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Thermal behavior of blends based on a thermoplastic-modified epoxy resin with a crosslinking density variation

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Abstract The thermal behavior of blends based on a polystyrene (PS) and several epoxy-amine systems where amino groups were provided by a monoamine (MA) and a diamine (DA) mixed in different proportions was investigated. This way, the crosslinking density of epoxy-amine polymer was controlled and continuously changed from a linear polymer (epoxy-MA) to a highly crosslinked polymer (epoxy-DA). The effect of the MA–DA proportion and PS modifier on the thermal stability, glass transition, and polymerization reaction was studied by differential scanning calorimetry and thermogravimetric analysis. The MA–DA ratio and modifier proportion did not affect the reaction heat but affected the reactivity. The thermal stability and glass transition temperature increased by increasing the DA proportion in the blend as a result of the higher degree of crosslinking. A study of miscibility of blends based on glass transitions was performed. The thermoplastic-modified materials generally showed two glass transitions with values close to the those of the pure materials, indicating that the mixtures were separated into phases.

Keywords Thermoplastic/thermoset blends · Thermal stability · Glass transition temperature · Polymerization reaction · Miscibility

Introduction

Despite the good properties and performance of epoxy resins, they have the disadvantage of being brittle materials. The toughness of epoxy resins may be improved by the incorporation of thermoplastic components that are initially miscible in the mixture of reactive monomers, but are separated in phases over the course of polymerization, leading to a randomly dispersed phase. This mechanism is known as Polymerization Induced Phase Separation (PIPS) [1, 2]. The final properties and thermal behavior of thermosets depend mainly on the degree of crosslinking of the polymer, which is determined by the functionality of the reactive monomers and the stoichiometry of the reaction [3]. The presence of the modifier can greatly affect and modify the properties of thermosetting material [4–13] being the degree of miscibility or immiscibility of the mixture a determining factor.

The techniques of differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) have proven to be successful for thermal characterization of polymers [14–19]. DSC analysis can also be used as an effective tool for evaluating the compatibility in polymer blends from glass transition measures [20–22].

The aim of the study is to investigate the thermal behavior of blends based on a thermoplastic modifier and an epoxy system polymerized with a monoamine (MA) and a diamine (DA) mixed in various proportions. This way, the molecular structure and the crosslinking density of epoxy-amine polymer is controlled with the formulation and continuously changed from a linear polymer (epoxy-MA) to highly crosslinked polymer (epoxy-DA) [23, 24]. In the present study, the effect of crosslinking density and modifier proportion on the glass transition, thermal stability, and polymerization reaction were analyzed. In

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addition, an analysis of the miscibility of blends based on glass transitions was performed.

Experimental

Materials

The epoxy-amine systems studied were always stoichiometric and were constituted by the precursor epoxy diglycidylether of bisphenol A (DGEBA) polymerized with different proportions of the MA α-aminodiphenylmethane (ADM), and the DA, 4,4′-methylenebis(2,6-diethylaniline) (MDEA). A total of five different epoxy-amine systems were studied, in which the origin of amino group was: 100%MA, 75%MA–25%DA, 50%MA–50%DA, 25%MA–75%DA, and 100%DA expressed as percentage of amino equivalents. The thermoplastic modifier was a polystyrene (PS) with a polydispersity index of 1.64. Compositions of blends in the range of 0 to 25 wt% PS were studied. The chemical structures and characteristics of materials are shown in Table 1.

Blends were prepared as follows: first, PS was dissolved in DGEBA using methylene chloride as solvent, which was later evaporated. In a second step, the PS/DGEBA blend was taken out of the oven at 120 °C and the corresponding amounts of the DA first and then the monomine were added at room temperature, then stirring for 2 min. Samples prepared in this way were tested to determine the reaction heats and glass transitions. To study the thermal stability, the samples were previously polymerized in an oven at 100 °C.

Techniques

A differential scanning calorimeter (DSC-7, Perkin Elmer) was used to measure the glass transition temperatures and the heats of reaction. Unreacted samples of about 5 mg were subjected to two successive scans in the DSC to a heating rate of 10 °C min^{-1}. The reaction enthalpies were calculated by integrating the exothermic peak obtained in the first scan and the glass transitions of polymerized materials were observed in the second scan.

A thermogravimetric balance (Perkin Elmer TGA-7 microbalance) was used to analyze the thermal and thermoxidative stability of the system. The analysis consisted of heating from 30 to 700 °C at a constant rate of 10 °C min^{-1} under two different atmospheres: inert (argon) and oxidizing (oxygen).

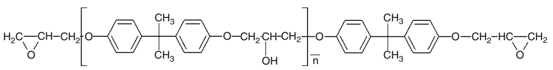
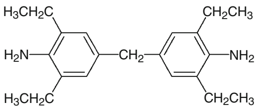
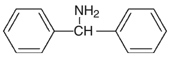
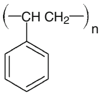
Results and discussion

Polymerization reaction

Dynamic tests were performed in the DSC for the five neat DGEBA/MA–DA systems and modified with various amounts of PS in order to study the polymerization reaction, and the effect of the proportion of MA–DA and PS modifier on the same.

The effect of the MA–DA proportion can be analyzed from Fig. 1 where the reaction exotherms obtained for the five DGEBA/MA–DA systems with different MA–DA ratio are shown. Exotherms were determined from the first DSC scans subtracted from the second and normalized by the mass. Figure 1 shows that the peak of the reaction of epoxy-diamine MDEA is around 220 °C, a higher temperature than the peak of the reaction epoxy-monoamine ADM, which is around 160 °C. As the position of the exotherm in the temperature axis is a measure of reactivity, it appears that the monoamine ADM is more reactive than the diamine MDEA with DGEBA.

Table 1 Characteristics of the materials

Material	Supplier	Structure	Molar mass/g mol^{-1}	Density/g cm^{-3}
DGEBA	Ciba–Geiby Araldite GY260		376 $n = 0.13$	1.20
MDEA	Aldrich		310.5	1.35[a]
ADM	Aldrich		183.26	1.064
PS	Aldrich		$M_n = 140000$ $M_w = 230000$	1.04

[a] From [35]

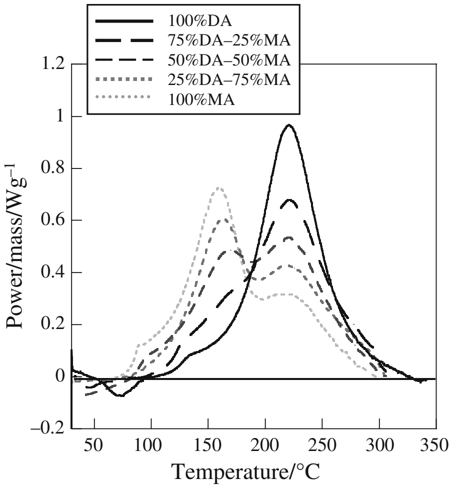


Fig. 1 Reaction exotherms obtained by DSC for various DGEBA/MDEA-ADM (1:1) systems with different proportions of MDEA (DA) and ADM (MA) equivalents

The epoxy-amine systems containing both MA and DA showed two peaks in their reaction exotherms corresponding to the reactions of epoxy-MA and epoxy-DA. The intensity of the peaks varied according to the proportion of MA–DA in the mixture.

The heats of polymerization reaction for the five DGEBA/MA–DA systems were calculated from the exothermic reaction in DSC and are listed in Table 2, expressed per mole of epoxy equivalents. Table 2 shows a reaction heat value similar for all DGEBA/MA–DA systems close to 106 kJ per mole of epoxy equivalents. This means that the proportion of MA–DA did not affect heat of polymerization reaction. The value obtained is in the range of heats reported in the literature for various epoxy-amine systems [25].

The effect of the PS proportion on the polymerization reaction can be observed in Fig. 2 where the reaction exotherms obtained for two epoxy-amine systems ((a) DGEBA/100% MDEA, (b) DGEBA/75%MA–25%DA) unmodified and modified with different proportions of PS are shown. Figure 2 shows that the area of the exothermic reaction decreases with increasing proportion of PS in the mixture. This is logical and expected because the amount of reactive blend is decreasing as a result of PS is an inert modifier. In addition, the maximum of reaction peak slightly shifts towards higher temperature when the proportion of PS increases, indicating that PS slightly delays the polymerization reaction. This delay can be attributed to increased viscosity in the mixing and dilution of reactive groups [26, 27]. The same results were obtained for other epoxy-amine systems studied. The heats of reaction for all the PS + DGEBA/MA–DA blends analyzed were calculated and are listed in Table 3, expressed in two ways: per gram of sample and per mole of epoxy equivalents.

Table 2 Heat of polymerization reaction in DGEBA/ADM(MA)–MDEA(DA) systems

Proportion of MA–DA	Heat of reaction/kJ mol equiv$_{\mathrm{EPOXY}}$$^{-1}$
100%MA	106.04
75%MA–25%DA	105.46
50%MA–50%DA	106.03
25%MA–75%DA	106.11
100%DA	106.00

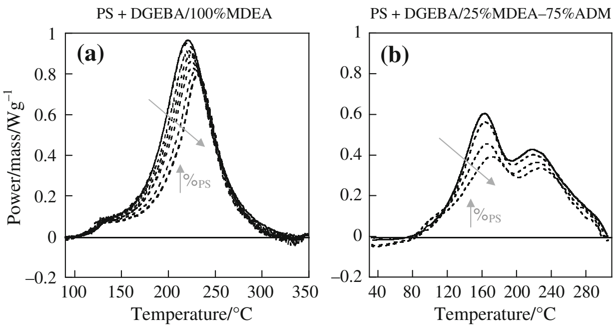


Fig. 2 Reaction exotherms obtained by DSC for two of the DGEBA/MDEA-ADM (1:1) systems unmodified (*solid line*) and modified with different proportions of PS (*dotted line*): **a** for DGEBA/100%MDEA system with 0,3, 6, 9, 12, 15, 20, and 25 wt% PS; **b** for DGEBA/75%ADM–25%MDEA system with 0, 6, 15, and 25 wt% PS

Table 3 shows that the reaction heat expressed per gram of sample decreases with increasing proportion of PS in the mixture. This was attributed, as mentioned above, to the decrease in the amount of reactive blend. However, the heat expressed by equivalent epoxy has almost the same value in all modified systems regardless of modifier proportion. It is therefore concluded that the PS did not affect the total reaction heat in the range of compositions analyzed.

Thermal stability

The effect of MA–DA proportion and PS modifier on the thermal stability of the epoxy-amine system was studied in both inert and oxidizing atmospheres.

The influence of furnace atmosphere and MA–DA proportion can be analyzed from Fig. 3 where the thermograms obtained by TGA for the neat DGEBA/MA–DA systems with different proportion of MA–DA are shown (a) in inert atmosphere and (b) in oxidizing atmosphere. Each thermogram was characterized by measuring several parameters: initial degradation temperature (T_{i}, calculated as the temperature at which 2% of the total mass is lost), onset of degradation temperature (T_{onset}), temperature at maximum rate of degradation (T_{P}, obtained from the

Table 3 Heat of polymerization reaction in DGEBA/ADM(MA)–MDEA(DA) systems modified with PS

%PS	Proportion of MA–DA				
	100%MA	75%MA–25%DA	50%MA–50%DA	25%MA–75%DA	100%DA
Heat of reaction in J/g_{SAMPLE}					
0	379.21	381.91	388.92	394.29	399.08
3	–	–	–	–	387.81
6	356.91	363.40	365.16	370.83	374.62
9	–	–	–	–	363.59
12	–	–	–	–	351.50
15	321.95	326.74	329.61	334.10	339.32
20	–	–	–	–	319.37
25	284.96	287.31	291.04	295.53	298.96
Heat of reaction in kJ/mol $equiv_{EPOXY}$					
0	106.04	105.45	106.03	106.11	106.00
3	–	–	–	–	106.19
6	106.17	106.75	105.90	106.16	105.85
9	–	–	–	–	106.12
12	–	–	–	–	106.09
15	105.91	106.14	105.71	105.77	106.03
20	–	–	–	–	106.03
25	106.24	105.78	105.79	106.04	105.87

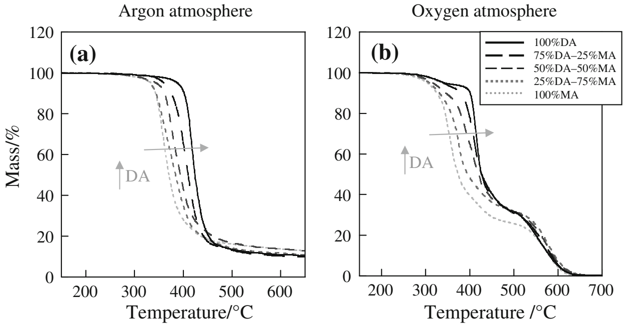


Fig. 3 Thermogravimetric curves obtained in both inert and oxidizing atmospheres for various DGEBA/MDEA-ADM (1:1) systems with different proportions of MDEA (DA) and ADM (MA) equivalents

derivative curve), and residual mass. Values obtained are listed in Table 4.

Comparing graphs (a) and (b) in Fig. 3 and data from Table 4, it is observed that the type of atmosphere affected the degradation of systems mainly in the shape of the thermogram, the residual mass obtained and the initial degradation temperature. Thus, degradation in an inert atmosphere occurred in a single step leading to a residual mass around the 10–14% of the total mass, while the degradation in oxidizing atmosphere mainly occurred in two or three steps leading to total mass loss around 620 °C. The degradation started slightly higher temperatures in inert atmosphere than in oxidizing atmosphere [18, 28], although the temperatures of onset and maximum degradation were not practically affected.

Table 4 Characteristic parameters of the degradation in inert and oxidizing atmosphere obtained for DGEBA/ADM(MA)–MDEA(DA) systems

Proportion of MA–DA	Characteristic parameters of degradation			
	T_i/°C	T_{onset}/°C	T_P/°C	%*R*
Inert atmosphere				
100%MA	286.1	337.5	360.0	13.8
75%MA–25%DA	289.6	339.6	373.3	11.7
50%MA–50%DA	310.4	356.2	378.9	13.8
25%MA–75%DA	321.5	376.4	406.1	10.4
100%DA	347.2	404.2	422.8	13.8
Oxidizing atmosphere				
100%MA	274.4	328.9	354.2	0
75%MA–25%DA	282.7	345.0	374.2	0
50%MA–50%DA	286.8	352.8	400.8	0
25%MA–75%DA	303.2	385.0	409.2	0
100%DA	304.8	399.4	414.2	0

The residue from degradation in an inert atmosphere is a consequence of the polymeric systems containing heteroatoms [29].

Analyzing the effect of MA–DA proportion on the thermal stability, Fig. 3 shows that the degradation curve in both atmospheres shifted to higher temperatures when the DA proportion increased, with a consequent increase of the initial, onset, and maximum degradation temperatures. Thus, in both atmospheres the temperature at maximum degradation increased about 60 °C, since for the system polymerized only with MA to system cured only with DA.

The increase in thermal stability of the epoxy-amine system with the amount of DA is expected and is a consequence of the increase occurring in the crosslinking density of the system. By increasing the crosslinking density of polymer, the heat required for its degradation will be higher, thus improving the thermal stability. However, the proportion of MA–DA did not affect the last step of thermoxidative degradation that occurred in all systems at similar temperatures near 575 °C, nor had a significant effect on the residual mass obtained.

The effect of PS modifier on the thermal stability can be analyzed from Fig. 4, which compares the thermograms and corresponding derivative curves obtained in an inert atmosphere for systems unmodified and modified with different proportions of PS (3, 6, 9, 12, 15, 20, and 25 wt%) for two systems: (a) the epoxy-MA system and (b) the epoxy-DA system. Furthermore, the thermogram of pure PS is shown.

Figure 4 shows that the degradation occurred at similar temperatures in unmodified systems and PS-modified systems. The same behavior was obtained for other epoxy-amine systems and in the presence of an oxidizing atmosphere. Therefore, PS did not worsen the thermal stability and thermooxidative of epoxy-amine systems. Figure 4 shows that the thermograms of systems polymerized only with MA had a second step of degradation (shown circled in Fig. 4a). This step of degradation should be attributed to the degradation of PS because the maximum degradation occurred at temperatures similar to that of PS, around 420 °C, and it increased with the proportion of PS in the blend (as shown derivative curves in Fig. 4a).

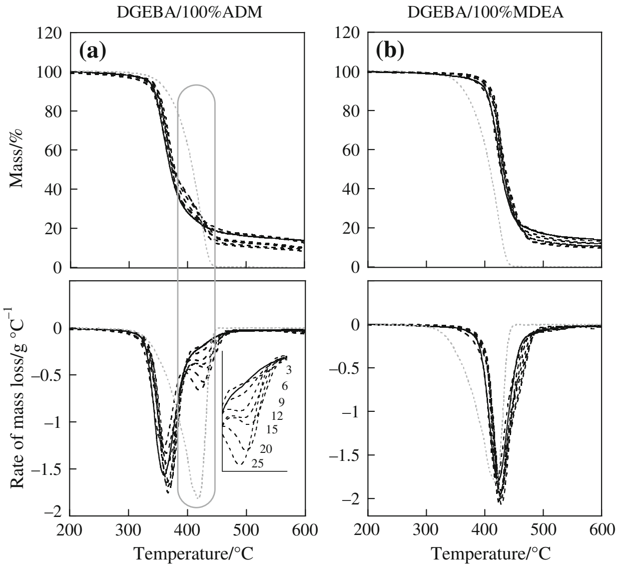


Fig. 4 Thermogravimetric and derivative curves obtained in an argon atmosphere for the systems **a** DGEBA/100%ADM and **b** DGEBA/100%MDEA unmodified (*solid line*) and modified with various PS proportions: 3, 6, 9, 12, 15, 20, and 25 wt% PS (*dotted line*). Curve obtained for the PS is also shown (*gray dotted line*)

This step of degradation was not observed in the system cured with only DA probably because there is overlap between the degradations of PS and epoxy-amine system as a result of displacement at higher temperatures of the degradation of epoxy-amine system.

Glass transition

The glass transitions of polymerized DGEBA/MA–DA blends were determined by DSC. Each glass transition was characterized by measuring the glass transition temperature and the change of specific heat at the glass transition.

The effect of the MA–DA proportion is shown in Fig. 5, where the glass transitions observed by DSC for the five neat DGEBA/MA–DA systems are shown. The curves were moved in the vertical axis for better viewing. The corresponding values of T_g and ΔC_p are listed in Table 5.

Figure 5 and Table 5 show that by increasing the proportion of DA, the glass transition temperature increased from about 83 °C for the system polymerized only with MA to 146 °C for the system polymerized only with DA, while the change in the specific heat decreased showing the opposite trend.

As in the thermal stability, variations in the glass transition temperature can be attributed mainly to the increase occurred in the crosslinking density of the material which causes the polymer networks are more rigid and therefore a higher energy (or temperature) is required for molecular segments begin to move [30, 31]. The increase in the

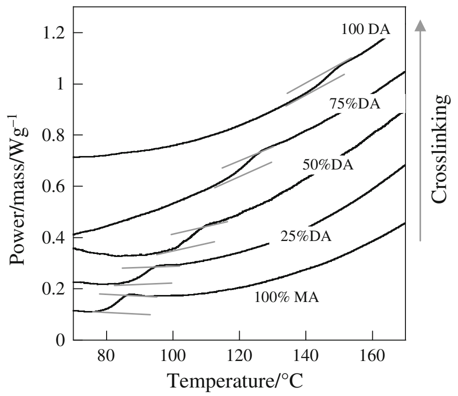


Fig. 5 Glass transitions obtained in various systems DGEBA/MDEA-ADM (1:1) with different proportions of MDEA (DA) and ADM (MA) equivalents

Table 5 Values of glass transitions (T_g and ΔC_p) obtained for DGEBA/ADM(MA)–MDEA(DA) systems

Proportion MA–DA	Glass transition	
	T_g/°C	ΔC_p/J g^{-1} °C^{-1}
100%MA	82.9	0.424
75%MA–25%DA	91.2	0.404
50%MA–50%DA	105.1	0.391
25%MA–75%DA	120.8	0.382
100%DA	146.2	0.317

degree of crosslinking also explains the decrease in ΔC_p since the heat capacity of the material increases with the number of active modes of movements and decreases with the rigidity of material.

The effect of PS modifier on the glass transition reached by the material will be discussed below and an analysis of the miscibility of blends based on glass transitions will also be performed. Figure 6 shows for each of the five DGEBA/MA–DA systems, the glass transitions obtained for the neat system (upper curve), the system modified with different proportions of PS (following curves displaced to down to increase the proportion of PS) and the pure PS (dotted line). Compositions analyzed were 0, 3, 6, 9, 12, 15, 20, and 25 wt% PS for the DGEBA/DA system and 0, 6, 15, and 25 wt% PS for other systems. The glass transitions were marked by a circle in Fig. 6. The corresponding values of T_g and ΔC_p are listed in Table 6.

Figure 6 shows that three of the epoxy-amine systems (DGEBA/100%DA, DGEBA/75%DA–25% MA, and DGEBA/100%MA) modified with larger amounts to 15 wt% PS showed two glass transitions at temperatures located close to those the pure components (PS and corresponding epoxy-amine system). This means, according to the criterion of miscibility based on the glass transitions [32, 33], that in these mixtures has been a phase separation, forming two phases, one rich in PS with a T_g close to that of PS, and the other rich in epoxy-amine with a T_g near that of the corresponding epoxy-amine system. Although these T_g are close to those of the pure components, they differ slightly coming toward the T_g of the other component, as shown in Table 6 data. This means that the separate phases are not pure and dissolved a part of another component [34].

In these three systems modified with minor proportions of 15 wt% PS, only a T_g next to the respective epoxy-amine system was observed. This does not indicate that these blends are immiscible, but it was attributed to that the proportion of the modifier-rich phase is so low that the signal corresponding to its glass transition was not able to be detected in the DSC.

The other two modified epoxy-amine systems (DGEBA/50%MA–50%DA and DGEBA/25%MA–75%DA) only had a single glass transition over the range of PS compositions. This could lead to wrongly think that they are miscible blends. However, if the difference between the T_g of the pure components that constituted the two mixtures is analyzed, both T_g are very close, in one case the difference is 5 °C and in the other, 9 °C. It is therefore expected that these two modified systems exist, as in the other mixtures, phase separation generating two glass transitions, but in these cases they are so close that come to overlap.

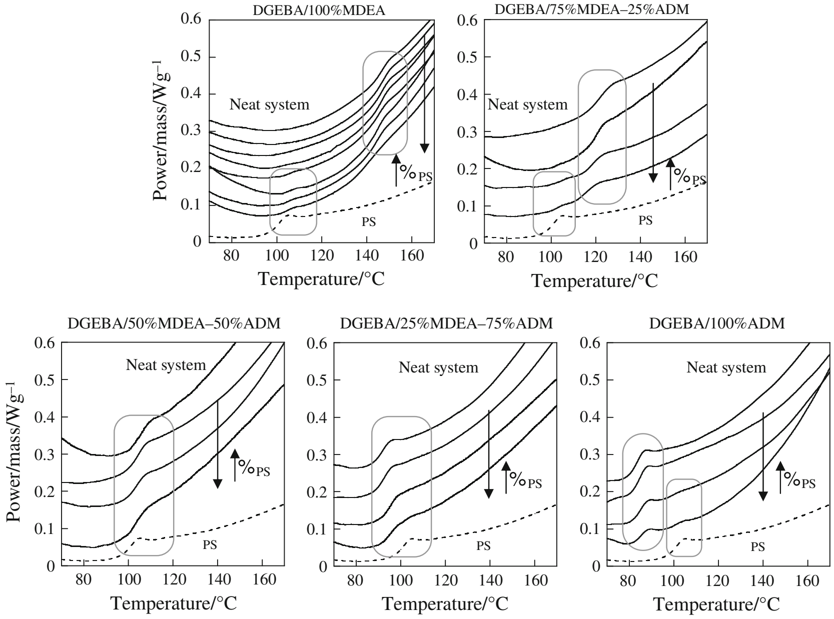


Fig. 6 Glass transitions obtained for five systems DGEBA/MDEA-ADM (1:1) with different MDEA-ADM ratio, unmodified and modified with various proportions of PS: 3, 6, 9, 12, 15, 20, and 25 wt% PS for the DGEBA/100%MDEA system, and 6, 15, and 25 wt% PS for other systems. The glass transition for pure PS is also shown. Glass transitions obtained are marked with a *circle*

Table 6 Values of glass transitions (T_g and ΔC_p) obtained for various DGEBA/ADM-MDEA modified with PS 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}
PS modifier				
PS	–	–	100.1	0.288
DGEBA/100%MDEA				
0	146.2	0.317	–	–
3	146.1	0.310	–	–
6	145.9	0.304	–	–
9	145.7	0.287	–	–
12	144.7	0.274	–	–
15	144.4	0.257	105.9	0.101
20	143.8	0.246	105.5	0.124
25	–	–	104.5	0.139
DGEBA/75%MDEA–25%ADM				
0	120.8	0.382	–	–
6	119.5	0.315	–	–
15	118.9	0.283	–	–
25	115.8	0.280	102.2	0.142
DGEBA/100%ADM				
0	82.9	0.424	–	–
6	83.5	0.362	–	–
15	84.4	0.334	–	–
25	84.8	0.324	99.7	0.145

	T_g/°C	ΔC_p/J g^{-1} °C^{-1}
DGEBA/50%MDEA–50%ADM		
0	105.1	0.391
6	104.0	0.384
15	103.4	0.377
25	103.1	0.361
DGEBA/25%MDEA–75%ADM		
0	91.2	0.404
6	92.3	0.396
15	94.5	0.392
25	95.5	0.389

Conclusions

The thermal behavior of blends based on a PS modifier and various epoxy-amine systems where the degree of crosslinking was continually changed and controlled through the formulation, with a MA and a DA mixed in different proportions, was investigated. The effect of MA–DA proportion (determining the crosslinking density) and the PS modifier on the polymerization reaction, thermal stability, and glass transition was determined and analyzed.

The heat of the polymerization reaction was not affected either by the ratio of MA–DA in the system or by the proportion of PS in the range of compositions studied, obtaining a value close to 106 kJ per mole of epoxy equivalents for all studied DGEBA/MDEA + ADM-PS blends. However, the reactivity of the epoxy-amine system was affected by these variables, resulting in the MA was more reactive than the DA and the PS slightly delayed reaction.

The thermal stability of blends was affected by the type of furnace atmosphere which affected the degradation mainly in the form of the thermogram, the final residue, and the initial temperature of degradation. Thus, the thermal degradation of the neat systems occurred in one step leading to a residual mass around the 10–14 wt%, whereas degradation thermoxidative started at temperatures slightly lower and occurred in two or three steps leading to total loss mass around 620 °C. In addition, the thermal stability and thermoxidative were considerably affected by the proportion of MA–DA in the system, increasing with the amount of DA. However, it did not change significantly with the presence of PS modifier.

The glass transition temperature of epoxy-amine systems increased with the proportion of DA in the system from 83 °C for the system polymerized only with MA (DGEBA/ADM) to 146 °C for the system cured only with DA (DGEBA/MDEA). The increase in glass transition temperature and thermal stability with the proportion of DA was attributed to the increase occurred in the crosslinking density.

PS-modified systems in general showed two glass transitions, indicating that the blends were immiscible and were separated into two phases, one phase rich in epoxy-amine system and the other phase rich in PS modifier. In some systems (DGEBA/75%ADM–25%MDEA and DGEBA/50%ADM–50%MDEA) and for some compositions of modifier (<15 wt% PS) only one glass transition was observed. This was not attributed to a miscibility of the blends, but an overlap of two transitions in the first case, and a lack of detectability in the second case.

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References

1. Williams RJJ, Rozenberg BA, Pascault JP. Reaction-induced phase separation in modified thermosetting polymers. In: Koenis JL, editor. Advances in polymer science, volume 128: polymer analysis, polymer physics. Berlin: Springer; 1997. p. 95–156.
2. Pascault JP, Williams RJJ. Formulation and characterization of thermoset-thermoplastic blends. In: Paul DR, Bucknall CB, editors. Polymer blends volume 1: formulation, chap 13. New York: Wiley; 2000. p. 379–415.
3. Ehrenstein GW. Polymeric materials: structure–properties-applications. Munich: Hanser Publishers; 2001. p. 55.

4. Cano J, Torres A, Abad MJ, Barral L, Díez FJ, López J. Characterization of an ABS-modified epoxy system. Polym Int. 2002; 51:1268–76.
5. López J, Ramírez C, Abad MJ, Barral L, Cano J, Díez FJ. Dynamic mechanical analysis of an epoxy/thermoplastic blend: polymerization-induced phase separation. Polym Int. 2002;51: 1100–6.
6. Girard-Reydet E, Vicard V, Pascault JP, Sautereau H. Polyetherimide-modified epoxy networks: influence of cure conditions on morphology and mechanical properties. J Appl Polym Sci. 1997;65:2433–45.
7. Torres A, López-de-Ullibarri I, Abad MJ, Barral L, Cano J, García-Garabal S, Díez FJ, López J, Ramírez C. Study of the effect of poly(acrylonitrile-co-butadiene-co-styrene) on the mechanical properties of an epoxy system. J Appl Polym Sci. 2004;92:461–7.
8. Arribas C, Masegosa RM, Salom C, Arévalo E, Prolongo SG, Prolongo MG. Epoxy/poly(benxyl methacrylate) blends: miscibility, phase separation on curing and morphology. J Therm Anal Calorim. 2006;86(3):693–8.
9. Schroeder WF, Borrajo J, Aranguren MI. Poly(methyl methacrylate)-modified vinyl ester thermosets: morphology, volume shrinkage, and mechanical properties. J Appl Polym Sci. 2007; 106:4007–17.
10. Dong JP, Huang JG, Lee FH, Roan JW, Huang YJ. Effect of poly(methyl methacrylate)-based low-profile additives on the properties of cured unsaturated polyester resins. I. Miscibility, curing behavior, and glass-transition temperatures. J Appl Polym Sci. 2004;91:3369–87.
11. Auad ML, Frontini PM, Borrajo J, Aranguren MI. Liquid rubber modified vinyl ester resins: fracture and mechanical behavior. Polymer. 2001;42:3723–30.
12. Auad ML, Proia M, Borrajo J, Aranguren MI. Rubber modified vinyl ester resins of different molecular weights. J Mater Sci. 2002;37:4117–26.
13. Zucchi IA, Galante MJ, Williams RJJ. Comparison of morphologies and mechanical properties of crosslinked epoxies modified by polystyrene and poly(methyl methacrylate) or by the corresponding block copolymer polystyrene-b-poly(methyl methacrylate). Polymer. 2005;46:2603–9.
14. López J, Rico M, Montero B, Díez J, Ramírez C. Polymer blends based on an epoxy-amine thermoset and a thermoplastic. J Therm Anal Calorim. 2009;95(2):369–76.
15. Radhakrishnan CK, Sujith A, Unnikrishnan G. Thermal behaviour of styrene butadiene rubber/poly(ethylene-co-vinyl acetate) blends TG and DSC analysis. J Therm Anal Calorim. 2007;90(1): 191–9.
16. Barral L, Cano J, López J, López-Bueno I, Nogueira P, Ramírez C, Torres A, Abad MJ. Thermal properties of amine cured diglycidyl ether of bisphenol A epoxi blended with poly(ether imide). Thermochim Acta. 2000;344:137–43.
17. Ramírez C, Rico M, López J, Montero B, Montes R. Study of an epoxy system cured with different diamines by differential scanning calorimetry. J Appl Polym Sci. 2007;103:1759–68.
18. Li Q, Zhong H, Wei P, Jiang P. Thermal degradation behaviors of polypropylene with novel silicon-containing intumescent flame retardant. J Appl Polym Sci. 2005;98:2487–92.
19. Vinnik RM, Roznyatovsky VA. Kinetic method by using calorimetry to mechanism of epoxy-amine cure reaction. Part VIII. A comparative study of some epoxy-amine reactions. J Therm Anal Calorim. 2006;85(2):455–61.
20. López J, López-Bueno I, Nogueira P, Ramírez C, Abad MJ, Barral L, Cano J. Effect of poly(styrene-co-acrylonitrile) on the curing of an epoxy/amine resin. Polymer. 2001;42:1669–77.
21. Del Río C, Acosta JL. Determination of the interaction parameter of partially or totally compatible systems through glass transition temperature measurements. Eur Polym J. 1996;32(7):913–7.
22. Remiro PM, Riccardi CC, Corcuera MA, Mondragon I. Design of morphology in PMMA-modified epoxy resins by control of curing conditions. I. Phase behavior. J Appl Polym Sci. 1999;74: 772–80.
23. Blanco M, López M, Fernández R, Martín L, Riccardi CC, Mondragon I. Thermoplastic-modified epoxy resins cured with different functionalities amine mixtures. Kinetics and miscibility study. J Therm Anal Calorim. 2009;97:969–78.
24. Blanco M, López M, Alvarez De Arcaya P, Ramos JA, Kortaberria G, Riccardi CC, Mondragon I. Thermoplastic-modified epoxy resins cured with different functionalities amine mixtures. Morphology, thermal behavior, and mechanical properties. J Appl Polym Sci. 2009;114:1753–60.
25. Klute CH, Viehmann W. Heat of polymerization of phenyl glycidyl ether and of an epoxy resin. J Appl Polym Sci. 1961; 13:86–95.
26. Girard-Reydet E, Riccardi CC, Sautereau H, Pascault JP. Epoxy-aromatic diamine kinetics. 2. Influence on epoxy-amine network formation. Macromolecules. 1995;28:7608–11.
27. Hoppe CE, Galante MJ, Oyanguren PA, Williams RJJ, Girard-Reydet E, Pascault JP. Transparent multiphasic polystyrene/ epoxy blends. Polym Eng Sci. 2002;42(12):2361–8.
28. Ramírez C, Rico M, Barral L, Díez J, García-Garabal S, Montero B. Organic/inorganic hybrid materials from an epoxy resin cured by an amine silsesquioxane. J Therm Anal Calorim. 2007;87(1):69–72.
29. Forrest MJ. Application to thermoplastics and rubbers. In: Gabbott P, editor. Principles and applications of thermal analysis, chap 6. Oxford: Blackwell Publishing; 2008. p. 191–212.
30. Eisenberg P, Lucas JC, Williams RJJ. Hibrid organic–inorganic polymer networks based on the copolymerization of methacryloxypropyl-silsesquioxanes and styrene. Macromol Symp. 2002; 189:1–13.
31. Schroeder WF, Auad ML, Barcia Vico MA, Borrajo J, Aranguren MI. Thermodynamic, morphological, mechanical and fracture properties of poly(methyl methacrylate) (PMMA) modified divinylester(DVE)/styrene(St) thermosets. Polymer. 2005;46:2306–19.
32. MacKnight WJ, Karasz FE, Fried JR. Solid state transition behavior of blends. In: Paul DR, Newman S, editors. Polymer blends, chap 5, vol. 1. San Diego: Academic Press Inc.; 1978. p. 185.
33. Fried JR. Applications of thermal analysis to the study of polymer blends. In: Dawkins JV, editor. Developments in polymer characterization, chap 2, vol. 4. London: Applied Science Publishers; 1983. p. 39–90.
34. Gardlund ZG. Properties and morphology of poly(methyl methacrylate)/bisphenol A polycarbonate blends. In: Han CD, editor. Polymer blends and composites in multiphase systems, Advances in chemistry series 206, chap 9. Washington, DC: American Chemical Society; 1984. p. 129–48.
35. Riccardi CC, Borrajo J, Meynie L, Fenouillot F, Pascault JP. Thermodynamic analysis of the phase separation during the polymerization of a thermoset system into a thermoplastic matrix. I. Effect of composition on cloud-point curves. J Polym Sci B. 2004;42:1351–60.