may be an indication of the influence of kinetic factors.

For epoxy/PVAc blends containing 15 wt % PVAc, the intermediate T_g observed after $t_c > 100$ min had a small intensity, but it was even detected after long curing times. This T_g increased steadily, as
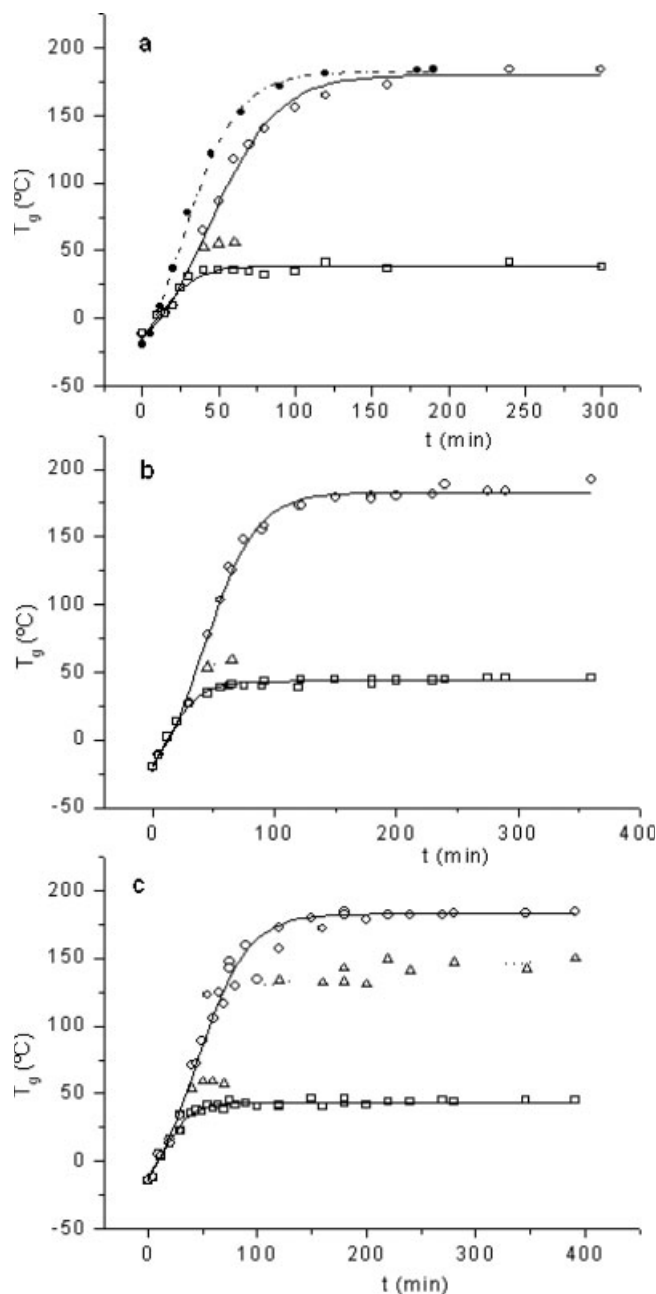
Figure 3 Glass-transition temperatures versus curing time for epoxy/PVAc blends cured at $T_c = 180°C$: (a) 0 wt % PVAc[24] (●) and 5 wt % PVAc—T_{g1} (□), T_{g2} (○), T_{g3} (△); (b) 10 wt % PVAc—T_{g1} (□), T_{g2} (○), T_{g3} (△); and (c) 15 wt % PVAc—T_{g1} (□), T_{g2} (○), T_{g3} (△).

can be seen in Figure 3(c). Thus, for blends containing 15 wt % PVAc isothermally cured at $T_c = 180°C$, minor, not totally cured epoxy domains could probably remain plasticized by PVAc. In contrast, the biphasic separation process seemed to be completed for blends with 5 and 10 wt % PVAc [see Fig. 3(a,b)]. Table I shows the final T_g values obtained after curing for $t_c \geq 180$ min.

It can be seen that for the epoxy/PVAc blend with 5 wt % PVAc, the final T_{g1} value was slightly less

than the T_g of pure PVAc ($T_g = 44°C$). This could reflect that some low-molecular-weight epoxy molecules had been dragged along the PVAc and acted as plasticizers. As will be shown later, the phase separation was detected when the conversion range was $0.3 < \alpha < 0.6$. This corresponds to high conversion for the primary amine groups, α_L, specifically $0.7 < \alpha_L < 0.95$, according to the data reported by Min, Stachurski, and Hodgkin.[25] Consequently, in this system when the phase separation was calorimetrically detected, most DDS molecules would be linked to epoxy molecules. Therefore, it was more likely that the curing agent (DDS molecules) would be in the rich epoxy phase and the PVAc plasticizer would be mainly unreacted DGEBA. Moreover, it should be also considered that strong tension stresses around PVAc particles (see section on morphological analysis) could lead to reduction in T_{g1} as in rubber-modified epoxies.[4]

DSC study: conversion analysis

The degree of conversion was obtained as:

$$\alpha = \frac{\Delta H_t - \Delta H_r}{\Delta H_t} \tag{1}$$

where ΔH_r and ΔH_t are the residual and total heats of reaction, respectively.

As we stated in a previous article,[24] during the DSC scans (from $-50°C$ to $360°C$), reactions involving PVAc took place at high temperature ($>250°C$). Consequently, to calculate the curing conversions in samples containing PVAc, it was necessary to correct the integrated areas of the exothermic peaks. To make this correction, longtime cured samples (180–300 min at 180°C) were scanned. A small wide exotherm in the 220°C–335°C range was detected in all the cured epoxy/PVAc blends. For blends containing 10 wt % PVAc, the reported value[24] was approximately 11 J/g. Although this was very small compared to the overall heat of curing (~380 J/g), it should be subtracted from the DSC peak areas to get H_t and H_r. For epoxy/PVAc blends with 5 and 15 wt % PVAc, the correction values obtained were 4 and 20 J/g respectively, that is, the effect was more important for higher PVAc content. Nevertheless the

TABLE I
Glass Transitions (T_g) of Cured Epoxy/PVAc Blends
$t_c > 180$ min at $T_c = 180°C$

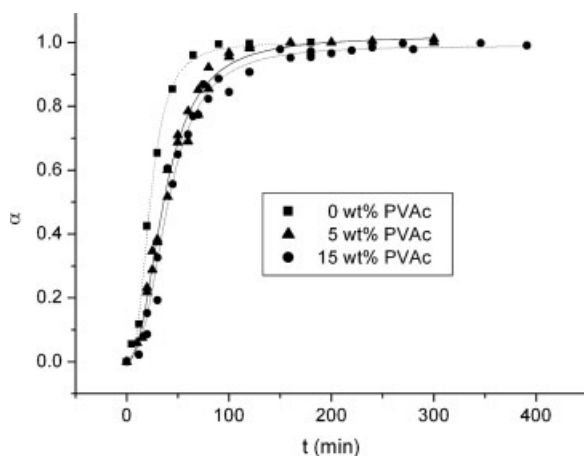| PVAc (wt %)	T_{g2}(°C)	T_{g1} (°C)
0	183	—
5	180	39
10	183	43
15	183/150	44

Figure 4 Conversion time plot for epoxy/PVAc blends containing 5 and 15 wt % PVAc ($T_c = 180°C$) together with that previously obtained for neat epoxy.[24]

conversion-versus-time curves did not change significantly relative to the uncorrected ones, except for a long curing time. Figure 4 shows the conversions calculated for blends containing 5 and 15 wt % PVAc plotted versus time, together with the data for neat epoxy.[24] As can be seen, PVAc slowed down the cure reaction. This could have been related to the dilution effect of reactants. However, a clear correlation between PVAc content and the delaying effect was not found.

The phenomenological model developed by Kamal[26] was used to analyze the isothermal kinetic data. The general equation assumed for the curing reaction of epoxy–amine systems was:[26,27]

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \qquad (2)$$

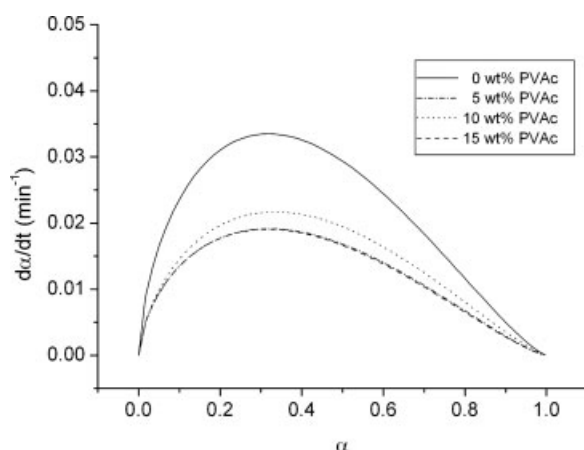where k_1 and k_2 are the apparent rate constants, m and n are the reaction orders, k_1 is the kinetic rate

Figure 5 Plots of $d\alpha/dt$ versus α for epoxy/PVAc blends containing different PVAc contents ($T_c = 180°C$) and for neat epoxy.

TABLE II
Kinetic Parameters for Epoxy/PVAc Blends Cured at 180°C

PVAc (wt %)	$k_1 \times 10^5 (s^{-1})$	$k_2 \times 10^3 (s^{-1})$	n	m
0	2	1.9	1.35	0.66
5	3	1.1	1.35	0.65
10	7	1.3	1.35	0.66
15	2	1.1	1.35	0.65

constant for the reaction catalyzed by the groups initially present, and k_2 is the kinetic rate constant associated with autocatalysis by the —OH groups generated in the epoxy–amine reaction.

On applying the kinetic model, all the α data could be considered because vitrification took place at the end of the isothermal curing ($T_c = 180°C$). Figure 5 shows the $d\alpha/dt$ versus α plots. As can be seen, the curing reaction was autocatalytic, displaying maximum rates at conversions close to 0.32. Although the presence of PVAc clearly decreased the reaction rate, there was no evident correlation with PVAc content. The values of the model parameters determined by an iterative procedure are listed in Table II. The reaction orders n and m were approximately 1.35 and 0.65, respectively, and did not seem to vary with the blend composition, with the total reaction order $m + n$ being close to 2. These values were in accordance with those previously reported in the literature.[28,29] For all blends, k_1 was noticeably lower than k_2. The neat epoxy showed the highest k_2 value; accordingly, it had the highest reaction rate.

Once the conversion has been calculated, it can be related to the phase separation process. The T_g and conversion values for reaction times at which the phase separation was detected are shown in Table III. Phase separation took place between 30 and 45 min, which corresponded to $0.35 < \alpha < 0.6$, that is, not far from gelation. According to the Flory–Stockmayer relation,[30] $\alpha_{gel} = 0.57$ for this kind of systems. Moreover, as T_{g2} reflected the T_g of the growing network phase, it could be correlated with the conversion. Figure 6 shows the plot of T_{g2} versus

TABLE III
T_g and Conversion Values at the Beginning of Phase Separation for Epoxy/PVAc Blends Cured at 180°C

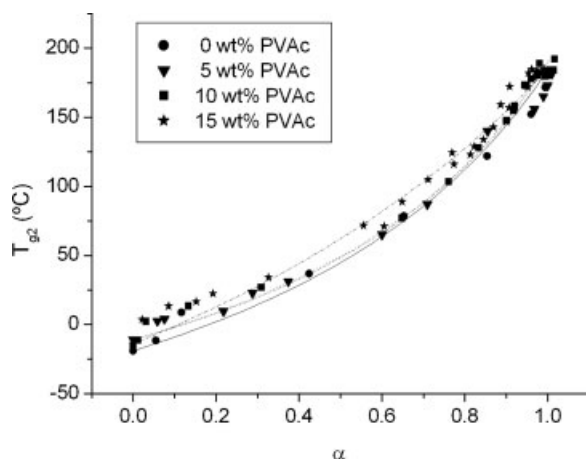| PVAc (wt %)	t_c (min)	T_{g1} (°C)	T_{g3} (°C)	T_{g2} (°C)	α
0	30	—	—	78	0.65
	45	—	—	122	0.85
5	30	—	—	31	0.37
	40	33	53	65	0.60
10	30	—	—	27	0.31
	45	34.5	54	77	0.65
15	30	—	—	34	0.33
	40	36	54	71	0.61

Figure 6 Glass-transition temperature of epoxy-rich phase (T_{g2}) versus conversion for epoxy/PVAc blends with different PVAc contents ($T_c = 180°C$): experimental points and Pascault-Williams fits.

conversion for all blend compositions. The behavior was that usually reported for thermosets.[3,25,31] The dispersion of the date for $\alpha < 0.5$ was a consequence of having miscible blends with different PVAc contents. In this range, $0 < \alpha < 0.5$, the T_g of the neat epoxy system was lower than the T_g of PVAc; therefore, the T_g values of the miscible epoxy/PVAc blends were higher than those corresponding to neat epoxy. When α approached 0.5, the T_g of the neat epoxy system would reach the PVAc T_g (44°C), and this effect should disappear. On the other hand, after complete phase separation (neat epoxy and neat PVAc), a unique T_{g2}-α profile would be expected. The dispersion observed for $\alpha > 0.5$ can be attributed to not having a neat phase separation and somewhat to experimental error. Aside from that for the epoxy/PVAc blends containing 15 wt % PVAc, only the data corresponding to the highest T_g values (T_{g2}) are plotted in Figure 6.

When the curing reaction is kinetically controlled there must be a one-to-one relationship between T_g and α. The relationship proposed by Pascault and Williams[32], derived from the Couchman expression,[33] considers the thermosetting system as a mixture of a fully cured network and a monomer:

$$\frac{T_g - T_g^0}{T_g^\infty - T_g^0} = \frac{\lambda\alpha}{1 - (1 - \lambda)\alpha} \qquad (3)$$

where T_g^0 is the glass-transition temperature of the unreacted mixture ($\alpha = 0$) and T_g^∞ is the glass-transition temperature of the fully reacted thermoset ($\alpha = 1$), $\lambda = \Delta c_p^\infty / \Delta c_p^0$ (where Δc_p^∞ and Δc_p^0 are the differences in heat capacity between the glassy-rubber and the glassy-liquid states, respectively), and it is usually taken as an adjustable parameter. This equa-

tion, sometimes referenced as the Di Benedetto relation,[34] has been successfully used to fit the T_g-α data of thermosets.

In carrying out the curing process, no vitrification took place until the end of curing ($T_c = 180°C \sim T_g^\infty$). Therefore, regardless of the phase separation that took place on curing, we applied eq. (3) to fit the T_g-α data. The lines on Figure 6 represent the fit of eq. (3) for each composition. The λ values obtained were 0.46, 0.45, 0.52, and 0.62 for neat epoxy and for the epoxy/PVAc blends containing 5, 10, and 15 wt % PVAc, respectively, which was in agreement with those previously reported for several amine epoxy systems.[3,32,35]

Morphological analysis

Environmental scanning electron microscopy (ESEM) was used to study the morphology of cured epoxy/PVAc blends with different PVAc contents. Figure 7 shows the micrographs obtained for cured samples (3 h at 180°C) having 5, 10, and 15 wt % PVAc together with the neat epoxy. The micrograph of the neat epoxy [Fig. 7(a)] shows, as was expected, no visible phase domains; however, the micrographs obtained for samples containing PVAc showed evidence of heterogeneous morphology. For cured epoxy/PVAc blends with 5 wt % PVAc [Fig. 7(b)], small spheres (number mean diameter of 1.5 ± 0.4 μm) were uniformly dispersed in a continuous matrix. Acetone-etched samples showed spherical holes in an unaffected matrix, confirming that the epoxy network formed the continuous phase and that the dispersed spherical particles were PVAc. Samples with 10 wt % PVAc presented a combined morphology [Fig. 7(c)] in which two types of regions could be distinguished. There were regions [Fig. 7(d)] that showed a morphology similar to that for samples containing 5 wt % PVAc. In these regions the number mean diameter of PVAc spheres was 1.6 ± 0.4 μm. Other regions [Fig. 7(e)] were formed by spherical nodules (number mean diameter 20 ± 10 μm) that occupied most of the volume and were wrapped by a continuous thin phase. Epoxy samples with 15 wt % PVAc [Fig. 7(f)] showed a distribution of spheres (number mean diameter 100 ± 30 μm) that were surrounded by a continuous thin phase. This morphology was similar to that observed in one of the regions of the samples containing 10 wt % PVAc, although in this case the spherical nodules were bigger. This agrees with an inverted morphology in which PVAc is the continuous phase. Accordingly, etching of these samples in acetone dissolved the PVAc phase and the samples disaggregated. With using higher magnification [Fig. 7(g)], very small spheres could be seen, which may be related to the intermediate T_g detected by DSC.
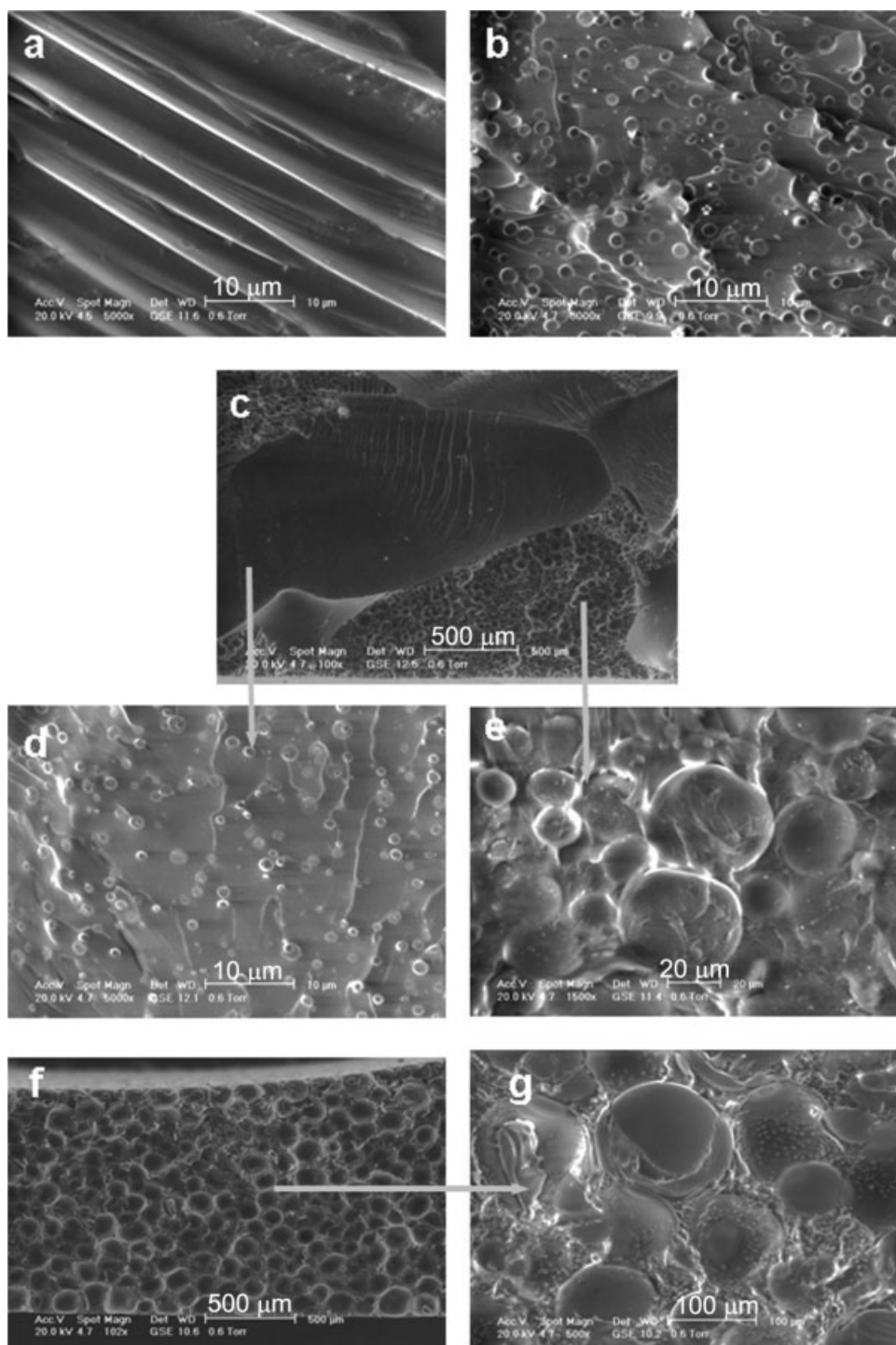
Figure 7 ESEM micrographs for epoxy/PVAc blends cured 3 h at 180°C: (a) neat epoxy, (b) 5 wt % PVAc, (c) 10 wt % PVAc showing combined morphology, (d) 10 wt % PVAc shown at higher magnification (e) 10 wt % PVAc shown at higher magnification, (f) 15 wt % PVAc, (g) 15 wt % PVAc shown at higher magnification.

The critical point was calculated according to Pascault[1] using the relation:

$$(\phi^c_{TP})^{-1} = 1 + \left[\frac{V_{TP}}{V_{TS}}\right]^{1/2} \frac{x_w(TP)}{(x_z(TP))^{1/2}} \quad (4)$$

where ϕ^c_{TP} is the volume fraction of the thermoplastic (PVAc) at the critical point, V_{TP} is the molar volume of the repeating unit of the thermoplastic, V_{TS} is the molar volume of the thermoset precursor taken as a single pseudomonomer (2/3 mol DGEBA and 1/3 mol DDS), and $x_w(TP)$ and $x_z(TP)$ are the degrees of
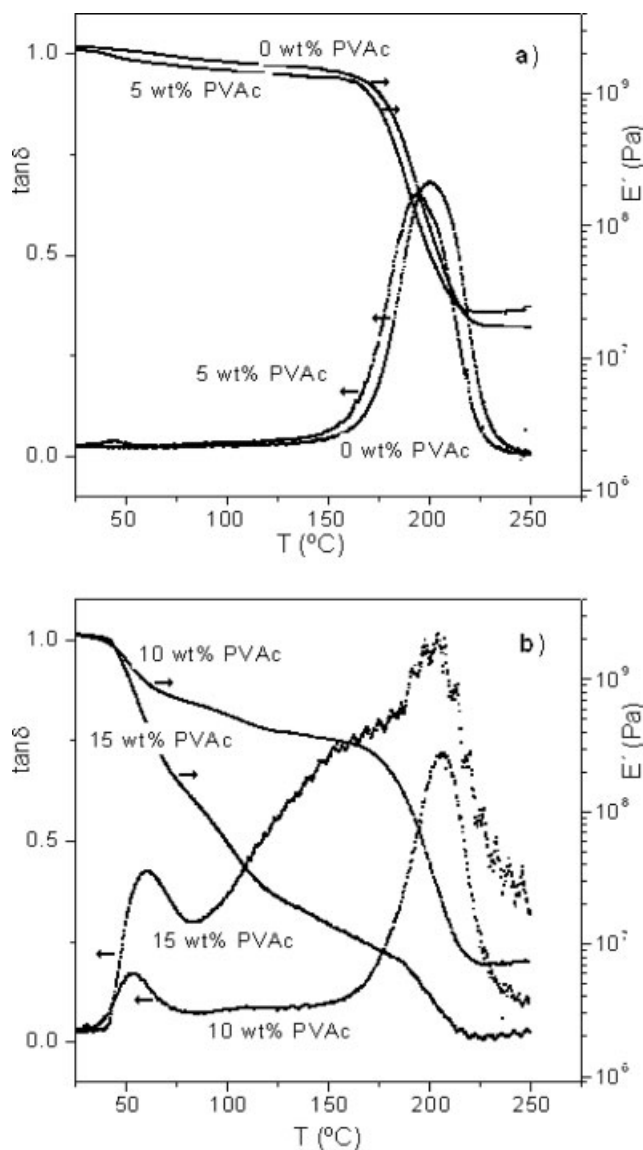
Figure 8 DMTA isochrones at 1 Hz: E' and tan δ versus temperatures for epoxy/PVAc blends cured 3 h at 180°C with different PVAc contents: (a) neat epoxy and 5 wt % PVAc and (b) 10 and 15 wt % PVAc.

polymerization of the thermoplastic. The molar volumes were obtained from the densities and the degrees of polymerization from GPC. A ϕ^c_{PVAc} of approximately 0.06 was obtained, which was in accordance with the experimental observations, that is, the inversion in morphology took place at a PVAc content of around 10 wt %. In this region a variety of morphologies may develop.[1] The morphology observed in the system studied here was similar to that previously reported for poly(ether imide)/epoxy blends cured with DDS.[36]

Dynamic mechanical thermal analysis

DMTA measurements were performed for cured samples (3 h at 180°C). Figure 8 shows the storage

modulus (E') and the loss tangent (tan δ) isochrones (1 Hz) for a specimen of each blend composition tested, which are plotted against temperature. Figure 8(a) shows the isochrones for the epoxy/PVAc blend containing 5 wt % PVAc and for neat epoxy, and Figure 8(b) shows the isochrones for blends containing 10 and 15 wt % PVAc. The storage modulus in the glassy state ($T < 40°C$) reached an E' of approximately 2×10^9 Pa, and as was expected, it was almost independent of PVAc content. The E' temperature of the isochrones for neat epoxy and for the samples with 5 wt % PVAc were very similar. However, for samples containing 10 wt % PVAc, a lowering of the modulus was detected in the PVAc glass-transition zone (40°C–60°C). From this temperature until approaching the T_g of the epoxy network, the modulus changed slightly, and the plateau between T_gs was approximately 5×10^8 Pa. In samples containing 15 wt % PVAc the effect of temperature was clearly remarkable—from 40°C the modulus decreased continuously with an increase in temperature. At 200°C both the epoxy and PVAc phases were above their T_g values, and the moduli were similar for the neat epoxy and the blend with 5 wt % PVAc ($E' \sim 2 \times 10^7$ Pa) but E' lowered to approximately 8 $\times 10^6$ and 2×10^6 Pa for samples containing 10 and 15 wt % PVAc, respectively. The E' temperature behavior could be related to sample morphology, that is, the blend containing 5 wt % PVAc and neat epoxy behaved similarly because the epoxy network formed the matrix. However, in samples with 15 wt % PVAc, in which the thermoplastic formed the continuous phase, a significant E' drop appeared when the temperature overrode the PVAc T_g. Samples composed of 10 wt % PVAc, which exhibited combined morphology, showed an intermediate behavior.

As can be seen in Figure 8(a), the neat epoxy showed a unique high tan δ peak (mean value for the three specimens tested of ~198°C) corresponding to the α-relaxation of the epoxy network. As expected, the calorimetric T_g values were about 10°C–20°C lower than the α-relaxation T_g values determined from the tan δ peak at 1 Hz. For the epoxy/PVAc blend with 5 wt % PVAc, the pronounced tan δ peak of the epoxy network appeared (~196°C), in addition to a small tan δ peak at about 44°C, which corresponded to the α-relaxation of the PVAc phase. For samples with 10 wt % PVAc, the large percentage of PVAc made it feasible to clearly detect the tan δ peak corresponding to PVAc, together with the epoxy network tan δ peak (~203°C). Tan δ isochrones for epoxy/PVAc blends containing 15 wt % PVAc were more complex. The isochrone clearly displayed two maxima that corresponded to a PVAc-rich phase and the cured epoxy network. The main difference with the isochrones of the other blends was the

much higher tan δ values from 50°C. This reflects that the capability of storing energy (E') decreased faster with temperature than the capability of dissipating it. This behavior was a consequence of the sample morphology, which was inverted, that is, PVAc was the matrix, and therefore when temperatures overrode the PVAc T_g, the matrix softened, and the sample could be seen as hard spheres (epoxy phase) dispersed into a viscous liquid that had a very low elastic response. Moreover, in this epoxy/PVAc blend (15 wt % PVAc), the epoxy network tan δ peak (~199°C) had a wide shoulder at about 160°C, which was attributed to the α-relaxation of the epoxy network domains with lower crosslinking density. This was in accordance with the T_g DSC results [see Fig. 3(c)] and with the slightly minor conversion reached in this blend composition (α = 0.98 after 3 h at 180°C). DMTA shoulders in the α-relaxation of epoxy network have been also observed in other epoxy-diamine thermosets[14,37] and attributed to having regions of not fully cured epoxy. In particular epoxy/polysulfone blends[14] with cocontinuous and inverted morphologies showed this behavior, whereas when the thermoplastic particles were dispersed in the epoxy matrix, the cure process could be completed and only one epoxy α-relaxation took place. The behavior of the epoxy/PVAc blends seemed to follow this pattern.

CONCLUSIONS

Epoxy (DGEBA + DDS)/PVAc blends with different PVAc contents (5, 10, or 15 wt %) showed a single T_g at the initial curing reaction stage, reflecting miscibility, but upon curing, more than one T_g occurred, indicating phase separation. Longtime cured epoxy/PVAc blends showed two T_g values, corresponding to a PVAc-rich phase and to the epoxy network. In the cured epoxy/PVAc blend with 15 wt % PVAc, a small intermediate T_g was detected, showing the presence of epoxy domains of a lower crosslinking density. The DMTA α-relaxations of cured epoxy/PVAc blends agreed with the T_g results by DSC.

The curing reaction was autocatalytic with maximum rates at conversions close to 0.32. The presence of PVAc slowed down the kinetic, but did not modify the reaction mechanism, with a total reaction order of about 2. T_g versus conversion data could be fitted to the Pascault and Williams relationship.

ESEM analysis showed that changing the PVAc content from 5 to 15 wt % led to an inversion in morphology. Cured epoxy/PVAc blends containing 5 wt % PVAc were composed of small PVAc spheres dispersed in an epoxy matrix; however, cured epoxy/PVAc blends containing 15 wt % PVAc showed an inverted morphology (epoxy spheres surrounded by a continuous PVAc phase), and the intermediate PVAc composition (10 wt %) showed a combined morphology.

The changes in the blend morphology with PVAc content had a clear effect on the DMTA behavior: blends in which the thermoplastic phase was dispersed in the epoxy matrix (5 wt % PVAc) behaved similarly to that of neat epoxy, whereas blends with inverted morphology (15 wt % PVAc) showed a dramatic decrease in the storage modulus and a high capability of dissipating energy from 40°C, because of the flow of the PVAc matrix at temperatures higher than its T_g.

References

1. Pascault, J. P.; Williams, R. J. J. In Polymer Blends; Paul, D.R.; Bucknall, C.B., Eds.; Wiley: New York, 2000; Vol. 1, p 379.
2. Yee, A. F.; Du, J.; Thouless, M. D. In Polymer Blends; Paul, D. R.; Bucknall, C. B., Eds.; Wiley: New York, 2000; Vol. 2, p 225.
3. Pascault, J. P.; Sautereau, H.; Verdu, J.; Williams, R. J. J. In Thermosetting Polymers; Marcel Dekker: New York, 2002; p 389.
4. Bucknall, C. B. In Polymer Blends; Paul, D. R.; Bucknall, C. B., Eds.; Wiley: New York, 2000; Vol. 2, p 83.
5. Williams, R. J. J.; Rosemberg, B. A.; Pascault, J. P. Adv Polym Sci 1997, 128, 95.
6. Kim, B. S.; Chiba, T.; Inoue, T. Polymer 1995, 36, 43.
7. Riccardi, C. C.; Borrajo, J.; Williams, J. J.; Girard-Reydet, E.; Sautereau, H.; Pascault, J. P. J Polym Sci, Part B: Polym Phys 1996, 34, 349.
8. Rong, M.; Zeng, H. Polymer 1997, 38, 269.
9. Girard-Reydet, E.; Sautereau, H.; Pascault, J. P.; Keates, P.; Navard, P.; Thollet, G.; Virgier, G. Polymer 1998, 39, 2269.
10. Lopez, J.; Ramirez, C.; Abad, M. J.; Barral, L.; Cano, J.; Diez, F. J. J Appl Polym Sci 2002, 85, 1277.
11. Bonnet, A.; Pascault, J. P.; Sautereau, H.; Taha, M.; Camberlin, Y. Macromolecules 1999, 32, 8517.
12. Bonnet, A.; Pascault, J. P.; Sautereau, H.; Camberlin, Y. Macromolecules 1999, 32, 8524.
13. Oyanguren, P. A.; Galante, M. J.; Andromaque, J.; Frontini, P.M.; Williams, J. J. Polymer 1999, 40, 5249.
14. Varley, R. J.; Hodkin, J. H.; Simon, G. P. Polymer 2001, 42, 3847.
15. Teng, K.; Chang, F. Polymer 1993, 34, 4291.
16. Teng, K.; Chang, F. Polymer 1996, 37, 2385.
17. Zheng, S.; Hu, Y.; Guo, Q.; Wei, J. Colloid Polym Sci 1996, 274, 410.
18. Quian, J. Y.; Pearson, R. A.; Dimonie, V. L.; Shaffer, O. L.; El-Hasser, M. S. Polymer 1997, 32, 21.
19. López, J.; Ramirez, C.; Abad, M. J.; Barral, L.; Cano, J.; Diez, F. Polym Int 2002, 51, 1100.
20. Ritzenhaler, S.; Girard-Reydet, E.; Pascault, J. P. Polymer 2000, 41, 6375.
21. Meynie, L.; Fenouillot, F., Pascault, J. P. Polymer 2004, 45, 1867.
22. Giannotti, M. I.; Foresti, M. L.; Mondragon, I.; Galante, M. J.; Oyanguren, P. A. J Polym Sci, Part B: Polym Phys 2004, 42, 3953.

23. Giannotti, M. I.; Foresti, M. L, Mondragon, I.; Galante, M. J.; Oyanguren, P. A. Polym Int 2004, 54, 807.
24. Lapprand, A.; Arribas, C.; Salom, C.; Masegosa, R. M.; Prolongo, M. G. J Mat Proc Tech 2003, 143–144, 827.
25. Min, B. G.; Stachurski, Z. H.; Hodgkin, J. H. Polymer 1993, 34, 4908.
26. Kamal, M. R. Polym Eng Sci 1974, 14, 23.
27. Sourour, S.; Kamal, M. R. Thermochim Acta 1976, 14, 41.
28. Keenan, M. R. J Appl Polym Sci 1987, 33, 1725.
29. Ryan, M. E.; Dutta, A. Polymer 1979, 20, 203.
30. Stepto, R. F. T., Ed. In Polymer Networks; Blackie Academic and Professional: London, 2000; p 18.
31. Rajagopalan, J. W.; Gillespie, J. R.; McKnight, S. H. Polymer 2000, 41, 7723.
32. Pascault, J. P.; Williams, R. J. J. J Polym Sci, Part B: Polym Phys 1990, 28, 85.
33. Couchman, P. R. Macromolecules 1987, 20, 1712.
34. Di Benedetto, A. T. J Polym Sci, Part B: Polym Phys 1987, 25, 1949.
35. Pascault, J. P.; Williams, R. J. J. Polym Bull 1990, 24, 115.
36. Cho, J. B.; Hwang, J. W.; Cho, K.; An, J. H.; Park, C. E. Polymer 1993, 34, 4832.
37. Ratna, D. Polymer 2001, 42, 4209.