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Effect of poly(styrene-*co*-acrylonitrile) on the curing of an epoxy/amine resin

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Abstract

The cure kinetics and the miscibility have been studied in blends of poly(styrene-*co*-acrylonitrile) (SAN) with tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM) and 4-4′-diaminodiphenylsulphone (DDS) as hardener. Differential scanning calorimetry (DSC) was the technique used for dynamic and isothermal experiments. Binary mixtures of SAN with the epoxy resin show complete miscibility over the whole composition range, displaying a single glass transition temperature. Kinetic analysis were performed using three kinetic models: Kissinger, Flynn–Wall–Ozawa and the phenomenological model developed by Kamal. Activation energies and kinetic parameters were determined by fitting experimental data. Diffusion control is incorporated to describe the cure in the latter stages, predicting the cure kinetics over the whole range of conversion. The autocatalytic mechanism was observed for the neat system and the epoxy-SAN blends. The reaction rates for the epoxy blends were found to be lower than of the neat epoxy. The reaction rates and the maximum conversions decreased when SAN contents increase, due to reduction of mobility of the reacting species.

Keywords: Cure kinetics; Poly(styrene-*co*-acrylonitrile)/epoxy blends; Miscibility

1. Introduction

Epoxy resins are nowadays widely used for composite materials in industry where properties such as high modulus, low creep, and reasonable high temperature performance are required [1]. The epoxy resins are generally brittle due to high crosslink densities, and this extensive use of epoxy systems has resulted in an increased interest in the modification of epoxy networks with high-performance ductile thermoplastics as an alternative to reactive rubbers for improving their toughness without sacrificing other useful properties such as glass transition temperature (T_g) and stiffness [2].

The reaction of epoxy resins curing is normally very complex because many reactive processes occur simultaneously. There are, also, other events that increase the complexity of the curing process, such as the gelation and vitrification phenomena, and the change from chemical kinetic control to control by diffusion with the advancement of curing [3].

A few reports on kinetic studies of blends with difunctional epoxy resins have recently appeared in the literature [4–7] but not much with tetrafunctional epoxy resins [8].

Isothermal and dynamic experiments by differential scanning calorimetry (DSC) were used to study the development of kinetics. In this work, we use two dynamic kinetic models and one isothermal model to study the cure kinetics of an epoxy system containing tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM) and 4-4′-diaminodiphenylsulphone (DDS) as curing agent, and its blends with the thermoplastic, poly(styrene-*co*-acrylonitrile) (SAN) at 10, 20, 30, and 40 phr (where phr represents the number of parts by mass quantity of SAN per hundred parts of TGDDM epoxy resin).

2. Experimental

2.1. Materials

The epoxy resin used was tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM) MY 720 from Ciba-Geigy, with weight per epoxy equivalent of 130 g eq^{-1} which was determined in our laboratory by hydrochlorination [9]. The neat epoxy resin and its blends with poly(styrene-*co*-acrylonitrile) (SAN), LNA-21, manufactured by Polidux (Repsol), were cured with an aromatic amine hardener, 4-4′-diaminodiphenylsulphone (DDS), from Fluka Chemie, with a molecular mass of 248.31 and purity >96% according to the

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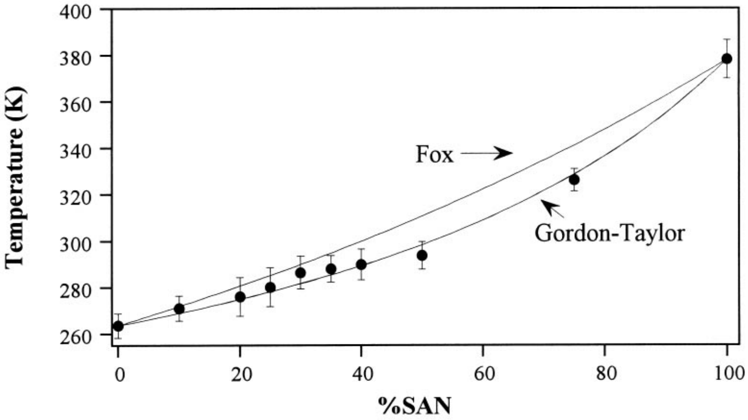

Fig. 1. Relationship between T_g (from DSC) and composition in TGDDM/SAN blends. (●●●) experimental points.

supplier. All components were commercial products, and were used without any further purification.

2.2. Technique

A DSC (Perkin–Elmer DSC 7, equipped with an intracooler and supported by a Perkin–Elmer computer for data acquisition/analysis) was used for the dynamic and isothermal cure experiments and data analysis. The thermal response and the temperature were calibrated with the heat of fusion and the melting point of pure indium. A dry nitrogen flow of 40 ml min^{-1} was used as purge gas. Samples of about 10 mg were enclosed in aluminium DSC capsules.

2.3. Miscibility studies

Initial miscibility of TGDDM/SAN mixtures were studied. SAN was weighted and dissolved in dichloromethane, and the resulting polymer solution was then mixed with 100 g of the epoxy resin at room temperature. The solvent in the mixture was removed in a vacuum oven for 12 h at 100°C. The solvent evaporation was controlled with a thermobalance. Blends of 0, 10, 20, 25, 30, 35, 40, 50, 75 and 100 phr were quenched at room temperature and then, scanning by DSC in order to determine the temperature of glass transition. The heating rate was 10°C min^{-1} for all the scans. In order to check reproducibility the procedure was repeated three times.

2.4. Cured blends

Epoxy resin/SAN mixtures with 10, 20, 30, and 40 phr of SAN, were prepared. SAN was weighted, dissolved in dichloromethane and mixed with the epoxy resin following the process described above. Subsequently, the mixture was placed in an oil bath at 120°C and a stoichiometric amount of DDS was slowly added, which continuous mechanical stirring until a homogeneous mixture was observed, which took about 10 min. The negligible extent of the curing reaction during the mixture process was controlled by isothermal DSC analysis. Samples were then cooled and stored in a freezer until required.

For dynamic heating experiments, six different heating rates were investigated: 5, 7.5, 10, 15, 20 and 30°C min^{-1} from 30 to 330°C in order to calculate the total heat of the reaction, ΔH_0, generated to reach full conversion. ΔH_0 was determined by the total area under the thermograms for each blend of SAN.

Isothermal experiments were conducted at five temperatures: 180, 190, 200, 210, and 220°C in order to obtain both the cure rate and the extent of cure as a function of time. The reaction was considered complete when the signal levelled off to baseline, which took from 10 to 120 min according to the isothermal temperatures. A second isothermal scan was performed to determinate the right baseline for each experiment. The isothermal conversion at time t, was defined as $\alpha(t) = \Delta H_t/\Delta H_0$, where ΔH_t is the heat under the exotherm curve at time t, calculated by integration of the DSC isothermal signal.

3. Results and discussion

3.1. Miscibility of TGDDM/SAN blends

Usually heterogeneous blends show separate glass transition temperatures [10], whereas the binary blends of SAN with TGDDM resin exhibited a single glass transition in the range of temperatures studied. Hence, one can assume that the blends constitute homogeneous systems, which indicate complete miscibility over the entire composition range.

The glass transition temperature data from DSC measurements are compared with the predictions of three equations relating the T_g of a miscible binary polymer to the weight fractions ω_1 and ω_2 of its components. Fig. 1 shows the relationship between T_g and composition for the blends

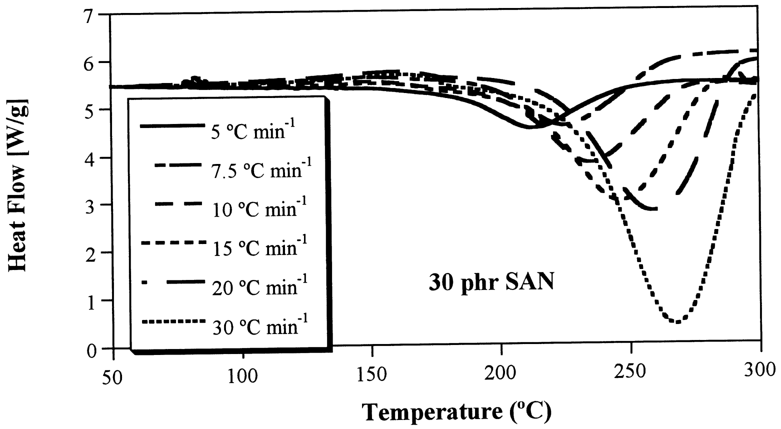

Fig. 2. Heat flow by DSC during cure at different heating rates: 5, 7.5, 10, 15, 20 and 30°C min^{-1} for the 30 phr SAN/epoxy blend.

studied. The first equation used was the Fox equation [11]

$$\frac{1}{T_g}=\frac{\omega_1}{T_{g_1}}+\frac{\omega_2}{T_{g_2}} \tag{1}$$

where T_{g_1} and T_{g_2} are the glass transition temperatures of the components, this value is −9.4 and 105.8°C for TGDDM and SAN, respectively.

The equation used by Gordon–Taylor [11] was

$$T_g=\frac{\omega_1 T_{g_1}+k\omega_2 T_{g_2}}{\omega_1+k\omega_2} \tag{2}$$

where k is an adjustable parameter depending on cubic expansion coefficient and the specific volume of each component.

Fig. 1 shows that the best fit is obtained from Eq. (2). Non-linear least squares regression was used. The value of k parameter from Gordon–Taylor equation is 0.44 and it is similar to the values of k obtained for other epoxy resin modified with SAN [12] and it is suggested that, the k value can be taken as a semiquantitative measure of the strength of interaction between the components of the blend. The low value of k suggests that the interaction forces between the epoxy and the thermoplastic are positive, but relatively weak [4,5]. The Fox equation has a good behaviour only for very low phr of SAN.

Table 1
Heats of reaction of epoxy blends with various SAN contents at different heating rates

q (°C min^{-1})	ΔH_0 (J g^{-1})				
	0 phr	10 phr	20 phr	30 phr	40 phr
5	529.5	525.2	490.2	484.0	451.2
7.5	522.3	495.0	485.5	484.6	457.7
10	535.1	512.5	476.4	485.6	447.9
15	536.0	497.7	489.0	471.3	465.7
20	528.9	494.6	486.8	450.6	452.5
30	534.5	511.7	476.1	458.1	469.9
Average value	531.1	506.1	484.0	472.4	457.5
Standard deviation	5.2	12.4	6.2	15.1	8.7
Q_0 (kJ mol^{-1} epoxy)	102.0	103.1	105.5	109.1	111.6
Standard deviation	1.0	2.5	1.4	3.5	2.1

3.2. Kinetic analysis procedures

The neat epoxy resin and its blends with 10, 20, 30, and 40 phr of SAN were tested at six different heating rates and were cured at five different isothermal temperatures. Kinetic analysis were performed using three kinetic models: Kissinger and Flynn–Wall–Ozawa [13,14] methods, that can be used to calculate kinetic parameters, such as the activation energy and it is not necessary to have a prior knowledge of the reaction mechanism; and the phenomenological model developed by Kamal [15], which has been successfully utilized to describe the cure of epoxy systems in our previous papers [6,7,16].

If one assumes that the extent of reaction, α, is proportional to the heat generated during reaction, the reaction rate can be expressed by means of the general law

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k(T)f(\alpha) \tag{3}$$

where t is the time, $k(T)$ is the Arrhenius rate constant, and $f(\alpha)$ is a function that depends of the reaction mechanism. An integrated form of the above equation often appears as

$$g(\alpha)=\int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)}=k(T)t \tag{4}$$

where $g(\alpha)$ is the integrated form of the conversion dependence function.

3.3. Dynamic kinetic methods

The Kissinger and Flynn–Wall–Ozawa methods were applied to the dynamic heating experimental data obtained at the heating rates between 5 and 30°C min^{-1}. Fig. 2 shows the heat flow measured by DSC during cure at these heating rates for 30 phr SAN/epoxy blend. To calculate the total heat of reaction generated to reach full conversion ΔH_0,

Table 2
Temperature of the peaks of the exotherms from DSC for all blends

q (°C min^{-1})	T_p (°C)				
	0 phr	10 phr	20 phr	30 phr	40 phr
5	211.8	215.2	213.6	212.8	216.5
7.5	223.3	226.6	226.1	226.2	230.6
10	232.2	235.9	232.5	234.8	238.5
15	243.2	247.3	242.8	246.4	249.7
20	256.4	256.7	257.6	259.0	261.2
30	266.3	270.3	269.7	267.3	274.2

the total area under the thermogram was determined for all blends.

The overall heat evolved in the reaction has been determined as the average value of reaction heats calculated in each thermogram, for each blend. It was observed that, these values do not vary too much with the heating rate, in any of the cases. The individual values of ΔH_0 and the average values are shown in Table 1. The total heat of reaction is influenced by the presence of SAN, and the average values of ΔH_0 decrease with the SAN content in the epoxy blends. The normalized values also are given in that table and the fact that the normalized values are practically constant, might be taken as an indication that the reaction mechanism does not change by the presence of SAN in the blends. These values are similar at those obtained in systems based in TGDDM [17,18].

According to the Kissinger method, the activation energy is obtained from the maximum reaction rate where d/dt (dα/dt) is zero under a constant-heating rate condition. The resulting relation can be expressed as

$$\frac{\mathrm{d}[\ln(q/T_p^2)]}{\mathrm{d}(1/T_p)} = -\frac{E}{\mathrm{R}} \tag{5}$$

where T_p is the maximum rate temperature, q is a constant heating rate, E is the activation energy and R is the gas constant. Therefore, a plot of $\ln(q/T_p^2)$ versus $1/T_p$ gives the activation energy without a specific assumption on the conversion-dependent function.

Based on the Doyle's approximation [19] for the integral $p(x)$ an alternative method was developed by Flynn–Wall–Ozawa for calculation of activation energy. They expressed equation $g(\alpha)$ as

$$\log(q) = \log\left[\frac{AE}{g(\alpha)\mathrm{R}}\right] - 2.315 - \frac{0.457E}{\mathrm{R}T} \tag{6}$$

where A is the pre-exponential factor. Without any assumptions on conversion-dependent functions, the Flynn–Wall–Ozawa method can provide activation energies for different conversion levels. In this study, this method was only applied to the maximum rate where the peak appears. A plot of logarithm of heating rate, q, as a function of the reciprocal of temperature, $1/T$, which slope is given by $-0.457\ E/\mathrm{R}T$ yields the activation energy. It is assumed that when the exothermic peak is reached the degree of conversion is independent of the heating rate [20].

Table 3
Activation energies obtained by Flynn–Wall–Ozawa and Kissinger methods for all blends of SAN/epoxy

SAN phr	E (kJ mol^{-1}) Flynn–Wall–Ozawa method	E (kJ mol^{-1}) Kissinger method
0	66.4 ± 2.1	61.3 ± 2.2
10	68.4 ± 0.6	63.4 ± 0.7
20	66.3 ± 3.0	61.1 ± 3.2
30	66.6 ± 2.9	61.5 ± 3.0
40	66.5 ± 1.6	61.3 ± 1.7

Table 2 gives the temperatures of the peaks, T_p, of DSC thermograms for all blends of epoxy/SAN. The peak shifts at higher temperatures as the heating rate increases. Applying the Flynn–Wall–Ozawa and Kissinger methods, the activation energies were determined from the slopes of the lines obtained by Eqs. (5) and (6) and they are shown in Table 3. It can be observed that the values obtained by the Flynn–Wall–Ozawa method are slightly higher than the values obtained by the Kissinger method for the all blends, being, however, very similar. These results show that the activation energy does not change with the content in SAN.

3.4. Isothermal kinetic analysis

To consider the autocatalytic reaction where initial reaction rate of an autocatalytic reaction is not zero, Kamal and Sourour [21] proposed the generalized expression

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = (k_1 + k_2\alpha^m)(1-\alpha)^n \tag{7}$$

where α is the conversion, k_1 and k_2, the rate constants with two different activation energies and two pre-exponential factors; m and n, the reaction orders; and $m + n$, the overall reaction order. The constant k_1 was graphically calculated as the initial reaction rate to at time zero, given by the intercept of plots of conversion rate versus time. The kinetic rate constants, k_1 and k_2 are assumed to be constant at a given temperature and following an Arrhenius temperature dependence.

For the determination of the cure kinetics by means of an autocatalytic model, first, the isothermal cure is performed at several temperatures, then the experimental rate equation (α, dα/dt) is determined for the complete course of the reaction, and finally, the experimental results are adjusted with the kinetic equation Thus, the reaction orders and the rate constants are obtained for each temperature. Finally, the activation energies and the frequency factors are determined by using the Arrhenius equation, for the dependence of the rate constants on the temperature. To compute the parameters in Eq. (7) from experimental data, several methods have been proposed previously [22,23]. In the present study,

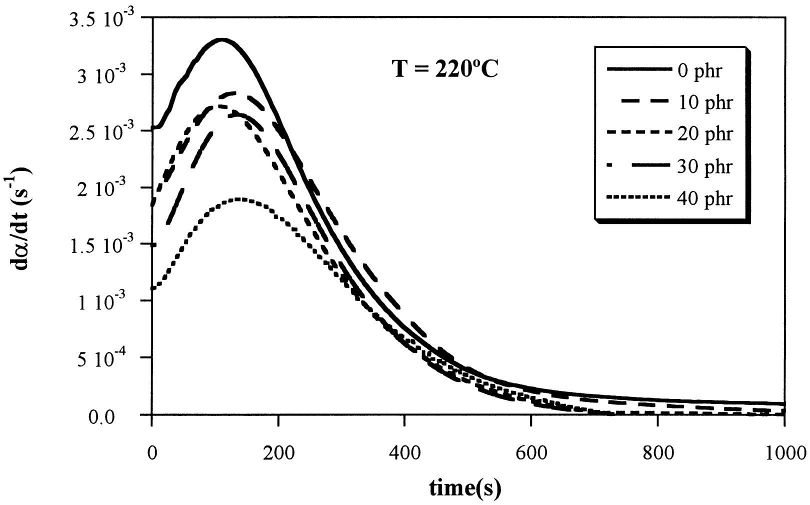

Fig. 3. Plots of the reaction rate versus time for the neat epoxy and its blends for the temperature of 220°C.

the parameters m, n, k_1 and k_2 were estimated without any constraints assumed using a least squares method.

Fig. 3 shows the reaction rates, dα/dt, versus time, t, measured directly by the analyzer, in isothermal mode at 220°C for the neat system and its blends with SAN. It can be observed the nature typically autocatalytic in all cases, with the maximum rate of conversion after the start of the reaction. The reaction rates are affected by the presence of SAN, decreasing as SAN contents increase, although the maximum of the reaction rates occurs practically at the same time for all the blends.

Table 4 shows the evolution of maximum conversions. The maximum conversion, $\alpha_{\max}$, for the neat system is higher than for all blends. $\alpha_{\max}$ increases with the temperature of cure and decreases with the SAN content. This last fact can be due to high viscosity of the blends with high SAN content, that hinders the reaction of reacting species.

Applying the Kamal model, Eq. (7), and through considerable iteration and graphic procedures, the reaction rate constants k_1 and k_2, moreover the parameters m and n and the overall reaction order, $m + n$, for the unmodified and modified systems by SAN were obtained. They are listed in Table 5. The parameter m is about 1 for the neat system and for all its blends and n is about 2 for the unmodified system and takes values from 1.3 to 3.5 for the different blends of SAN and different cure temperatures. The anomalous values of n, and subsequently of $m + n$, at high phr of SAN can mean that the autocatalytic model is not entirely applicable in these cases.

Table 4
Maximum conversion for all the isotherms and for all blends with SAN/epoxy

	$\alpha_{\max}$				
Isotherm temp (°C)	180	190	200	210	220
0 phr	0.71	0.79	0.86	0.93	0.98
10 phr	0.65	0.77	0.83	0.91	0.96
20 phr	0.62	0.73	0.77	0.80	0.86
30 phr	0.54	0.60	0.62	0.69	0.79
40 phr	0.42	0.54	0.61	0.64	0.65

Table 5
Values of the parameters k_1 and k_2 and the reaction orders m, n and $m + n$

T (°C)	$k_1 \times 10^3$ (s^{-1})	$k_2 \times 10^3$ (s^{-1})	m	n	$m + n$
Epoxy/SAN (0 phr)					
180	0.3	4.3	1.1	2.0	3.1
190	0.6	4.9	1.1	1.8	2.9
200	0.9	7.4	1.1	1.9	3.0
210	1.2	11.0	1.2	1.9	3.1
220	1.7	14.6	1.1	1.9	3.0
Epoxy/SAN (10 phr)					
180	0.3	2.1	0.9	1.7	2.6
190	0.5	2.6	0.8	1.4	2.2
200	0.8	4.7	0.9	1.3	2.2
210	1.3	7.7	1.1	1.5	2.6
220	1.9	9.3	1.0	1.3	2.3
Epoxy/SAN (20 phr)					
180	0.3	3.6	1.1	2.4	3.5
190	0.5	5.5	1.2	2.2	3.4
200	0.6	7.4	1.2	2.1	3.3
210	1.2	11.3	1.2	1.8	3.0
220	1.9	18.9	1.3	2.0	3.3
Epoxy/SAN (30 phr)					
180	0.2	3.9	1.1	3.1	4.2
190	0.4	9.3	1.3	3.2	4.5
200	0.5	11.0	1.2	3.3	4.5
210	1.1	13.6	1.3	2.1	3.4
220	1.5	23.0	1.3	2.3	3.6
Epoxy/SAN (40 phr)					
180	0.1	2.1	0.8	2.8	3.6
190	0.2	4.8	0.9	3.5	4.4
200	0.5	7.2	1.1	2.7	3.8
210	0.7	11.0	1.1	3.3	4.4
220	1.1	14.6	1.1	2.8	3.9

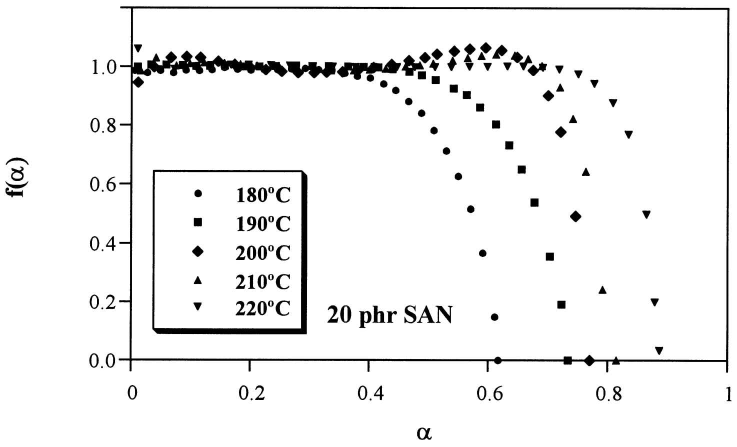

Fig. 4. Plot of diffusion factor, $f(\alpha)$, versus conversion, α, for 20 phr SAN/epoxy blend.

The activation energies, E_1 and E_2, and pre-exponential factors, A_1 and A_2, associated to the parameters k_1 and k_2 obtained for the neat amine cured system and its blends are shown in Table 6. The epoxy resin/SAN blends exhibit higher activation energies for E_1 and E_2 than for the neat system, being constant for the blends of 10, 20, and 30 phr of SAN and notably higher as the content in SAN is of 40 phr, due to the fact that the SAN hinders the reaction of the resin with the hardener.

After vitrification any further progress in the cure reaction is virtually stopped, and so, the extent of cure is limited. This event indicates that the cure kinetics in the later stage was indeed subjected to diffusion control as a result of vitrification. Differences between model predictions and experimental data are bigger at low cure temperatures because the reaction is controlled by diffusion rather than by chemical factors an account of the high viscosity of blends.

To consider diffusion effect we have used a semiempirical relationship based on free volume considerations applied successfully by Khanna and Chanda [24,25]. It relates the diffusion controlled rate constant, k_d, to the chemical rate constant, k_c, by the expression

$$k_d = k_c \exp[-C(\alpha - \alpha_c)] \tag{8}$$

where C is a fitted parameter and α_c, the critical conversion, being two empirical parameters. Eq. (8) corresponds to an abrupt onset of diffusion control at $\alpha = \alpha_c$, while, in reality, the onset is gradual and there is a region where both chemical and diffusion factors are controlling. An overall effective rate constant, k_e, can be expressed in terms of k_d and k_c by the relation

$$\frac{1}{k_e} = \frac{1}{k_d} + \frac{1}{k_c} \tag{9}$$

Table 6
Activation energies and pre-exponential factors for all the epoxy blends

SAN (phr)	E_1 (kJ mol^{-1})	E_2 (kJ mol^{-1})	ln A_1	ln A_2
0	78.3 ± 5.1	60.3 ± 5.4	12.8 ± 1.3	10.5 ± 1.4
10	84.0 ± 2.0	75.8 ± 7.6	14.2 ± 0.5	13.9 ± 1.9
20	89.0 ± 6.4	69.1 ± 6.6	15.9 ± 1.6	12.8 ± 1.7
30	91.5 ± 7.4	68.4 ± 12.0	15.8 ± 1.9	12.8 ± 3.0
40	112.7 ± 16.3	87.1 ± 7.6	20.8 ± 4.2	17.1 ± 1.9

Table 7
Values of critical conversion, α_c, and of C parameter at different curing temperatures for each SAN/epoxy blend

T (°C)	α_c	C
Epoxy/SAN (0 phr)		
180	0.66	29.1
190	0.74	20.9
200	0.80	36.5
210	0.85	51.4
220	0.95	36.6
Epoxy/SAN (10 phr)		
180	0.60	23.0
190	0.71	19.9
200	0.78	22.3
210	0.88	68.1
220	0.94	35.8
Epoxy/SAN (20 phr)		
180	0.58	23.4
190	0.69	23.3
200	0.74	72.6
210	0.87	44.8
220	0.92	70.9
Epoxy/SAN (30 phr)		
180	0.50	28.8
190	0.58	45.4
200	0.62	42.9
210	0.77	67.4
220	0.81	10.8
Epoxy/SAN (40 phr)		
180	0.43	23.3
190	0.50	25.4
200	0.56	28.6
210	0.57	74.6
220	0.61	25.8

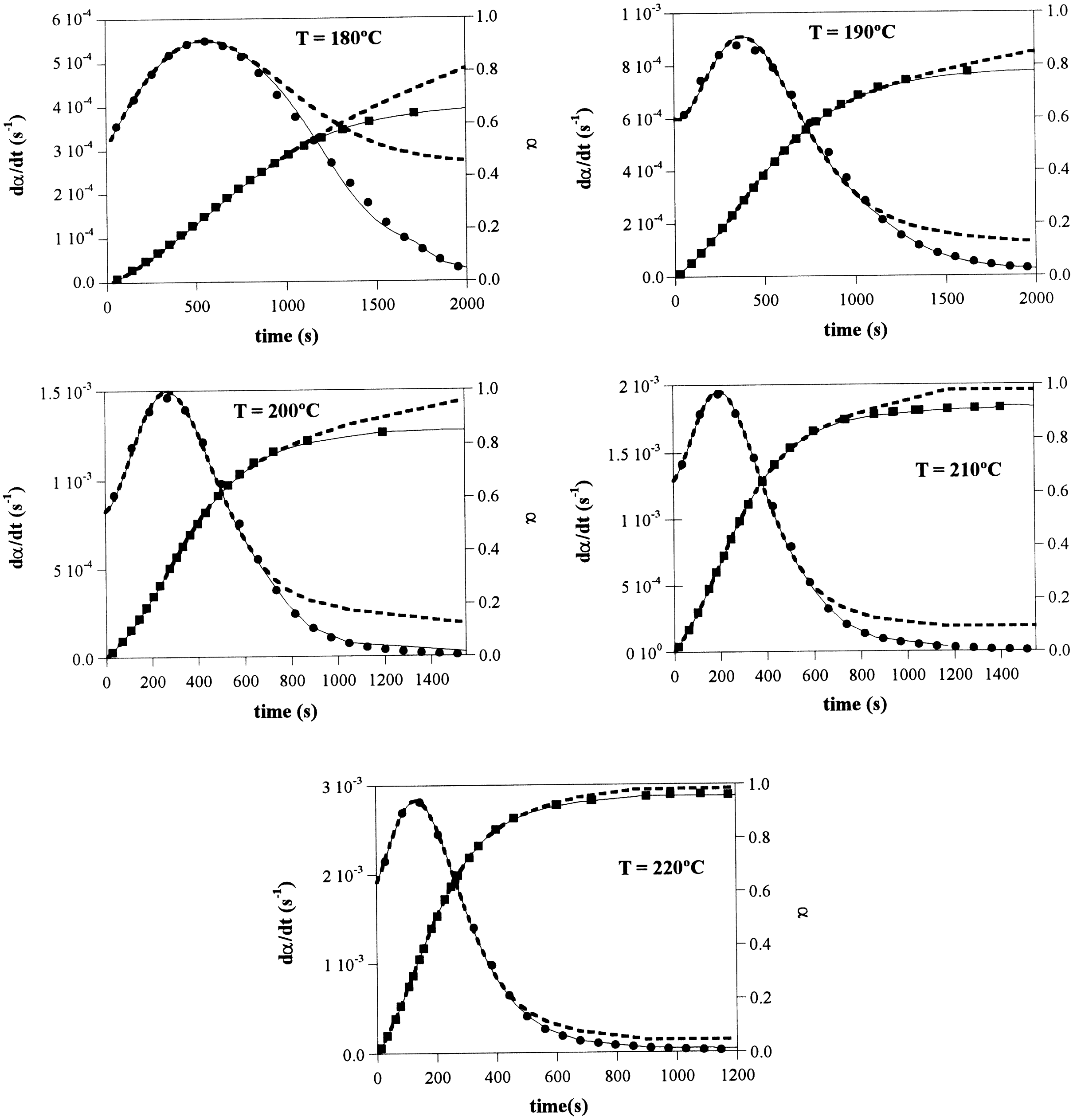

Fig. 5. Comparison of experimental data with model predictions: reaction rate, $d\alpha/dt$, (●●●) and conversion, α, (■■■) versus time for 10 phr SAN at all temperatures. (dashed line), autocatalytic model; (solid line), autocatalytic model with diffusion.

it can be combined with Eq. (8), to obtain the diffusion factor $f(\alpha)$

$$f(\alpha) = \frac{k_e}{k_c} = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \tag{10}$$

When α is much smaller than the critical value, $\alpha \ll \alpha_c$, then $f(\alpha)$ approximates unity, the reaction is kinetically controlled and the effect of diffusion is negligible. As α approaches α_c, $f(\alpha)$ begins to decrease and approaches zero as the reaction effectively stops. The effective reaction rate at any conversion is equal to the chemical reaction rate multiplied by $f(\alpha)$. The diffusion factor was obtained as the ratio of experimental reaction rate to the reaction rate predicted by the autocatalytic model in Eq. (7). Fig. 4 shows the behaviour of $f(\alpha)$ with the conversion for 20 phr SAN/epoxy blend at all curing temperatures. The decrease in $f(\alpha)$ and, consequently, in the effective reaction rate due to onset of diffusion at higher conversions is seen.

Application of non-linear regression to $f(\alpha)$ versus α data to Eq. (10) gives values of α_c and C which are shown in Table 7. An increase in α_c was observed in the neat system and its blends with increasing temperature. No discernible trend is found for the coefficient *C*, in agreement with the studies of Cole et al. [17] on epoxy–amine systems.

It may be noted that the critical conversion is not an adjustable parameter because it reflects the onset of diffusional limitation that occurs only in the latter stages of reaction. It is also not an observable quantity since the transition to the diffusion regime is gradual. As cure proceeds, the mobility of the reacting species is reduced and this leads to diffusional effects. Hence, α_c would reflect the state of cure of the system rather than the temperature of cure.

Fig. 5 displays the experimental values of reaction rate and conversion against time for the blend of 10 phr of SAN and for all curing temperatures and the corrected data comparing the data calculated by the autocatalytic model, coupled with the diffusion factor, according to Eq. (10). Good agreement between experimental data and the autocatalytic model with diffusion was found over the whole curing temperature range and for each concentration of SAN.

4. Conclusions

A resin based on tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM) modified with poly(styrene-*co*-acrylonitrile) (SAN) (10, 20, 30, and 40 phr) and diaminodiphenylsulphone (DDS) as a curing agent was studied in this work. The miscibility and kinetic analysis were developed. The miscibility between SAN and TGDDM was analyzed using the Fox and the Gordon–Taylor equations. Kinetic analysis was performed using three kinetic models: Kissinger, Flynn–Wall–Ozawa and the phenomenological model developed by Kamal. Diffusion control is incorporated to describe the cure in the latter stages predicting the cure kinetics over the whole range of conversion.

The results presented here show that uncured epoxy resin, TGDDM, is miscible with SAN over the entire blend composition range. Dynamic scanning calorimeter technique is an useful tool for developing and studying the miscibility. The total heats of reaction are influenced by the presence of SAN and the average values decrease with the SAN content in the epoxy blends, however, the normalized values of the total heats of reaction by equivalent epoxy are practically constant. This fact can be taken as an indication that the reaction mechanism does not changes by the presence of SAN in the blends. The obtained results for dynamic experiments suggest that the systems with SAN need the same energy than the neat system in order to accomplish total cure.

An autocatalytic mechanism was observed for both the neat system and the epoxy–SAN blends over a range of compositions. Kinetic parameters for the epoxy blends were obtained and the kinetic model proposed by Kamal was found to describe well the cure behaviour of the epoxy and its blends up to the vitrification point. The maximum conversions decreased with the increase of content in SAN. Although the reaction mechanism of the epoxy blends remained the same as that of the neat epoxy, the reaction rates of the blends were found to be lower than the latter. The results show that when the SAN contents increase there is a reduction of the rates of conversion and the final conversions obtained, due to reduction of mobility of the reacting species imposed by the SAN. The thermoplastic hinders the reaction of epoxy with the amine hardener.

In order to describe the cure in the later stages of reaction (post-vitrification region) a diffusion factor has been introduced. By combining the Kamal model and a diffusion factor, it was possible to predict the cure kinetics over the whole range of conversion. It was observed that, the behaviour of the blends is the same as that for the neat system.

Based on the research work of this paper and our previous, it can be said that this model is a starting point to discuss the kinetics of many epoxy resins modified by thermoplastics.

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