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Thermal properties of amine cured diglycidyl ether of bisphenol A epoxy blended with poly(ether imide)

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Abstract

Thermal properties of an epoxy system containing diglycidyl ether of bisphenol A (DGEBA) and 1,3-bisaminomethylcyclohexane (1,3-BAC) as curing agent modified with poly(ether imide) (PEI) were studied using both dynamic mechanical (DMA) and thermogravimetric (TG) analysis. The effect of thermal degradation in air and in vacuum on the dynamic mechanical and thermogravimetric properties for the DGEBA/1,3-BAC/PEI system was investigated. The results showed that this system can be considered miscible for PEI contents up to 10 phr (phr: number of parts of PEI per hundred parts of the DGEBA epoxy resin), and also that even very small contents of PEI in the blends reduced the thermal stability of the material. Thermal degradation during a short period of time of this material both, in air or in vacuum yields a decrease of thermal stability and an increase of the glass transition temperature with respect to the material without degradation.

Keywords: Blend; DMA; Epoxy resin; Poly(ether imide); TG; Thermal degradation

1. Introduction

Thermosetting epoxies possess properties such as high tensile strength and modulus, dimensional and thermal stability and excellent chemical and solvent resistance. So, epoxy resins have been used extensively as matrices in fibre-reinforced composites. However, these materials are generally brittle due to high crosslink densities.

Polymeric thermoplastics can enhance fracture toughness without sacrificing the glass transition temperature, strength, stiffness or other desirable properties of thermosetting resins. Rubber modification of epoxies [1], firstly realised, became ineffective because toughness improvements in most rubber-modified thermosetting systems usually result in a significant decrease in the glass transition temperature of the cured resins.

Polymeric materials are subjected to various types of degradation, ranging from thermal degradation to biodegradation. Degradation of polymers is an undesirable process involving a deterioration of their properties. This view, however, is a limited one since it is possible to utilise degradation process for the creation of new materials with useful properties [2].

In this work the thermal properties of an epoxy system containing diglycidyl ether of bisphenol A (DGEBA) and 1,3-bisaminomethylcyclohexane (1,3-BAC) as curing agent modified with a high perfor-

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mance thermoplastic poly(ether imide) (PEI) were investigated using both dynamic mechanical (DMA) and thermogravimetric (TG) analysis. The PEI has been used specially in the modification of tetrafunctional epoxy resins [3,4] but it was less used with DGEBA, where the success in the improvement of the mechanical properties is not guaranteed initially [5].

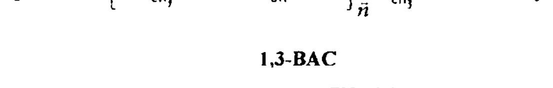
The cure kinetics of the DGEBA/1,3-BAC system [6], and some of their thermal and mechanical properties [7–9] have been previously reported. This work is part of a larger study on the modification of DGEBA/1,3-BAC system with different thermoplastics. The objective of this part was to study the influence of PEI contents on thermal stability, glass transition temperature, and modulus of the DGEBA/1,3-BAC/PEI system via DMA and TG analysis. Also, the influence of thermal degradation on the DMA and TG properties was investigated for the DGEBA/1,3-BAC/PEI system when carried out in air or in vacuum during a relatively short time.

2. Experimental

2.1. Materials

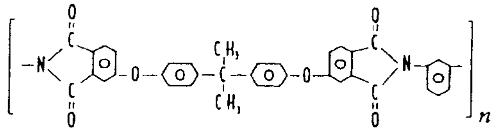
The three components used for the blends were the resin diglycidyl ether of bisphenol A (DGEBA), Shell Epikote 828, with weight per epoxy equivalent of 192.2 g eq^{-1} which was determined by hydrochlorination [10], the curing agent 1,3-BAC, Mitsubishi Gas Chem., with molecular weight of 142.18 and manufacturer purity value of >99% according to the supplier, and the thermoplastic poly(ether imide) (PEI), General Electric Ultem 1000. The structures of these components are as follows

DGEBA



1,3-BAC

PEI



All components were commercial products, and were used as received without purification. Formulation of DGEBA/1,3-BAC was 100 g DGEBA for 18.5 g 1,3-BAC. Epoxy/PEI blended mixtures with 1, 2.5, 5, 7.5, and 10 phr of PEI were prepared (where phr represents the number of parts of PEI per hundred parts of the DGEBA epoxy resin).

2.2. Procedure, cure and degradation of the material

All the blends with PEI were prepared following the same procedure: the PEI was holded in an oven at 70°C in order to be dehydrated, then it was dissolved in dichloromethane and the resulting polymer solution was mixed with the epoxy resin at room temperature. The solvent in the mixture was vapourised in a thermic bath at 80°C. Then, the 1,3-BAC was slowly added with continuous stirring to the resin–PEI mixture at room temperature.

The mixture was then poured into a rectangular mould to obtain a homogeneous sheet of the material. The mould was introduced in a forced air convection oven pre-heated at 40°C. The mixture was cured 5 h at 40°C, followed by 8 h at 60°C and a post-cure of 2 h at 120°C.

Each sheet was cut in three parts. One was degraded in a forced air convection oven during 24 h at 160°C, the second one was degraded in a vacuum oven at identical conditions, and the remaining part was tested without degradation.

2.3. Techniques

Dynamic mechanical measurements were performed with a DMA-7 analyser connected to a liquid nitrogen cooling accessory CCA-7 from Perkin Elmer. Samples were prepared as rectangular shapes suitable for DMA tests. Dimensions of the cut specimens were 18.0 mm × 4.3 mm × 4.3 mm. All the experiments were carried-out in three-point bending mode with a frequency of 1 Hz over the temperature range 25–250°C under a helium flow of 40 ml min^{-1}. The temperature ramping rate was 5°C min^{-1}. The DMA calibration have different routines. These automatic routines allow to calibrate the height, furnace temperature and force. The temperature calibration was made using the melting point of high purity indium.

TG analysis was performed with a Perkin Elmer TGA-7 microbalance coupled with a 1022 Perkin Elmer microprocessor. The experiments were conducted in an argon atmosphere flowing at a rate of 100 ml min^{-1}. The temperature range of the experiments was between 35°C and 700°C. The heating rate was 20°C min^{-1}. Small discs of about 12 mg mass were cut from the sheets to use in these experiments. This microbalance was calibrated by using the discontinuous change in magnetic properties with temperature of metals such as nickel and perkalloy. As the temperature increases, the individual metal samples lose their ferromagnetic properties at well-defined temperatures and they are no longer influenced by the magnet. The Curie point of every metal can be calculated and therefore the microbalance can be calibrated at different heating rates.

3. Results and discussion

3.1. DMA and TG properties of the DGEBA/1,3-BAC/PEI system

Fig. 1 displays the dynamic storage modulus, E', and the loss factor, tan δ, curves for two of the dynamic mechanical tests. It is appreciable that the glass transition region is less broad for: (a) the neat system than for (b) the modified one. No second peak in tan δ was detected in the glass transition region of PEI, around 220°C [11], for any of the studied blends, i.e., there was no sign of the existence of two phases in the blends.

In Table 1 are shown the glass transition temperatures, T_g, the values of the loss factor at the maximum, tan δ_{max}, and the values of E' before (glassy region) and after (rubbery zone) the glass transition temperature for the neat and the modified systems. The values of T_g from DMA data were determined from the tan δ peak, and the values of E' at the glassy and rubbery regions were determined, respectively, at 50°C and 200°C. It is appreciable for an increase of T_g and E' with the PEI contents up to 5 phr, but for contents higher than 5 phr there is a clear diminution of these values. However, for all the contents of PEI studied T_g is relatively high, above 130°C, and the drop of E' in the glass transition region given by the rate E'_{50}/E'_{200} is around 20, indicative of high crosslinking [12].

Table 1
DMA parameters for the DGEBA/1,3-BAC/PEI system

PEI (phr)	T_g (°C)	tan δ_{max}	E'_{50} (10^8 Pa)	E'_{200} (10^8 Pa)
0	138.2	0.49	2.2	0.11
1	139.0	0.45	2.5	0.13
2.5	138.5	0.45	3.0	0.14
5	139.5	0.39	3.1	0.18
7.5	134.7	0.28	1.9	0.10
10	136.7	0.30	1.5	0.07

Fig. 2 shows the TG and derivative curves for some tests. The loss of mass happens with only one step. Neither the presence of absorbed water nor the traces of the disolvent used to prepare the different blends were found.

Table 2 presents the temperatures of degradation at the beginning, T_{on1}, at the final T_{on2}, and at the maximum rate of degradation, T_{max}, for the neat and the modified systems. T_{on1} was determined from the onset of the TG curve realized before and after of the sudden drop at the start of the step of degradation. T_{max} was determined from the maximum of the derivative curve, such temperature coincides with the inflection point of the degradation curve. This point was used for the determination of T_{on1} and T_{on2}. The residual mass remaining as char was calculated at 600°C in all the tests realized. The results showed that a decrease of thermal stability was appreciable while increasing the PEI contents. Very small percentages of

Table 2
TG parameters for the DGEBA/1,3-BAC/PEI system

PEI (phr)	T_{on1} (°C)	T_{max} (°C)	T_{on2} (°C)	Residual mass at 600°C (%)
0	477	492	508	9.6
1	440	463	491	14.7
2.5	436	464	495	13.6
5	409	438	479	9.3
7.5	400	435	483	9.6
10	395	423	465	8.7

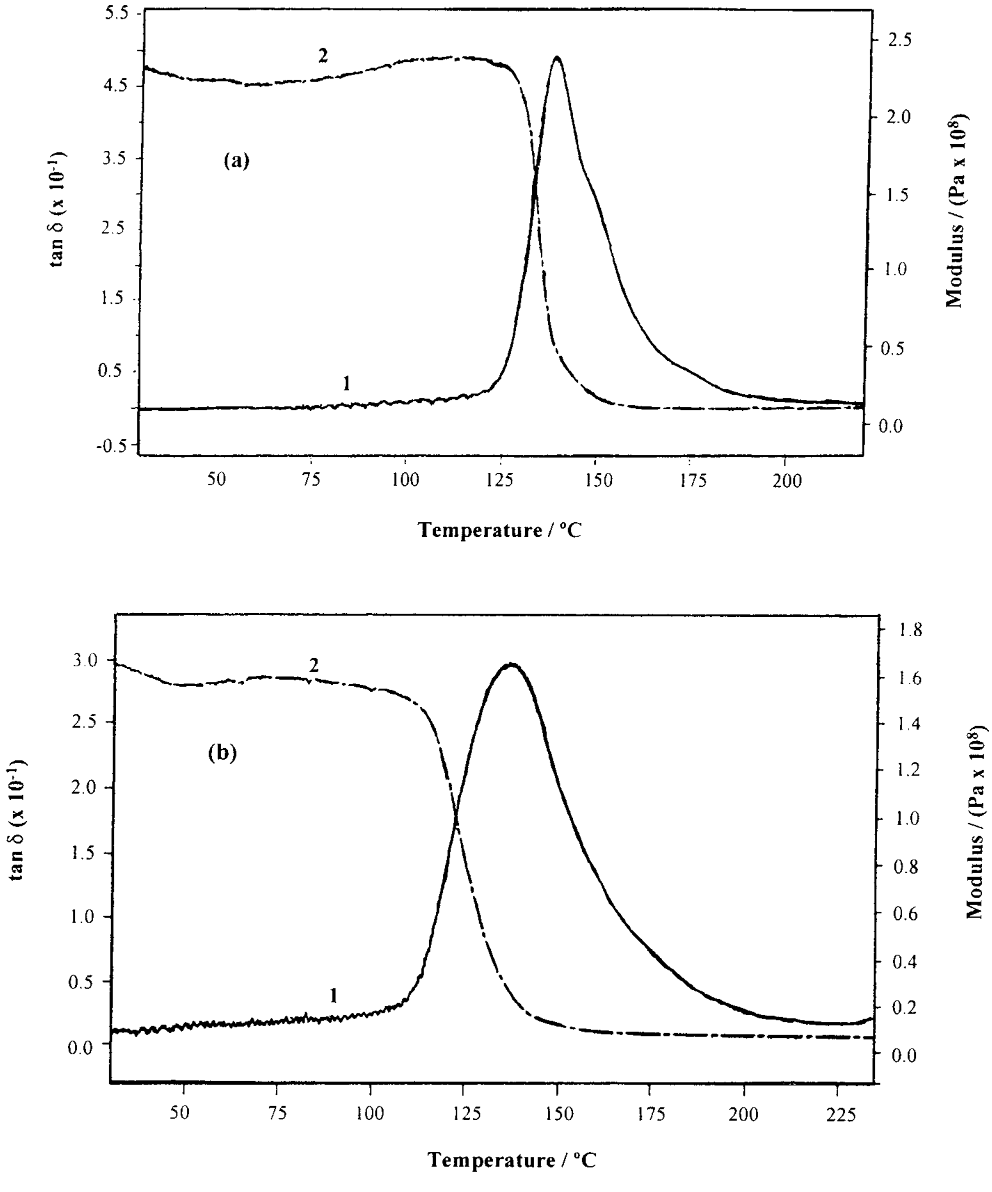


Fig. 1. DMA parameters. (1) tan δ, (2) storage modulus: (a) 0 PEI phr, (b) 10 PEI phr.

PEI caused a decrease of T_{on1}, T_{on2}, and T_{max} of some tens of degrees. This decrease is less marked for PEI contents higher than 5 phr.

3.2. Effect of thermal degradation on the DGEBA/ 1,3-BAC/PEI system

Table 3 gives the dynamic mechanical properties of the blends tested, when the samples were kept 24 h at 160°C in a forced air convection oven. An increase of T_g and E' with the PEI content up to 5 phr was observed, similar behaviour as in the system without degradation. When the T_g values of the degraded material in air are compared with those of the material with the same content of PEI without degradation, a clear increase in T_g was observed in all the blends. These results agree with previous values [8] obtained for the degradation of the neat system, for this system

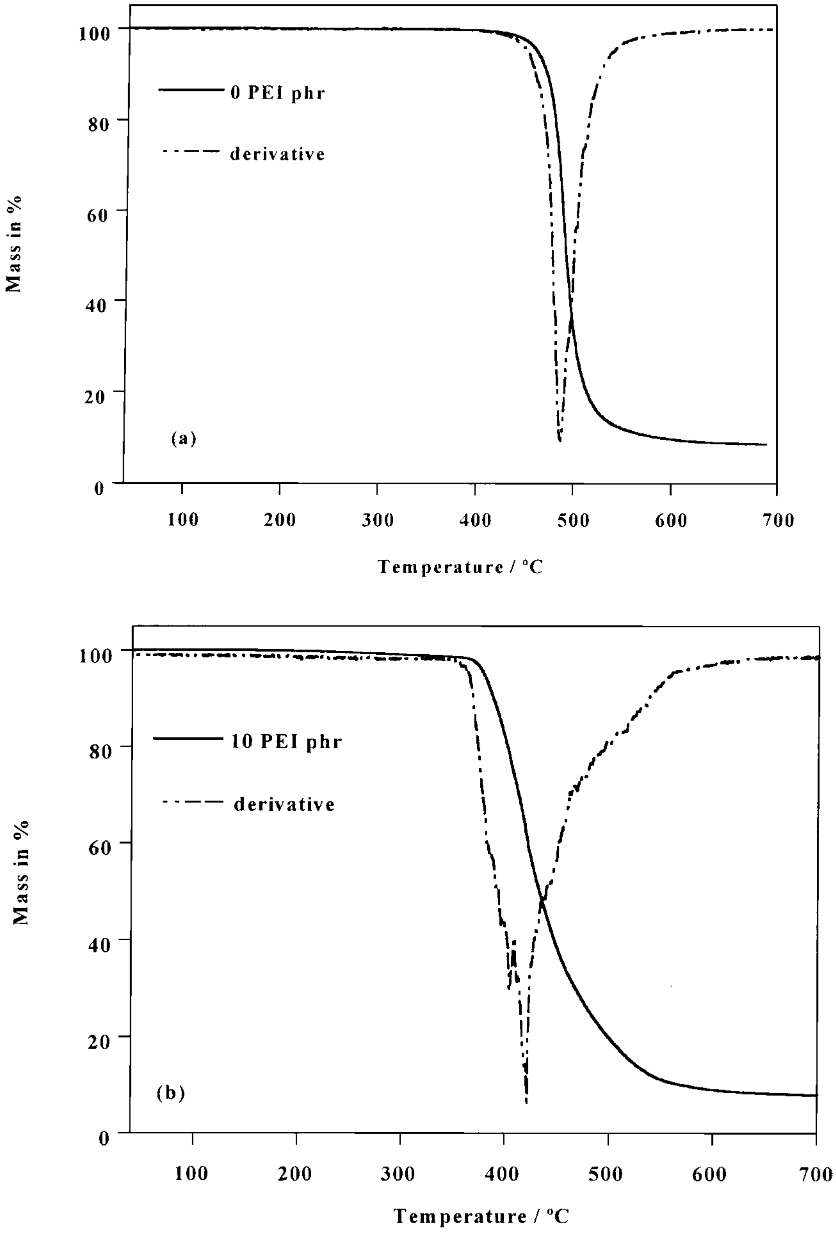


Fig. 2. TG curves: (a) 0 PEI phr, (b) 10 PEI phr.

an increase in T_g during the first 100 h followed by a decrease for many hours of aging was reached. As the blends were kept at 160°C during 24 h, an additional crosslinking occurs, making the reaction more complex and increasing T_g. Then, such process can be considered like a post-cured, that is, there is an improvement for the value of T_g.

Table 4 shows the relevant parameters of the TG tests of all blends maintained 24 h at 160°C in a forced air convection oven. There is a decrease in T_{on1}, T_{on2}, and T_{max} while the PEI contents increase, the same trend that in the blends without degradation. In all the blends the residual mass was approximately 11%. Comparing the values of T_{on1} for the material degraded

Table 3
DMA parameters for the DGEBA/1,3-BAC/PEI system degraded in air

PEI (phr)	T_g (°C)	tan δ_{max}	E'_{50} (10^8 Pa)	E'_{200} (10^8 Pa)
0	146.1	0.47	1.4	0.08
1	146.1	0.45	1.4	0.09
2.5	151.8	0.40	2.6	0.13
5	153.4	0.54	5.7	0.21
7.5	139.4	0.49	1.2	0.05
10	149.7	0.62	3.5	0.08

Table 4
TG parameters for the DGEBA/1,3-BAC/PEI system degraded in air

PEI (phr)	T_{on1} (°C)	T_{max} (°C)	T_{on2} (°C)	Residual mass at 600°C (%)
0	459	477	514	10.4
1	445	463	502	11.4
2.5	433	458	500	14.0
5	406	437	477	10.1
7.5	366	396	454	10.8
10	383	415	463	10.6

in air with the values obtained without degradation, it was observed that the values are smaller for the degradation material during 24 h, that is, the degradation process implies a loss of thermal stability.

To study the influence of the atmosphere on the samples during the process of isothermal degradation, some DMA and TG tests were realized for blends with 24 h at 160°C of degradation in a vacuum oven. Tables 5 and 6 present the results obtained for the blends with PEI contents of 0, 5, and 10 phr.

The values of T_g and T_{on1} for the material degraded in vacuum are, respectively, higher and smaller than the corresponding values of the material without degradation for the same contents of PEI, such as in the case of the degradation in air. So, the variations of T_g and T_{on1} during the degradation can be mainly attributed to the high temperatures and the times of degradation. However, other effects such as the changes of colour of the samples during thermal degradation are due to the atmosphere. The material without PEI is transparent and colourless, when it was degraded in vacuum no change of colour was detected, but when it was degraded in air the material obtained an intense brown colour. The blends with PEI are amber-coloured. This material, when the PEI contents increase, becomes more amber-coloured and opaque for the degradation in air. These changes of colour during thermal degradation in air are originated by thermooxidative reactions.

Table 5
DMA parameters for the DGEBA/1,3-BAC/PEI system degraded in vacuum

PEI (phr)	T_g (°C)	tan δ_{max}	E'_{50} (10^8 Pa)	E'_{200} (10^8 Pa)
0	143.9	0.46	1.6	0.09
5	141.3	0.41	4.8	0.18
10	156.9	0.43	2.5	0.09

Table 6
TG parameters for the DGEBA/1,3-BAC/PEI system degraded in vacuum

PEI (phr)	T_{on1} (°C)	T_{max} (°C)	T_{on2} (°C)	Residual mass at 600°C (%)
0	438	458	489	7.9
5	411	435	476	9.4
10	382	419	472	10.5

Fig. 3 shows the increase of T_g with thermal degradation when it is compared with the material without degradation for the blend with 10 phr of PEI.

4. Conclusions

From all the results obtained it can be concluded that even small contents of PEI in the blends reduce the thermal stability of the material, having a less effect on T_g.

Only one peak was observed in tan δ curves for all the blends so, the DGEBA/1,3-BAC/PEI system can be considered miscible for PEI contents up to 10 phr, i.e., there is a single-phase structure for these materials.

Thermal degradation of the material in air or in vacuum at a temperature above the glass transition temperature during 24 h yields a decrease of the thermal stability and an increase of T_g with regard to the material without degradation. Degradation in vacuum gives less increase of T_g, and also a less

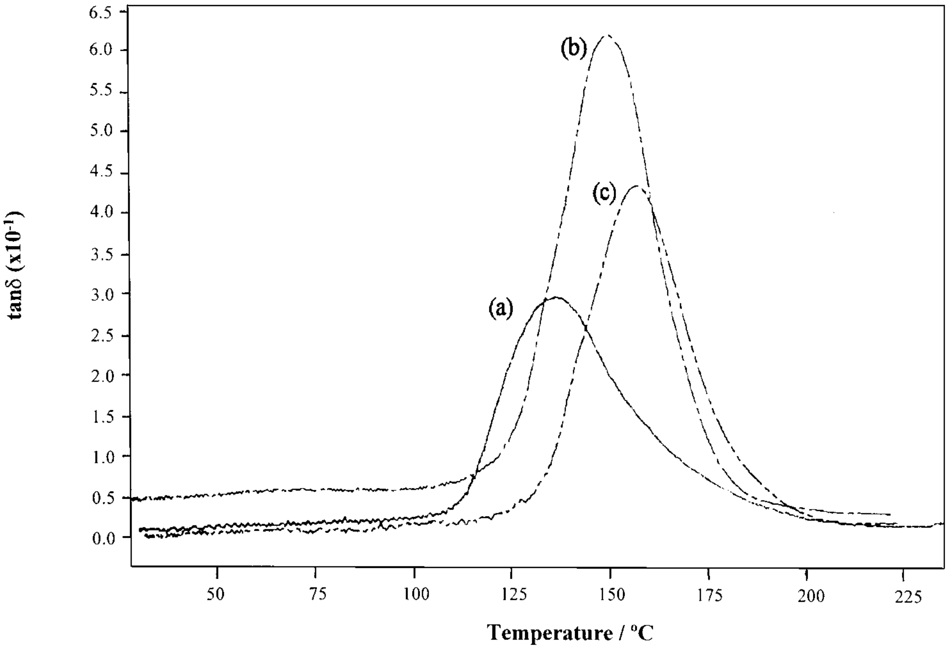


Fig. 3. tan δ curves of DGEBA/1,3-BAC/PEI 10 phr: (a) without degradation, (b) degraded in air, (c) degraded in vacuum.

change in the colour of the samples than when the degradation was realised in air.

Acknowledgements

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