

Using PA11 and 12 as Curing Agents for Epoxy Networks: Influence of Reactivity on Miscibility and Properties

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ABSTRACT: The Rilsan PA11 prepolymer was evaluated as a curing agent of a diepoxy prepolymer (DGEBA). The miscibility, the glass transition temperature, and the melting of the blend were studied as a function of time at 200°C. A gelation phenomenon was evidenced by dynamic mechanical analysis and the gel time was determined at 200°C. The participation of amide groups to the reaction process at this temperature was confirmed by the study of the PA12 Orgasol®/DGEBA system and a reaction mechanism was elucidated by the study of a model system composed of ethylacetamide/phenyl glycidyl ether. The mechanical properties of DGEBA/Rilsan networks cured 7 h at 200°C were evaluated and indicate very high Young's modulus and critical stress intensity factor. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 857–865, 2000

Key words: polyamide; epoxy; kinetics; miscibility; mechanical properties

INTRODUCTION

In previous studies, we used polyamide (PA) fine powders as toughening agents for epoxy networks and the low improvement was, in part, due to a lack of adhesion between the two phases.¹ Some physical treatments of PA particles may improve the adhesive properties.² These networks were cured at a temperature below the PA melting temperature so the morphologies remained the same. Conversely, if we mixed epoxy prepolymers and PAs at higher temperatures, a reaction can occur. Numerous PAs containing free amino groups have been synthesized as curing agents for the epoxy prepolymer.^{3–9} These systems are used

as coatings presenting high toughness and good adhesion to numerous substrates. For these systems, a problem of compatibility between the PA and the epoxy prepolymer is sometimes noticed⁹ and the reactivity does not depend, in the range of temperature in which they are used, on the amide functions but on the secondary amine functions in the backbone chains and on the primary amine functions at the chain ends.^{6,7} Their high functionality leads to highly crosslinked polymers.⁵

Concerning the reactivity of amide functions toward an epoxy group, it seems, according to the literature, only possible at high temperature or with the use of a base catalyst.^{10,11} The reaction mechanism between the amide functions and the oxirane group is not yet totally elucidated, but most studies consider that the first step involves the nucleophilic attack on the oxirane ring by the amide nitrogen and report the formation of ester

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groups.^{10,12} These last groups are attributed to the isomerization of the hydroxylated molecule formed during the first step of reaction¹² or directly to the coordination of the epoxy group with amide followed by the break of the NHCO bond.¹¹

In this article, we present the results of studies on blends of an epoxy prepolymer, that is, diglycidyl ether of bisphenol A (DGEBA), with two different PAs: Rilsan PA11 PA, which presents three kinds of potentially reactive functions, that is, acid, amine, and amide functions, and Orgasol®, which possesses only amide functions. Special attention was paid to the study of the miscibility, the kinetics, and also the reactivity of amide functions toward oxirane rings, and for this goal, an additional system composed of a model secondary amide and a monofunctional epoxy was studied. The mechanical properties of DGEBA/Rilsan blends after curing were also determined.

EXPERIMENTAL

Materials

The Rilsan particles are PA11 prepolymers supplied by Elf Atochem obtained by the polycondensation of amino-11 undecanoic acid with an \bar{M}_n value equal to 10,000 g/mol. The Orgasol® particles are PA12 type from Elf Atochem (France). They are obtained directly by an anionic polymerization process of ϵ -caprolactam and ω -caprolactam. To limit the polymerization degree, a hydrocarbonaceous chain regulator is used and it constitutes the chain ends of the polymer.

Ethylacetamide from Aldrich was the amide chosen as the secondary amide model. Two epoxies were used in this study: a difunctional epoxy prepolymer, DGEBA (DER 332 from Dow Chemical) with $\bar{n} = 0.03$, and a monofunctional epoxy, the phenyl glycidyl ether (PGE).

Differential Scanning Calorimetry (DSC)

Glass transition temperatures (T_g) and melting temperatures (T_f) were determined using DSC with a Mettler TA 3000 apparatus. DSC specimens (10–20 mg) cured during various times at 200°C and quenched to room temperature were analyzed. They were heated from -70 to 250°C under an argon atmosphere with a heating rate of 10 K min^{-1} . T_g was taken as the temperature corresponding to the onset of the heat-capacity baseline change. T_f was taken as the temperature

corresponding to the maximum of the melting peak.

IR Analysis

IR spectra were recorded in the wavelength range of $400\text{--}4000\text{ cm}^{-1}$ on a Nicolet magna-IR550 setup. The PA/epoxy blend was placed between two KBr plates in a hot cell from a Power Process Controls 355-A. IR spectra were recorded after various times at 200°C and each spectrum was the result of 32 individual scans. The epoxy conversion was calculated using the peak relative to the epoxy groups at 915 cm^{-1} , the reference peak relative to phenyl groups at 830 cm^{-1} , and applying the following equation:

$$X = [1 - h(t)]/h(t = 0)$$

where $h(t)$ represents the ratio of the height of the peak at 915 cm^{-1} to the height of the peak at 830 cm^{-1} at time t and $h(t = 0)$ is the same ratio at the initial time.

Size-Exclusion Chromatography (SEC) Analysis

SEC analysis was performed on the ethylacetamide/phenyl glycidyl ether system with a Waters 717T injector equipped with a pump from Spectra Physics and with microStyragel columns (100 and 500 \AA). Experiments were carried out with tetrahydrofuran as a mobile phase and polystyrene (PS) was used as a standard.

Scanning Electron Microscopy (SEM)

The dissolution of the Rilsan PA powders in the epoxy prepolymer was studied by SEM on the fracture surface. After different times at 200°C , the blends were quenched to room temperature and fractured at liquid nitrogen temperature.

Dynamic Mechanical Analysis (DMA)

Rheological Study

The dynamic shear modulus G^* of the blend (storage modulus G' , loss modulus G'' , and loss factor $\tan \delta$) and the complex viscosity η^* were recorded at 200°C with a Rheometrics RDA 700 viscoelasticimeter as a function of time at different frequencies using parallel plates (diameter 40 mm).

Study in the Solid State

In the solid state, the dynamic tensile modulus E^* was recorded as a function of temperature

using a Rheometrics RSAII viscoelastimeter at 1 Hz. Rectangular specimens ($0.7 \times 6 \times 38 \text{ mm}^3$) were tested in the tensile mode from -150 to 250°C with a heating rate of 1 K min^{-1} .

Elastic Properties

The Young's modulus was obtained at room temperature in the tensile mode using an Adamel Lhomargy DY25 testing machine. Dogbone specimens were tested with an EX10 extensometer at a strain rate of $\dot{\epsilon} = 1.67 \times 10^{-3} \text{ s}^{-1}$. The Poisson ratio was determined with cross-strain gauges of Vishay Micromeasures.

Yielding Properties

The compression stress-strain curves were obtained with an Adamel Lhomargy DY25 testing machine equipped with a compression cage. Upper-yield stresses were measured at room temperature at a strain rate of $8 \times 10^{-4} \text{ s}^{-1}$.

Linear Elastic Fracture Mechanics

Single-edge notched specimens (SEN) (thickness $t = 6 \text{ mm}$ and width $w = 12 \text{ mm}$) were machined

in plates and tested in a three-point bending mode (span-to-length = 48 mm) at 25°C . Cracks of length a were made at ambient temperature using a diamond saw and finished with a razor blade. The crack length was measured by optical microscopy. The stress deflection curves are typical of a brittle fracture without stick-slip propagation.

The critical stress intensity factor (K_{IC}) was calculated using the following formula:

$$K_{\text{IC}} = \sigma c \sqrt{\pi a} f(a/w)$$

The fracture energy, G_{IC} , can be related to the critical stress-intensity factor, K_{IC} , in plane strain conditions by the equation

$$G_{\text{IC}} = K_{\text{IC}}^2(1 - \nu^2)/E$$

RESULTS

DGEBA $\bar{n} = 0.03$ /PA11 blends containing 30 phr of PA were prepared at room temperature and

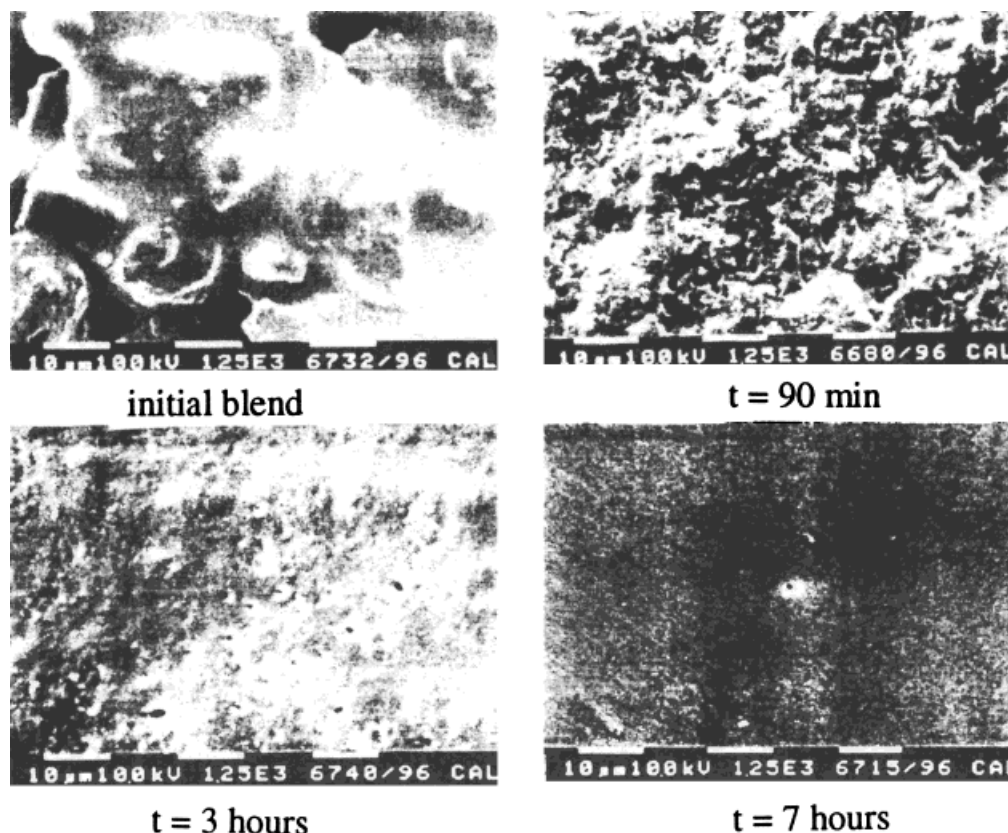


Figure 1 SEM micrographs of DGEBA $\bar{n} = 0.03$ /PA11 blends cured during various times at 200°C .

observed at different temperatures with an optical microscope. The initial blend is constituted by a homogeneous dispersion of angular Rilsan particles of about $100\ \mu\text{m}$ size in the epoxy prepolymer. At 140°C , thus below the melting temperature of PA, any evolution of the size of the particles is noticed as a function of time, in agreement with previous works.¹ On the other hand, as the temperature becomes higher than the melting temperature of PA, a rapid dissolution is noticed. The SEM micrographs of samples quenched at room temperature after various times at 200°C and fractured at nitrogen temperature clearly show a decrease of the size of the dispersed particles as a function of time at 200°C (Fig. 1). After 7 h at 200°C , the blend is transparent, no particles were evidenced by SEM, and the material is insoluble even in the best solvent of PA such as hexafluoroisopropanol. This result suggests the occurrence of a gelation phenomenon.

The evolution of the dynamic shear modulus and of the complex viscosity of the DGEBA $\bar{n} = 0.03/\text{PA}$ blend as a function of time at 200°C confirms this hypothesis. Figures 2 and 3 show that the increase of the viscosity of the blend cannot be attributed to an increase of the molecular weight of Rilsan alone due to the continuation of the PA polycondensation in these conditions. Indeed, the increase of viscosity is much much higher for the blend and the value measured at $1\ \text{rad s}^{-1}$ is equal to about $5000\ \text{Pa s}$ after 60 min at 200°C . This evolution is not related to a vitrification phenomenon but to a gelation phenomenon as confirmed by the crossing of the $\tan \delta$ curves as a function of time at different frequencies (Fig. 4). The intersection point determines the gel time,^{13,14} which is equal to 50 min. For the

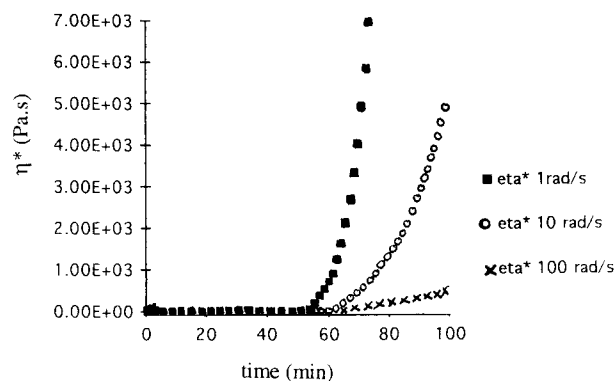


Figure 2 Evolution of the complex viscosity of DGEBA $\bar{n} = 0.03/\text{PA11}$ blends at different frequencies as a function of time at 200°C .

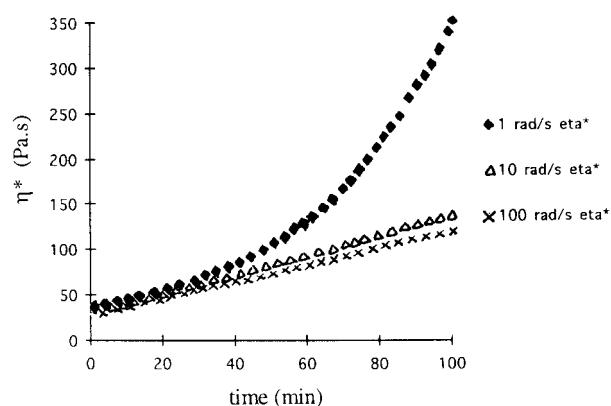


Figure 3 Evolution of the complex viscosity of PA11 at different frequencies as a function of time at 200°C .

time corresponding to the gel point, the proportionality between $G'(\omega)$, $G''(\omega)$, and the pulsation ω raised to the power Δ is verified, leading to a value of the critical factor Δ (Fig. 5) equal to 0.65, a value in the range of those commonly found on epoxy networks in the literature (0.6–0.75).^{14–16}

Concerning the reactive dissolution of PA in the epoxy prepolymer, DSC and dynamic mechanical measurements on samples cured during various times at 200°C gave further information. Whereas no evolution of the DGEBA glass transition temperature is noticed as a function of time during 15 h at 200°C , the glass transition of the DGEBA/PA11 blend increases as the time at 200°C increases and the melting enthalpy decreases until the PA melting peak completely disappears (Fig. 6). These results are confirmed by

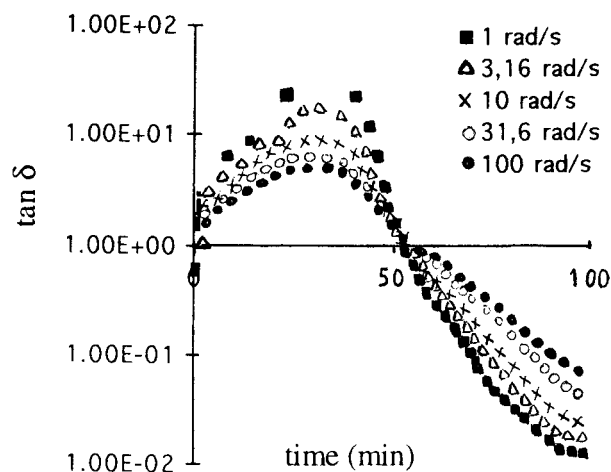


Figure 4 $\tan \delta$ curves for DGEBA $\bar{n} = 0.03/\text{PA11}$ blends as a function of time at 200°C and for different frequencies.

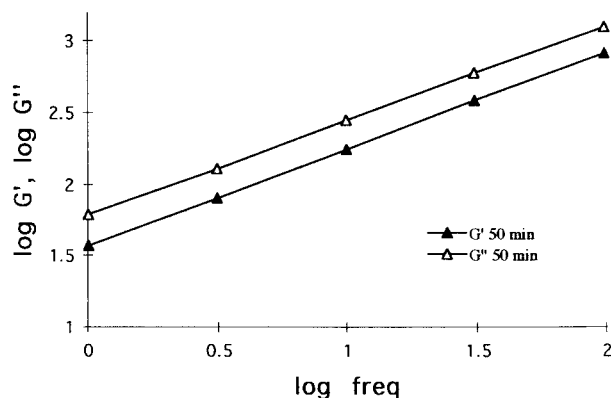


Figure 5 Evolution of the logarithm of G' and G'' as a function of the logarithm of the frequency.

DMA (Fig. 7). Indeed, after 3 h at 200°C, two decreases of the modulus are noticed: the first one related to the glass transition temperature of the blend and the second one related to the melting of the PA dispersed particles. After 7 h at 200°C, the decrease of the modulus corresponding to the main relaxation of the blend is shifted to higher temperature, whereas the second decrease of the modulus disappears, confirming, in agreement with SEM observations, the total dissolution of PA, with the limit of sensitivity.

The shift of T_g to higher temperature as a function of time at 200°C was related to a decrease of the peak relative to epoxy groups at 915

cm^{-1} , an increase of the peaks relative to ester groups at 1740 cm^{-1} , and ether groups at 1100 cm^{-1} . As shown by Figure 8, the conversion of epoxy groups seems quite complete after 180 min, whereas the concentration of ester groups still increases. Whereas homopolymerization of epoxy can explain the increase of the height of the ether peak, three mechanisms can be at the origin of the formation of ester groups: The first one implies the acid chains ends of Rilsan and the hydroxyl groups of the epoxy, the second one implies an isomerization of the molecule formed by the reaction between the epoxy and the amide as proposed by Komarova et al.¹⁰ and Iwakura and Izawa,¹² and the last one implies a reaction between amide groups and hydroxyl groups. To confirm the participation of amide groups in the formation of the reaction products, two systems were studied: The first one is composed of Orgasol® PA and the DGEBA epoxy prepolymer, the content of PA being equal to 30 phr. In that case, the chain ends of Orgasol® are not reactive and, consequently, only amide groups can be involved in the reaction process. The second one is a model system composed of a monofunctional epoxy:phenyl glycidyl ether, and a secondary amide: ethylacetamide. It lets us propose a reaction mechanism.

Concerning the DGEBA/Orgasol® epoxy prepolymer system, a phase separation occurs when the Orgasol® particles are molten. This behavior

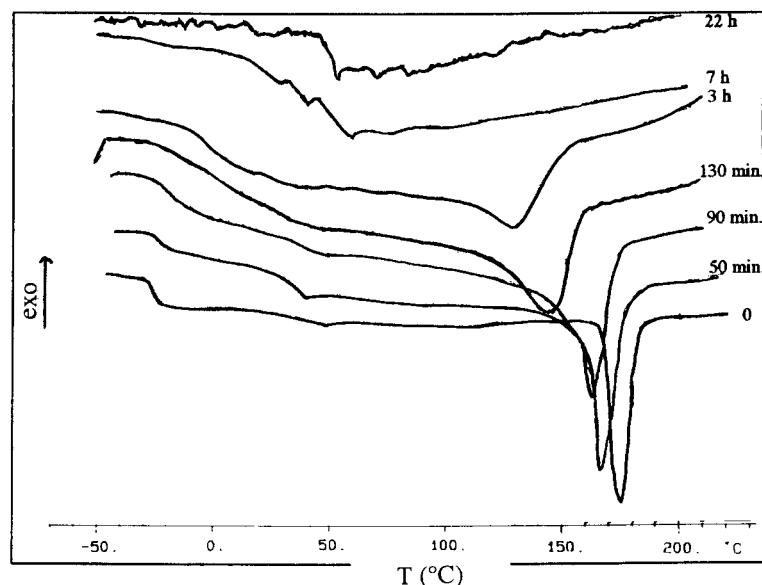


Figure 6 DSC thermograms at $10^\circ\text{C min}^{-1}$ of the DGEBA $\bar{n} = 0.03/\text{PA11}$ blends after different times at 200°C.

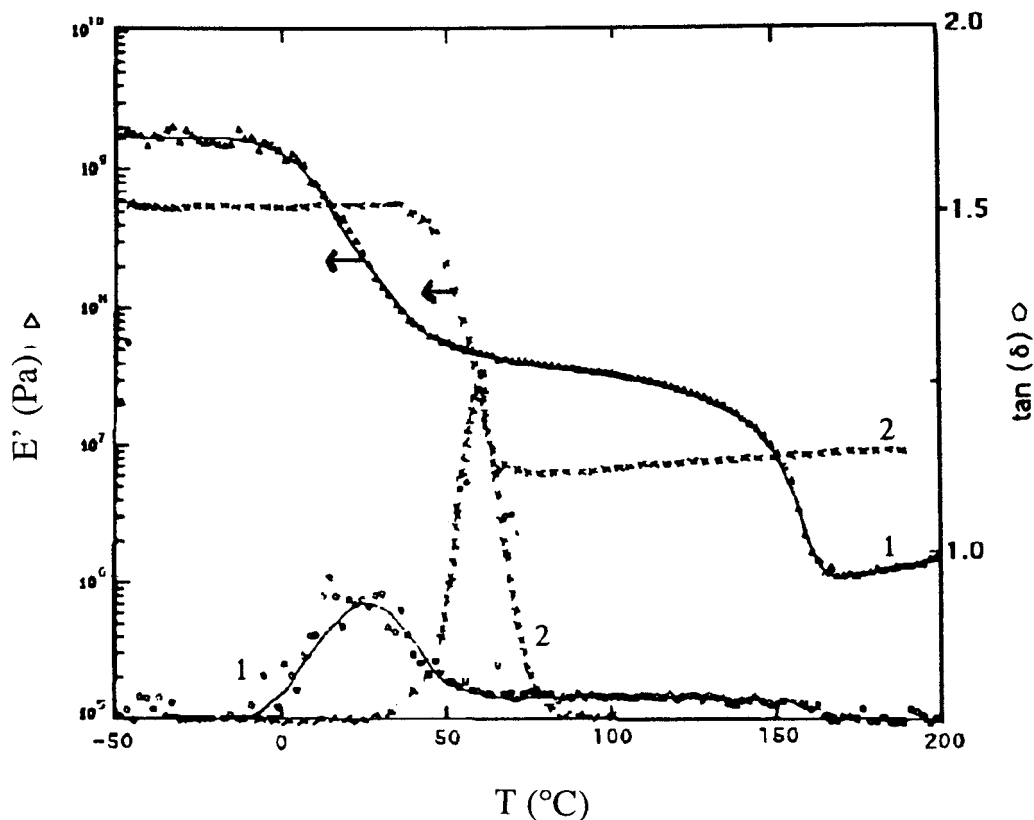


Figure 7 Evolution of E' and $\tan \delta$ as a function of the temperature at 1 Hz for DGEBA/PA11 blends cured (1) during 3 h at 200°C and (2) during 7 h at 200°C.

has already been observed on several epoxy/amide systems in the literature.^{9,17} Nevertheless, at the interface between PA and epoxy, as for the DGEBA/Rilsan blend, the conversion of epoxy functions is total after 230 min at 200°C and ester

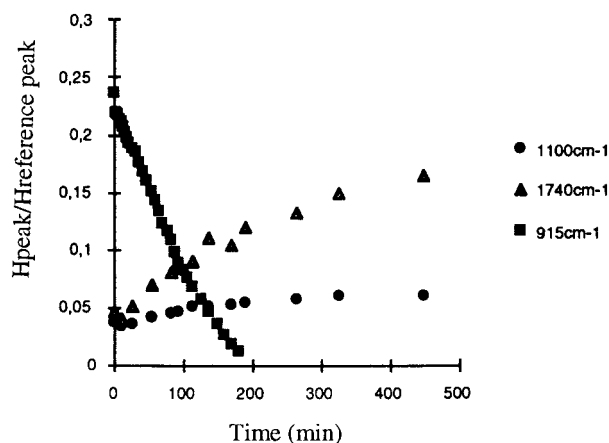


Figure 8 Evolution of the (■) epoxy peak, (●) ether peak, and (▲) ester peak normalized to a reference peak as a function of time at 200°C.

and ether groups are formed. An increase of the glass transition temperature is also noticed as a function of time and the melting peak disappears after 1 h at 250°C. In the meantime, in the two separated phases of the system, no modification of either DGEBA or Orgasol® is noticed. These results confirm the participation of amide groups to the reaction process as will also the model system.

This system composed of ethylacetamide and phenyl glycidyl ether in a stoichiometric ratio was studied as a function of time at 150°C by IR and SEC. It remains homogeneous. As for the two other systems, a decrease of the peak relative to epoxy groups and an increase of the peaks relative to ether and ester groups are noticed by IR analysis, whereas no modification of PGE or ethylacetamide taken separately is noticed during 15 h at 150°C. After 15 h at 150°C, the epoxy conversion is equal to 88%. The SEC chromatograms of the blend at the initial time and after 15 h at 150°C are presented in Figure 9. The peak at 19 mL noted as 1 is representative of PGE and the peak at 18.5 mL noted as 2 is representative

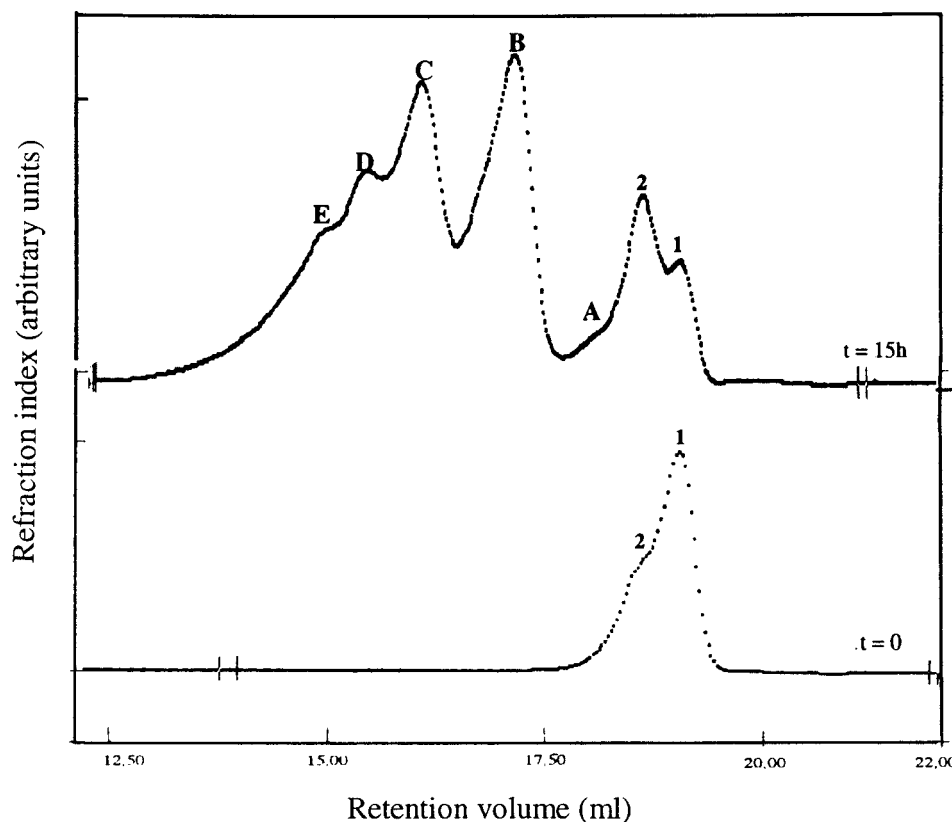


Figure 9 SEC chromatograms of phenyl glycidyl ether/ethylacetamide blends at initial time and after 15 h at 150°C.

of ethylacetamide. After 15 h at 150°C, a decrease of these two peaks is noticed and the ratio of the height of each peak to the initial one lets us calculate the conversion. It is, respectively, equal to 87% for PGE and 61% for ethylacetamide. The result obtained for PGE is then in good agreement with the value of conversion calculated by IR spectroscopy.

The comparison of the conversion calculated for PGE and for ethylacetamide shows that the reaction mechanism concerns, in part, the amide groups but essentially epoxy functions. It leads to the formation of higher molecular weight products noted from A to E in the order of increasing weight in Figure 9. According to the different results reported in the literature, different species can be formed during the reaction between PA and epoxy and Figure 10 summarizes some of them. Assuming that each component from A to E experimentally obtained corresponds to one species of Figure 10, we can associate the molecular weight of the considered species to the experimental retention volume of the species. The plot of the logarithm of the molecular weight of these species

as a function of their retention volume determines, as for the PS standards, a straight line (Fig. 11), showing that this attribution seems to be correct. Thus, the first step of the reaction should consist of the nucleophilic attack on the oxirane ring by the amide nitrogen. The second step consists of either the reaction of this species with a phenyl glycidyl ether unit or the isomerization of the hydroxylated molecule formed during the first step of reaction and the reaction of this species with a phenyl glycidyl ether. Both these mechanisms lead to the formation of a compound with a molecular weight equal to 387 g/mol, and in the case of reaction 2', the formed species has an ester group. After this second step, the homopolymerization of oxirane functions seems to be the main mechanism, confirming the higher consumption of epoxy groups compared to amide groups.

The mechanical properties of the DGEBA \bar{n} = 0.03/Rilsan system containing 30 phr of Rilsan were evaluated after a cure cycle of 7 h at 200°C. Indeed, this system stays homogeneous and it was then interesting to evaluate Rilsan as a

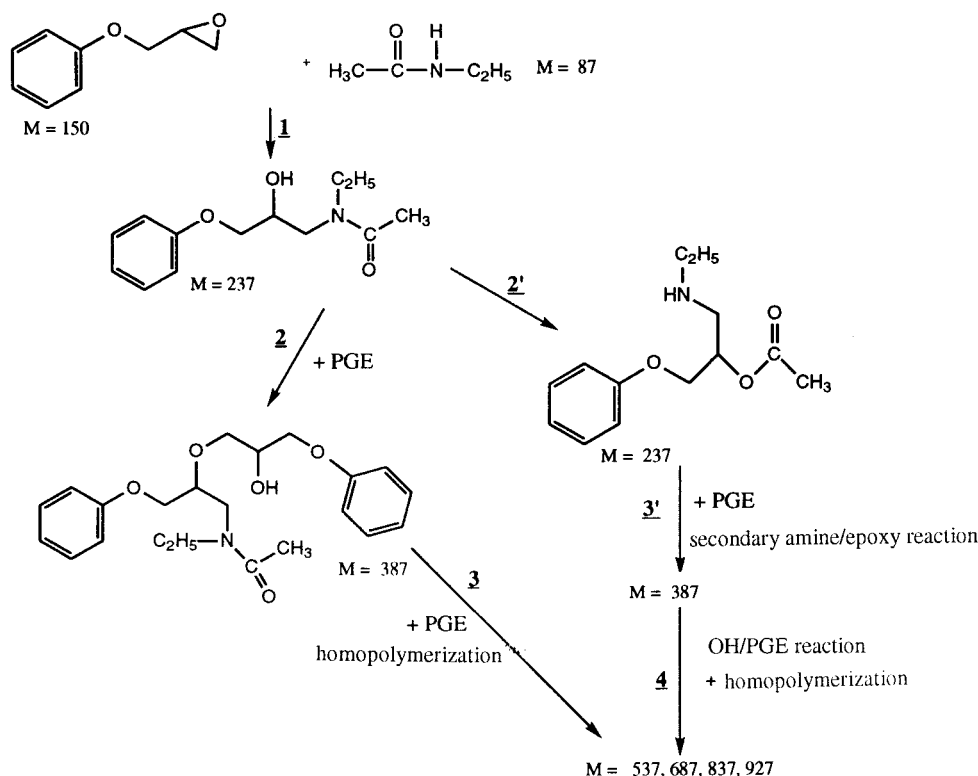


Figure 10 Reaction mechanism proposed for epoxy-amine reaction.

comonomer of DGEBA. The properties of the network are presented in Table I. The system has a relatively low glass transition temperature (about 60°C), a high Young's modulus compared to classical epoxy networks, and a yield stress in the order of magnitude of that commonly found for epoxy systems. The major result is the high value of the critical stress intensity factor obtained. It is twofold higher than the value obtained for example with Jeffamine T403, comonomer leading to

almost the same glass transition temperature of the network.

CONCLUSIONS

The reactive dissolution of PA11 in an epoxy prepolymer was evidenced at 200°C by the disappearance of the PA particles, the disappearance of the PA melting peak, and the occurrence of a

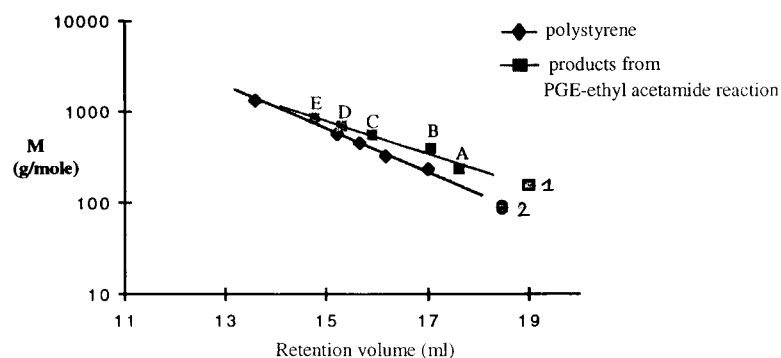


Figure 11 Evolution of the logarithm of the molecular weight as a function of the retention volume for (a) the species obtained by the reaction between PGE and ethylacetamide and (b) for different PS standards.

Table I Thermal and Mechanical Properties of Homogeneous DGEBA \bar{n} = 0.03/PA11 Blend Containing 30 phr of Rilsan After 7 H at 200°C

Blend	E (GPa)	σ_y (MPa)	K_{IC} (MPa m ^{1/2})	G_{IC} (J/m ²)	T_g (°C)
DGEBA/ Rilsan	3.1	106	3.19	2890	58

gelation phenomenon and increase of the glass transition temperature of the blend. The evidence for the participation of amide functions to the chemical reaction was shown. The formation of ester groups was observed for the PA11/DGEBA \bar{n} = 0.03 system but also for the Orgasol®/DGEBA \bar{n} = 0.03 blend, Orgasol® having no reactive chain ends, and for a model system composed by a secondary amide (ethyl acetamide) and a mono-functional epoxy (phenyl glycidyl ether). For all these systems, the reaction of amide groups with oxirane groups was confirmed, but the main mechanism remains epoxy homopolymerization.

The potentiality of PA11 as a toughening agent was underlined and different approaches are now envisaged:

1. As in this work, the total dissolution of PA11 leads to a high increase of the critical stress intensity factor; using different amounts of Rilsan could lead to networks with tailored properties.
2. Controlled and not total PA11 dissolution

can also be envisaged in order to improve epoxy/PA interactions, keeping thermoplastic particles.

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