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POLYMER BLENDS BASED ON AN EPOXY-AMINE THERMOSET AND A THERMOPLASTIC

Effect of thermoplastic on cure reaction and thermal stability of the system

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The effect of thermoplastic modification of an epoxy–amine system on the cure reaction, miscibility and thermal stability of the system was investigated. The cure kinetics showed an autocatalytic behavior. Modifier did not affect either the total reaction heat or the achieved maximum conversion but delayed the kinetics. The model of Horie–Kamal corrected by diffusion factor was used to adjust kinetics in the whole range of conversions. The modified systems showed two glass transitions indicating two separated phases, whose compositions were estimated using the Fox and Couchman equations. Modifier did not affect the thermal and thermooxidative stability of the system.

Keywords: *cure kinetics, miscibility, thermal stability, thermoplastic/epoxy–amine blends*

Introduction

Epoxy resins are generally used as advanced composite matrix materials due to their properties and performances. However these materials are brittle. The toughness of these materials may be improved by the incorporation of thermoplastic components which are initially miscible with the monomers, but are segregated in the course of polymerization leading to a randomly dispersed phase. This mechanism is denominated polymerization induced phase separation (PIPS) [1, 2].

The separated phases by the PIPS mechanism are not pure but to dissolve part of another component and they may be forming different types of morphologies [3].

The modification of thermosets can affect a large extent to the processing, cure reaction and properties of epoxy resins [4–8].

The knowledge of cure reaction of thermosets and in particular the effects of temperature, time and modifier on the same is essential to control their properties and applications. In this regard, it is necessary to have a model that is capable of adequately describe the advance of the reaction in the whole range of conversions. In general, the curing reactions in epoxy resins show complex kinetics characterized by an initial acceleration due to autocatalysis and by a retardation in the later stages due to the vitrification [9–11].

Various kinetics models have been developed in the last years [12]. Among them, the model of Horie–Kamal proves to be appropriate to adjust the kinetics of epoxy–amine resins. The description of the complete kinetics of these systems, typically require the modification of the Horie–Kamal model with the correction due to the control by diffusion [13, 14].

The aim of this work is to investigate the effect of the modification of an epoxy–amine thermoset with a thermoplastic on the cure reaction, thermal stability and miscibility of the epoxy–amine system. The Horie–Kamal model corrected by diffusion factor was used to describe the obtained cure kinetics for the epoxy–amine systems neat and modified with different proportions of thermoplastic.

Experimental

Materials

The epoxy–amine thermoset studied was constituted by stoichiometric amounts of a diglycidylether of bisphenol A (DGEBA) and an aromatic diamine, the 4,4’-methylenebis(2,6-diethylaniline) (MDEA). The used DGEBA, was Araldite GY-260 from Ciba-Geigy, with mass per epoxy equivalent of 188 g eq^{-1}, the MDEA was supplied by Aldrich. The thermoplastic modifier was a polystyrene (PS) from Aldrich with a number and mass average molecular mass of 140000 and 230000, respectively.

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

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Blends preparation

The blends were prepared as follows: first, the PS was dissolved in the epoxy prepolymer using methylene chloride (CH_2Cl_2) as a solvent, which was later evaporated for a day at room temperature followed by several hours at 140°C. In a second step, the PS/DGEBA blend was taken out of the oven at 120°C and the corresponding amount of diamine was added at room temperature, then mixing for 2 min. Blends for testing in the DSC were cooled and stared in a freezer until required. Blends for analyzing in the TG were cured at different temperatures and then were tested.

Techniques

A DSC (PerkinElmer DSC-7, supported by a Perkin Elmer computer for data acquisition) was used to study the cure reaction [15, 16] and miscibility of system. The cure reaction was studied through both dynamic and isothermal experiments. In the dynamic experiments, the total heat of reaction was calculated for the DGEBA/MDEA (1:1) system neat and modified with different amounts of PS. They consisted of two consecutive heatings at a constant rate of 10°C min^{-1} under inert atmosphere. The isothermal experiments were realized to the system neat and modified with 6 and 15 mass% of PS conduced at three temperatures: 150, 160 and 170°C to obtain the reaction rate and the extent of cure as a function of time. The glass transitions, for the miscibility study, were observed in the second dynamic experiment in the DSC.

A TG balance (PerkinElmer TGA-7 microbalance coupled with a 1022 Perkin Elmer microprocessor) was used to analyze the thermal and thermooxidative stability of the system. The analysis consisted of heatings at a constant rate of 10°C min^{-1} under two different atmospheres: inert (argon) and oxidant (oxygen).

Results and discussion

Cure reaction

The study of the cure reaction of epoxy–amine system was realized through both dynamic and isothermal experiments.

Dynamic tests in DSC were realized at the DGEBA/MDEA (1:1) system neat and modified with 3, 6, 9, 12, 15, 20 and 25% in mass of PS. They were conducted in order to determine the total heat of reaction and the effect of PS in the same [17]. The results of the dynamic tests subtracted from the second scans and normalized by the mass are shown in Fig. 1.

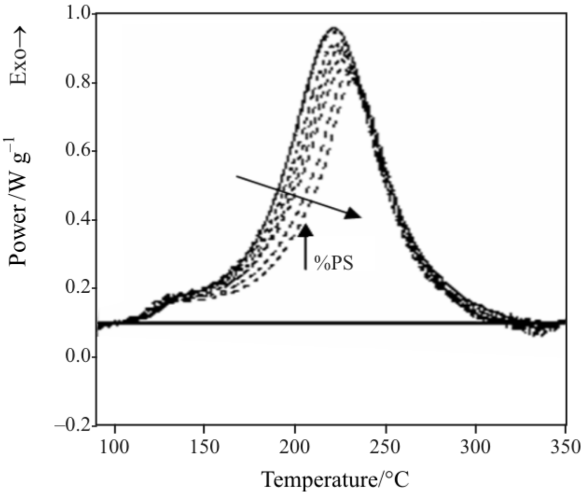

Fig. 1 Dynamic DSC curves for the DGEBA/MDEA system neat and modified with 3, 6, 9, 12, 15, 20 and 25 mass% of PS

If the cure reaction is the only event involved in the exchange of heat, the total area under the curve each system gives the total heat involved in the cure reaction of epoxy–amine system. Table 1 shows for each of the systems, the peak temperature of exotherm and the total heat of reaction expressed both, per mass of sample and per mass of epoxy equivalent.

The total heat per mass sample decreased when the percentage of PS increased. This is logical because PS is an inert modifier and does not react with resin. But if the total heat is expressed per mass of epoxy equivalent, the same value is practically obtained for all systems. This means PS does not affect the total heat reaction in the range of concentrations studied. The overall heat involved in the epoxy–amine reaction was determined as the average value of reaction heats expressed per epoxy equivalent mass obtained in the different systems. A value of 106.02±0.12 kJ eq_{epoxy}^{-1} was obtained.

Table 1 Total heat and peak temperature of the exotherms from DSC for all blends

PS/%	Reaction heat		Peak temp./ °C
	J g^{-1} sample	kJ (eq ep)$^{-1}$	
0	399.08	106.00	220.68
3	387.81	106.19	220.67
6	374.62	105.85	222.46
9	363.59	106.12	222.87
12	351.50	106.09	223.87
15	339.32	106.03	226.08
20	319.37	106.03	229.27
25	298.16	105.87	231.26

On the other hand, the maximum of exothermic peak shifted slightly to higher temperatures when the proportion of PS in the system increased. This means that PS produces a delay in the reaction, probably due to an increase in the viscosity of the blend and a dilution effect.

In conclusion, the PS did not affect the total reaction heat but delayed the cure reaction.

The isothermal experiments enabled monitoring and studying the kinetics of cure reactions.

The results of the isothermal tests, treated to obtain the reaction rate and conversion [14] are shown respectively in Figs 2 and 3, for the DGEBA/MDEA (1:1) system neat and modified with 6 and 15% of PS at there temperatures 150, 160 and 170°C.

Figure 2 shows a nature typically autocatalytic in all the isotherms with the maximum rate of conversion after the start of the reaction [11, 18]. The reaction rates are affected by the presence of PS, decreasing in general as the PS content increases and increasing the time where the reaction rate is maximal. As for the effect of temperature on the reaction rate, increasing the temperature, the reaction rate increased and the time when the rate is zero decreased.

Figure 3 shows the effect of temperature and PS on the extent of reaction. The maximum conversion reached by the system increased with the cure temperature but was not affected by the addition of PS in the range of compositions studied. However, in general PS increased the time needed to achieve it, meaning that PS produces a retardant effect on the kinetics.

Next, we will try to get some equations of reaction rate that adequately describe the cure kinetics of the various systems studied at cure temperature tested.

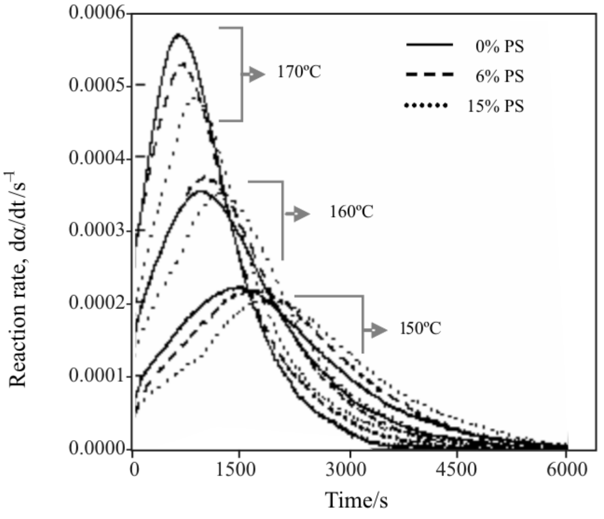

Fig. 2 Reaction rate, dα/dt, *vs.* time curves for the DGEBA/MDEA system neat and modified with 6 and 15 mass% of PS at three different temperatures

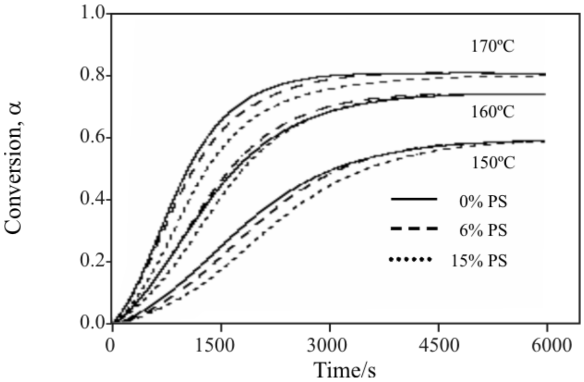

Fig. 3 Conversion, α *vs.* time curves for the DGEBA/MDEA system neat and modified with 6 and 15 mass% of PS at three different temperatures

Different models have been developed to describe the cure reaction of thermosets. The model proposed by Kamal [19] for autocatalytic reactions is appropriate to describe the kinetics of epoxy–amine systems at low extents of reaction. It suggests the following rate equation,

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

where k_1, k_2, m and n are adjustable parameters of the model. k_1 and k_2 are the rate constant for the externally catalyzed and autocatalytic processes, respectively. They are assumed to follow an Arrhenius temperature dependences. m and n are the reaction orders, $m+n$ is the overall reaction order.

In order to determine the equations of reaction rate, the autocatalytic Kamal model was applied to the experimental data of reaction rate *vs.* conversion (dα/dt *vs.* α) obtained for each isotherm. Figure 4 shows the experimental data of kinetics with the corresponding adjustment resulting from the application of Kamal model.

Good fits were obtained for the initial stages of reaction. However, the model predicted higher conversions and reaction rates for the latter stages of the cure reaction. Deviations observed are attributed to the reaction, becoming diffusion controlled in that conversion range.

From adjustment of the theoretical equation to each experimental isotherm, the adjustable parameters were obtained for each system and temperature, without any constraints assumed using a least squares method. They are listed in Table 2.

The obtained values of reaction orders were too high, increasing with the proportion of PS. The anomalous values can mean that this autocatalytic model is not entirely applicable in these cases. An Arrhenius temperature dependence was applied to the rate constants (k_1, k_2) of each system, obtaining the corres-

Table 2 Rate constants, k_1 and k_2, and reactions orders, m and n, for the neat and modified systems at different temperatures

T/°C	$k_1 \cdot 10^3$/s^{-1}	$k_2 \cdot 10^3$/s^{-1}	m	n	$m+n$
Neat system					
150	0.0859	1.861	1.06	2.98	4.04
160	0.1653	2.233	1.06	2.37	3.44
170	0.2604	3.430	1.07	2.09	3.16
Modified system with 6% PS					
150	0.0740	2.200	1.15	3.07	4.22
160	0.1817	3.345	1.25	2.54	3.80
170	0.2810	4.227	1.24	2.39	3.63
Modified system with 15% PS					
150	0.0681	3.768	1.41	3.76	5.17
160	0.1580	4.145	1.41	2.70	4.11
170	0.2158	5.363	1.37	2.67	4.04

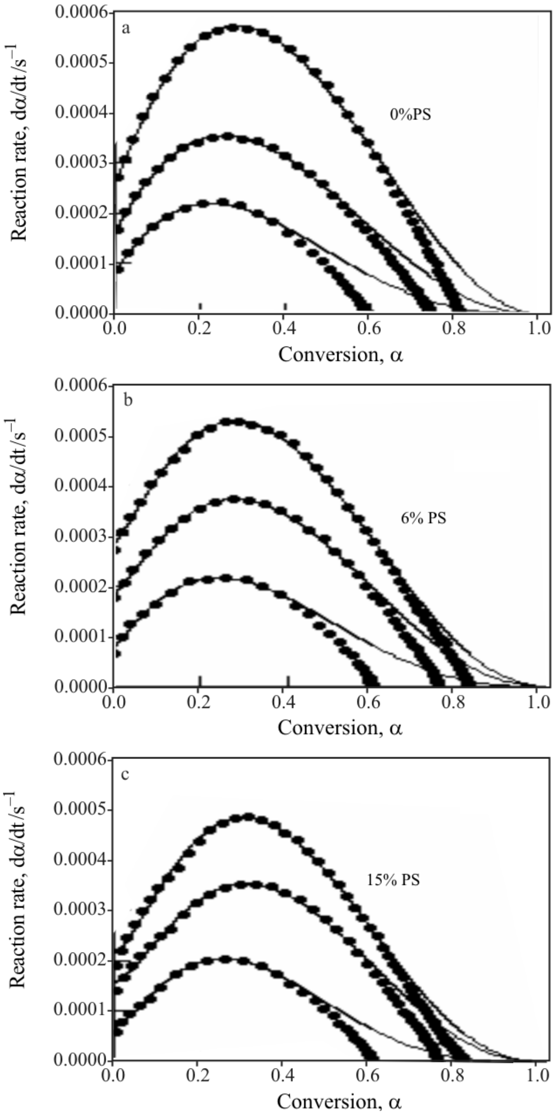

Fig. 4 Comparison of ● – experimental with –– – predictions of Kamal model for the a – system neat and b – modified with 6 and c – 15% PS at different temperatures

Table 3 Activation energies and pre-exponential factors for the neat and modified systems

PS/%	E_a/kJ mol^{-1}		A/s^{-1}	
	E_{a1}	E_{a2}	A_1	A_2
0	86.52	47.51	4.27e+6	1.33e+3
6	104.18	51.07	5.82e+8	4.58e+3
15	90.18	27.39	1.01e+7	8.85

ponding activation energies and pre-exponential factors. They are listed in Table 3.

The activation energy and the pre-exponential factor for the externally catalyzed process (Ea_1, A_1) were greater than those of autocatalytic process (Ea_2, A_2) in any of the system studied.

To obtain a kinetic equation that adequately describes the advance of cure reaction in the whole range of conversions, the Kamal model was corrected by the diffusion factor. In this way, the effect of both chemical kinetics and diffusion are considered. The rate equation of the Kamal model corrected by diffusion factor is given by

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = (k_1 + k_2\alpha^{\mathrm{m}})(1-\alpha)^{\mathrm{n}} F(\alpha) \tag{2}$$

$F(\alpha)$ is the so-called diffusion factor and is a function of conversion given by,

$$F(\alpha) = \frac{1}{1+\exp[C(\alpha - \alpha_{\mathrm{C}})]} \tag{3}$$

where C and α_C are again adjustable parameters of the model. α_C is the critical conversion. $F(\alpha)$ was experimentally determined by dividing the experimental reaction rate between the reaction rate determined with the Kamal model (Eq. 1) [20].

From adjustment of theoretical $F(\alpha)$ (Eq. 3) to experimental $F(\alpha)$ *vs.* α data of each isotherm, the respective values of C and α_C parameters were estimated. They are showed in Table 4.

In all systems α_C increased with temperature, but practically unchanged with the composition of PS. For the C coefficient no discernible trend is found [21].

Table 4 Parameter C and critical conversion, α_C, for the neat and modified systems at different temperatures

T/°C	C/%			α_C/%		
	0	6	15	0	6	15
150	25.79	29.80	30.15	0.541	0.550	0.554
160	28.71	30.98	28.82	0.698	0.706	0.706
170	31.90	34.04	29.02	0.769	0.777	0.757

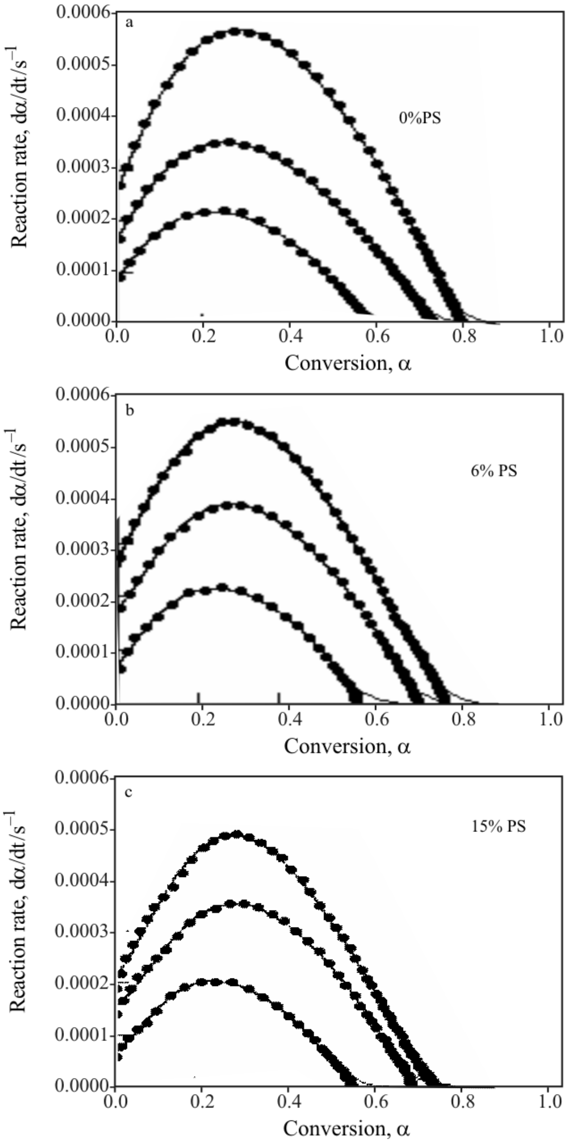

Fig. 5 Comparison of ● – experimental with —– predictions of Kamal model corrected by diffusion factor for the a – system neat b – modified with 6 and c – 15% PS at different temperatures

Substituting the values of adjustable parameters (k_1, k_2, m, n, C, α_C) obtained for each isotherm, in the Kamal model corrected given by the Eq. (4), the corresponding kinetic equation is obtained.

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=(k_1+k_2\alpha^{\mathrm{m}})(1-\alpha)^{\mathrm{n}}\frac{1}{1+\exp[C(\alpha-\alpha_{\mathrm{C}})]} \tag{4}$$

Figure 5 shows the result for each isotherm, where experimental dα/dt values are compared with those calculated by the Kamal model corrected with diffusion factor.

Excellent agreement was found over the whole conversion range in all isotherms.

Study of miscibility

The miscibility of the modified epoxy–amine systems was analyzed by means of measuring the glass transitions in the mixtures completely cured. The values of glass transition temperatures (T_g) and the corresponding changes in specific heat (Δc_p) obtained from DSC, for the blends systems (%PS+DGEBA/MDEA (1:1)) and for the neat system DGEBA/MDEA (1:1) and PS, are shown in Table 5.

The PS/epoxy–amine blends with percentages of PS higher than 12 mass% showed two glass transitions: one located between 142 and 146°C and another, with a minor Δc_p, located between 104 and 106°C. This indicates that a phase separation has occurred [22]. Each phase is characterized by a different T_g. Thus, the T_g close to 145°C corresponds to the thermoset rich phase while the T_g close to 105 stand for the PS rich phase.

The glass transition temperatures of the separated phases, although nearby, differ from those of the pure components. This is because the phases are not pure, containing quantities of other component. In blends with proportions of PS lower than 12 mass%,

Table 5 Values of glass transition temperature (T_g) with the corresponding change of specific heat (Δc_p) for the neat and modified systems

PS/%	Epoxy rich phase		PS rich phase	
	T_g/°C	Δc_p/ J g^{-1} °C^{-1}	T_g/°C	Δc_p/ J g^{-1} °C^{-1}
0	146.18	0.317		
3	146.08	0.310		
6	145.87	0.304		
9	145.74	0.287		
12	144.72	0.274	105.96	0.075
15	144.39	0.257	105.89	0.101
20	143.84	0.246	105.49	0.124
25	142.41	0.229	104.55	0.139
100			100.11	0.288

we were able only to distinguish the T_g of epoxy-rich phase. The explanation is that the volume of PS rich phase is so small that the signal corresponding to its glass transition is not appreciated by DSC.

Each of these separated phases may be considered as a totally miscible system. By application of the Fox equation or Couchman equation to each phase, the compositions of separated phases can be theoretically estimated [23–25].

The Fox equation applied to this system is given by,

$$\frac{1}{T_g} = \frac{(1-W_{PS})}{T_{gTE}} + \frac{W_{PS}}{T_{gPS}} \quad (5)$$

The Couchman equation is given by,

$$\ln T_g = \frac{(1-W_{PS})\Delta c_{pTE} \ln T_{gTE} + W_{PS}\Delta c_{pPS} \ln T_{gPS}}{(1-W_{PS})\Delta c_{pTE} + W_{PS}\Delta c_{pPS}} \quad (6)$$

where T_{gPS}, Δc_{pPS} and T_{gTE}, Δc_{pE} are respectively the glass transition temperature and the corresponding change in specific heat for PS and for the pure thermoset. T_g represents the T_g of each separated phase, and W_{PS} is the mass fraction of PS present in that phase.

Both equations were applied to the separated phases of the different PS/thermoset blends. By replacing data from Table 5 in the Eqs (5) and (6), the mass fraction of PS were obtained and then they were stated in volume fractions using the equation,

$$\phi_{PS} = \frac{W_{PS}/\rho_{PS}}{(1-W_{PS})/\rho_{TE} + W_{PS}/\rho_{PS}} \quad (7)$$

where ρ_{TE} and ρ_{PS} represent the densities of thermoset (1.20 g cm^3) and PS (1.04 g cm^3), respectively.

Figure 6 shows the composition of PS in each separated phase estimated from both equations, Fox and Couchman, for different initial PS/thermoset mixtures.

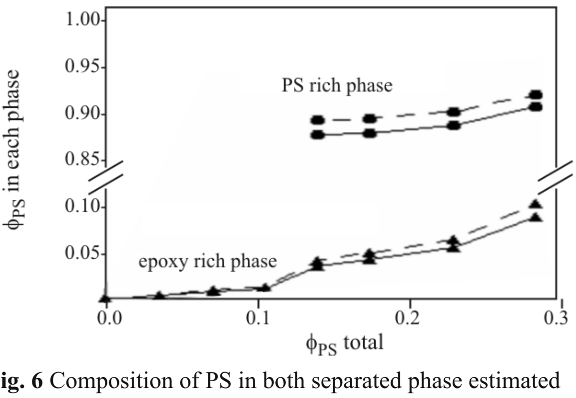

Fig. 6 Composition of PS in both separated phase estimated from —– Fox equation and - - - - Couchman equation

The PS composition values obtained by the Couchman equation were slightly higher than those obtained by the Fox equation.

When the initial proportion of PS in the system increased, the epoxy rich phase dissolved much PS being less pure, while the PS rich phase was more pure.

Although the phases are not pure, only dissolve small amounts of another component. Thus, according to the Fox and Couchman equations, the thermoset-rich phase contain only between 0 and 10% of polystyrene and the PS-rich phase between 8 and 12% of thermoset in the range of compositions studied, as is shown in Fig. 6.

Thermal stability

The effect of modifier on the thermal stability of the epoxy–amine system was studied in both inert and oxidant atmospheres [26]. The curves obtained by TG for the neat system and some modified systems are shown in Fig. 7, a) in inert atmosphere and b) in oxidant atmosphere.

The degradation was different in both atmospheres. Thus, in oxidant atmosphere, the degradation proceeded by a several-steps process, leading to the

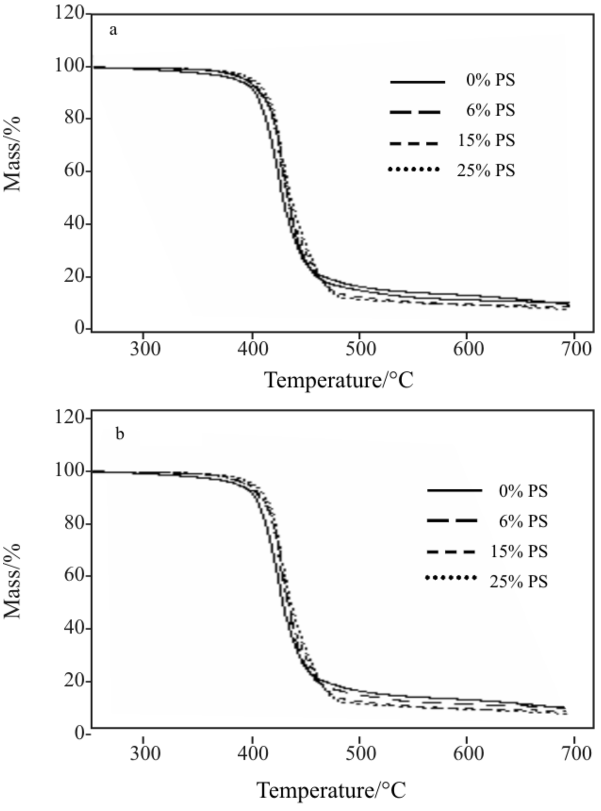

Fig. 7 Experimental TG curves for the DGEBA/MDEA system neat and modified with 6, 15 and 25 mass% of PS. a – in argon; b – in oxygen atmosphere

total mass loss about 650°C. On the contrary, in inert atmosphere, the process of degradation happened by an only step leading to a residue for the neat system of about 13% of the total mass at 650°C. The residue in inert atmosphere decreased slightly when the percentage of modifier in the system increased.

The temperature of maximum degradation of PS is about 420°C in argon and 410°C in oxygen. These temperatures are close to the degradation of the epoxy–amine system in these atmospheres. Comparing the curve of the neat system with those obtained for the modified systems, there are not displacements of the degradation curve. Only minor changes are observed which should be attributed to the degradation of PS.

Accordingly, PS did not affect either the thermal or thermooxidative stability of the epoxy–amine system.

Conclusions

The effect of the modification of an epoxy–amine thermoset system with a thermoplastic was examined from the standpoint of the cure reaction, miscibility and thermal stability.

The study of cure reaction of the epoxy–amine system was realized though both, dynamic and isothermal experiments. In the dynamic experiments, the total reaction heat and the effect of PS on it were determined, resulting that PS did not affect the total reaction heat but delayed the cure reaction. Isothermal experiments were realized to the systems neat and modified with 6 and 15 mass% of PS at different temperatures in order to monitoring the reaction kinetics. The kinetics of all systems showed an autocatalytic behaviour. PS did not affect the maximum conversion achieved by the systems but increased the time required to achieve it, delaying the cure kinetics. When the cure temperature increased, the reaction rate and the conversion achieved by the system increased. The Horie–Kamal model was applied to each of the isotherm, being necessary for adjusting the whole kinetics, to introduce a correction due to the diffusion.

The model estimated, among other parameters, rate constants, activation energies and reaction orders. The activation energy for the externally catalyzed process was greater than that obtained for the autocatalytic process in all the cases. The overall reaction orders decreased with cure temperature but increased with the proportion of PS.

The miscibility of modified epoxy systems was studied by means of measuring the glass transition temperatures (T_g). Two T_gs were observed in the modified systems at temperatures close to the T_g of pure components. This indicates that a phase separation has occurred resulting in a thermoplastic rich phase and an epoxy rich phase not pure. Calculations of the compositions in each separated phase were estimated from the values of T_g and by means of the Fox and Couchman equations; resulting that, when the initial proportion of PS in the system increased, the epoxy rich phase dissolved much PS while the PS rich phase was purest.

Finally, the thermal stability of the systems was studied in both, inert and oxidant atmospheres, resulting that PS did not affect either the thermal or thermooxidative stability of the epoxy-amine system, since the PS degradation occurs at temperatures close to the degradation of thermoset.

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