

CURE KINETICS OF EPOXY RESIN AND THERMOPLASTIC POLYMER

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The cure kinetics and morphology of diglycidyl ether of bisphenol A (DGEBA) modified with polyvinyl acetate (PVAc) using diaminodiphenylmethane (DDM) as hardener were investigated through differential scanning calorimetry (DSC) and environmental scanning electron microscopy (ESEM). Isothermal curing measurements were carried out at 150, 120 and 80°C. The kinetic parameters were obtained using the general autocatalytic chemically controlled model. The comparison of the kinetic data indicates that the presence of PVAc does not change the autocatalytic nature of the cure reaction. Two T_g 's were observed in the fully cured samples of the modified systems. ESEM micrographs confirm the biphasic morphology.

Keywords: cure kinetics, epoxy/polyvinyl acetate blends, morphology

Introduction

Epoxy resins are used for a wide range of applications, including major matrix material for carbon fiber composites. Among their relevant properties are specific strength, high temperature and chemical resistance and easy processing. However, the epoxy resins are generally brittle due to high crosslink densities. In the literature [1–8] it can be found many studies in which the epoxy resins are blended with other materials like thermoplastic polymers in order to improve their fracture toughness without sacrificing the glass transition temperature, T_g , strength stiffness, or other desirable properties of thermosetting systems. Toughness improvement requires the formation of a heterogeneous material with thermoplastic rich and thermosetting rich phases. In these systems, the toughening has been suggested [8, 9] to arise from crack pinning and plastic deformation of the rich thermoplastic phase. Generally, phase separation of the thermoplastic polymer takes place during the curing reaction. The reaction-induced phase separation process can generate a variety of morphologies (bicontinuous or inverted structures) depending on thermodynamic and kinetic factors, namely, the modifier concentration and its molar mass, the curing temperature, the reaction rate and the viscosity during phase separation [8, 10]. The thermoplastics addition to epoxy resins is expected not only to alter the morphology but also the cure kinetics.

In previous works [11, 12] we have studied the curing reaction and morphology of an epoxy resin, diglycidylether of bisphenol A (DGEBA), modified with ductile thermoplastic, polyvinyl acetate (PVAc) with a moderate $T_g \sim 45^\circ\text{C}$. The hardener used was

4,4'-diaminodiphenylsulfone (DDS) and the reaction was carried out at 180°C. It has been proved [11] that DGEBA/PVAc blends are homogeneous in the whole composition range. PVAc allows obtaining homogeneous reacting mixtures with adequate viscosity values that makes easier the processing regarding to other blends formed with thermoplastic polymers with higher T_g .

In the present work we have investigated the isothermal cure kinetics of DGEBA and their blends with PVAc (5, 10, 15 mass%) using 4,4'-diaminodiphenylmethane (DDM) as hardener, through differential scanning calorimetry measurements (DSC). The reactions were conducted at three temperatures, 150, 120 and 80°C. The reaction rates and the total orders of the curing reactions have been determined for neat epoxy (DGEBA+DDM) and its blends with PVAc at 150 and 120°C. DDM is a hardener that allows performing the curing reactions at lower curing temperatures than DDS, preventing the possible thermal degradation of PVAc. The aim of this paper is to investigate the effect of curing conditions and blend compositions on the curing kinetics of DGEBA+ DDM+PVAc blends comparing the results with those obtained for DGEBA+DDS+PVAc. Also, the morphology of the totally curing samples will be analyzed by environmental scanning electron microscopy (ESEM). In these systems the final phase morphology is the consequence of two competitive processes: phase separation and vitrification that take place in the course of curing reaction, and therefore it depends on the reaction temperature. Consequently, the morphologies of the cured samples will be compared with those obtained for analogous samples cured with DDS at higher temperature.

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Experimental

Materials and sample preparation

The epoxy resin used in this work is diglycidyl ether of bisphenol A (DGEBA) manufactured by Ciba under commercial name of Araldite. The number average relative molecular mass $M_n=360$ was obtained from epoxy equivalent 180 g/eq, that was determined by chemical titration of the end groups. The amine curing agent was 4,4'-diaminodiphenylmethane (DDM) manufactured by Aldrich of 97% purity. Poly(vinyl acetate) with $M_n=9 \cdot 10^4$ and polydispersity index 2 was purchased from Polysciences. Acetone Panreac (0.3% water content) was used as solvent. The chemical structures of the three components are shown in Fig. 1.

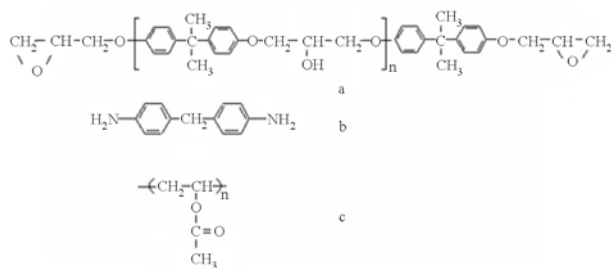


Fig. 1 Chemical structure of a – epoxy resin (DGEBA), b – DDM and c – PVAc

The blends DGEBA+DDM and DGEBA+DDM+PVAc were prepared by mixing appropriate amounts of their respective solutions in acetone. The epoxy prepolymer and DDM in the blends were always in stoichiometric ratio amino-hydrogen to epoxy. Three blend compositions, with different percentages of PVAc (5, 10, 15 mass%) in the final samples, have been prepared besides the unmodified epoxy. The mixtures were cast into aluminium pans for differential scanning calorimetry measurements (DSC). The solvent in the mixture was vaporized under vacuum at room temperature for 24 h. Samples for environmental scanning electron microscopy, ESEM, were prepared in a similar way.

Methods

Differential scanning calorimetry

In order to determine the glass transition temperature and the heat of reaction, a Mettler-Toledo mod 822e differential scanning calorimetry was used. Prior to DSC runs, the temperature and heat flow were calibrated using indium and zinc standards. The measurements were conducted under nitrogen atmosphere. The sample mass used was kept in the 10 to 25 mg

range. The heating rate used in the different scans was $10^\circ\text{C min}^{-1}$.

To study the kinetics of the curing reactions, a set of identical samples for each composition were prepared. The DGEBA+DDM and DGEBA+DDM+PVAc samples were isothermally cured in an air oven at the curing temperatures $T_c=150, 120$ and 80°C , and then withdrawn at different time intervals and quenched immediately to room temperature to ‘freeze’ the reaction. Afterwards, they were scanned in DSC apparatus from -60 to 300°C to determine the residual heat of reaction (ΔH_R). The exothermal peak area of uncured samples ($t_c=0$ min) was taken as the total heat of the reaction (ΔH_T). The conversion, α , as a function of the curing time (t_c) was obtained as:

$$\alpha = \frac{\Delta H_T - \Delta H_R}{\Delta H_T} \quad (1)$$

To determine the T_g of the present phases in the total cured system all the samples were rescanned from -10 to 200°C at $10^\circ\text{C min}^{-1}$. The T_g value was taken at the midpoint of the heat capacity transition.

Environmental scanning electron microscopy

Environmental scanning electron microscopy, ESEM, has been used to study the morphology of the cured resin, as well as their blends. Due to the non conducting nature of the samples, the environmental mode was selected. A Phillips XL 30 instrument was used with beam energy of 20 kV, being verified that these experimental conditions did not produce severe damage on the samples. The water vapour pressure was 0.5–0.8 Torr, corresponding to a relative humidity of $\approx 5\%$.

Results and discussion

Heat of reaction and conversion

Blends of DGEBA+DDM and DGEBA+DDM+PVAc were cured at three different temperatures, 80, 120 and 150°C . The reaction kinetics and the glass transition temperatures can be investigated from the curves of the blends after the isothermal cure for different reaction times, t_c . Figure 2 shows the set of curves obtained for DGEBA+DDM samples cured at $T_c=120^\circ\text{C}$ for different times. As it can be observed the glass transition temperature (T_g) increases, whereas the area of exothermal peak, corresponding to the residual heat of reaction, ΔH_R reduces as a function of t_c . The presence of a single T_g in the curves indicates the existence of a unique amorphous phase. DGEBA+DDM cured at 80 and 150°C shows a similar behaviour. Figure 3 exhibits the DSC curves obtained at different t_c for DGEBA+DDM+PVAc (15 mass%) at $T_c=150^\circ\text{C}$.

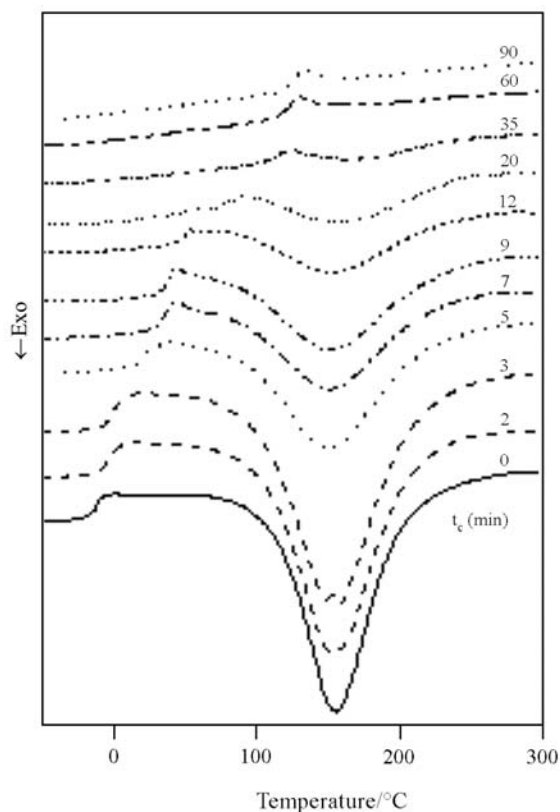


Fig. 2 DSC curves of DGEBA+DDM cured at $T_c=120^\circ\text{C}$ for different curing times, t_c

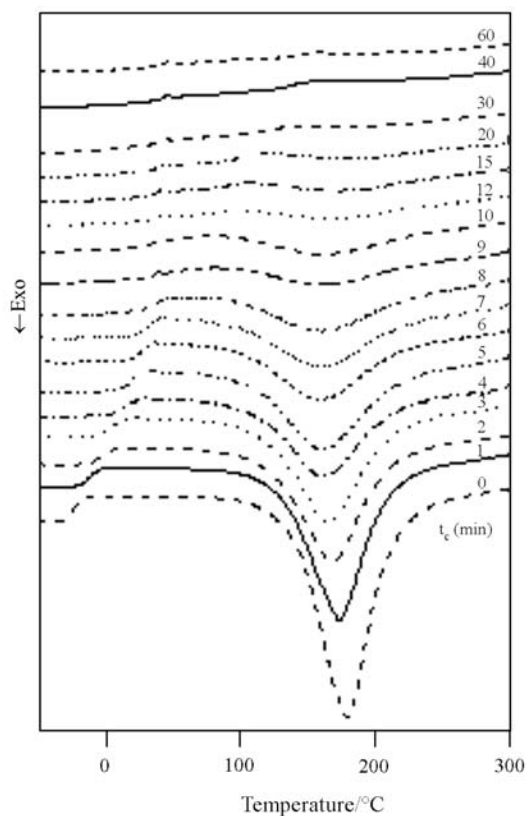


Fig. 3 DSC curves of DGEBA+DDM+15 mass% PVAc cured at $T_c=150^\circ\text{C}$ for different curing times, t_c

The pattern of the curves is similar to those obtained for DGEBA+DDM blends, although when the reaction time increases two T_g 's are detected. The lowest T_g is nearly constant and slightly minor than the corresponding to pure PVAc; therefore it could be assigned to a phase enriched in PVAc. The highest T_g increases with the reaction time and consequently should be mainly composed of epoxy (DGEBA+DDM). Similar results are obtained changing the content of PVAc in the blend (5 and 10 mass%) and the curing temperature ($T_c=120$ and 80°C).

Figure 4 shows the heating curves for the system DGEBA+DDM+PVAc (0, 5, 10 and 15 mass%) corresponding to uncured samples ($t_c=0$ min). These samples can be considered as miscible, if it is admitted as miscibility criterion the existence of a single T_g .

From the area of the broad exothermal peak of the curves in Fig. 4 it is possible to calculate the total heat of the reaction, ΔH_T . Table 1 shows ΔH_T for each blend per gram of the blend. The decrease of ΔH_T is a consequence of the presence of PVAc. However, ΔH_T almost remains constant when is calculated per epoxy equivalent. The average value of $\Delta H_T \sim 95 \text{ kJ ee}^{-1}$ obtained is in agreement with those reported in [13, 14].

The temperature value corresponding to the minimum of the exothermal peak T_{peak} , is also given in Table 1. This minimum corresponds to the maximal heat flow due to the exothermic epoxy-amine reac-

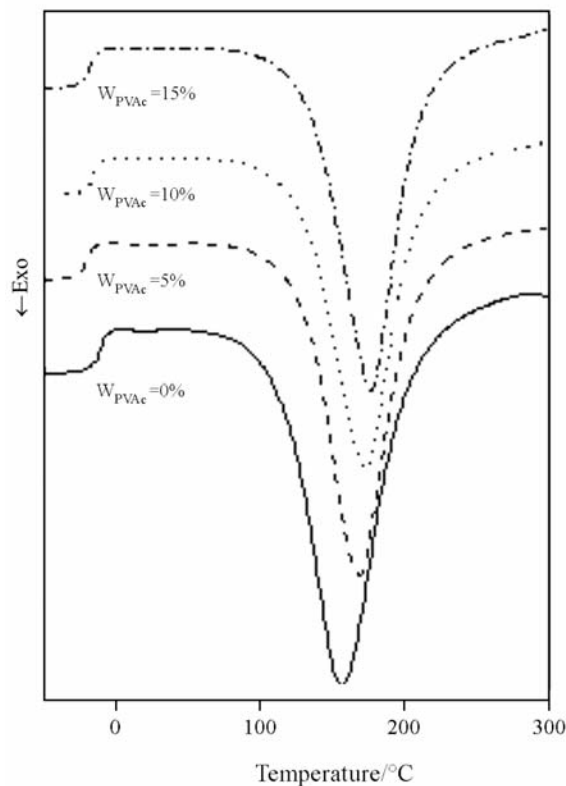


Fig. 4 DSC curves obtained for uncured samples DGEBA+DDM+PVAc

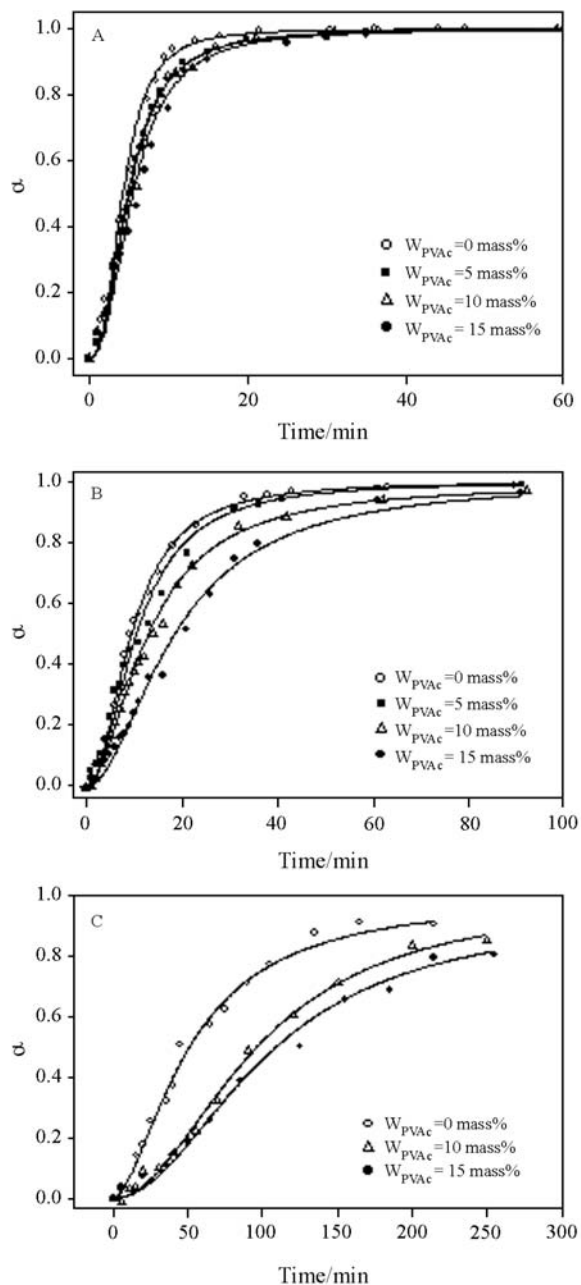
Table 1 Total heat of the reaction, ΔH_T , and temperature value corresponding to the minimum of the exothermal peak, T_{peak} , for DGEBA+DDM+PVAc obtained at $10^\circ\text{C min}^{-1}$

PVAc/ mass%	$T_{peak}/$ $^\circ\text{C}$	$\Delta H_T/$ J g^{-1}	$\Delta H_T/$ $\text{kJ (epoxy equiv.)}^{-1}$
0	164	-425	-98
5	168	-390	-95
10	178	-362	-93
15	181	-346	-94

tion. The peak temperature increases with the content of PVAc in the blend showing that the kinetics becomes slower when the PVAc is present.

From the DSC measurement the conversion as a function of the curing time is calculated using Eq. (1). The results for the neat epoxy and its three blends with 5, 10, and 15 mass% of PVAc are plotted in Fig. 5 at $T_c=150, 120$ and 80°C . It can be seen that the kinetics become slower when the PVAc is present. As it was demonstrated in a previous work [11] the blends DGEBA+PVAc are initially homogeneous, with a single glass transition temperature over the entire composition range. The addition of a non reactive thermoplastic as PVAc to the DGEBA+DDM provokes a dilution effect of reactive groups and therefore a decrease of epoxy-amine reaction rate. Figure 5 also indicates that, at $T_c=150^\circ\text{C}$ is necessary around 30 min to reach final conversion ($\alpha\sim 1$) for modified and unmodified systems. For $T_c=120$ and 80°C , the value of the reached conversion remains practically constant below unity. At these curing temperatures the isothermal reaction occurs below the glass transition temperature, T_g^∞ , corresponding to the fully reacted material and the reactive material transforms to glassy state during the curing reaction. As a consequence of the vitrification a lower conversion is reached, mainly at $T_c=80^\circ\text{C}$.

The vitrification time (t_v) is defined as the reaction time at which the glass temperature becomes equal to curing reaction temperature. In Table 2 the t_v and the corresponding values of conversion (α_v) are shown for unmodified DGEBA+DDM systems at $T_c=150, 120$ and 80°C . The value of T_g^∞ for this system is 147°C . Table 2 also summarizes the maximum T_g reached at each curing temperature (T_g^{\max}). At $T_c=150^\circ\text{C}$ the curing reaction is chemically controlled due to the value of the T_g^{\max} is coincident with T_g^∞ . However at $T_c=120$ and 80°C the values of T_g^{\max} obtained are lower than T_g^∞ , accordingly, at later stages, the reaction becomes diffusion controlled. It would be expected that the diffusion control over the reactive system was more significant at $T_c=80^\circ\text{C}$.

**Fig. 5** Conversion (α) – time curves for DGEBA+DDM+PVAc blends at A – $T_c=150^\circ\text{C}$; B – $T_c=120^\circ\text{C}$; C – $T_c=80^\circ\text{C}$ **Table 2** Vitrification time, t_v , vitrification conversion, α_v , and glass transition temperature obtained at the end of curing reaction, T_g^{\max} as a function of the curing temperature, T_c for neat epoxy

$T_c / ^\circ\text{C}$	t_v / min	α_v	$T_g^{\max} / ^\circ\text{C}$
150	45	1	147
120	63	0.98	125
80	135	0.88	92

Kinetic analysis

The reaction rates have been calculated from the conversions curves in Fig. 5. The reaction rate vs. curing time curves for DGEBA+DDM+PVAc (0, 5, 10 and 15 mass%) are shown in Fig. 6a, b, at 150 and 120°C respectively. All the rate curves display a maximum indicating an autocatalytic behaviour. The maximum reaction rate value decreases with the content of PVAc. This maximum is displaced towards higher times as the thermoplastic content increases.

Table 3 reports the values of conversion corresponding to the maximum reaction rate for neat epoxy and its blends cured at 150 and 120°C. The presence of PVAc does not modify the autocatalytic behaviour; however, the reaction rate of DGEBA+DDM is clearly reduced by the presence of PVAc. At each T_c the maximum reaction rate reached is lower when PVAc is present in the blends.

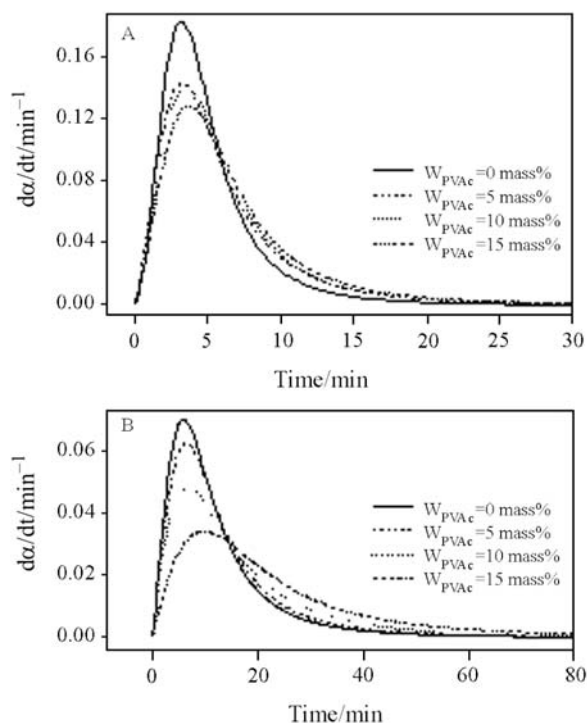


Fig. 6 Reaction rate – time curves for DGEBA+DDM+PVAc blends at A – $T_c=150^\circ\text{C}$; B – $T_c=120^\circ\text{C}$

Table 3 Conversion at the maximum reaction rate for DGEBA+DDM+PVAc (0, 5, 10, 15 mass%) blends

PVAc/ mass%	$T_c=150^\circ\text{C}$		$T_c=120^\circ\text{C}$	
	Max. rate/ min^{-1}	α	Max. rate/ min^{-1}	α
	0.183	0.31	0.070	0.26
5	0.143	0.28	0.063	0.25
10	0.141	0.30	0.047	0.23
15	0.128	0.30	0.034	0.23

Table 4 Kinetic parameters for DGEBA+DDM+PVAc (0, 5, 10, 15 mass%) blends at different curing temperatures, T_c

System	$T_c/^\circ\text{C}$	$k_2/$ min^{-1}	m	n
Neat epoxy	120	0.203	0.51	1.48
	150	0.505	0.64	1.37
Epoxy+PVAc 5 mass%	120	0.160	0.47	1.48
	150	0.461	0.57	1.44
Epoxy+PVAc 10 mass%	120	0.133	0.48	1.62
	150	0.371	0.60	1.42
Epoxy+PVAc 15 mass%	120	0.101	0.47	1.54
	150	0.367	0.58	1.43

The kinetic data of DGEBA+DDM+PVAc (0, 5, 10 and 15 mass%) obtained at $T_c=150$ and 120°C have been analyzed by the phenomenological model [15–17] habitually used to describe autocatalytic curing reactions chemically controlled of epoxy–amine systems:

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

where α is the conversion; m and n are partial reaction order, k_1 represents the kinetics rate constant for the reaction between groups initially present and k_2 represents the kinetics rate constant associated with the autocatalysis by the $-\text{OH}$ groups generated in the epoxy–amine reaction. The kinetic data obtained at $T_c=80^\circ\text{C}$ have not been analyzed by these model due to the reaction becomes diffusion controlled as it has been explained above (Table 2).

The kinetic parameters have been calculated by an iterative procedure and their values are shown in Table 4. The kinetic analysis demonstrates that the values of k_1 are always near to zero in both modified and unmodified samples indicating that the initial rate can be neglected, and then the autocatalytic mechanism is predominant. The partial orders m and n do not seem to change significantly as a function of the content of PVAc; a total order of the reaction $m+n$ close to 2 is obtained in all the blends studied. These results are in agreement with the literature values [18–22] for curing reaction of epoxy–amine systems. The values of k_2 at $T_c=150^\circ\text{C}$ in Table 4 are higher than the values of k_2 at $T_c=180^\circ\text{C}$ obtained for DGEBA+DDS+PVAc [12]; therefore the reaction rate using DDM as hardener is higher than the reaction rate using DDS. Also DDM allows reaching full conversion at lower curing temperatures. This circumstance may represent an advantage when a thermoplastic like PVAc, liable to suffer thermal degradation, is used as modifier of the epoxy resin.

Morphology of total cured samples

The blends DGEBA+DDM+PVAc (0, 5, 10 and 15 mass%) totally cured were rescanned to determine the glass transition temperatures. As is expected [2, 13] during the cure reaction the phase separation between the thermoplastic PVAc and the forming epoxy polymer occurs. The existence of two T_g s in the samples reveals the biphasic morphology of the totally cured epoxy+PVAc blends. The values of the two T_g s indicate the coexistence of one phase fundamentally formed by PVAc ($T_{g1} \sim 44^\circ\text{C}$) with another phase enriched in cured epoxy ($T_{g2} \sim 150^\circ\text{C}$).

Environmental scanning electron micrographies of the fully cured blends with PVAc (5 and 15 mass%) cured at $T_c = 150^\circ\text{C}$ for 2 h are shown in Fig. 7. Phase separated morphology was observed when PVAc is present. For epoxy resin+PVAc (5 mass%) the thermoplastic rich phase is dispersed as small spheres in epoxy rich phase. For 15 mass% in PVAc morphology is more complex. A combined morphology is obtained, in which the inversion begins to appear. The morphology obtained under these cure conditions is in agreement with that obtained under more complex cure schedules [23]. Moreover, a similar morphology is observed for DGEBA+DDS+PVAc cured at 180°C , but in this case the inversion is completed for 15 mass% PVAc content.

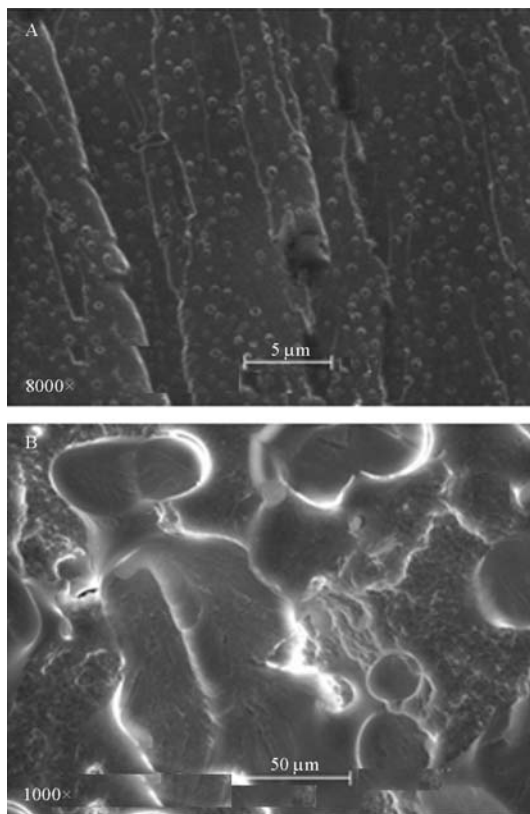


Fig. 7 Micrographies for DGEBA+DDM+PVAc blends; A – 5 mass% PVAc; B – 15 mass% PVAc

Conclusions

The isothermal curing process of DGEBA+DDM+thermoplastic non reactive PVAc (5, 10 and 15 mass%) blends at $T_c = 150, 120$ and 80°C was investigated by DSC. Prior to curing the blends were fully miscible. The effect of dilution of PVAc in the reactive system (DGEBA+DDM) provokes a decrease in the reaction rate at all the curing temperatures studied.

An autocatalytic mechanism was observed for all the blends. Kinetic parameters of DGEBA+DDM and its blends with PVAc (5, 10 and 15 mass%) were obtained at $T_c = 150$ and 120°C using the autocatalytic model for chemically controlled reactions. A total reaction order ($n+m$) close to 2 was obtained for all the blends. The values of k_1 were near to zero indicating that the initial reaction rate could be neglected and the autocatalytic mechanism was predominant.

DSC measurements revealed heterogeneous morphologies for blends with PVAc. Two phases were detected in the totally cured samples. The T_g values showed the coexistence of one phase formed mainly by PVAc and another phase corresponding to epoxy resin. ESEM micrographies for epoxy resin+PVAc (5 and 15 mass%) cured at $T_c = 150^\circ\text{C}$ demonstrated a change in the morphology of the samples as a function of the PVAc content.

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