

Physical and Mechanical Behavior of Tetraglycidyl Diaminodiphenyl Methane (TGDDM)/*m*-Phenylene Diamine (*m*-PDA) Epoxy Systems

J. J. IMAZ,¹ M. J. JURADO,² M. A. CORCUERA,¹ and I. MONDRAGON^{1,*}

¹Escuela Universitaria Ingeniería Técnica Industrial, Departamento Ingeniería Química y M. Ambiente (Universidad del País Vasco/Euskal Herriko Unibertsitatea), Avda. Felipe IV, 1 B, C. P. 20011. Apdo. 1379, San Sebastián, Spain; ²Inasmet, B² Igara, San Sebastián, Spain

SYNOPSIS

The rheological behavior of a tetraglycidyl diaminodiphenyl methane with a tetrafunctional aromatic diamine has been studied in terms of the influence of curing agent content and temperature. In this work, critical times corresponding to gelation are used as a measure of activation energy. The dynamic mechanical behavior has been used to analyze the curing extent of these epoxy systems with different amine contents before and after thermal post-treatment. The β -relaxation peak temperature is found to increase with the curing agent content and also after thermal posttreatment. This has been related to the rise of cross-linking extent. Dependence of flexural mechanical properties on curing agent content and the postcure process has also been determined.

INTRODUCTION

Composite materials application increasingly requires the development of systems with good thermal and mechanical properties, together with low- and medium-temperature manufacturing possibilities. Whenever the materials are submitted to strong structural requirements, the main role is played by the fiber. However, the matrix will also be taken into account with regard to the following points of view:

- A suitable stress transfer is assured along the material protecting the fiber from thermal, chemical, and environmental effects
- Thermal properties of the material will depend mainly on the matrix.
- The matrix will also determine the manufacturing method and the different curing times of the material.

Final properties of thermostable matrix composites depend strongly on manufacturing conditions.

Because of this, knowledge of kinetics and mechanisms of the curing reactions and how they are carried out are very important in order to know the final properties of these materials. Temperature, polymerization time, pressure conditions, and the proportion of curing agent and catalyst greatly influence the polymerization and, consequently, the properties of the final product.¹⁻³ At the same time, postcuring heat treatment may have a strong incidence on the ultimate behavior of the material.⁴

Such behavior will be even more complex considering the epoxy-cured resins, as they are usually highly cross-linked resins. These are amorphous solids prepared by chemical reaction of epoxy monomers or oligomers with curing agents having relatively small molecules. The variation of the rheological behavior⁵⁻¹⁰ as well as the final properties of the material¹¹⁻¹⁷ have been extensively studied to analyze the influence of stoichiometry modifications, different curing agent contents, and curing temperature. Sometimes results turn out to be somewhat contradictory, e.g., certain systems show insensitivity concerning the mechanical behavior with respect to the resin/hardener ratio,¹² whereas others show significant variations on elastic modulus or on strength with respect to such a ratio.¹¹⁻¹³ Because

* To whom correspondence should be addressed.

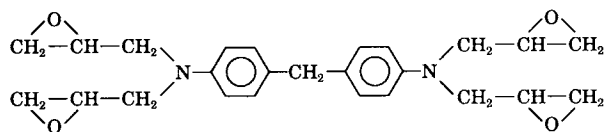
of such contradictory results, certain authors proposed a specific study of the mechanical and physical behavior for each epoxy/hardener system. Those studies also refer to the influence of different variables that take part in the curing process.¹⁸

A study of rheological behavior throughout the curing process of an epoxy/amine-type curing agent system has been carried out. Epoxy resins show very good thermal and mechanical properties and are widely used as matrices of structural composite materials. Tetraglycidyl 4,4'-diaminodiphenyl methane (TGDDM) resin is very often used in high-performance applications. Many bibliography references can be found concerning this resin with different curing agents.¹⁹⁻²³ The system employed in this work has been the TGDDM with an aromatic amine, *m*-phenylene diamine (*m*-PDA) as curing agent.

This study intends to analyze the rheological behavior of that system. The influence of both the resin/hardener ratio and the processing temperature will also be examined with respect to such behavior. A further study will be carried out concerning properties of different processed materials employed, before and after heat treatment, using either dynamic-mechanical thermal techniques or static-mechanical ones.

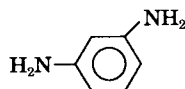
EXPERIMENTAL

The TGDDM employed is a Ciba-Geigy product named MY 720, with the following formula:



It has a glass transition temperature of -8.5°C , measured by differential scanning calorimetry with a calorimeter Dupont 2000.

The curing agent employed is an aromatic commercial diamine, the *m*-phenylene diamine (*m*-PDA) of Fluka with the following formula:



Samples employed in the different analyses were prepared by mixing different proportions of both resin and hardener. The hardener was added in small quantities until the total homogenization of the

product was obtained. Mixtures were carried out at 70°C for 10 min in order to avoid noncontrolled reactions. Previous to the rheological analysis, samples were kept safe at -10°C in order to stop the cross-linking process.

A Haake RV 20 static rheometer with a permanent run was used for measuring the viscosity of different resin/hardener mixtures. The different mixtures were placed among two coaxial cylinders. The external cylinder is static while the inner one rotates at a rate of 4.8 s^{-1} . The viscosity evolution of different mixtures employed was obtained by measuring the couple at temperatures ranging from 50 to 90°C .

Compositions of TGDDM/*m*-PDA mixtures were the following: 1 : 0.37, 1 : 0.55, 1 : 0.74, 1 : 1.11, and 1 : 1.48. These systems and temperatures under which they were studied are given in Table I.

For both dynamic-mechanical thermal and static-mechanical studies, plates of $150 \times 150 \times 3.5\text{ mm}$ were prepared using a steel mold. Commercial Ciba-Geigy product QZ 11 was used as a releasing agent. The mixtures were prepared as follows: Mixtures were kept at 80°C for 2 h; temperature was then subsequently increased to 120°C and maintained for another 2 h to be further submitted to a postcure treatment, in certain samples, at 170°C for 2 h. The specimens used for dynamic-mechanical thermal study were subsequently mechanized (dimensions were $60 \times 12 \times 3.5\text{ mm}$). Dynamic-mechanical thermal analysis was carried out in a Metravib viscoanalyzer provided with a three-point flexion device. The applied sinusoidal strain was 5 Hz at temperatures ranging from -100 to 300°C and a heat rate of $2^{\circ}\text{C}/\text{min}$.

The static-mechanical study was performed by a flexural test following standard ASTM D-790 with Instron equipment, Model 4206, and a test rate of $1.7\text{ mm}/\text{min}$. Dimensions of specimens employed were $80 \times 12 \times 3.5\text{ mm}$.

Table I TGDDM/*m*-PDA Contents and Temperatures Employed for the Rheological Analysis

<i>m</i> -PDA	<i>T</i> ($^{\circ}\text{C}$)				
	50	60	70	80	90
1:0.37	—	×	×	×	×
1:0.55	—	×	×	×	×
1:0.74	×	×	×	×	×
1:1.11	×	×	×	×	—
1:1.48	×	×	×	—	—

RESULTS AND DISCUSSION

Work began with a previous study of cross-linking reactions through viscosity measurements. By such means, the different systems were characterized rheologically for those compositions and temperatures shown in Table I. Figure 1 displays initial viscosity of TGDDM/*m*-PDA systems and its variation with temperature concerning different resin/hardener ratios employed. The curves obtained allow the rheological characterization of the different systems studied throughout their curing reactions.

Figure 2 shows viscosity profiles all through the curing process of the five systems analyzed. Each system was analyzed according to its rheological behavior at different temperatures. The relevance of these two factors (i.e., composition and temperature) during the curing evolution of the compounds may be observed in Figure 2. Rheological behavior of the reactive system is very sensitive to molecular modifications. An increase in the molecular weight and subsequently over the cross-linking degree through the curing of different systems will influence the progressive viscosity increase at a macroscopic level. The mixture of TGDDM resin with an amine-type hardener within the different systems will result

in a nucleophilic reaction of the primary amines of the *m*-PDA curing agent.¹⁹ Such an addition will result in a moderate viscosity increase at the beginning of the curing process because at this stage the chains are mainly linear and the cross-linking process has not been started.⁵ Such a moderate increase corresponds to the first zone of linear increase in Figure 2. The higher the reaction conversion, the higher is the polymerization extent of the molecular structures. This cross-linking process implies an increase of the rate of viscosity variation in the system.²⁴

The system gels in the process of increasing viscosity, i.e., the molecular weight achieved could be theoretically considered as infinite.⁶ In most cases, tests were stopped for those viscosities falling between 500 and 2000 Pa s. From Figure 2 it may be observed that for each case the temperature increase will result in an increase in the rate of viscosity variation. This variation is a consequence of the increase in the kinetics constant of the nucleophilic addition reaction with temperature.¹ Because of the same reasons, the higher the temperature, the lesser the gelation time in the studied interval. To observe the composition influence of the system over the kinetics of reaction, viscosity profiles for different TGDDM/

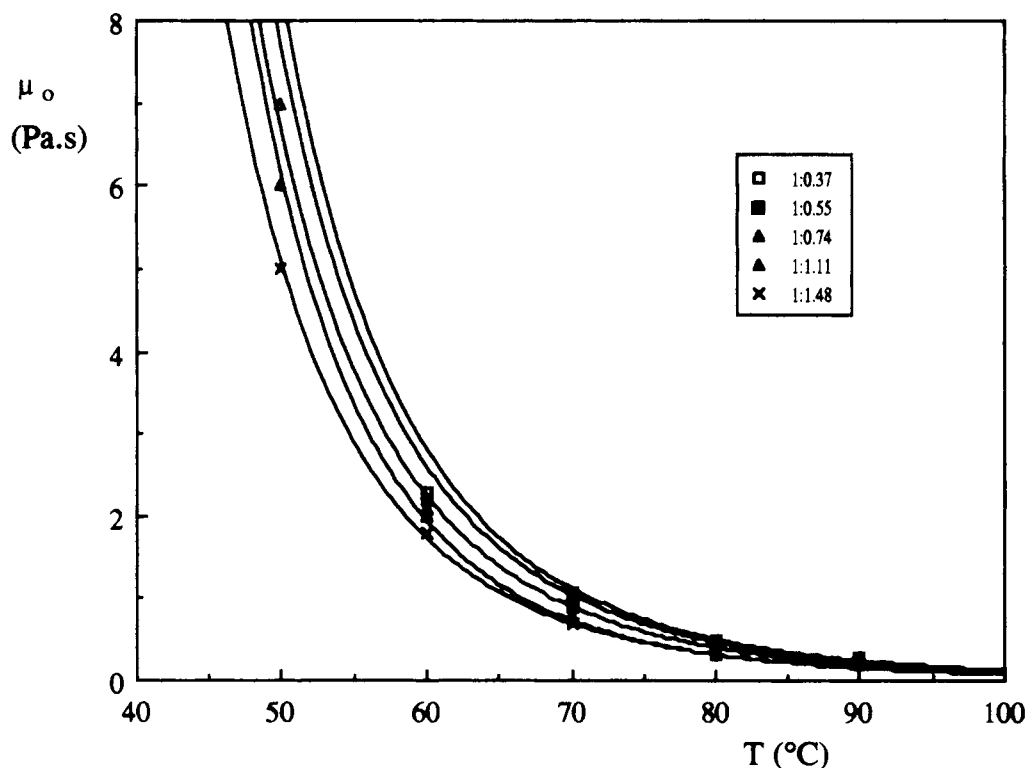


Figure 1 Initial viscosity against temperature for different resin/hardener ratios.

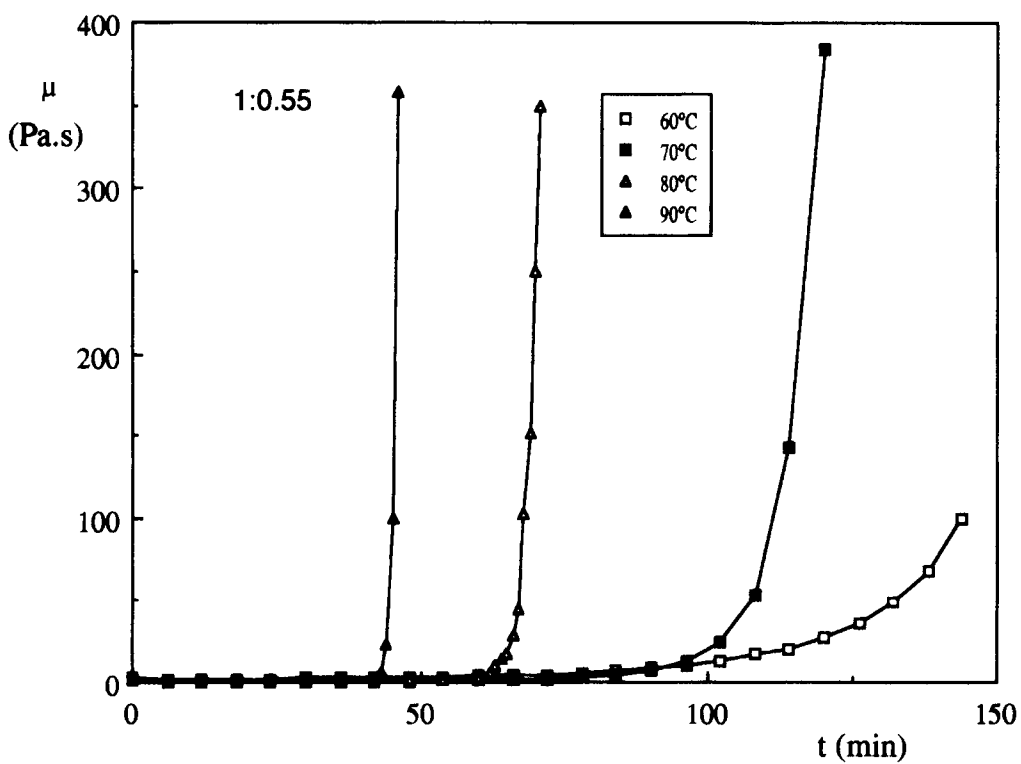
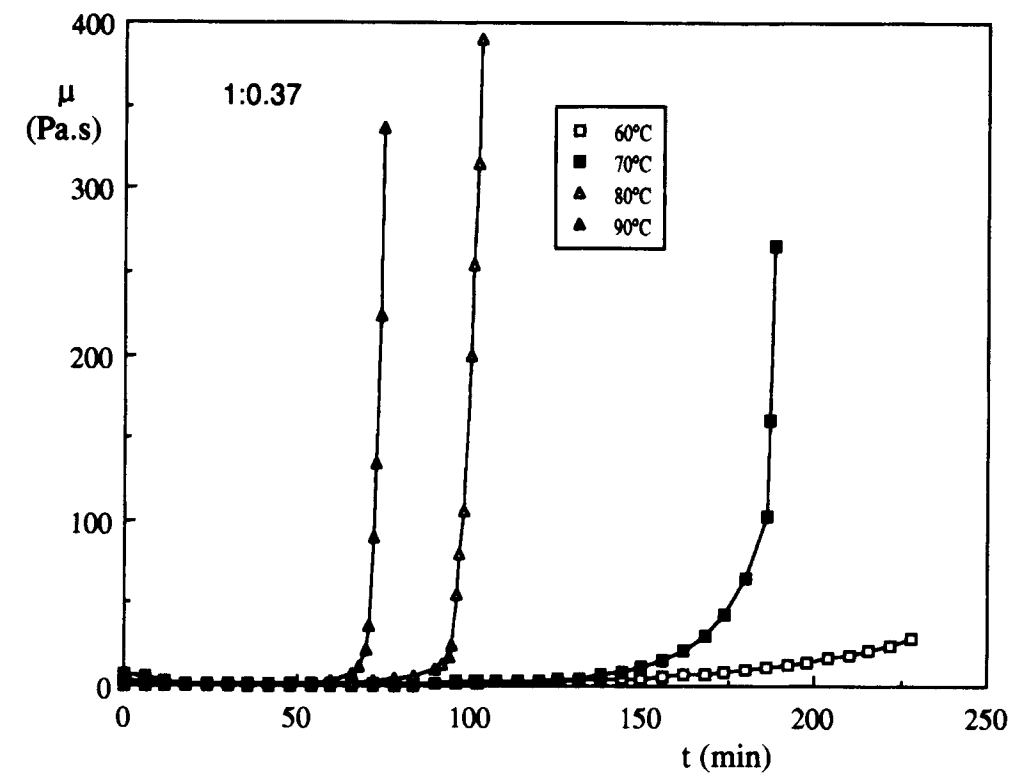


Figure 2 Viscosity profiles at different temperatures for various TGDDM/*m*-PDA ratios: (a) 1 : 0.37; (b) 1 : 0.55; (c) 1 : 0.74; (d) 1 : 1.11; (e) 1 : 1.48.

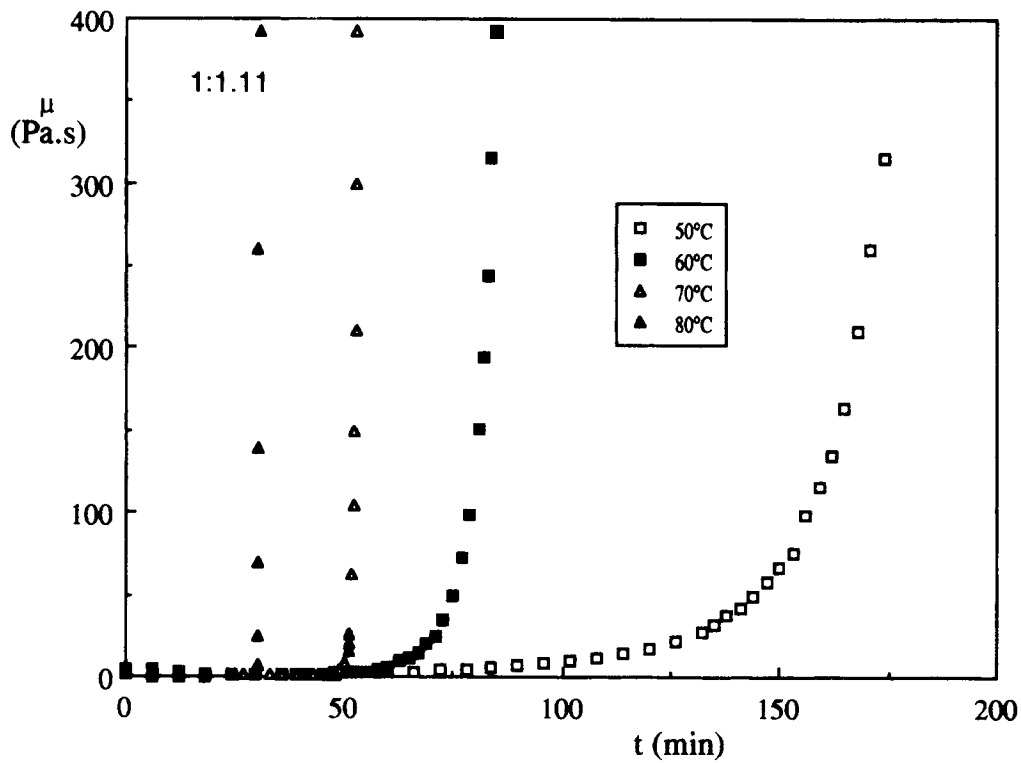
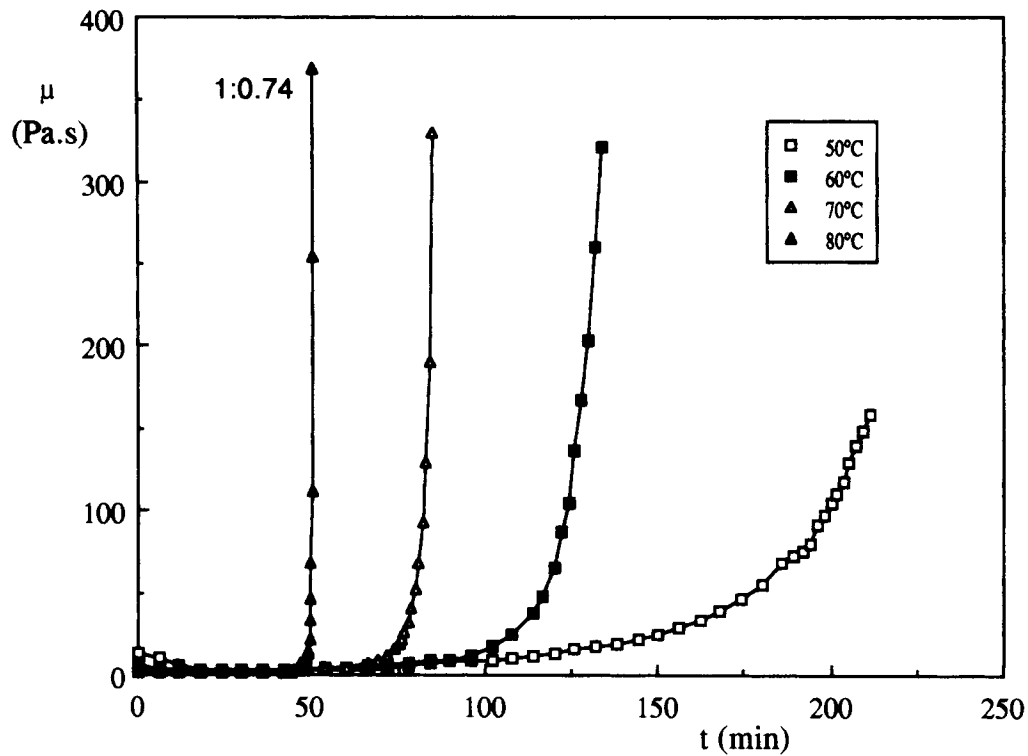


Figure 2 (Continued from the previous page)

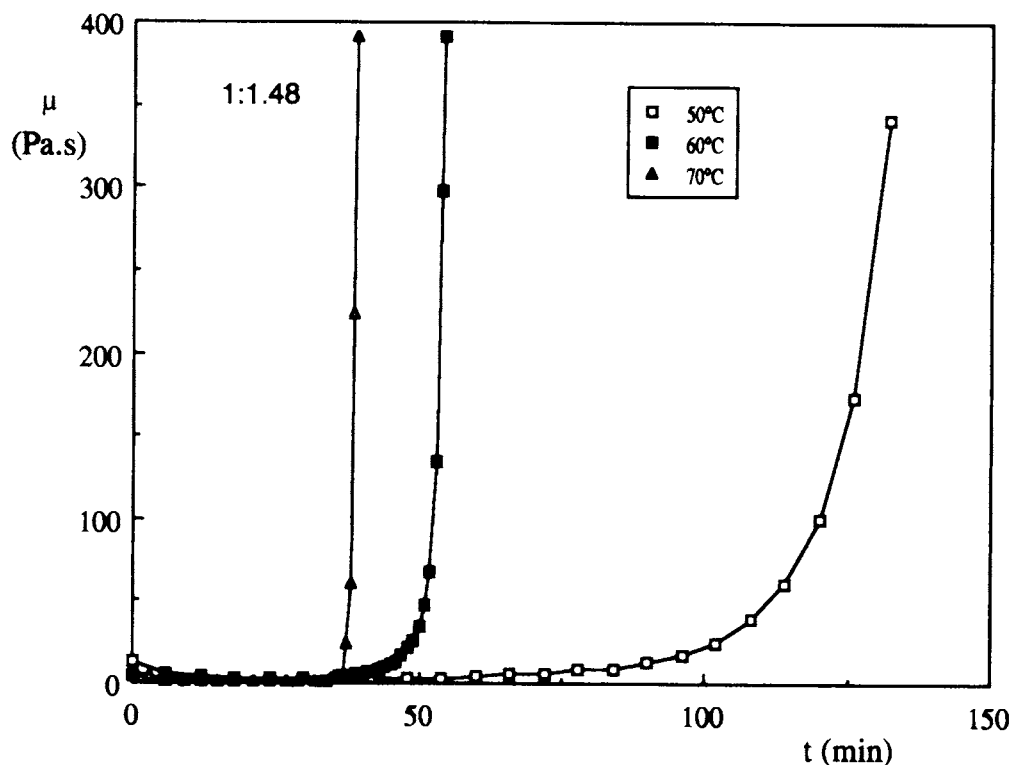


Figure 2 (Continued from the previous page)

m-PDA systems in the temperature range employed are given in Figure 3. Within the studied composition range, the decrease of gel time according to the increase of the proportion of amine-type hardener may be clearly observed. The parameter employed for measuring the gel time is the one called critical reaction time, t_0 ,⁵ determined by the intersection of the final linear prolongation of the curve $\log \mu$ vs. time, and the straight line with the equation $\mu = \mu_0$, where μ_0 is the initial steadied viscosity of the mixture. The t_0 time is characteristic of the system and slightly precedes the gel point.²⁵ Figure 4 shows the evolution of critical times with respect to temperatures of different compositions studied. Figure 5 displays the development of that critical time at a certain temperature according to *m*-PDA content used. As may be observed, t_0 variation with the inverse of temperature is adjusted to a straight line. The rate of the reaction agrees with an Arrhenius-type law with an exponential rate increase with respect to the absolute temperature of the system. Activation energies obtained for our systems have an approximate value of 13,500 cal/mol. This value corresponds to a value close to the opening reaction of an epoxy ring by nucleophilic attack of primary amines.⁵ As already mentioned, this is the process produced until gelation and t_0 are reached.

The viscosity increase rate at the first and final zones of the viscosity–time curves is an interesting variable when studying characterization of rheological behavior. The initial straight line of the curves may be identified with the reaction step corresponding to the formation of linear chains, while from the critical time, another linear zone is achieved that is qualitatively identified with the formation of the tridimensional structure.⁵ Variation of both parameters, $d \log \mu_1/dt$ and $d \log \mu_2/dt$, against temperature is plotted in Figure 6. Because of linearity of these curves, an Arrhenius kind of behavior may be identified in the kinetics of both sides of the curing process, either in the zone corresponding to linear growth of molecular chains or in the zone corresponding to the branching and cross-linking process. However, temperature will act in both cases, leading to a similar effect over the reaction rate.

Figures 7–10 show dynamic-mechanical thermal scans of the different samples studied. The evolution of both E' storage modulus and $\tan \delta$ through analyzed temperature scanning is plotted in the above-mentioned figures. Figure 7 shows modulus evolution for TGDDM/*m*-PDA systems of 1 : 0.37, 1 : 0.55, and 1 : 1.11 compositions without postcuring. Figure 8 shows the evolution of $\tan \delta$ for the same systems with respect to temperature, also without postcuring.

In Figures 9 and 10, test samples were previously submitted to a postcuring process. The thermal treatment consists of maintaining the previous specimens at 170°C for 2 h and then slowly cooling to ambient temperature in order to avoid the sudden contraction of the material. Figure 9 shows the evolution of modulus E' for the three systems described once they are postcured. Figure 10 shows the variation of $\tan \delta$ for the same systems once they are submitted to the described heat treatment.

Three main transitions may be described by observing Figures 8 and 10, where $\tan \delta$ vs. temperature is displayed. The behavior agrees with other observations.²⁶ A first broad peak, called β relaxation,¹⁸ is located between -80 and 40°C, slightly varying its position according to both the composition of the system and whether a heat treatment has been carried out. This peak may be attributed to the crankshaft rotation of the glycidyl amine linkage after the reaction of the epoxy ring with the amine group.^{20,27} In principle, the greater the reaction extent of the epoxy-amine reaction, the higher the extension of the β peak.²⁸ This can be observed in Figure 10; after postcuring, a broader transition is observed with respect to Figure 8, where the same samples are given before thermal posttreatment.

The α peak is normally identified as the glass transition temperature of the material. This peak is associated with the movement of a relevant number of segments of the molecular chain. This α transition was observed—as shown in Figure 8—in two peaks called α_1 and α_2 .²⁶ The α_2 peak is concerned with the extension of cross-linking of molecular chains.²⁰ As can be seen from Figures 8 and 10, the temperature corresponding to this peak is higher as curing extent increases. The α_1 peak is associated with the glass transition temperature of highly cross-linked material.²⁰ Therefore, the α_2 transition is concerned with the reaction conversion and may be observed approximately at 115°C in Figure 8. This transition is continuously affected by additional curing as a consequence of heat treatment. Hardener content also affects the extension of the α_2 peak, as can be observed in Figures 8 and 10. As deduced from these figures, such α_2 peaks associated with T_g tend toward higher temperatures, diminishing the peak area as the proportion of the curing agent increases.

Figure 7 shows the evolution of storage modulus for the three systems previous to postcuring. Concerning the 1 : 1.11 ratio, E' modulus smoothly decreases down to 230°C, where it drastically falls [Fig. 7(c)]. That point corresponds to the zone of ultimate glass transition temperature, $T_{g\infty}$. With regard to the 1 : 0.55 mixture [Fig. 7(b)], E' decreases

slowly down to approximately 110°C. From 110 to 250°C, it first diminishes, then later increases. All these changes indicate the additional curing reactions that take place when the scan temperature exceeds the zone of the initial α_2 transition temperature. Because of this, the postcuring heat treatment performed—and as the temperature used was 170°C—will result in an additional curing of the studied systems. During the initial cycle of the curing, the system vitrifies at a temperature inferior to the one that makes all the epoxy groups react. When the original α_2 temperature is exceeded, there is enough molecular mobility and thermal energy in the epoxy network to allow for further reactions. Therefore, E' increases from 170 to 250°C in the 1 : 0.55 system (Fig. 7(b)) due to the new cross-links that take place²⁰ until the reaction of all the epoxy groups is complete and, finally, E' decreases drastically when the $T_{g\infty}$ corresponding to the system is reached. Finally, and concerning the 1 : 0.37 mixture [Fig. 7(a)], the cross-linking extent is clearly inferior to the previous compositions, due to the higher excess of epoxy groups without reaction. Therefore, the α_2 peak corresponding to the transition temperature of the original system will be more prominent as can be deduced from Figures 7(c) and 8(c). For the 1 : 1.11 system, the heat treatment will cause only a slight increase in the cross-linking extent, as the treatment temperature, 170°C, is close to the original α_2 temperature.

A displacement of the drop of the modulus toward higher temperatures with respect to Figure 7 is observed in Figure 9 after postcuring. Concerning the 1 : 0.55 system, it is possible to observe how modulus increases at temperatures exceeding the α_2 peak temperature. The α_2 peak moves toward higher temperatures with an increase in cross-linking degree. However, postcuring modifications are more sensitive when considering the variation of $\tan \delta$ (Fig. 10). Observing the transition temperature values of those samples, with and without postcuring from Figures 8 and 10, the influence of the heat treatment over the resin cross-linking process becomes clear (Table II).

We may conclude that by increasing the proportion of *m*-PDA hardener the molecular weight between the cross-links will become smaller because the amine groups will react with the epoxy groups. It will result in the formation of more glycidyl amine links and so more crankshaft rotations will be possible. As a result of this, when the ratio of *m*-PDA increases, the $\tan \delta$ and the surface under the β peak increase. This is observed in Figure 8. In this figure, there is also an increase of the temperature on which

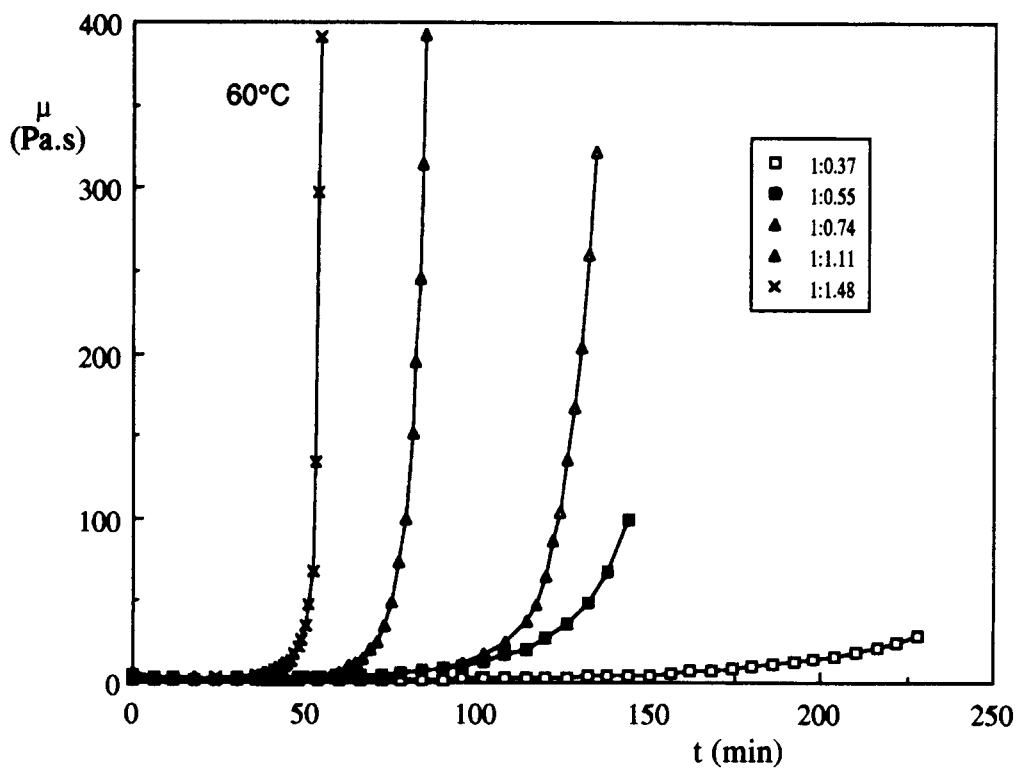
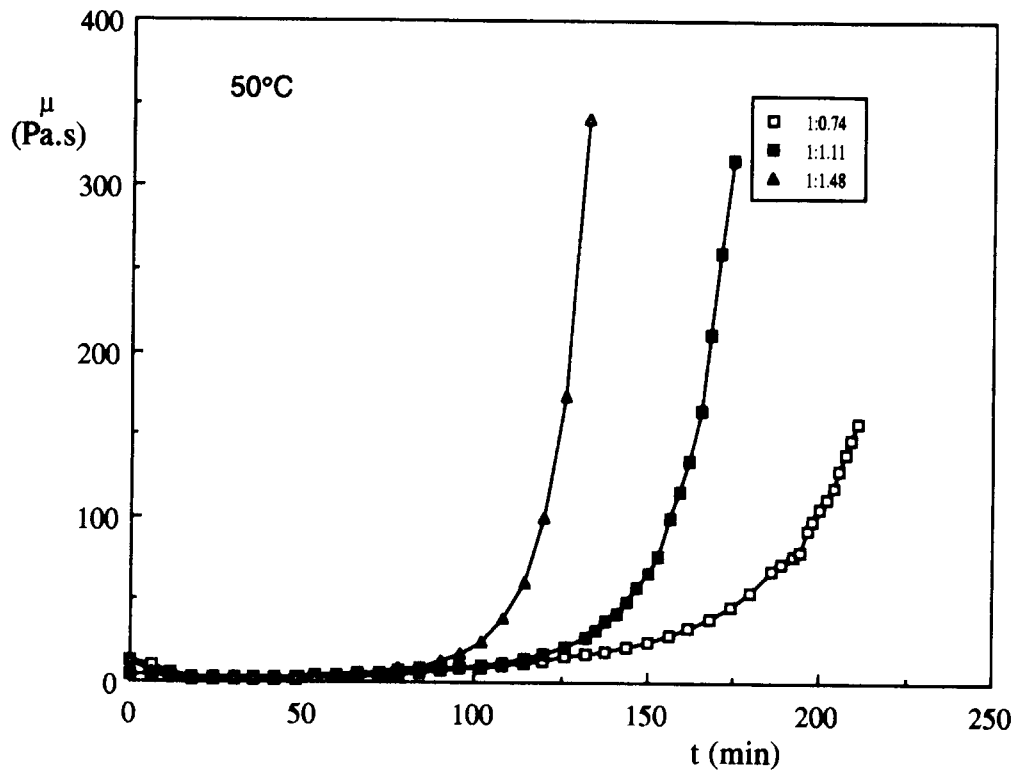


Figure 3 Viscosity profiles of different compositions at employed temperatures: (a) 50°C; (b) 60°C; (c) 70°C; (d) 80°C; (e) 90°C.

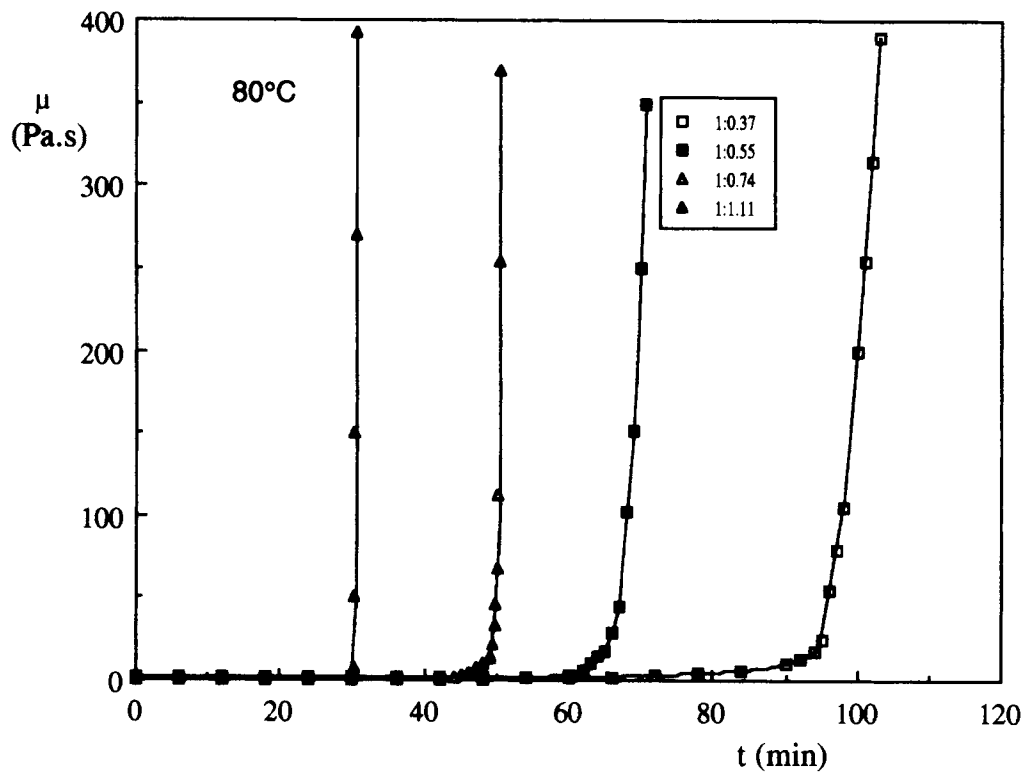
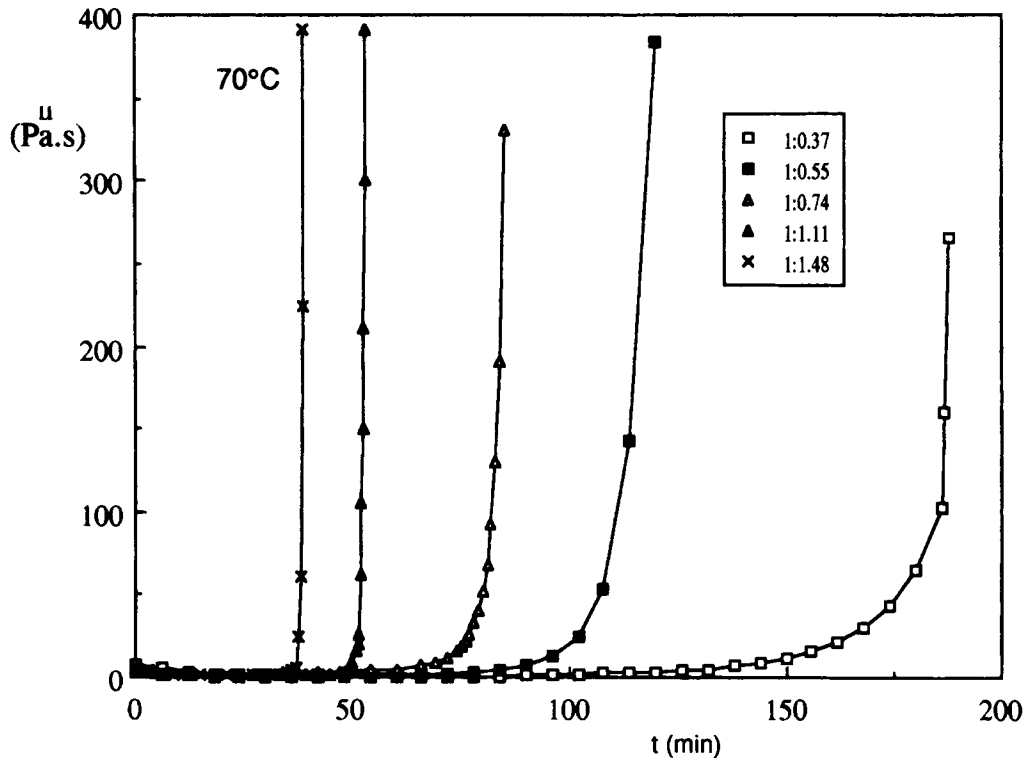


Figure 3 (Continued from the previous page)

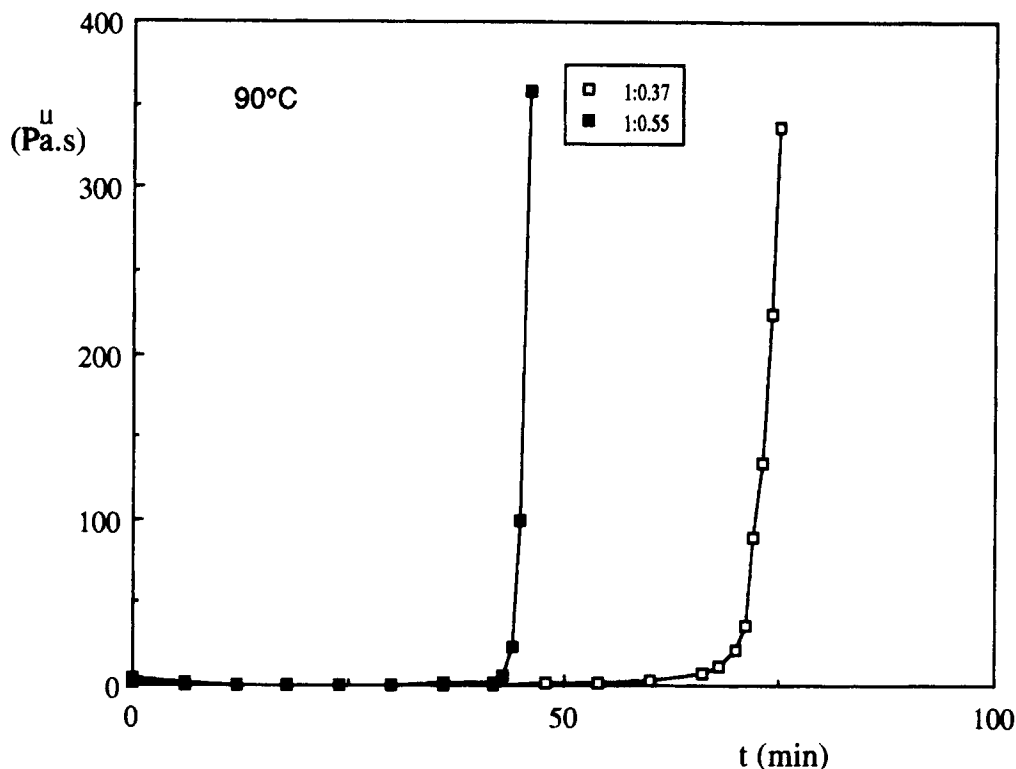


Figure 3 (Continued from the previous page)

the β peak is located, proportional to an increase of the curing agent content. This could be explained by the fact that the reaction extension goes up in the studied range as the hardener ratio increases. When more groups react, the density of the cross-linking increases. As a result, the crankshaft rotation is more difficult because of the higher cross-linking degree when the curing agent content increases. So, more energy or a higher temperature is necessary to generate the crankshaft rotation. But when the curing agent content varies, the value of the modulus does not change a lot. That means that the modulus is not very sensitive to cross-linking extension at low temperatures. These observations agree with similar effects shown in the bibliography.²⁰

In the same way, when postcuring is carried out (Fig. 10), the β transition moves to higher temperatures. In this case, the movement is also because postcuring will produce a higher cross-linking degree, resulting in less mobility for the crankshaft rotation, and so the latter will need more energy and also a higher temperature.

In the case of 1 : 0.55 and 1 : 0.37 mixtures, the displacement of the α_2 peak due to the thermal treatment to higher temperatures is clearer than in the case of the 1 : 1.11 mixture. In these mixtures,

the curing is not as complete as in the case of the 1 : 1.11 mixture and an additional curing (Fig. 10) will cause an increase of the tridimensional structure of the network, responsible for the α_2 transition, needing more energy and higher temperatures to produce the movement, moving the α_2 peak to higher temperatures.

The behavior shown suggests that mixtures with a hardener content inferior to that corresponding to the stoichiometric ratio are far from reaching a full cross-linked network, although postcuring at 170°C increases the cross-linking degree. This fact explains the important decreasing in E' at temperatures not exceeding $T_{g\infty}$ in systems 1 : 0.55 and 1 : 0.37. However, results for the 1 : 1.11 system are quite satisfactory, as, having a closer ratio to the stoichiometric one, the reaction extension between amine and epoxy groups is higher than for the non-stoichiometric systems employed.

Mechanical behavior of studied systems is given in Figures 11–13. The mechanical behavior was studied by beam tests measuring elastic modulus, strength, and deformation to failure. Figure 11 shows the variation of elastic modulus, E , according to the used hardener content in the different systems analyzed. It is observed that the higher the employed

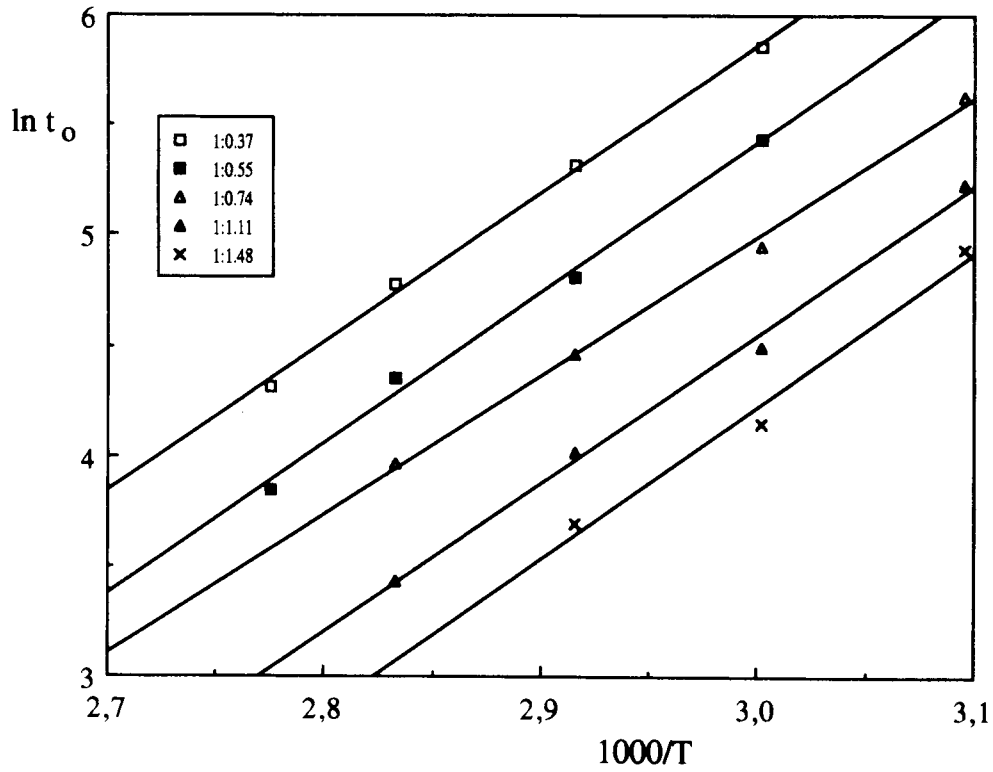


Figure 4 Dependence of critical times on temperature for employed compositions.

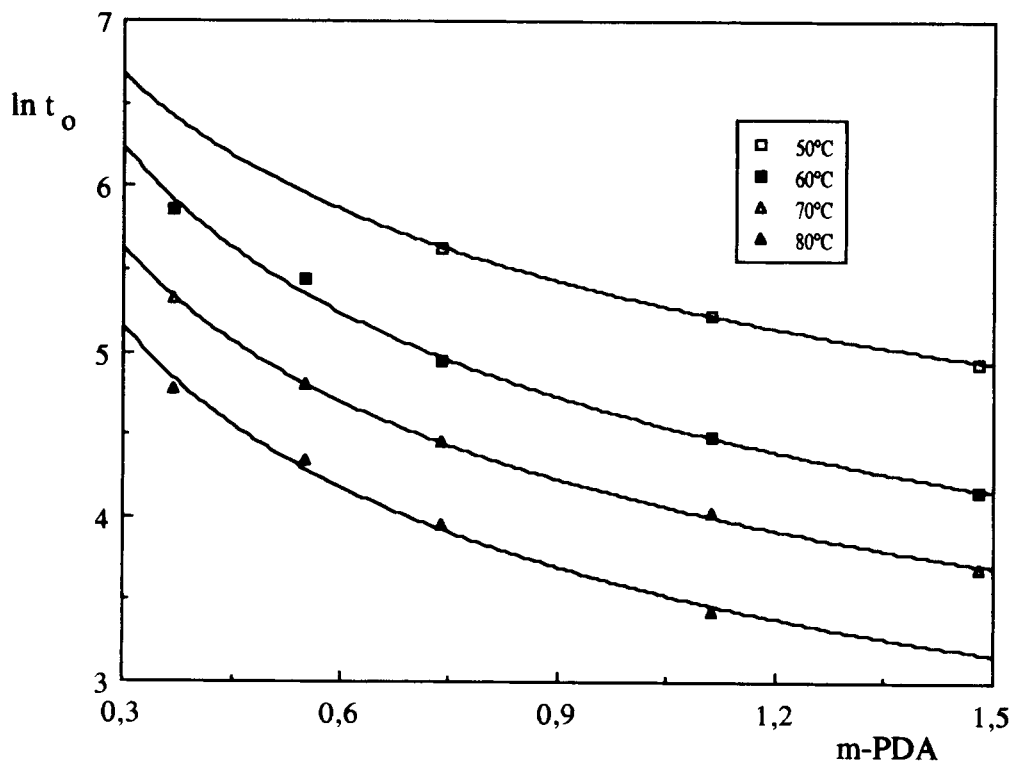


Figure 5 Critical times variation against *m*-PDA content at different temperatures.

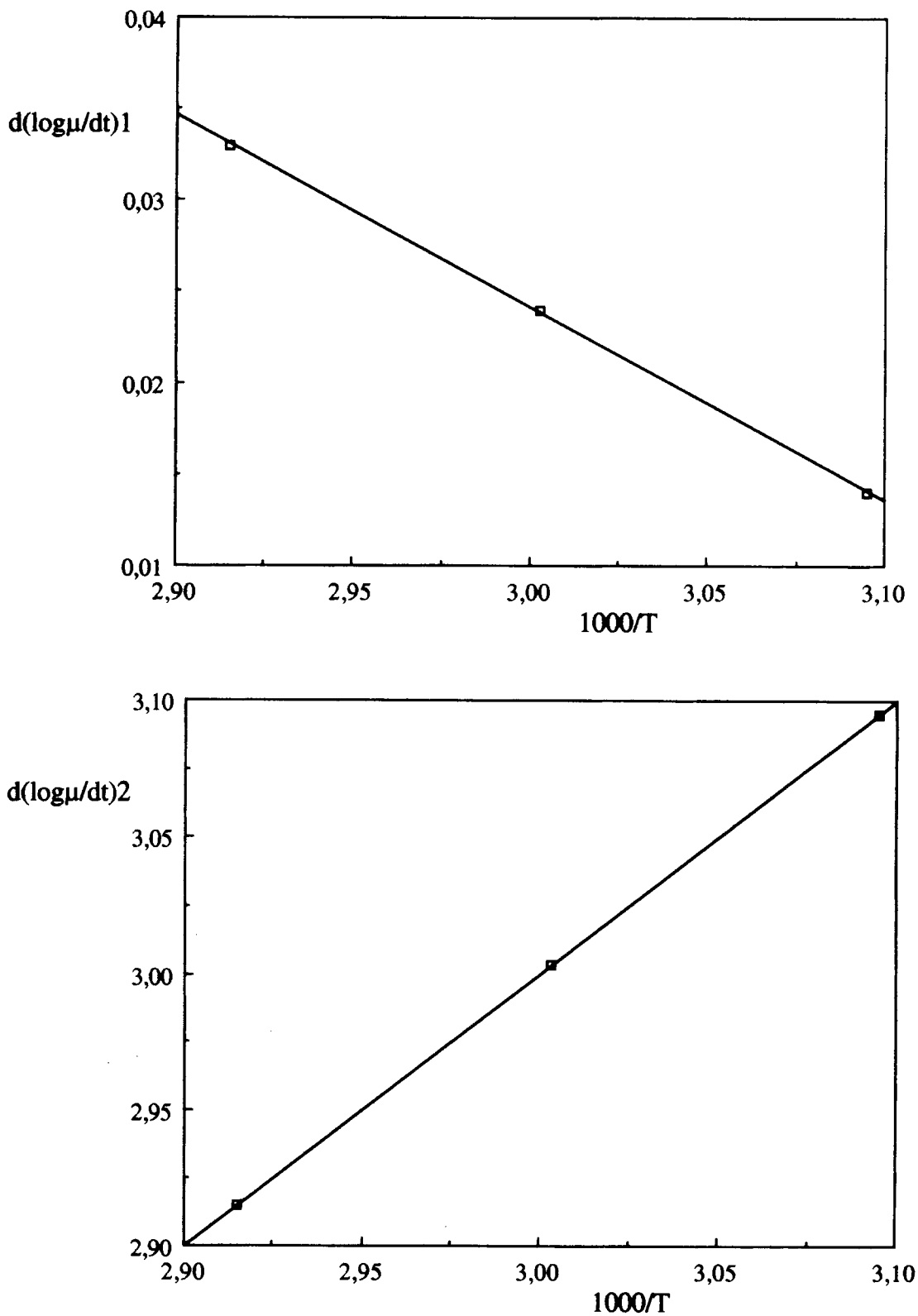


Figure 6 Viscosity increase rate vs. temperature for the systems employed: (a) before critical time; (b) at the final zone of viscosity–time curves.

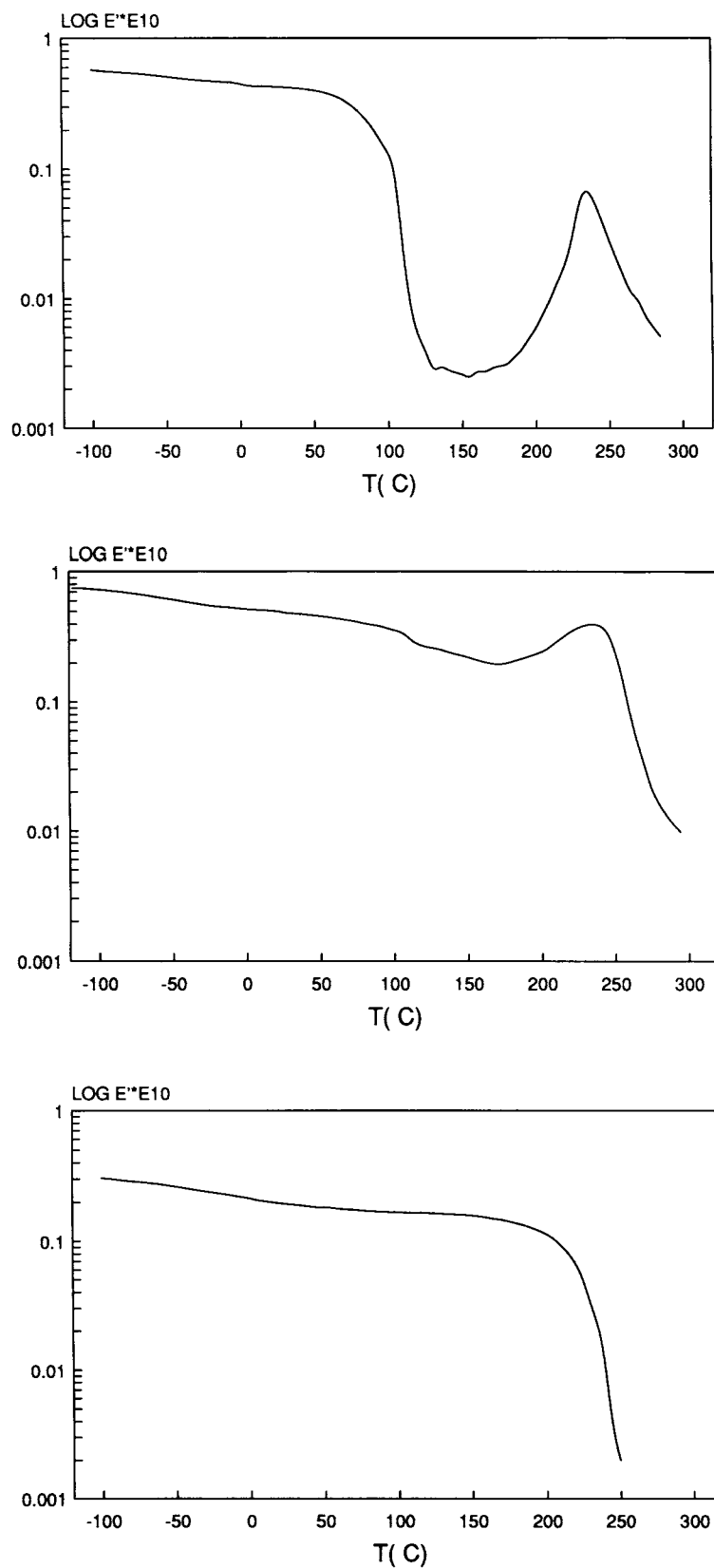


Figure 7 Dependence of storage modulus on temperature for systems without postcuring at various resin/curing agent ratios: (a) 1 : 0.37; (b) 1 : 0.55; (c) 1 : 1.11.

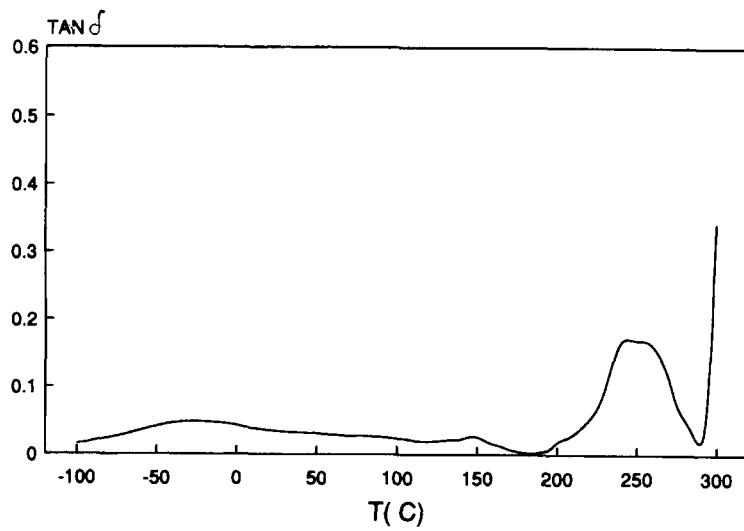
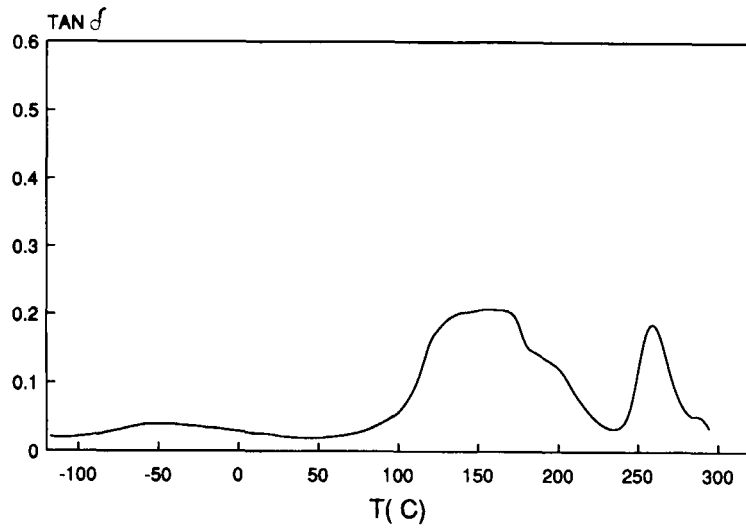
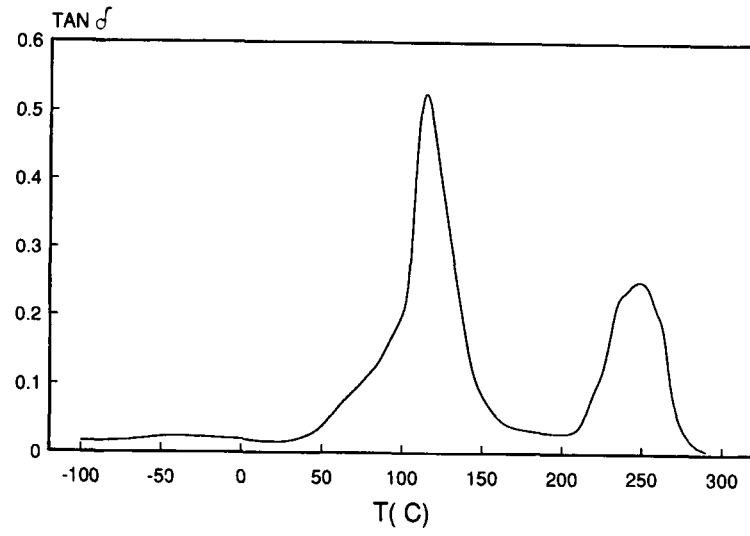


Figure 8 Loss factor vs. temperature for systems without postcuring at various resin/curing agent ratios: (a) 1 : 0.37; (b) 1 : 0.55; (c) 1 : 1.11.

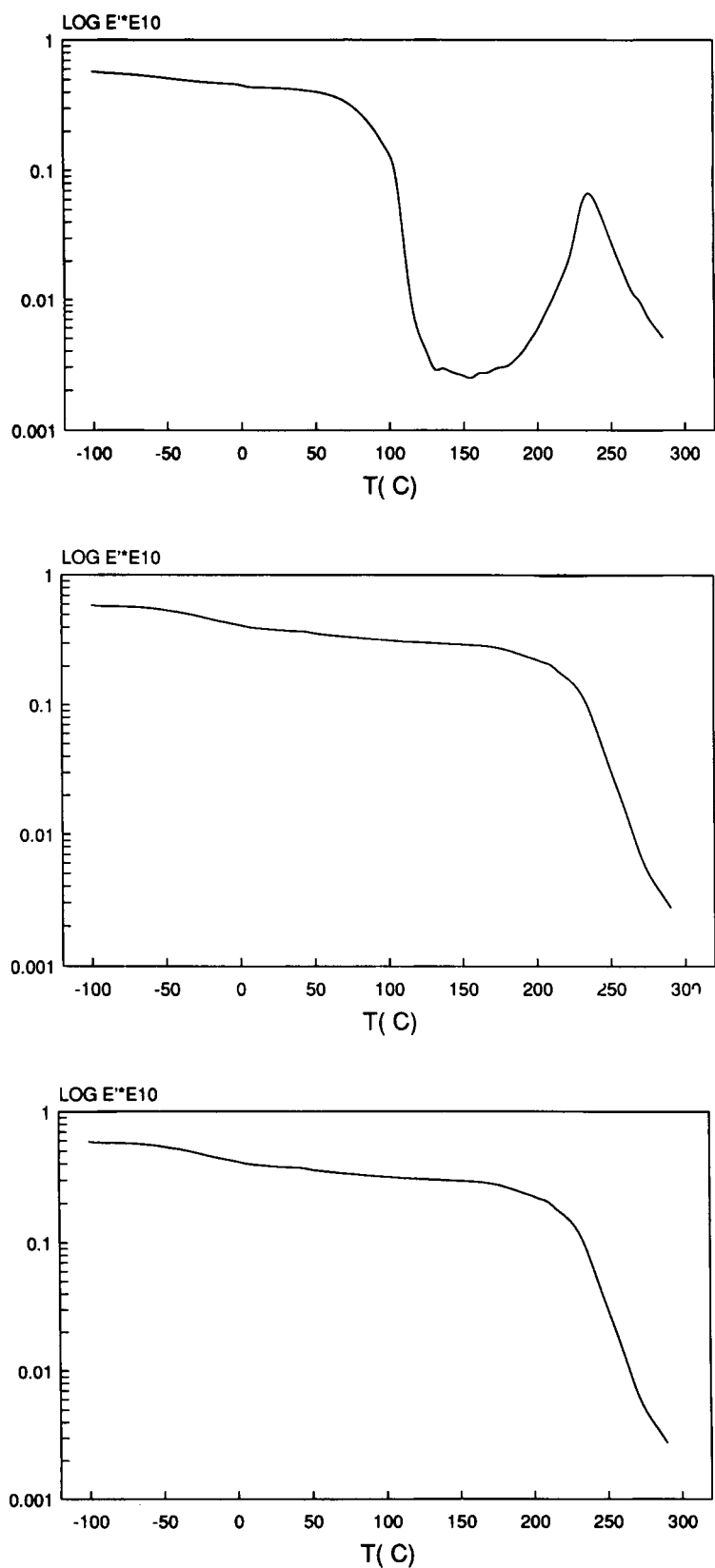


Figure 9 Dependence of storage modulus on temperature for systems after thermal post-treatment at various resin/curing agent ratios: (a) 1 : 0.37; (b) 1 : 0.55; (c) 1 : 1.11.

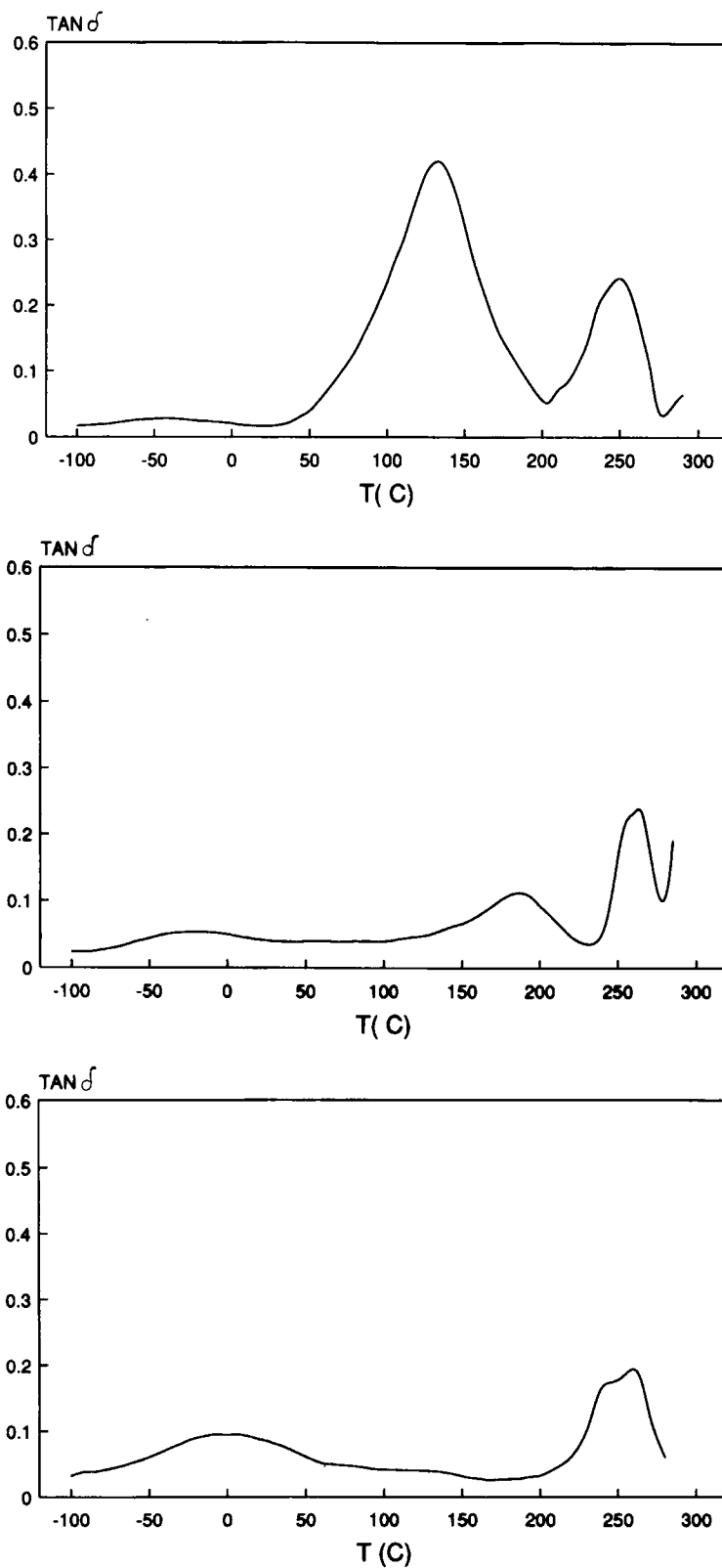


Figure 10 Loss factor vs. temperature for systems after thermal posttreatment at various resin/curing agent ratios: (a) 1 : 0.37; (b) 1 : 0.55; (c) 1 : 1.11.

Table II Influence of Postcuring on α_1 Relaxation Temperature

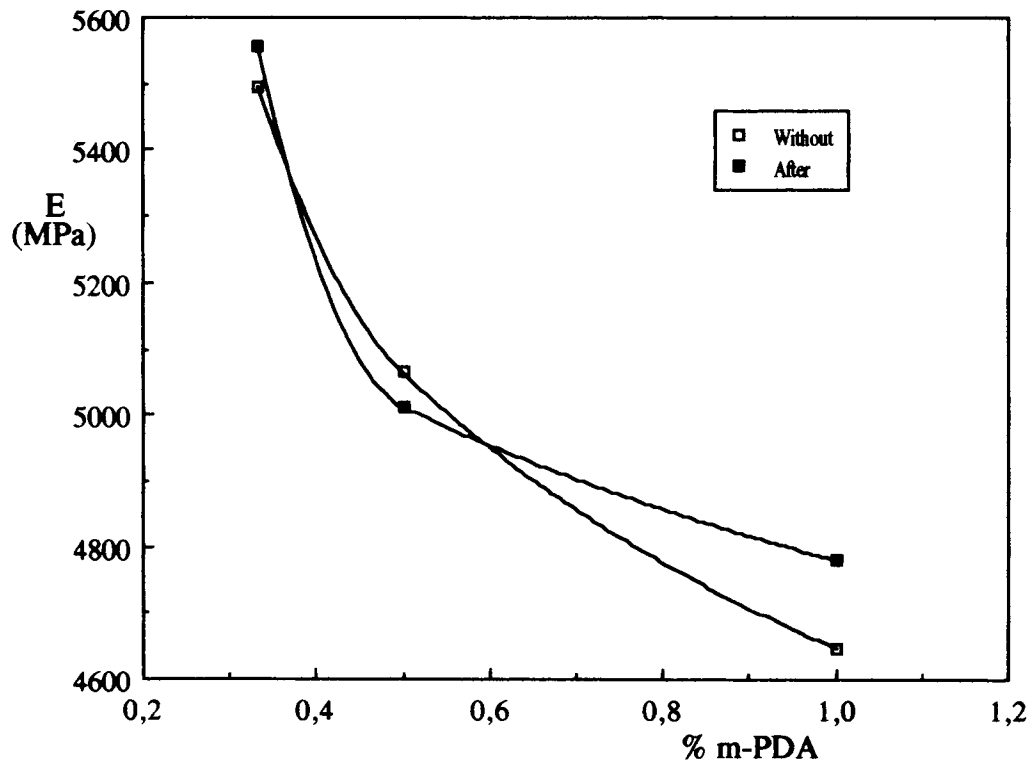
TGDDM/ <i>m</i> -PDA Weight Ratio	T_{α_1} before Postcuring	T_{α_1} after Postcuring
1:1.11	242	245
1:0.55	160	190
1:0.37	115	135

m-PDA content the lower is the rigidity. At the present time, we do not have a coherent explanation for these results, but they could be related to the broadness of the β peak as well as to the relaxation broadness increase when *m*-PDA content increases, i.e., at the highest *m*-PDA contents, a higher possibility of small molecular displacements exists. These displacements could lead to a decrease in the stiffness of these materials.

Figure 11 also offers the modulus variation when systems have been postcured. It may be observed that such treatment does not basically vary the behavior of these systems, as, although the cross-link-

ing degree increases, their chemical nature is hardly modified. The modulus values obtained for such systems—approximately 5000 MPa—show potential interest as they are similar to those obtained by TGDDM/diamine diphenyl sulphone (DDS) systems, largely employed in those applications where high-performance composites are required, and are clearly superior to the diglycidyl ether of bisphenol A (DGEBA) systems, which are the most commonly ones used.

Figure 12 shows the bending strength according to content of *m*-PDA employed. A clear rise in strength is observed when increasing the curing agent content. This is quite obvious, as the higher the cross-linking degree, the higher the need for external energy that can cause a rupture of those generated links²⁰ and result in a higher strength. In Figure 12, the postcuring influence over bending strength can be seen. After postcuring, a slight strength diminution is observed. Such diminution can be associated with internal stresses generated during the heat treatment. However, the influence of the β relaxation of these systems shall also be taken into account when discussing deformability of those materials. It can be observed that strength

**Figure 11** Evolution of elastic modulus with *m*-PDA content for samples before and after thermal posttreatment.

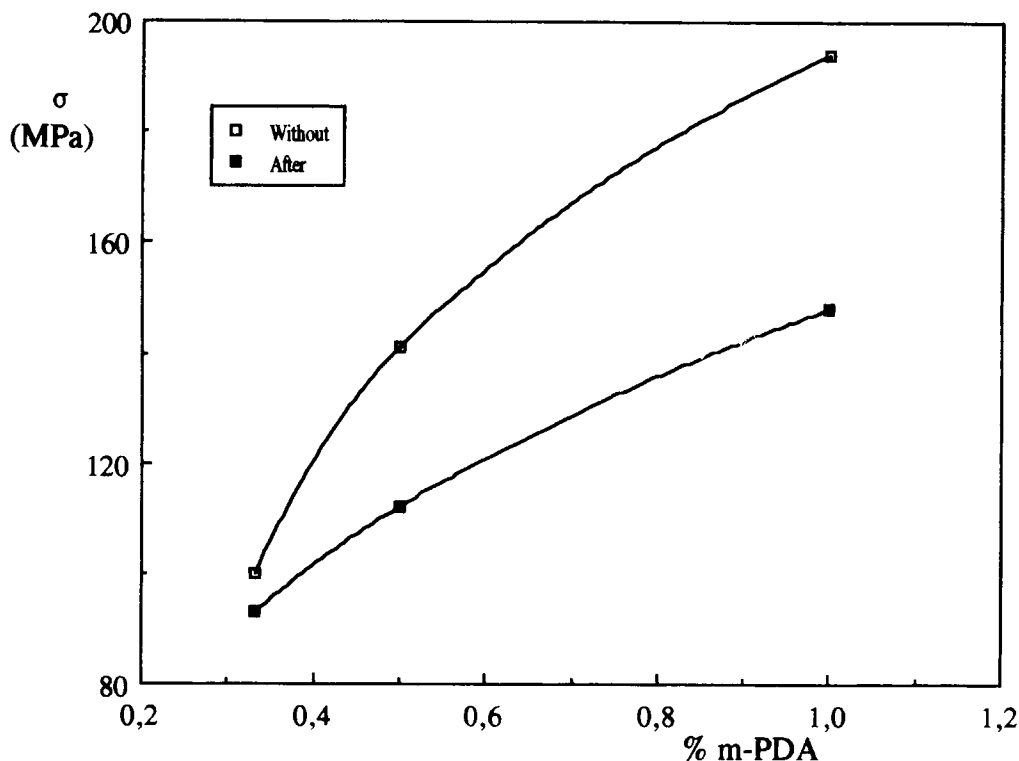


Figure 12 Dependence of bending strength on *m*-PDA content for samples before and after thermal posttreatment.

values obtained are high, about 160–180 MPa for stoichiometric compositions.

Deformation at failure of these systems is displayed in Figure 13. The brittleness of these materials, similar to those of all nonmodified epoxy systems, is clearly observed. Brittleness is lesser in those cases where systems have a low *m*-PDA content. This fact might be concerned with physical defaults of those materials and due to uncompleted curings. Deformability can also be related to β relaxation of these materials. It can be observed that β relaxation is broader in those systems with a higher content of *m*-PDA, as stated by certain authors.²⁰ A reduction of deformability of these systems with the heat treatment is observed in Figure 13. That may be due to modifications suffered by β peaks with the heat treatment. As observed in Figures 8 and 10, postcuring results in a relaxation displacement toward higher temperatures, as that employed for mechanical tests. As that relaxation allows the rotation of glycidyl amine linkages,²⁸ displacement toward ambient temperature will result in a decrease of movement capacity of chains at this temperature, which implies a decreasing of material deformability. This observation matches the experimental reality.

CONCLUSIONS

A TGDDM/*m*-PDA epoxy/hardener system was characterized. The evolution of the curing process using different epoxy/amine ratios and different temperatures was analyzed. After the rheological study, employed materials were characterized by analysis of E' modulus and $\tan \delta$ and also by a static-mechanical study of stiffness modulus, break strength, and deformation at failure. The most important conclusions obtained are the following:

The polymerization kinetics of the systems in the studied interval is very sensitive to both temperature and resin/curing agent ratio. The increase of temperature and also of aminic curing agent content will accelerate the curing process throughout all the steps. The rheological behavior with respect to temperature follows an Arrhenius-type law.

A critical time indicating the beginning of the cross-linking process can be defined. That critical time, obtained from data of viscosity–time curves, decreases when the temperature increases and/or when the curing agent content increases.

The rate of viscosity increase has clearly two dif-

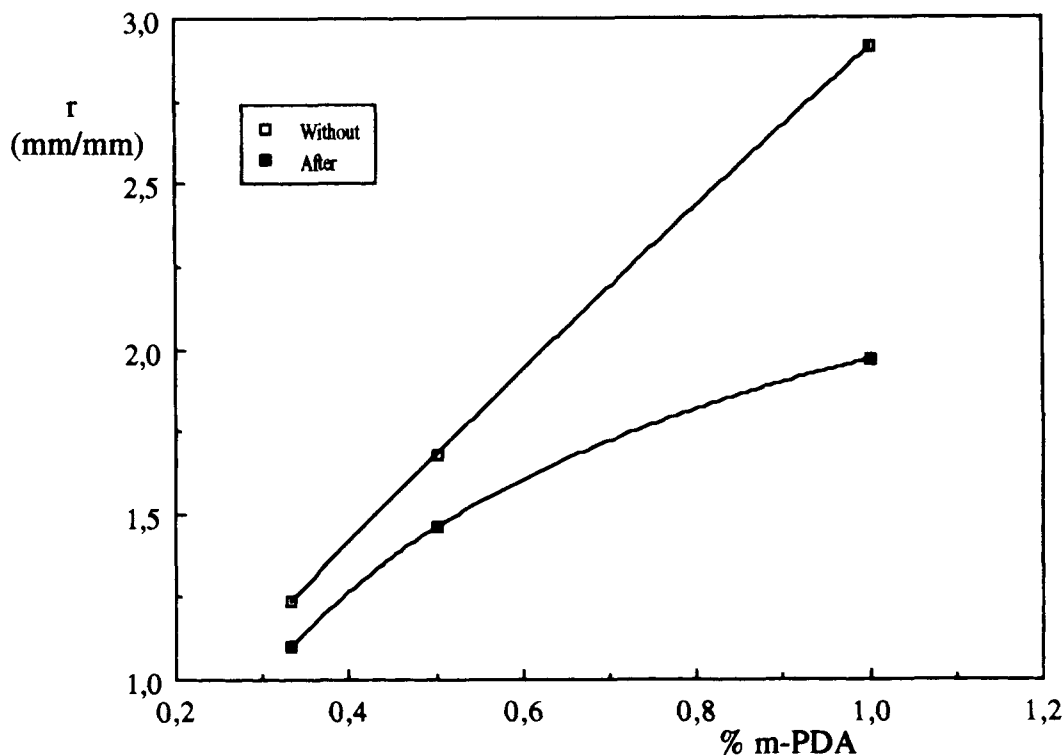


Figure 13 Evolution of deformability with *m*-PDA content for samples before and after thermal posttreatment.

ferent steps: The first one corresponds to a linear growth of chains, and the second one, after the critical time, to tridimensional network formation. Both rates will also increase in accordance with a rise in the temperature.

The systems have also been studied by dynamic-mechanical thermal analysis. The molecular transitions and the glass transition temperature corresponding to the uncured phase and whose peak magnitude decreases when the curing agent content is higher, as a result of which it is displaced toward the $T_{g\infty}$, corresponding to the fully cross-linked network, have been analysed. For 1 : 1.11 composition, the results obtained indicate a high cross-linking extent, although for lower curing agent contents, the obtained curing conversion apparently has been uncompleted. For those systems, a further heat treatment has clearly improved material properties as it has been inferred by observing the variation of transitions corresponding to these not fully cured systems.

The β relaxation clearly shows the reaction extent in the studied systems since its magnitude increases and it is displaced to higher temperatures as the cross-linking process advances.

Mechanical properties of these systems, such as strength and modulus, are very interesting. The observed brittleness is similar to that shown by other unmodified epoxy systems. The postcuring heat treatment has increased fragility in all systems. That behavior can be related to the β transition displacement to higher temperatures.

Briefly, the studied system shows acceptable kinetics at low temperatures and its mechanical and thermal properties can be considered satisfactory.

The authors are grateful to the Diputación Foral de Gipuzkoa for financial support of this study.

REFERENCES

1. A. Moroni, J. Mijovic, E. M. Pearce, and C. Ching Foun, *J. Appl. Polym. Sci.*, **32**, 3761 (1986).
2. S. A. Bidstrup and C. W. Macosko, *J. Polym. Sci. Part B Polym. Phys. Ed.*, **28**, 691 (1990).
3. M. Ochi, H. Iesako, S. Nakajima, and M. Shimbo, *J. Polym. Sci. Polym. Phys. Ed.*, **24**, 251 (1986).
4. K. P. Pang and J. K. Gillham, *J. Appl. Polym. Sci.*, **39**, 909 (1990).

5. A. Apicella, P. Masi, and L. Nicolais, *Rheol. Acta*, **23**, 291 (1984).
6. D. Harran, M. F. Grenier-Loustalot, and Ph. Monge, *Eur. Polym. J.*, **24**, 225 (1988).
7. Y. G. Lin, H. Sauteaureau, and J. P. Pascault, *J. Polym. Sci. Part A Polym. Chem.*, **24**, 2171 (1986).
8. C. D. Wingard and C. L. Beatty, *J. Appl. Polym. Sci.*, **40**, 1981 (1990).
9. D. Serrano and D. Harran, *Polym. Eng. Sci.*, **29**, 531 (1989).
10. A. C. Senhaji and D. Harran, *Makromol. Chem. Macromol. Symp.*, **30**, 109 (1989).
11. S. Mostovoy and E. J. Ripling, *J. Appl. Polym. Sci.*, **10**, 1351 (1966).
12. J. P. Bell, *J. Appl. Polym. Sci.*, **14**, 1901 (1970).
13. S. L. Kim, M. D. Skibo, J. A. Manson, R. W. Hertzberg, and J. Janiszewski, *Polym. Eng. Sci.*, **18**, 1093 (1978).
14. K. Selby and L. E. Miller, *J. Mater. Sci.*, **10**, 12 (1975).
15. S. Yamini and R. J. Young, *J. Mater. Sci.*, **15**, 1814 (1980).
16. R. J. Morgan, J. E. O'Neal, and D. B. Miller, *J. Mater. Sci.*, **14**, 109 (1979).
17. R. J. Morgan, F. M. Kong, and C. M. Walkup, *Polymer*, **25**, 375 (1984).
18. V. B. Gupta, L. T. Drzal, C. Y. C. Lee, and M. J. Rich, *Polym. Eng. Sci.*, **25**, 812 (1985).
19. J. M. Kenny, A. Apicella, and L. Nicolais, *Polym. Eng. Sci.*, **29**, 973 (1989).
20. H. S. Chu and J. C. Seferis, *Polym. Compos.*, **5**, 124 (1984).
21. E. M. Woo, L. B. Chen, and J. C. Seferis, *J. Mater. Sci.*, **22**, 3665 (1987).
22. T. W. Wilson, R. E. Fornes, R. D. Gilbert, and J. D. Memory, *J. Polym. Sci. Part B Polym. Phys. Ed.*, **26**, 2029 (1988).
23. P. Delvigs, *Polym. Compos.*, **7**(2), 101 (1986).
24. J. J. Imaz, N. Markaide, A. Rubio, R. Llano-Ponte, A. Valea, and I. Mondragon, in *Comptes-Rendus des Septièmes Journées Nationales sur les Composites*, November 6-8, 1990, Lyon, France, p. 763.
25. D. Serrano, Thèse de Docteur 3e cycle, Pau, France, 1987.
26. J. D. Keenan, J. C. Seferis, and J. T. Quinlivan, *J. Appl. Polym. Sci.*, **24**, 2375 (1979).
27. A. J. Kinloch, S. J. Shaw, D. A. Tod, and D. L. Hunston, *Polymer*, **24**, 1341 (1983).
28. C. A. May and F. E. Weir, *SPE Tech. Pap.*, **8**, 2 (1962).

Received June 24, 1991

Accepted October 15, 1991