

Synthesis, by Reactive Extrusion, of High Molar Mass Epoxy Prepolymers Containing Rubber Preformed Particles

M. TAHA, V. PERRUT, A. A. ROCHE, J. P. PASCAULT

Laboratoire des Matériaux Macromoléculaires, CNRS UMR No. 5627, Institut National des Sciences Appliquées de Lyon, Bât 403, 20 Avenue A. Einstein, 69621 Villeurbanne Cedex, France

Received 19 July 1996; accepted 16 October 1996

ABSTRACT: High molar mass epoxy prepolymers containing rubber dispersions based on carboxyl-terminated butadiene–acrylonitrile random copolymer (CTBN) were prepared from initially miscible solution of low molar mass epoxy prepolymers, bisphenol A and CTBN-based rubber. During chain extension inside a twin-screw extruder due to epoxy–phenoxy and epoxy–carboxy reactions, a phase separation process occurs. Epoxy–phenoxy and epoxy–carboxy reactions were catalyzed by the triphenyl phosphine. The effect of reaction parameters (temperature, catalyst, reactant stoichiometry) on the reactive extrusion process were analyzed. The structure of the prepolymers showed low branching reactions (2–5%). Low molar mass prepolymers have a Newtonian rheological behavior. Cloud-point temperature of different reactive liquid butadiene acrylonitrile random copolymer (RLP)/epoxy resin blends were measured for different RLP concentrations. It was shown that rubber particles remain insoluble in a range of temperature from room temperature to 180°C, typical of temperatures used for epoxy curing reactions. Prepolymers containing different rubber concentrations were cured using dicyandiamide as the hardener. The practical adhesion of the issued networks to an aluminium alloy increased with rubber concentration. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2447–2456, 1997

INTRODUCTION

The intrinsic properties of epoxy resins, chemical and corrosion resistance, good electrical capacities, flexibility, and outstanding adhesion to various substrates, are the main reasons for the regular growth rate of these polymers.¹ Recently, epoxy coatings have been adapted to environmental regulations regarding solvent-emission requirements. Higher molar mass solid epoxy resins are thus used in industrial solid coatings.

Unmodified epoxy resins exhibit brittleness after curing with hardeners. They are often toughened by an elastomer dispersion in the form of

particles of micrometer order.^{2,3} The enhancement of the toughness by the rubber incorporation is mainly due to the plastic deformation of the material at the crack tip and depends on the ability of the matrix plastic deformation during the fracture process.⁴ When liquid epoxy prepolymers are used, the elastomer phase is generally introduced by the initially miscible additive method. The additive is dissolved in the monomer and a phase separation occurs when the molar mass of the reactive product increases. Hycar[®] reactive liquid butadiene–acrylonitrile random copolymers (RLP) are the oldest and still most widely used low-viscosity soluble additives to liquid epoxy resins. Morphologies of RLP-modified systems result from the competition between the phase separation and epoxy reaction processes. It thus depends mainly on the monomer's reactivity and processing conditions, principally the curing temper-

Correspondence to: M. Taha.

Journal of Applied Polymer Science, Vol. 65, 2447–2456 (1997)
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ature.^{5,6} On the other hand, properties of the material obtained are related directly to the morphology of the dispersed phase.⁶ This means that processing conditions are, when the reaction induced phase separation method (RIPS) is adopted, the most important parameters.⁷

The classical carboxyl terminated butadiene-acrylonitrile random copolymer (CTBN), even the one with the higher acrylonitrile content (26%), are not miscible with high molar mass epoxy prepolymers at low temperatures.⁸ The RIPS method cannot be used for the elaboration of fine rubber dispersions in these prepolymers. However, a mechanical mixing of the CTBN and the epoxy prepolymer is also possible. In this case, the morphology of the blend depends on mixing conditions. This makes the obtention of finely dispersed stable rubber particles and the quality control of the issued morphology difficult.

When the rubber dispersion is present before any epoxy reaction, and if the structure and the dispersion remains unchanged during the epoxy network formation, the rubber particles can be considered to be preformed. The direct effect of this method is that the material properties, depending on the rubber addition, should be independent of curing temperature.

The system used in this study was thoroughly investigated by Romanchick et al.⁸ The RIPS method was used for the preparation in bulk of high molar mass epoxy prepolymers containing finely dispersed CTBN-based rubber particles. The reaction used was polycondensation of a liquid low molar mass diepoxy, in which the RLP is initially miscible, with a diphenol.

The main objective of this study is to do this reaction inside a twin-screw extruder. The structure and some properties of the prepared prepolymer blends were also studied. Prepolymer blends applied onto aluminium sheets were cured using dicyandiamide as the hardener, and the practical adhesion of the issued network was measured.

EXPERIMENTAL

Materials

The liquid diglycidyl ether of bisphenol A (DGEBA) epoxy prepolymer used in this study was Bakelite[®] 164 with an equivalent weight of epoxy groups equal to 188 g · mol⁻¹ as determined by acid titration ($\bar{n} = 0.15$). The ratio of the sec-

ondary hydroxyl group to the epoxy group is equal to 0.075. The high molar mass epoxy prepolymer was DER[®] 667 with an equivalent weight of epoxy groups equal to 2000 g · mol⁻¹ ($\bar{n} = 5.85$). The triphenyl phosphine (TPP) was from Aldrich. The bisphenol A was supplied by Shell Chemicals. Dicyandiamine and Diuron (3-(3-4-dichlorophenyl)-1-dimethylurea) were respectively Dyhard[®] 100S and Dyhard[®] UR200 from SKW Trotsberg.

The rubber was CTBN Hycar[®] 1300 × 8 (BF Goodrich) with a number-average molar mass of 3500 g · mol⁻¹, an acrylonitrile content of 18%, and COOH functionality equal to 1.8. CTBN Hycar[®] 1300 × 13 (BF Goodrich) with a number-average molar mass of 3200 g · mol⁻¹, an acrylonitrile content of 26% and COOH functionality equal to 1.8 was also used.

All reactants were used as received without any purification.

Extrusion

A modular intermeshing corotating twin-screw extruder CLEXTRAL BC21 was used in this study. The screw diameter was 25 mm and the total barrel length 900 mm. Screw and temperature profiles are presented in Figure 1. Bisphenol A and the catalyst were dry blended before the extrusion. Liquid DGEBA prepolymer was injected through barrel 1 and the Bisphenol A and catalyst mixture through the extruder hopper. In experiments where RLP was used, it was mixed with liquid DGEBA prepolymer and injected through barrel 1. The stationary state (constant pressure, temperature, and output) was established in approximately 15 min. Products were then taken from the extruder die. Portion of them (approximately 1 g) were immediately frozen in liquid nitrogen while others (1 g or 2 kg) were kept at room temperature.

For residence time distribution studies, the biphenyl was used as a UV tracer. 0.5 grams were injected as an impulse in the field hopper to the extruder. Products were collected from the extruder die, diluted in THF, and analyzed by SEC. The tracer concentration at time t (C_t) was measured using a calibration curve. The extruder response to the inlet pulse, the residence time distribution E_t is expressed in eq. (1).

$$E_t = C_t / \sum_0^{\infty} C_t \cdot \Delta t \quad (1)$$

We can also calculate the number average residence time

$$\bar{t}_m = \sum_0^{\infty} t \cdot E_t \cdot \Delta t \quad (2)$$

A dimensionless time θ

$$\theta = t/\bar{t}_m \quad (3)$$

The variance σ_t^2 and a dimensionless variance σ_θ^2

$$\sigma_t^2 = \sum (t - \bar{t}_m)^2 \cdot E(t) \cdot \Delta t \quad (4)$$

$$\sigma_\theta^2 = \sigma_t^2 / \bar{t}_m^2 \quad (5)$$

The time average residence time

$$\bar{t}_w = \sum t^2 \cdot C_t / \sum t \cdot C_t \quad (6)$$

and a dispersity index I

$$I = \bar{t}_w / \bar{t}_m \quad (7)$$

Apparatus

Infrared transmission spectra were obtained using the KBr pellet technique with an FT-IR spectrometer (Nicolet 205) at a resolution of 4 cm^{-1} .

The dynamic mechanical spectra of networks were recorded in the tension mode using a RSA II viscoelasticimeter (from Rheometrics) at 10 Hz. The storage moduli (E'), loss moduli (E''), and the loss factor ($\tan \delta$) were recorded as a function of the temperature. The rheological study of the DGEBA was made using an RDA II rheometer (from Rheometrics) in the cone and plate steady shear flow (diameter = 25 mm, cone angle = 0.02 Rad., gap = 50 mm).

A Mettler TA3000 was used for differential

scanning calorimetry (DSC) at a $10^\circ\text{C}/\text{min}$ heating rate under argon atmosphere.

Size Exclusion Chromatography (SEC) was performed in a Waters device equipped with UV (at 254 nm) and refractive index detectors. The solvent used was THF at a 1.5 mL/min flow rate and a pressure of 5×10^6 Pa. Columns of PL (Polymer Laboratories) gel 1000 Å, 500 Å, 100 Å, and 100 Å were used. Number- and mass-average molar masses were calculated using calibration with polystyrene standards. When rubber containing specimens were analyzed, number- and mass-average molar masses include the rubber.

$^1\text{H-NMR}$ spectra were recorded with a Bruker AC 200 at 200 MHz at room temperature. Deuterated chloroform was used for field lock. Chemical shifts are reported with trimethylsilane (TMS) at 0 ppm being used as the internal reference.

Cloud-Point Curves (CPC) were obtained using a home-made device.⁹ Mixtures of liquid DGEBA, Bakelite[®] 164, and the prepolymer blends prepared in Experiments 4 and 7 (Table I) and postcured for 1 h at 100°C were made at 90°C . Mixtures of solid DGEBA, DER[®] 667, and the prepolymer blend prepared in Experiment 7 (Table I) and postcured for 1 h at 100°C were made at 190°C . The mixture was heated to a temperature approximately 15°C superior to the cloud point, as judged by the transparency of the specimen. The temperature was kept constant for 5 min and then decreased with a cooling rate of $1^\circ\text{C}/\text{min}$. The cloud-point temperature (T_{cp}) was determined as the temperature at which the system changed from being transparent to cloudy. This technique begins to detect particles when average diameters measure approximately $0.1 \mu\text{m}$.

The practical adhesion was measured using a tensile machine FLEX 3 from TECHLAB. The substrate used was an aluminium alloy, die-cut to $10 \times 50 \text{ mm}^2$ from 1.5 mm-thick sheets. A sulfochromic acid bath (20 min at room temperature) was used as chemical surface treatment of the

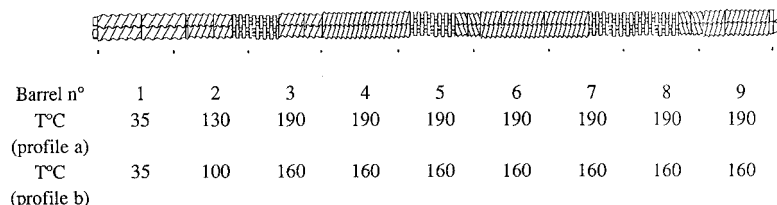


Figure 1 Screw and temperature profiles used in reactive extrusion. (a) 190°C , (b) 160°C .

substrate. The practical adhesion (or adherence) measurement of the epoxy network layers was evaluated by a three-point flexure test^{10–12} carried out according to the French standard AFNOR T 76143. After application of the epoxy reactive system and its curing cycle, a parallelepipedic epoxy bloc was applied to the coated surfaces as stiffener and cured at 80°C during 2 h. The used stiffener was CIBA AW134 with hardener HY994 based on a liquid DGEBA (700 g·mol⁻¹) and 3-(dimethylamino)-propylamine). Samples were stocked for 48 h at 20°C and 50% HR, and then tested. Parameters taken as representative of the practical adhesion were the ultimate load (F_{\max}) and the ultimate displacement (D_{\max}). The variation of the slope of the load/displacement curves within the linear region is characteristic of the stiffness sample variation. The locus of failure after mechanical testing was done using an optical microscope. When no polymer coating was observed on the failed metallic surface the term metal/polymer fracture was used. When fracture was observed between the polymer coating and the stiffener, the term polymer/stiffener fracture was employed.

RESULTS AND DISCUSSION

Synthesis by Reactive Extrusion

Fitting the Reaction to the Twin-screw Extrusion Process

Epoxy–Phenol, Epoxy–Carboxy, and Epoxy–Hydroxy condensation reactions are involved in the reactive system.

The small mean residence time of reactants within the extruder (1–5 min) reduce the number of reactions that can be processed in a twin-screw extruder. Fitting the epoxy–phenol reaction chosen for this study to the extrusion process implies simultaneously taking into account technical limitations and others concerning the different reactions involved in the system. Rapid kinetic evaluations made at different temperatures in a batch reactor shows that, even at relatively high temperatures (180°C) the epoxy monomer conversion after 10 min reaction is too low (lower than 30%). For this reason a catalyst was used.

In addition to the reaction of DGEBA with phenol and carboxy leading to linear chains, an etherification side reaction can occur between epoxy groups and the secondary alcohol. This reaction

can form branches and may change the epoxy functionality of final prepolymers. In extreme conditions, a crosslinked product can be obtained.¹³ The percentage of side branching reactions increases with the temperature¹⁴ and with the addition of large amounts of tri-*n* butyl amine catalyst.¹⁵ The use of the Triphenyl Phosphine (TPP) catalyst seems to limit this branching reaction.¹⁶ For this reason TPP was used in this study.

As shown in Figure 2, a conversion higher than 80%, calculated by FT–IR, can be obtained within a reasonable time limit at 180°C with the use of 1 wt % of TPP. This shows that the reaction can reasonably be made, from a kinetic point of view, by reactive extrusion.

The reaction parameters used in this study (temperature, % catalyst) were chosen taking into consideration this kinetic evaluation (Table I). The rubber content is expressed as the initial CTBN content introduced during the extrusion.

Screw Rate Choice

The screw profile of the extruder was designed to quickly mix the reactants and increase the mean residence time of reactants within the extruder. For epoxy–amine reactions, it was shown that the residence time of the reactive extrusion is proportional to kneading-discs and left-handed screw elements length.¹⁷ Therefore, long kneading-discs portions were used and the second and third kneading areas were followed by left-handed screw elements. However, because the transport in kneading-blocks is too small and that a high pressure must be used in order to pass the left-handed screw elements, this choice reduce the transport capacities of the profile. The Residence Time Distribution (RTD) and characteristics of the extruded epoxy blends are given in Table II. For all experiments where a liquid rubber was used, a cloudy product was obtained on the extruder die, showing that a phase separation occurred during extrusion. Conversion (x_E) and glass transition temperature (T_{gE}) are those of the epoxy rich phase. Mass average molar masses include the rubber.

In Experiments 1 to 4 the viscosity of the products at the extruder die is relatively low. For Experiments 1 and 2, this is a results of the low concentration of catalyst leading to low conversions. For Experiments 3 and 4, the low viscosity is due to the value of the epoxy to phenol plus carboxylic acid ratio r . The r value ($r = 0.88$)

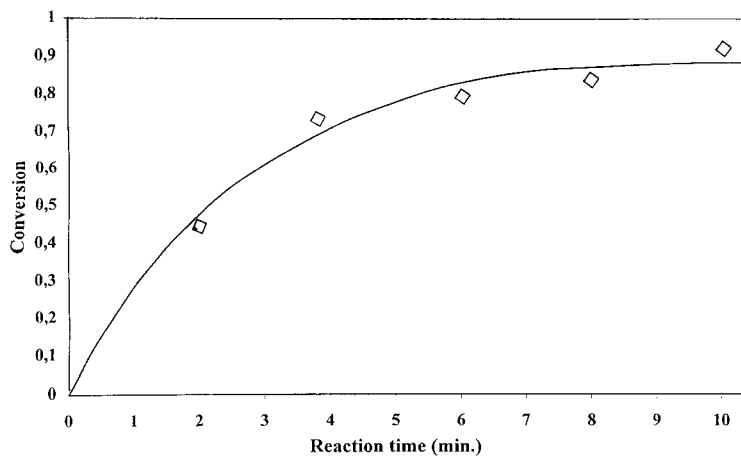


Figure 2 DGEBA/bisphenol A condensation reaction at 180°C. 1 wt % TPP catalyst. Conversions measured by FTIR.

leading to low molar mass oligomers. In those cases, it was possible to operate at a low screw rotation rate ($v = 35$ rpm). In Experiments 5 and 6 ($r = 1.01$), the molar mass of the overall product is much higher, resulting in higher viscosity. In this case, with the same input as in Experiments 1 to 4, the transport of the reactants was not possible at 35 rpm. The screw rate was increased to 100 rpm. In Experiment 7 ($r = 1.32$), at the extruder die the viscosity of the product was lower than the viscosity of those issued from Experiments 5 and 6 (Fig. 3). Nevertheless, it was impossible to operate at 100 rpm. A regular transport was obtained only at screw rates higher than 200 rpm. This is a result of the high elasticity of the product showing that the transport within the extruder is not only the result of the viscosity, but of the viscoelastic behavior of the mixture.

Residence Time Distribution

One can note that equivalent information is given by the dispersity index $I = \overline{t_w}/\overline{t_m}$ and the dimensionless variance σ_{θ}^2 . An increase in the reaction temperature has two opposite effects on the viscosity of the mixture: the first leads to a decrease of the viscosity at a constant molar mass of the product, the second to an increase of the kinetic rate, and consequently, of the molar mass and of the viscosity at the extruder die. In case of Experiments 3 and 4 or 5 and 6, the second effect is predominant. This increase of viscosity, with a constant transport capacity of the screw profile, leads to an increase of the number average residence time ($\overline{t_m}$). However, different evolutions are observed in Experiments 1 and 2 when the catalyst concentration is low. The increase of viscosity

Table I Reactive-Extrusion Parameters of the Condensation of Bisphenol A(OH) and Diglycidyl Ether of Bisphenol A(e) in Presence of CTBN(COOH) · ($r = e/OH + COOH$)

Experiment No.	Screw Rate (rpm)	Input kg/h	T °C	Additive		TPP wt %	r
				Type	wt %		
1	35	6	190	CTBN × 8	14.5%	0.1	0.96
2	35	6	160	CTBN × 8	14.5%	0.1	0.96
3	35	6	190	CTBN × 8	14.5%	1	0.88
4	35	6	160	CTBN × 8	14.5%	1	0.88
5	100	6	160	—		0.9	1.01
6	100	6	190	—		0.9	1.01
7	210	6	190	CTBN × 13	16%	0.8	1.32

Table II Characterisation of the Reactive Extruded Oligomer Blends

Experiment No.	Extrusion Characteristic			Epoxy and Epoxy/Rubber Blend Characteristic					
	$\overline{t_m}$ s	$\overline{t_w}/\overline{t_m}$	σ_θ^2	x_E	T_{gE} (°C)	$\overline{M_w}^a$	$\overline{M_w}^b$	η_o^b (pa·s) 145°C	η_o^b (pa·s) 185°C
1	129	1.08	0.69	0.69	16.5	722			
2	156	1.11	0.106	0.5	-1.5	620			
3	208	1.03	0.032	0.93	45	3280	6700	12	2.5
4	160	1.12	1.12	0.83	37	1320	7500	21	1.5
5	145	1.45	1.45	0.43	49	1970	34000		740
6	199	1.18	1.18	0.79	79	5340	38000		1250
7	193	1.15	1.15	0.75	50	1790	25000	40	6

x_E (FTIR), T_{gE} (DSC), and $\overline{M_w}$ (SEC, PS standard).

^a On the extruder die.

^b After thickening (1 h at 100°C).

due to an increase of the molar mass with the conversion smaller than the fluidification effect due to the temperature. This results in a higher $\overline{t_m}$ for the experiment conducted at low temperature (160°C) than the one at 190°C. It is also important to note that experiments processed at 160°C (particularly Experiment 5), leads to broader distributions of products than those run at 190°C. The consequence of this evolution is that

the conversion distribution, as defined by Cassagnau et al.,¹⁸ will be broader for experiments at 160°C, leading to more heterogeneous products. It was also clearly observed that the screw rotation rate is not the main factor affecting $\overline{t_m}$. For example, going from Experiment 1 to 7 even when the screw rate is six times higher, $\overline{t_m}$ increases ($\overline{t_m}$ is 1.5 times higher in Experiment 7 than for Experiment 1). In a nonreactive extrusion pro-

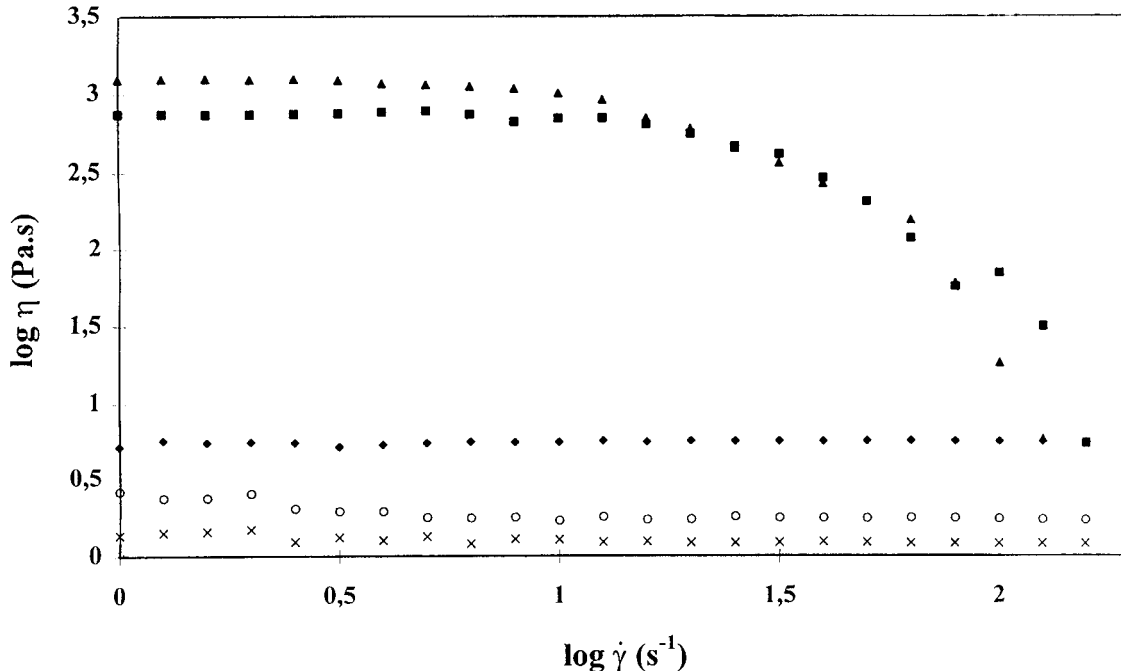


Figure 3 Viscosity as a function of shear rate at 140°C for prepolymers prepared in Experiment 3 (○), 4 (×), 5 (■), 6 (▲), and 7 (▲) thickened for 1 h at 100°C.

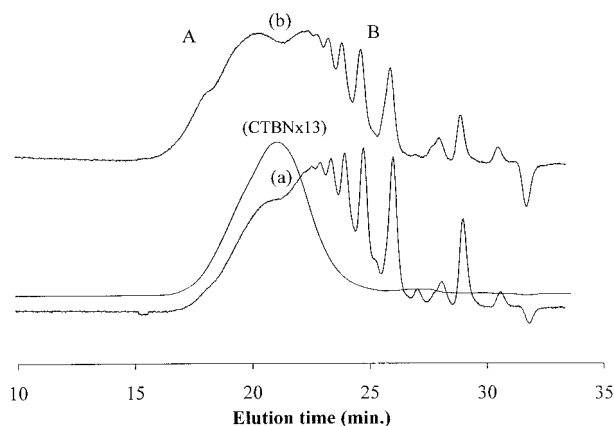


Figure 4 SEC of CTBN \times 13 and epoxy prepolymers/RLP blend prepared in Experiment 7. (a) On the extruder die; (b) postcured (1 h at 100°C).

cess, an opposite effect should be observed. This leads to believe that residence time evolution in reactive extrusion is too complex to be examined using only the nonreactive twin-screw extrusion modeling.

Phase Separation During Reactive Extrusion

In Experiment 5, the epoxy conversion is low. Postcuring of the obtained product (1 h at 100°C) results in a high increase of the molar mass of the epoxy prepolymer. In Experiment 6, conversion at the extruder die is much higher than in Experiment 5, and the conversion increase with maturation is lower. As expected, the products obtained after maturation of the prepolymers issued from Experiments 5 and 6 leads to oligomer having equivalent molar mass. When a RLP is used, the evolution of the reaction is different. The SEC of the prepolymer obtained at the extruder die in Experiment 7 is shown in Figure 4. First, one notes that there is no residual BPA. The figure is divided in two parts, indicating two populations of molecules. Peaks from part B are eluted at higher elution times than initial CTBN 13. The two molecule population can be described as follow:



The epoxy conversion is 0.75, indicating that the reaction is not total.

The blend of A and B is opaque, indicating a two-phase system. Experiments (see later) indi-

cate that the blend is still cloudy at the reaction temperature inside the twin-screw extruder. During the twin-screw extrusion, the reactive system goes from a one-phase to a two-phase system. Experiments have not been done to localize the phase separation on the processing line, but one can anticipate the fact that this will disturb the reaction rate.

At the extruder die, the product contains a rubber-rich particles well dispersed in a high molar mass epoxy prepolymer. During the postcure, the reaction continues inside each phase resulting in an important increase of the molar mass of A) and B) [Fig. (4b)].

Rubber/Epoxy Prepolymer Miscibility

Cloud-point temperature increase, for a given composition of RLP/epoxy prepolymer, with the mean molar mass of the epoxy was analyzed by Verchere et al.⁹ They reported for a CTBN \times 8/epoxy prepolymer blend that an increase of the epoxy prepolymer molar mass from 349 to 383 $\text{g} \cdot \text{mol}^{-1}$ leads to an increase of the precipitation temperature of 14°C. In this study, the high increase of the epoxy prepolymer molar mass leads to important change of the miscibility of the RLP/epoxy prepolymer blend.

The cloud point were first measured for a blend containing CTBN \times 13, issued from Experiment 7. The epoxy phenol reactions were completed in an oven at 100°C for 1 h to avoid any evolution of components due to chemical reactions during the study. Higher DGEBA concentrations were obtained by dilution in high molar mass DGEBA [DER[®] 667 ($\bar{n} = 5.85$)]. Results are reported in Table III. For the undiluted product, and those containing 12 and 10 wt % RLP, the cloud-point temperature was expected to be higher than the degradation temperature. For other concentrations, high cloud-point temperatures were obtained.

Because acrylonitrile content in CTBN \times 8 is lower than in CTBN \times 13, the solubility of the product issued from Experiment 4 is lower than the one issued from Experiment 7. The cloud points of blends containing 4 to 16 wt % CTBN \times 8 RLP, diluted in high molar mass DGEBA [DER[®] 667 ($\bar{n} = 5.85$)] were expected to be higher than degradation temperature. When diluted in low molar mass DGEBA [Bakelite[®] 164 ($\bar{n} = 0.15$)], lower cloud point temperature were observed (Table III). These results clearly show

Table III Cloud-Point Temperature of RLP/Epoxy Resin Blends

RLP wt %	1	2	4	6	8	10
Cloud point temperature (°C) ^a	—	—	214	220	235	—
Cloud point temperature (°C) ^b	55	82	140	175	185	190

^a Prepolymer mixture from Experiment 7 (CTBN × 13) diluted in high molar mass DGEBA [DER[®] 667 (\bar{n} = 5.85)].

^b Prepolymer mixture from Experiment 4 (CTBN × 8) diluted in liquid DGEBA [Dakelite[®] 164 (\bar{n} = 0.15)].

that these epoxy resin blends containing 4 to 15 wt % of CTBN × 13 and blends containing 4 to 15 wt % of CTBN × 8 remains nonmiscible at usual epoxy curing temperatures (lower than 160°C) when diluted in high molar mass epoxy prepolymer. This indicates that the rubber behaves as preformed particles during the curing of the resin.

When the blend containing CTBN × 8 is diluted in low molar mass epoxy, the rubber behaves as preformed particles during the curing of the resin only for RLP concentrations higher than 6 wt %.

Structure of the Epoxy Prepolymer

In this study, extreme temperature and catalytic conditions were used to increase the reactivity and to produce high molar mass prepolymers in the reactive extrusion. This may lead to branched oligomers. To characterise the functionality of the products obtained, their structure were analyzed by NMR using the method developed by Baltzer and Zahir.¹⁹ For Experiments 5 and 6, the branching amount (epoxy/secondary alcohol to epoxy/phenol reaction ratio) increases with the reaction temperature from 2.3 to 4.4%. When 2 kg samples were left at room temperature, the reaction continues. The analysis of the thickened

product showed larger amounts of branching reactions for the product issued from Experiment 5 (up to 3%). The branching amount of the product issued from Experiment 6 remained unchanged (4.5%). This indicates that the synthesis of a solid epoxy prepolymer with low amount of branching reactions can be made by reactive extrusion.

Rheology of Epoxy Prepolymers and Epoxy–Rubber Blends

Here also and to avoid any evolution of components due to chemical reactions during the rheological study, the products issued from reactive extrusion were postcured in an oven at 100°C for 1 h. The total reaction conversion was then obtained. The viscosity evolution of different epoxy and epoxy–rubber blend is given in Figure 3. As expected, the smallest molar mass prepolymers showed a Newtonian behavior. For higher molar mass, a Newtonian behavior was only observed for shear rates lower than 10 s⁻¹. The viscosity then decreases, and the n value of the power law equation $\eta = K\dot{\gamma}^n$ was found to be equal to 0.76.

Properties of the Networks Based on the High Molar Mass Epoxy Prepolymers

The epoxy–rubber blend issued from Experiment 7 was diluted with high molar mass epoxy prepolymer [DER[®] 667 (\bar{n} = 5.85)], and blends containing different amounts of rubber were prepared. These prepolymers were cured with dicyandiamide (DDA). Diuron was used as a catalyst (2 wt % of the DDA). The amine hydrogen to epoxy function ratio was 0.8. The curing conditions were 1 h 30 min, at 100°C and 1 h 30 min at 150°C.

With the addition of 5 wt % of rubber, the elastic modulus decreases from 5900 to 3700 MPa. For higher elastomer concentrations, only a small decrease to 3500 MPa was observed. Films were prepared using the same curing conditions (#100

Table IV Characteristics of Rubber-Modified DGEBA–DDA Networks

RLP (wt %) ^a	$T_{\alpha E}$ ^b (°C)	$T_{\alpha R}$ ^b (°C)	T_{gE} ^c (°C)
0	—	—	104
5	—	−40	103
10	97	−40	95
16	89	−40	86

^a (RLP is initially CTBN × 13. Rubber-modified DGEBA with different rubber content were prepared mixing epoxy/rubber from Experiment 7 (CTBN × 13) and high molar mass DGEBA [DER[®] 667 (\bar{n} = 5.85)].

^b Dynamic Mechanical Spectroscopy (max. tan δ).

^c DSC.

Table V Practical Adhesion Measurement of the Epoxy Network and Rubber-Modified Epoxy Network to Aluminium Alloy and Locus of the Failure

RLP (wt %) ^a		Slope (N/mm)	F_{\max} (N)	D_{\max} (mm)	Failure
0	$t = 0$	$1037 \pm 3\%$	$310 \pm 32\%$	$0.30 \pm 30\%$	metal/polymer
	aged ^b	$1180 \pm 3\%$	$289 \pm 32\%$	$0.24 \pm 32\%$	metal/polymer
5	$t = 0$	$1020 \pm 2\%$	$530 \pm 15\%$	$0.53 \pm 16\%$	metal/polymer
	aged ^b	$1158 \pm 5\%$	$532 \pm 7\%$	$0.46 \pm 7\%$	metal/polymer
10	$t = 0$	$1031 \pm 2\%$	$610 \pm 22\%$	$0.63 \pm 25\%$	metal/polymer
	aged ^b	$1186 \pm 2\%$	$542 \pm 11\%$	$0.43 \pm 12\%$	metal/polymer
16	$t = 0$	$972 \pm 2\%$	$897 \pm 8\%$	$1.34 \pm 16\%$	polymer/stiffener
	aged ^b	$1186 \pm 1\%$	$578 \pm 11\%$	$0.50 \pm 12\%$	metal/polymer

^a RLP is initially CTBN \times 13. Rubber-modified DGEBA with different rubber content were prepared mixing epoxy/rubber from Experiment 7 (CTBN \times 13) and DER[®] 667.

^b 24 h in water at 40°C.

η m thickness). They were analyzed by DSC and dynamic mechanical spectroscopy in the tension mode at 0.1 Hz. By DSC, only the T_g of the epoxy rich phase (noted T_{gE}) was observed. The dynamic mechanical spectra display the main relaxation associated with the glass transition of epoxy network (noted a_E) and the relaxation associated with the glass transition of the rubber-rich dispersed phase (noted a_R). The temperatures at maximum of $\tan \gamma$ corresponding to these relaxations are given in Table IV. The T_{gE} of the non-modified DGEBA–DDA network is relatively low (104°C) compared to the one prepared using low molar mass DGEBA. Maazouz et al.⁷ obtained a $T_{gE} = 153^\circ\text{C}$ for a network prepared using liquid DGEBA ($\bar{n} = 0.15$) and DDA. The T_{gE} decreasing when the epoxy–rubber blend is added, indicates that (a) part of the elastomer is dissolved in epoxy matrix, (b) or/and epoxy prepolymer with higher molar mass is introduced. Equivalent effect was illustrated in many articles.^{6,7,20–22}

The practical adhesion measurements of the epoxy network to an aluminium alloy are reported in Table V. It can be observed that without aging, the practical adhesion increases with the % of rubber. To take into account the locus of the failure, the failed metallic surface was observed. In the case of a system modified with 16 wt % of rubber, rubber was initially CTBN \times 13, the practical adhesion of the epoxy network onto the metallic substrate is higher than the practical adhesion of the epoxy network layer onto the epoxy stiffener. From the slope values of the load/displacement curves, it is noted that the addition of the rubber within the epoxy resin induces a slight decrease in the stiffness of the polymeric layer. Elsewhere,

it is shown that the elastic modulus of the polymeric layer slightly decrease when the ratio of the elastomer increase. After aging (24 h in water at 40°C), the failure takes place, for all specimens tested, at the metal/polymer interface. The adherence values decrease after aging. The highest values are observed for the system modified with 16 wt % CTBN \times 13. It is also observed that during aging the stiffness of the rubber-modified epoxy network layer increase.

CONCLUSION

High molar mass epoxy prepolymers can be prepared using epoxy–phenol condensation reactions by reactive extrusion. When CTBN is mixed with reactants, a phase separation occurs during the reaction. During the curing of these rubber-dispersed prepolymers with an amine hardener, no solubilization of rubber particles is observed. The practical adhesion of the issued network increase with the addition of rubber.

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