

Rheological Behavior of Reactive Miscible Polymer Blends: Influence of Mixing and Annealing Before Crosslinking

C. Serra, M. Bouquey, G. Schlatter, R. Muller

Laboratoire d'Ingénierie des Polymères pour les Hautes Technologies, Ecole de Chimie Polymères et Matériaux, 25 rue Becquerel, F-67087 Strasbourg Cedex 2, France

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ABSTRACT: We followed crosslinking reactions in the blends of two miscible reactive polymers by either torque rheometry or dynamic rheological measurements. Functional polymers with controlled glass-transition temperatures (T_g 's), chain lengths, and number of reactive groups per chain were synthesized by bulk radical polymerization. The blends were prepared either in a batch mixer or directly in the parallel plate geometry of a dynamic rheometer. Because of the low T_g of the blend components, it was possible to separate the mixing step from the crosslinking reaction, which was followed by small amplitude dynamic measurements at a higher temperature. The kinetics of the crosslinking reaction were determined by the study of the variations of the storage modulus (G') as a function of the reaction time. In this study, we focused on investigating the influence of blend composition, crosslinking reaction temperature, and amount of shear generated during the mixing step on the reaction kinetics. The influence of annealing time after the preshear step was also investigated. We found that the mixing procedure in the internal mixer produced homogeneous blends for which G' was dependent on the reaction time. Moreover, the reaction rate increased as the tempera-

ture and the chain functionality increased. A first approach showed that reduced variables could be defined from G' and reaction time with the initial concentration of the functional units to obtain a master curve independent of the species concentration. For blends prepared directly between the parallel plates of the dynamic rheometer, G' and the subsequent reaction rate were strongly dependent on the amount of shear generated during the mixing step. However, at high enough shear, the blend was perfectly mixed and the increase in G' versus reaction time was comparable to that obtained for the blend prepared in the internal mixer. Surprisingly, the higher the annealing time was, the lower the increase in G' was. However, we could explain this by considering the fact that the reaction started during the annealing step, which therefore, led to a thin crosslinked layer, which prevented any further diffusion of the polymer chains. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1978–1995, 2005

Key words: blends; crosslinking; miscibility; mixing; rheology

INTRODUCTION

This study was initiated in the frame of a project for the production of flexible and thick molded parts for optical applications. A crosslinkable formulation with acrylic and methacrylic esters had to be developed. There are two main ways to synthesize such a product. The first one consists of a one-step polymerization of a crosslinkable formulation with a dimethacrylic ester as the crosslinking agent. The second one consists of a crosslinking reaction between two suitably functionalized polymers. We were interested in the second method, for which shrinkage during processing is less important.

The network was to be obtained in three steps: two linear functional polymers bearing mutually reactive groups were first synthesized. These two functional

polymers were then melt-mixed, and finally, the crosslinking reaction occurred at the blend interphase at higher temperatures. To obtain a homogeneous material, the two reactive polymers had to be miscible. The results presented in this article are thus restricted to miscible blends.

In this study, we aimed to carry out the mixing step independently of the crosslinking reaction. As a consequence, the chemical system was chosen so that the kinetics of the reaction were slow enough compared to the mixing time at the mixing temperature [T_1 ; which had to be above the glass-transition temperature (T_g) of both components].

Therefore, a preliminary step consisted of the choice of a suitable chemical system, which led us to synthesize random copolymers with small amounts of reactive comonomer. The underlying chemistry chosen for the crosslinking reaction was the addition esterification between an epoxy group and a carboxylic acid group. This reaction has been widely studied in commercial blends in industry in the framework of the chemical compatibilization technique.^{1–11}

Correspondence to: R. Muller (mullerr@ecpm.u-strasbg.fr).

TABLE I
Compositions of the Terpolymers: Weight Fractions (and Molar Fractions) of the Comonomers

Code	M_f (g/mol)	BA (%)	MMA (%)	GMA (%)	AA (%)
GMA2	2000	56.0 (51.0)	37.3 (43.5)	6.7 (5.5)	0
GMA5	5000	58.3 (52.7)	38.9 (45.0)	2.8 (2.3)	0
GMA8	8000	58.9 (53.2)	39.3 (45.4)	1.8 (1.4)	0
AA2	2000	57.9 (51.0)	38.6 (43.5)	0	3.5 (5.5)
AA5	5000	59.1 (52.7)	39.4 (45.0)	0	1.5 (2.3)
AA8	8000	59.5 (53.2)	39.6 (45.4)	0	0.9 (1.4)

It has been shown in the literature that dynamic mechanical measurements in the melt can be used to characterize the formation of grafted and crosslinked polymers at the interphases of a molten blend.^{6,11-16} We investigated the kinetics of the crosslinking reaction by following the evolution of the storage modulus (G') as a function of the reaction time at a fixed frequency (ω).

This study was devoted to the investigation of the influence of several parameters on the reaction kinetics: the crosslinking reaction temperature, the number of functional units per chain in each blend component, the blend composition, the amount of shear generated during the mixing step, and the time of the annealing step following the mixing process. This study focused on investigations of rheological changes that occurred in the blend as a result of the chemical reaction at the interphase.

EXPERIMENTAL

Materials

The backbone of both blend components was a random butyl acrylate (BA)-methyl methacrylate (MMA) copolymer with a BA-MMA molar ratio of 54/46, which according to Fox's relation, led to a T_g of about 0°C. Acrylic acid (AA) and glycidyl methacrylate (GMA) were used as functional comonomers for each blend component, respectively. With this system, the mixing step could be carried out at moderate temperatures (ca. 50°C), well below the temperature at which the kinetics of the interchain reaction becomes significant in the time range of rheological experiments (ca. 100°C).

BA-MMA-GMA and BA-MMA-AA terpolymers were synthesized with various amounts of functional monomer by bulk radical copolymerization. The monomers were purchased from Aldrich Chemical Co (S^t Quentin Fallavier, France). Both BA and MMA were first treated with basic alumina to remove inhibitors. GMA and AA were used as received. Azobisisobutyronitrile was used as initiator, and the reaction was thermally activated. Calculations were made on the transfer agent (butanethiol) concentration to

obtain a number-average molar mass of about 50,000 g/mol.

All reagents were introduced in sealed polypropylene tubes with a diameter of 2 cm and a volume of 10 cm³. These tubes were immersed into a large water bath maintained at 80°C, which allowed the dissipation of the reaction heat and a nearly isothermal reaction. Conversions of about 90-95% were obtained after 3 h of reaction, and the composition of the copolymers was assumed to correspond to the molar fractions of the initially introduced monomers.¹⁴ All terpolymers were dried *in vacuo* at 80°C for 16 h to extract the residual monomers.

The functionality of a given terpolymer was characterized by the number-average molar mass between two consecutive functional units (M_f ; where the functional units were GMA or AA). Two series of terpolymers were synthesized with three different functionalities corresponding to M_f values of 2000, 5000, and 8000 g/mol. The three BA-MMA-GMA terpolymers were coded GMA2, GMA5, and GMA8, respectively, whereas the corresponding BA-MMA-AA terpolymers were coded AA2, AA5, and AA8, respectively. The compositions of all of the terpolymers, expressed in weight and molar fractions, are given in Table I.

Pure terpolymers were characterized by dynamic mechanical measurements performed in the range 0.1-100 rad/s and 30-150°C to draw master curves.¹⁶ The samples were shaped in the form of small discs 8 mm in diameter and put in the parallel plate geometry of a rheometer (thickness = 2 mm). Experiments were also done on samples that were not dried. It appeared that the presence of residual monomer could introduce significant variations (up to about 10%) in the measured values of G' . All pure terpolymers were, therefore, systematically dried after their synthesis.

The temperature dependence of the shift factors obeyed an Arrhenius-type equation with the same activation energy (E_a ; ca. 110 kJ) for both the terpolymer of butyl acrylate and methyl methacrylate (GMAx) and the terpolymer of butyl acrylate and methyl methacrylate (AAy). For example, the master curves for G' and the loss modulus (G'') at 30°C are shown in Figure 1 for GMA2 and AA2. The results show that both GMA2 and AA2 had the same vis-

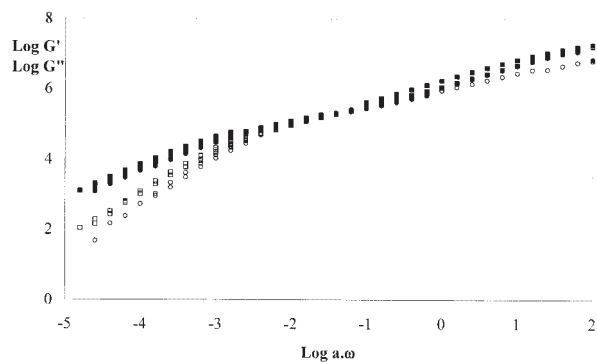


Figure 1 Master curves for G' [(■) GMA2 and (●) AA2] and G'' [(□) GMA2 and (○) AA2] at a reference temperature of 30°C.

coelastic behavior in the range of $aT \rightarrow T_0$ from 10^{-3} to 1 rad/s. However, a small discrepancy was observed for lower frequencies, which led to a zero-shear viscosity ratio of 50%, which led to a zero-shear viscosity ratio of 15% and a weight-average molar mass ratio of 15%. Also, in the temperature range 130–180°C, where the crosslinking reaction was studied, the dynamic moduli of the pure phases appeared to be very low (terminal or flow region), with the shift factor from 30 to 180°C being equal to $10^{-6.25}$.

Blend preparation

For all of blends examined in this study, the volume (or mass) fractions of the GMA_x and AA_y terpolymers (Φ_{GMA_x} and Φ_{AA_y} , respectively) were chosen so that the acid and epoxy functions were present in stoichiometric amounts. The following relation then held between Φ_{GMA_x} , Φ_{AA_y} and the M_f values:

$$\frac{\Phi_{GMA_x}}{M_{f_{GMA_x}}} = \frac{\Phi_{AA_y}}{M_{f_{AA_y}}} \quad (1)$$

A blend coded a2g2 was prepared with AA2 and GMA2 and corresponded, according to eq. (1), to a 50/50 composition of the two components.

The blends were prepared either in a batch mixer or directly in the parallel plate geometry of the mechanical spectrometer.

Internal mixer

The blends were prepared in a 60-cm³ batch mixer (Haake Rheocord 9000, Thermo Haake, Karlsruhe, Germany). Mixing was carried out at 120 or 30 rpm and a set temperature (T_{set}) of 30°C (i.e., $T_g + 30^\circ\text{C}$). The melt temperature was measured in the mixing chamber, and it increased from its initial value of 30°C up to $T_1 = 60^\circ\text{C}$ due to viscous dissipation. As shown later, for mixing times of the order of 30 min, the

reaction between the epoxy and acid functions could be neglected. This was not the case if the blend stayed for much longer times at the same temperature, as discussed later.

Dynamic rheometer

Shearing step. Discs (diameter = 25 mm, thickness = 2.5 mm) of the pure terpolymers (GMA5 or AA5) were first compression-molded at 70°C for 3 min. To obtain a 50/50 blend composition, these discs were cut in two parts along the diameter, and two semidisks (one of GMA5 and one of AA5) were placed side by side between the plates of the rheometer. Before shearing, the thickness of the sample was reduced to 1.9 mm to make sure that the whole gap between the plates was filled with polymer.

The mixing was carried out by a steady rotation of one plate of the rheometer (ARES, TA Instruments, Guyancourt, France), which led to a multilayer morphology, as shown in Figure 2,¹⁵ in which the thickness of the layers (e) was easily controlled by the amount of applied shear. The choice of the shear rate ($\dot{\gamma}$) and T_1 had to satisfy two conditions: (1) interchain reactions needed to be avoided during the mixing step, and (2) torque and normal force during shearing had to be kept low enough to stay in the measuring range of the transducer. We met these conditions by taking $T_1 = 50^\circ\text{C}$ and a $\dot{\gamma}$ at the outer rim of the discs of 0.5 s^{-1} . All specimens were kept at 50°C for 15 min before shearing to keep the same temperature in the whole sample.

Annealing step. For some samples, an additional step was introduced: once the mixing step was achieved, the annealing temperature (T_1) was increased up to $T_1 = 60^\circ\text{C}$, and the sample was kept at rest for a certain diffusion time (t_D). During this time, the diffusion of the chains at the interfaces between layers may have occurred, provided that no significant grafting or crosslinking took place at this temperature.

Analysis methods

Several methods were used to characterize the components and blends. The interchain reaction was char-

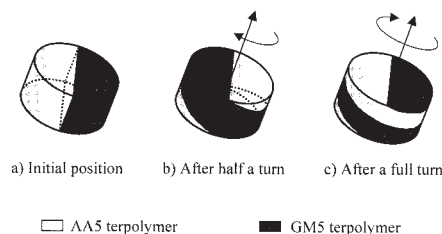


Figure 2 Preparation of the multilayer samples in the parallel plates of the rheometer.

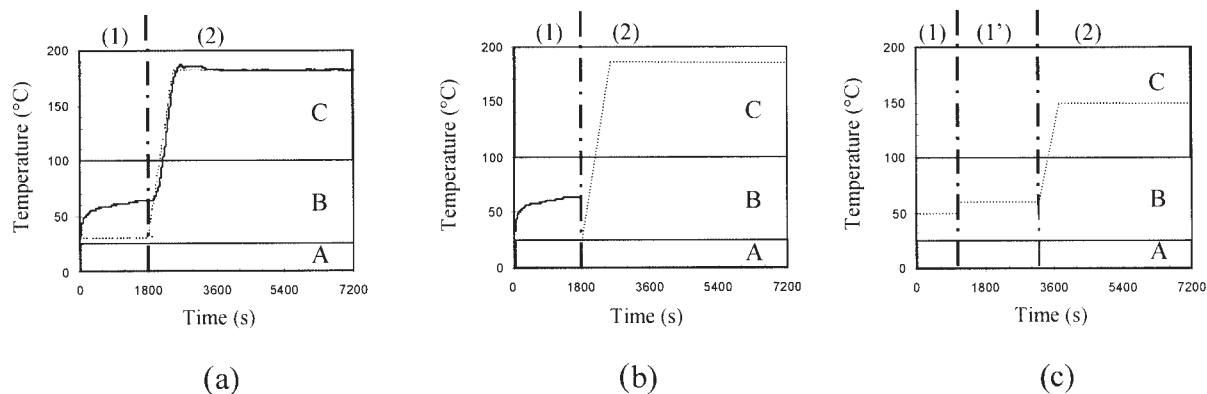


Figure 3 Temperature history as a function of time: (A) temperature range in which the terpolymers could not be mixed, (B) temperature range in which the mixing step was carried out independently of the crosslinking reaction, and (C) temperature range in which crosslinking began. (a) Mixing within the internal mixer: (1) mixing step and (2) the reaction with analysis by torque rheometry [(—) recorded temperature and (---) T_{set}]. (b) Mixing within the internal mixer: (1) mixing step and (2) the reaction with analysis by mechanical spectrometry. (c) Mixing between the parallel plates of the rheometer: (1) mixing step, (1') annealing step, and (2) reaction with analysis by mechanical spectrometry.

acterized by IR spectroscopy, torque rheometry, and rheological measurements, the blend morphology was characterized by X-ray microtomography, and the crosslinked fraction was characterized by a gel extraction technique.

IR spectroscopy

IR spectroscopy was performed on a2g2 blends and GMA2 at room temperature with a Nicolet Fourier transform infrared spectrometer (Impact 40, Thermo Electron, Courtaboeuf, France) equipped with an attenuated total reflection Golden Gate single-reflection diamond, which allowed us to analyze bulk samples without further preparation. All spectra were recorded at a resolution of 1 cm^{-1} and 16 accumulations. Because of the strong similarities between the different terpolymers, only the 912-cm^{-1} absorption peak of the GMA epoxy group did not interfere with the other peaks and could be used to follow the interchain grafting reaction.

The a2g2 blends and GMA used for this study were mixed for 30 min at 30 rpm and $T_{set} = 30^\circ\text{C}$ in the internal mixer. The reaction took place in an oven at 150°C . Samples were then removed at different reaction times.

Torque rheometry

After 30 min of mixing at 120 rpm and $T_{set} = 30^\circ\text{C}$, the temperature was increased up to 180°C to promote the crosslinking reaction, and the rotor speed was slowed to 80 rpm. The time evolution of the torque was then continuously recorded for 80 min, where $t = 0$ corresponded to the beginning of the experiment as the pure terpolymers were introduced into the mixing

chamber. Figure 3(a) shows the evolution of temperature with time for the whole experimental procedure.

Dynamic mechanical measurements

Recently, dynamic rheological measurements have been used as a powerful method for studying crosslinking reactions, namely, curing processes, gelation of thermoset resins, and the formation of grafted and crosslinked polymers at the interphases of a molten blend,^{6,8,11–23} in network-forming systems.

Therefore, for most samples, the rheological properties during the reaction were characterized by small-amplitude dynamic mechanical measurements in the parallel plate geometry of a rheometer (ARES, Rheometrics). Although the structure of the sample was modified by the crosslinking reaction, this analysis method offered the advantage of being a nondestructive method, unlike torque rheometry, because the samples were analyzed within the linear viscoelastic domain, that is, under very small amplitude oscillations.

For the blend prepared with the internal mixer, samplings (of about 1 g) were made at different times, and samples were immediately stored at 0°C to prevent chain diffusion and interchain reaction before the measurements. They were then shaped in the form of small (diameter = 8 mm) discs and put in the parallel plate geometry of the rheometer (thickness = 2 mm).

Finally, for both samples, either prepared with the internal mixer or directly mixed between the parallel plates of the dynamic rheometer, the crosslinking reaction was promoted by a rapid increase in the temperature (at a rate of $100^\circ\text{C}/\text{min}$) up to T_2 (130, 150, or 180°C). Once this temperature was reached, we measured the dynamic viscoelastic properties as a function

of reaction time (t_R) by carrying out a ω sweep test in the range 0.1–100 rad/s every 10 min. Figure 3(b,c) presents the temperature history of the samples.

Morphology characterization

X-ray microtomography (Skyscan 1072 microtomograph) was used to characterize the multilayer structure generated during the mixing step between the rheometer plates. It is a nondestructive method that allows the building of three-dimensional images, with a resolution of a few micrometers, of the internal structure of the sample. The method combines (1) X-ray radiography, which produces two-dimensional transmission pictures, and (2) tomography, which allows one to rebuild the internal structure of the sample calculated from radiographies taken at successive angular positions of the sample. The X-ray beam operated at 80 kV and 100 μ A. A charge coupling device camera with a resolution of 1024×1024 pixels allowed us to record the transmission pictures. To obtain an X-ray contrast between the two blend components, we dispersed 5 wt % lead stearate into one phase with a batch mixer (Haake Rheocord 9000). The observed blends were prepared with a semidisc of AA5 and a semidisc of AA5 labeled with lead stearate. The observed blends were thus nonreactive blends, as the two sheared terpolymers were both AA5 terpolymers.

Crosslinked fraction

For a reacted blend, the crosslinked fraction was determined by the extraction of the uncrosslinked fraction in a Soxhlet apparatus. This was done by the dissolution of about 1 g of the blend in a large volume of tetrahydrofuran at 80°C for 72 h. For longer times, no further evolution of the amount of extracted fraction was observed. The undissolved fraction was then dried at 80°C under dynamic vacuum, weighed, and compared with the initial mass of the blend.

RESULTS AND DISCUSSION

Reactions of the epoxy group

In this study, the GMAx and AAy terpolymers were both multifunctional in terms of the epoxy and carboxylic acid groups. So the addition esterification reaction between the carboxylic acid and epoxy groups should have eventually led to a crosslinked structure located at the interphase.^{6,8,10,23} Carboxylic acid and epoxy groups react via epoxy ring opening, which generates a secondary hydroxyl group. This group may react with another epoxy ring (cf. Fig. 4), and due to the multifunctionality of the GMAx terpolymers,

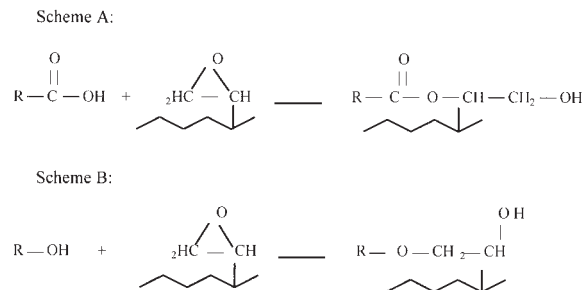


Figure 4 Potential reactions of the epoxy units: (Scheme A) reaction with carboxylic acid units and (Scheme B) reaction of the epoxy units with themselves.

this reaction could have also led to the formation of a crosslinked structure within the GMAx phase.

Characterization by IR spectroscopy

IR spectroscopy was performed on a2g2 blends to explore the crosslinking reactions occurring in the melt. The peak at 912 cm^{-1} disappeared progressively as a function of the reaction time. However, the absorption peak was not high enough to allow a quantitative characterization or to access to the kinetics of the reaction.

GMA2 itself was also heat-treated under similar conditions because it could undergo crosslinking reactions. Because the IR spectrographs did not reveal any alteration of the GMA2 composition over time, we concluded that without any initiator, the absence of hydroxyl groups inhibited such crosslinking reactions. This was also confirmed by rheological studies because there was no time evolution of G' of the pure GMA2 terpolymer sample at 180°C.

Torque rheometry

The network raised from the crosslinking reaction was characterized by torque rheometry. In the internal mixer, the mixing torque was continuously monitored as a function of the blending time. As the crosslinking reaction proceeded, the molecular weight increased and, thus, the viscosity increased, resulting in an increase in the mixing torque.^{1,2,5,7,9–11}

A low-molecular-weight compound that was monofunctional in terms of carboxylic acid groups content could be used to investigate the potential reactions. Thus, a monoacid compound (hydrocinnamic acid) was melt-blended with the GMA8 compound in a batch mixer operating at 50 rpm and a T_{set} of 50°C. Carboxylic acid and epoxy groups were introduced in stoichiometric amounts. We also followed the time evolution of the mixing torque for a a8g8 blend: GMA and AA groups were introduced in the batch mixer in stoichiometric amounts. They were then melt-blended

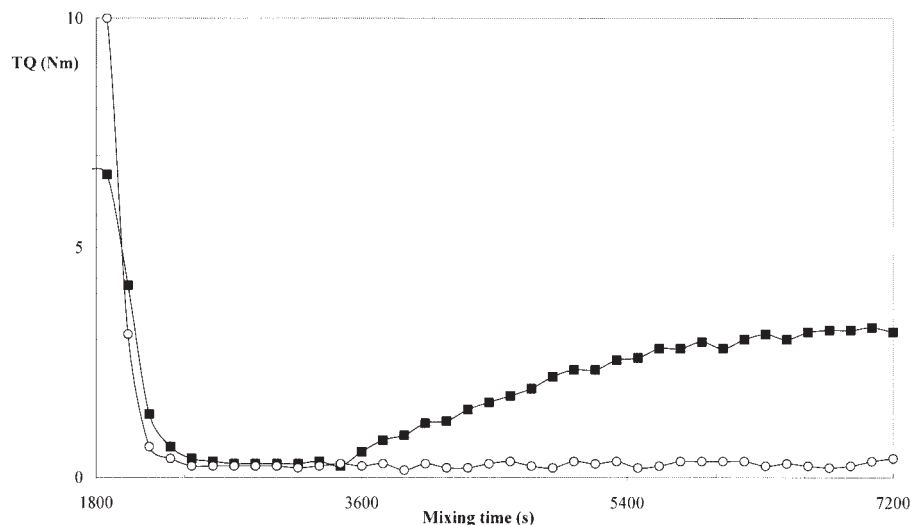


Figure 5 Effect of the carboxylic acid functionality: torque (TQ) versus mixing time at 180°C. Blends of GMA8 with (○) hydrocinnamic acid and (■) AA8.

at 120 rpm and 30°C. After a mixing step of 30 min, the temperature was increased to 180°C.

In the absence of reactions of epoxy units with themselves, the grafting of the monofunctional low-molecular-weight compound onto the GMA8 pure terpolymer should have induced little rheological change, whereas the reaction with the multifunctional compound AA8, which led to a crosslinking reaction, should have resulted in a large torque increase in the batch mixer.

As seen in Figure 5, the monofunctional compound had no effect on the torque, whereas the multifunctional compound AA8 produced a torque increase.

Dynamic mechanical measurements

Furthermore, mechanical spectrometry was carried out on pure GMA2, which was the compound with the highest amount of epoxy functions. The G' value at 100 rad/s was recorded for the following thermal

cycle: 6 h at 180°C and then 0.5 h at 220°C. As seen in Figure 6, G' did not significantly increase during the 6 h at 180°C. When the temperature increased to 220°C, we observed first a decrease in G' due to the thermal effect on the viscosity and then a sharp increase (up to 2 decades in 10 min), which was attributed to the crosslinking reaction between the epoxy functions.

From both the torque rheometry and dynamic mechanical measurements, we concluded that the crosslinking of the epoxy functions with themselves could be neglected for temperatures below 180°C. Then, the torque increase shown in Figure 5 was due to the reaction between the epoxy and the carboxylic acid units of the multifunctional terpolymers. These experiments provided evidence for the fact that the reaction indeed occurred between the epoxy and carboxylic acid functions in the melt.

Kinetics of the interchain crosslinking reaction

Torque rheometry

Many research groups have used a torque rheometer, such as a Brabender plasticorder or a Haake rheometer, to characterize grafting or crosslinking reactions occurring in reactive polymer blends at high temperatures.^{1,2,5,7,9-11} As seen before, the formation of a crosslinked structure results in an increase in the mixing torque.

We were interested in studying the influence of the functionality of the blend components on the kinetics of the crosslinking reaction. Three different blend compositions were explored: a2g2, a5g5, and a8g8 blends.

As soon as the temperature was increased to promote the crosslinking reaction, the mixing torque fell

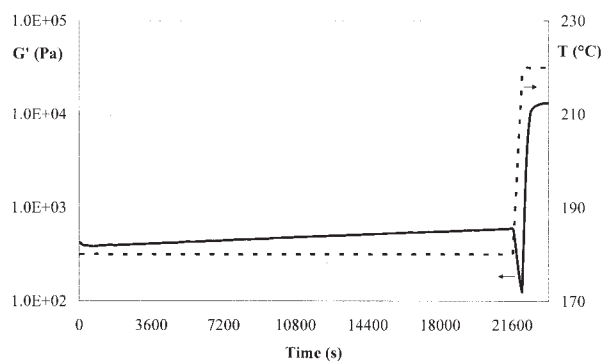


Figure 6 (---) Thermal cycle and (—) evolution of G' for GMA2 at 100 rad/s.

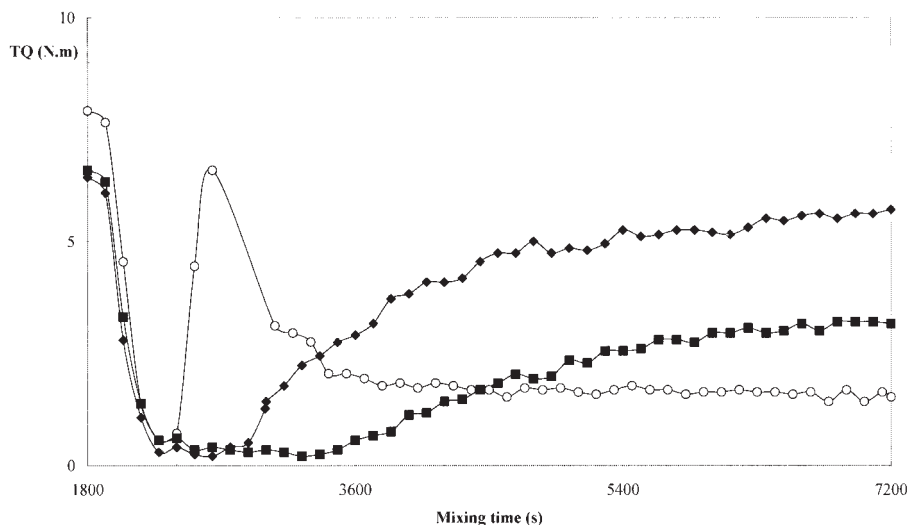


Figure 7 Torque (TQ) versus mixing time at 180°C for (○) a2g2, (◆) a5g5, and (■) a8g8 blends.

to zero. After various times, which we will call *induction times*, the torque increased sharply and finally reached a plateau value. Consequently, the crosslinking reaction could be characterized by two parameters: the induction time and the plateau value. As expected and shown in Figure 7, the length of the induction period decreased with increasing functionality, that is, by increasing functional group concentration.

We also expected that the smaller the mass between two functional units was, the higher the plateau value should have been. This trend was only observed for the a5g5 and a8g8 blends. However, as shown in Figure 7, the form of the curve obtained for the a2g2 blend strongly differed from the others. After the beginning of the torque increase, the torque suddenly fell and reached a lower plateau value than those measured for the a5g5 and a8g8 blends. The aspect of the product at the end of the experiment was also quite different. The a5g5 and a8g8 blends were rubbery, whereas the a2g2 blend was friable, almost like a powder. The observed fall in torque was due to the mechanical degradation of the sample, as the highly crosslinked sample was still mixed in the batch mixer when the crosslinking reaction proceeded.

As discussed, the torque rheometry had some limitations and could be only used as a qualitative method to characterize the crosslinking reaction. As a result, we had to choose another analysis method to follow the crosslinking reaction occurring in the melt in our reactive polymer blends, namely, dynamic rheological studies.

Dynamic mechanical measurements on reactive blends prepared in the internal mixer

In the following paragraphs, to distinguish the samples prepared under various operating conditions, we

code them in the following way: a sample coded 150a2g2m15r30 means that the sampling was made in the batch mixer operating at 30 rpm after a mixing time of 15 min on a a2g2 blend and that the reaction kinetics were studied at 150°C in the rheometer.

The curves for G' measured for the reactive blends were well above those of the pure terpolymers. In the presence of a crosslinking reaction, the G' versus ω curves reached a plateau at low frequencies. When the reaction time was long enough, a true plateau behavior was observed in the whole ω range investigated, as shown in a previous article,¹⁶ and the value of this plateau increased with the reaction time. For this reason, we followed the crosslinking reaction by drawing G' versus reaction time at a fixed ω . The highest ω of 100 rad/s was chosen because, at short reaction times, it was only at this ω that the torque level reached the minimum value of 0.02 g/cm required for accurate measurements. On the other hand, in a previous article,¹⁶ it was shown that even in the early stages of the crosslinking reaction, the values of G' are almost independent of ω in the range from 10^{-1} to 100 rad/s. In the same study, it was also found that in the range of temperatures in which the crosslinking reaction was studied, the dynamic moduli of the pure terpolymers were strongly ω -dependent and well below the plateau values found for the reactive blends. This confirmed that the values of moduli observed for the reactive blends were only due to the intermolecular crosslinking reaction.

Influence of the mixing time. The influence of the amount of shear during the mixing step was investigated. Takings were made at three different mixing times, 15, 20, and 30 min, at a rotor speed of 120 rpm. As indicated previously, we followed the crosslinking reaction by drawing G' versus reaction time at a ω of 100 rad/s. These experiments were carried out at dif-

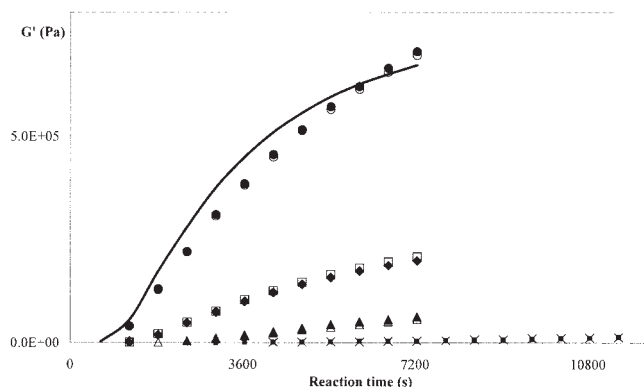


Figure 8 Influence of mixing time for blends prepared in the internal mixer at 120 rpm and 30°C: G' versus reaction time for (●) 150a2g2m15r120, (○) 150a2g2m20r120, (◆) 180a5g5m15r120, (□) 180a5g5m20r120, (◇) 180a5g5m30r120, (▲) 180a8g8m15r120, (△) 180a8g8m30r120, (×) 150a8g8m15r120, (■) 150a8g8m30r120, and (—) 150a2g2m ∞ r120.

ferent temperatures (150 and 180°C) for different blend compositions (a2g2, a5g5, and a8g8) and for different mixing times. From the results shown in Figure 8, we can conclude that the mixing time in the range investigated had no influence on the kinetics of the interfacial crosslinking reaction. This means that the morphology reached after 15 min of mixing was either homogeneous or independent of mixing time.

To confirm this result, experiments were performed on homogeneous samples prepared in the following way: the two pure terpolymers, bearing, respectively, acid and epoxy groups, were both dissolved in methylene chloride, and the solution was then dried *in vacuo* at 20°C so that the crosslinking reaction did not occur during the preparation of the sample, as shown in Figure 8. There was no significant difference be-

tween the curve of the homogeneous sample coded a2g2m ∞ and the curve of the previously studied blends. So we concluded that at the operating conditions, the reached morphology was homogeneous.

Adjustments were then made on the rotor speed to generate amounts of shear in a range as wide as possible and to investigate their influence on the reaction kinetics. The speed was then decreased to 30 rpm. a8g8 blends were explored for this series of experiments as the effect of mixing time should have been more pronounced for blends with the lowest functionality. The reaction temperature was set at 180°C, and samplings were made at different mixing times. The experimental results are shown in Figure 9. We concluded that a general trend was observed. That is, G' increased more rapidly as the mixing time increased, but discrepancies up to 20% were observed. Indeed, for example, the 180a8g8m8r30 curve fell between the 180a8g8m10r30 and 180a8g8m30r30 curves.

The homogeneity of the mixing in the batch mixer was then investigated. Reproducibility experiments were performed on different samplings made in the batch mixer for identical mixing times. Differences of about 10% appeared, differences of the same order of magnitude as those observed for different mixing times at low rotor speed. Consequently, the experiments with a mixing step in the batch mixer could not allow us to make conclusions about the influence of the amount of shear generated during the mixing step on the reaction kinetics.

As a result, samples prepared from samplings made in the batch mixer operating at 120 rpm allowed us to study the influence of the other parameters, such as the reaction temperature and the blend composition, on samples with a homogeneous morphology.

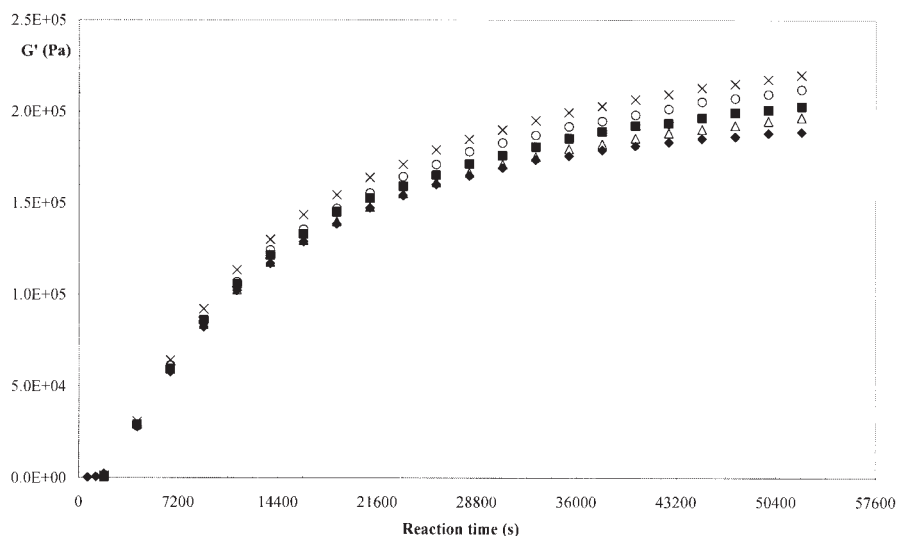


Figure 9 Influence of mixing time for blends prepared in the internal mixer at 30 rpm and 30°C: G' versus reaction time for (◆) 180a8g8m4r30, (△) 180a8g8m10r30, (■) 180a8g8m8r30, (○) 180a8g8m30r30, and (×) 180a8g8m20r30.

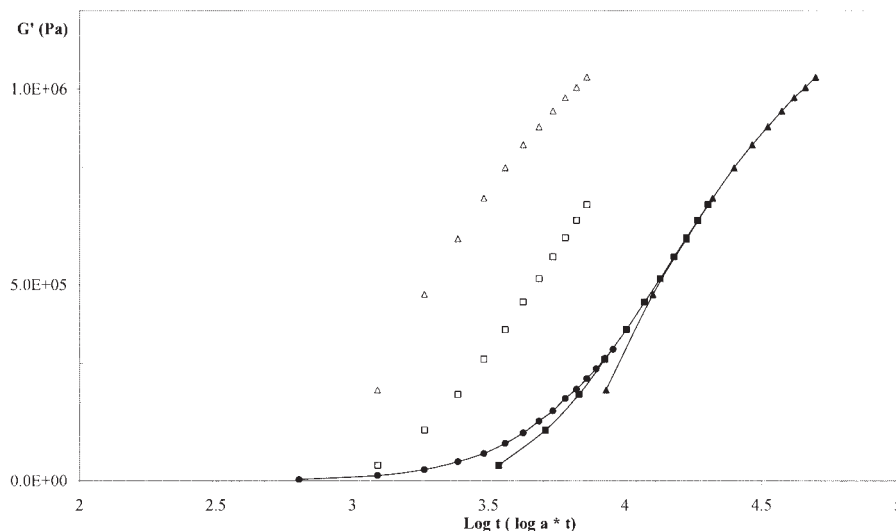


Figure 10 Influence of the reaction temperature: G' versus $\log t$ for (●) 130a2g2m20r120, (□) 150a2g2m20r120, and (△) 180a2g2m15r120 with time–temperature superposition and G' versus $\log (a_{T-T_0} t)$ where $T_0 = 130^\circ\text{C}$ for (●) 130a2g2m20r120 (reference), (■) 150a2g2m20r120, and (▲) 180a2g2m15r120.

Kinetics of the reaction in homogeneous blends: Influence of the temperature. The influence of the reaction temperature on the kinetics of the reaction was investigated in homogeneous blends prepared in the Haake instrument operating at 120 rpm as described previously. For each blend composition, two reaction temperatures were studied: 150 and 180°C . A third temperature (130°C) was also used for the most reactive blend: a2g2.

As mentioned in a previous article,¹⁶ all curves had the same typical form: after a given induction period, G' increased linearly as a function of the reaction time and finally reached a plateau value. This induction time increased with decreasing reaction temperature and functionality. The induction time measured for the 130a2g2 sample, that is, for the most functional blend, was 30 min. As a result, we assumed that no crosslinking occurred during the mixing step because the measured T_1 was $50\text{--}60^\circ\text{C}$ and the highest mixing time was 30 min.

The results for the evolution of G' as a function of the reaction time are shown in Figure 10 (semilogarithmic scales). As expected, the reaction rate increased with temperature because G' increased more rapidly as the temperature increased. As shown in Figure 10, it was possible to draw a master curve by the introduction of a reduced time (t_{reduced}) according to the time–temperature equivalence. The temperature dependence of the experimentally determined shift factors obeyed an Arrhenius-type equation. As a result, we calculated the apparent activation energy of the reaction from the master curves drawn for the different functionalities (E_{a1}). The results are summarized in Table II.

As seen before, after a given induction period, G' increased linearly as a function of the reaction time.

The apparent activation energy of the reaction could also be determined from the slope of the tangent to the $G' = f(t)$ curve after this induction period (E_{a2})^{17,18,21,23} because the temperature dependence of these slopes obeyed an Arrhenius-type equation. The apparent activation energies estimated in this way for the different functionalities are shown in Table II.

The E_a 's of the crosslinking reaction calculated from both methods were quite similar. The apparent E_a of the crosslinking reaction increased with decreasing functionality but remained lower than the E_a of viscosity and self-diffusion estimated from the master curves for the viscoelastic properties of the pure terpolymers (ca. 100 kJ/mol).

Kinetics of the reaction in homogeneous blends: Influence of the blend composition.

Symmetric blends. Several blend compositions were explored. At the beginning, we were interested in studying blends prepared with pure terpolymers with the same functionality. Three different blend compositions were explored, a2g2, a5g5, and a8g8, and the results for the G' versus reaction time curves at 180°C are shown in Figure 11 (filled symbols).

It has been shown in the literature that the total reaction time can be determined by drawing G' versus time,¹² at the end of the reaction, the $G' = f(t)$ curve reaches a plateau. We tried to obtain this plateau for

TABLE II
 E_a Values Determined from Different Methods

Code	E_{a1} (kJ/mol)	E_{a2} (kJ/mol)
a2g2	58	66
a5g5	63	68
a8g8	84	88

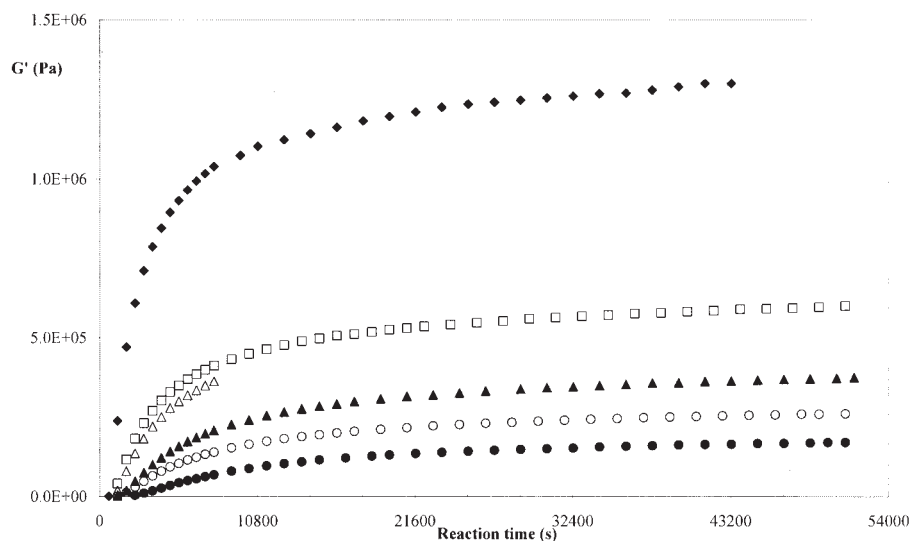


Figure 11 Influence of blend composition: G' versus reaction time for (◆) 180a2g2m15r120, (□) 180a2g5m15r120, (△) 180a5g2m15r120, (▲) 180a5g5m20r120, (○) 180a8g2m20r120, and (●) 180a8g8m15r120.

the a2g2, a5g5, and a8g8 blends, and the results are shown in Figure 11. According to classical rubber elasticity theory, we calculated the number-average molar mass between two crosslinked units (Mf_{exp}) from the value of G' at the plateau. We compared this experimental value (Mf_{exp}) with the theoretical value of the number-average molar mass between two functional units (Mf_{th}). The results are summarized in Table III: for the highest functionality, Mf_{exp} was equal to 3000 g/mol, which was close to the Mf_{th} value of 2000 g/mol, whereas the deviation between both values was higher for the other blends. In fact, the deviation increased when the functionality decreased. Because G' was proportional to the fraction of reacted units, this means that the lower the functionality was, the lower the fraction of reacted functional units was. The fact that Mf_{exp} determined from the plateau modulus was of the same order of magnitude as Mf confirmed the conclusion on the homogeneity of the blends at the end of the mixing step. This was further confirmed by solvent extraction measurements carried out in acetone for which gel fractions of 100% within experimental error were found after only 2 h of reaction time.

TABLE III
 Mf_{th} Values [Eq. (3)], Limiting Values of G' for Long Reaction Times, and Mf_{exp} Values

Code	Mf_{th} (g/mol)	G' (Pa)	Mf_{exp} (g/mol)
a2g2	2000	1.30×10^6	3,000
a5g5	5000	4.60×10^5	9,000
a8g8	8000	2.28×10^5	18,000
a5g2-a2g5	3500	6.00×10^5	7,000
a8g2	5000	2.61×10^5	16,000

Nonsymmetric blends. These blends were prepared with terpolymers with different functionalities and were called *nonsymmetric blends*. A blend coded a5g2 means that it was prepared with AA5 and GMA2, but the acid and epoxy functions were still introduced in stoichiometric amounts. Different blend compositions were explored (a2g5, a5g2, and a8g2), and the results for G' are shown in Figure 11 (open symbols). We might have expected that these nonsymmetric blends would have intermediate reaction kinetics and structures compared to the two corresponding symmetric blends: for instance, the G' curve corresponding to a2g5 should have been between the curves corresponding to a2g2 and a5g5, which was indeed confirmed by the experiments.

On the other hand, as shown in Figure 11, the curves corresponding to a2g5 and a5g2 were almost identical, which means that under stoichiometric conditions, the network structure and the kinetics of its formation only depended on the volume concentration of the functional monomers and tended to prove that the synthesized terpolymers were indeed statistical.

It was possible to estimate a Mf_{th} value for nonsymmetric blends again with the classical rubber elasticity theory: for a complete reaction, the number of elastic strands per unit volume (ν_e) in the crosslinked sample is equal to the sum of the initial numbers of acid and epoxy units per unit volume. If the elastic modulus (G) of the crosslinked network was still given by $G = \nu_e k_b T$, where k_b is the Boltzmann constant, it can be expressed as a function of Φ_{GMAx} and Φ_{AAy} :

$$\nu_e = N_A \left(\frac{\rho \Phi_{\text{GMAx}}}{Mf_{\text{GMAx}}} + \frac{\rho \Phi_{\text{AAy}}}{Mf_{\text{AAy}}} \right) \quad (2)$$

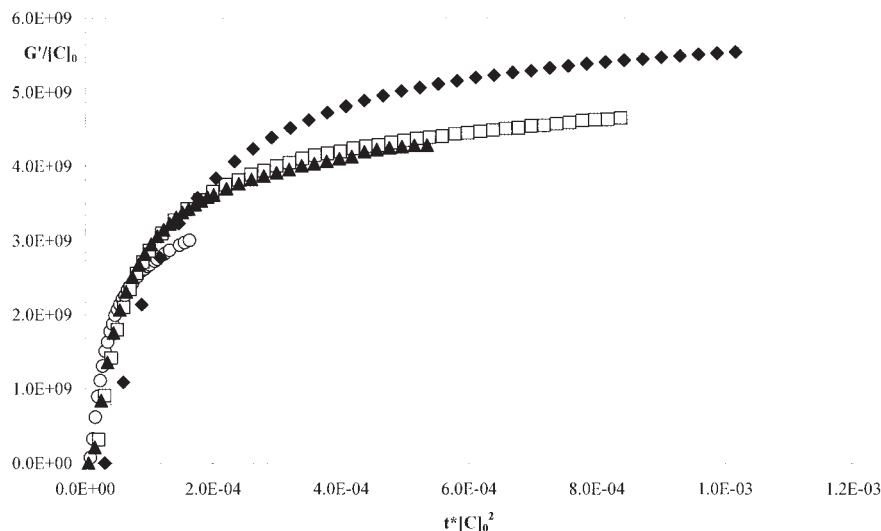


Figure 12 Data of Figure 8 plotted with reduced variables $\{G'/[C]_0 = f(t[C]_0^2)\}$: (\blacklozenge) 180a2g2m15, (\square) 180a2g5m15, (\blacktriangle) 180a5g5m20, and (\circ) 180a8g8m15.

where ρ is the density (mass per unit volume) and N_A is Avogadro's number.

Considering the fact that the acid and epoxy functions are present in stoichiometric amounts [cf. eq. (1)], we finally obtained the following expression:

$$G = \rho RT \frac{2\Phi_{GMAX}}{Mf_{GMAX}} = \rho RT \frac{2\Phi_{AAy}}{Mf_{AAy}} \quad (3)$$

Mf_{th} is given by

$$Mf_{th} = \frac{Mf_{GMAX}}{2\Phi_{GMAX}} = \frac{Mf_{AAy}}{2\Phi_{AAy}} \quad (4)$$

It can be calculated and compared with Mf_{exp} :

$$Mf_{exp} = RT \frac{\rho}{G} \quad (5)$$

The results are summarized in Table III: we see in particular that the a8g2 and a5g5 blends should have led to the same values of modulus, corresponding to $Mf_{th} = 5000$ g/mol, because their concentrations of acid and epoxy functions were the same. However, the experimental values of Mf were both higher than the expected value. Moreover, the measured values of G' for the a8g2 blend were always lower than those of the a5g5 blend, and the deviation between Mf_{exp} and Mf_{th} was higher. This meant that the network structure not only depended on the concentration of functional units but also on the chain functionality or, more precisely, on Mf .

Finally, we made an attempt to draw a master curve for stoichiometric blends by introducing reduced variables involving the concentration of functional units.

Because G' was expected to be proportional to the initial concentrations of the functional units ($[GMA]_0 = [AA]_0 = [C]_0$, where $[GMA]_0$ is the initial concentration of glycidyl methacrylate and $[AA]_0$ is the initial concentration of acrylic acid), a reduced modulus was obtained by the division of G' by $[C]_0$. If one assumes that the reaction is autocatalyzed by the acid functions,²⁴ the reaction rate is proportional to $[AA]^2$:

$$-\frac{d[AA]}{dt} = k[AA]^2[GMA] \quad (6)$$

where k is the crosslinking kinetics constant.

Equation (6) assumes that all AA functions catalyze the reaction. In stoichiometric conditions

$$-\frac{d[C]}{dt} = k[C]^3 \Leftrightarrow 2kt = \frac{1}{[C]^2} - \frac{1}{[C]_0^2} \quad (7)$$

where C_0 is the initial concentration of functional unit (either AA or GMA).

The corresponding $t_{reduced}$ will, therefore, be defined as t multiplied by $[C]_0^q$, which is only function of the reaction extent. If the structure of the crosslinked blends only depends on the initial concentrations of reactive functions, a single master curve should be obtained for all stoichiometric blend compositions if the previously defined reduced variables are used. As shown in Figure 12, the results are quite satisfactory, especially at short reaction times, where all reduced curves are superimposed. Attempts to construct a master curve were made with different expressions of the $t_{reduced}$ of the type $t \times [C]_0^q$, and the best results were obtained for $q = 2$, which thus confirmed the assumption that the reaction was catalyzed by one of

the reactive components. Forthcoming measurements on nonstoichiometric blends will give more information on the chemical nature of the catalyzing species.

However, the value of the G' plateau at long reaction times seemed to be still dependent on the chain functionality and the blend composition. This result could be explained by the following arguments: (1) G' was proportional to the volume concentration of elastic network strands and, therefore, to the amount of reacted functional units, and (2) the previous experimental results show that the lower the initial concentration of functional units (or the higher the M_f) was, the lower was the fraction of functional units that eventually reacted (at long reaction times). This means that if the distance between the reactive units was increased by a reduction in the chain functionality, the final proportion of functions that were able to react was decreased.

Dynamic mechanical measurements on reactive blends prepared between the parallel plates of the dynamic rheometer

The internal mixer was not able to produce blends with intermediate mixing states but only homogeneous states. Because the amount of shear generated during the mixing step should have had a great influence on the reaction kinetics, we thought about a new mixing technique to produce heterogeneous blends. The mixing step was carried out directly between the parallel plate geometry of the rheometer to control and generate various amount of shear. In this way, we obtained different mixing states. Additionally, to the mixing and reaction steps, we also introduced a further step in the process (a t_D or annealing time just after the mixing step), and we studied the influence of this diffusion step on the reaction kinetics.

Morphology. With the mixing process we used (see Blend Preparation section), we should have generated a multilayer sample.¹⁵ The amount of shear generated during the mixing or preshear step was related to e , expressed in units of radius of gyration (R_g):

$$e = \frac{\pi R}{\dot{\gamma} t} \quad (8)$$

where $\dot{\gamma}$ is the shear rate, t is the shear time, and R is the radius of the disc sample. R_g was assumed to be about 7 nm with a polystyrene equivalent.^{25,26} Then, the theoretical number of layers (n_{th}) was simply calculated with the following equation:

$$n_{th} = \frac{h}{e} \quad (9)$$

where h is the total thickness.

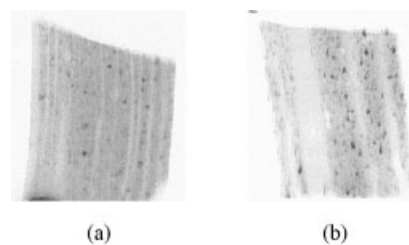


Figure 13 Microtographs of the multilayer structure generated during the mixing step in the parallel plate geometry of the mechanical spectrometer: (a) structure of a $10,000-R_g$ sample ($n_{th} = 27$, $n_{exp} = 22$) and (b) structure of a $30,000-R_g$ sample ($n_{th} = 9$, $n_{exp} = 9$).

As shown in Figure 13(a,b), the microtographs indeed exhibited a multilayer structure. We concluded that eq. (8) gave quite an accurate value of e because the experimental layers number (n_{exp}) approached n_{th} as calculated by eq. (9).

Kinetics of the reaction in heterogeneous blends: Influence of the mixing time. We were interested in studying the influence of the amount of shear generated during the mixing step on the reaction kinetics.

Samples coded a5g5 prepared by the previously described process with various amounts of preshear ($e = 1000, 2000, 5000$, and $10,000 R_g$) but without the annealing step were then investigated. The reaction temperature was fixed at 150°C . The increases in G' for the different samples are shown in Figure 14.

Calculations were also made to determine the distance that the polymer chains may have diffused during the different steps of the process. These steps were (1) the mixing step at 50°C , (2) the temperature ramp, and (3) the reaction step at 150°C before the grafting or crosslinking reaction took place (because the resulting grafted or crosslinked structure should have prevented further diffusion). Calculations were then made with the assumption that no further diffusion was possible in the blend after the reaction induction period observed in the $G' = f(t)$ curves. The mean diffusion distance (x) was determined with the following relations:

$$R_g^2 = D(T)\lambda(T) \quad (10)$$

$$(R_g x)^2 = D(T)t \quad (11)$$

$$x = \sqrt{\frac{t}{\lambda(T)}} \quad (12)$$

where x is expressed in units of R_g , t is the time, and $D(T)$ and $\lambda(T)$ are the diffusion constant and the terminal relaxation time at a certain temperature (T), respectively. These relations assume that the time during which the chains diffuse on a distance equivalent to their R_g corresponds to their longest relaxation time

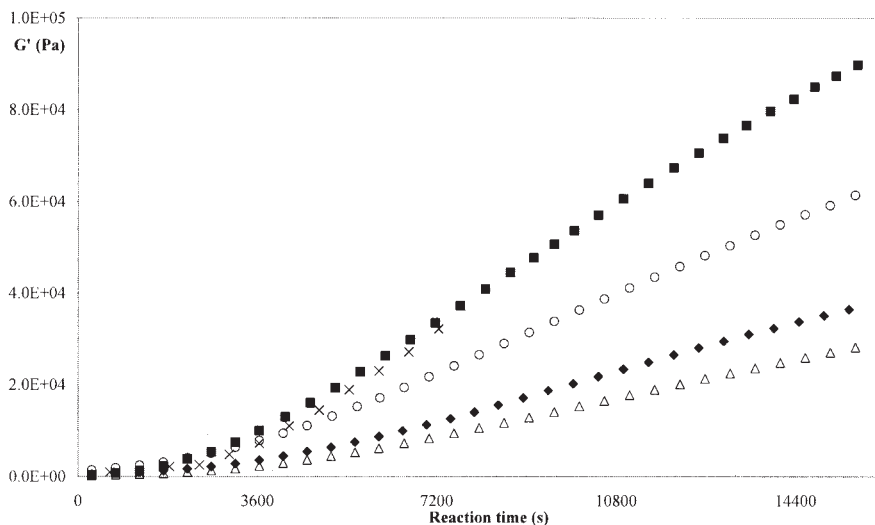


Figure 14 Effect of the amount of shear generated during the mixing step. Evolution of the G' versus reaction time at 100 rad/s as a function of e . $t = 0$ corresponds to the end of the mixing step: (x) a5g5 prepared in an internal mixer and $e =$ (■) 1000, (○) 2000, (◆) 5000, and (△) 10,000 R_g .

(λ). The λ 's were estimated from the master curves drawn at an initial temperature (T_0) of 30°C with the fact that

$$\lambda(T_0) = \frac{1}{\omega_c} \quad (13)$$

where ω_c is the frequency crossover of the G' and G'' curves and

$$\lambda(T) = a_{T \rightarrow T_0} \lambda(T_0) \quad (14)$$

where $a_{T \rightarrow T_0}$ is the shift factor from temperature T to T_0 .

We also introduced t_{reduced} because x was determined at 50°C, whereas the successive steps occurred at different temperatures:

$$t_{\text{reduced}} = \sum \frac{t_{\text{real}}}{\left(\frac{a_{T \rightarrow T_0}}{a_{50 \rightarrow T_0}} \right)} \quad (15)$$

where t_{real} is the real time. Finally, x is given, with eqs. (12) and (15), by the following equation:

$$x = \sqrt{\frac{t_{\text{reduced}}}{\lambda(T = 50^\circ\text{C})}} \quad (16)$$

The total x was calculated to be equal to around 8400 R_g . As a result, we expected that only the $G' = f(t)$ curve drawn for $e = 10,000 R_g$ should have differed from the others, whereas the other curves drawn for $e = 1000, 2000,$ and $5000 R_g$ should have been superimposed. However, as shown in Figure 14, the increase in G' as a function of the reaction time was strongly

dependent on the amount of preshear generated during the mixing step, which indicated that x was overestimated. This could be explained because the molar mass sharply increased with the reaction time and because the grafting reaction results in a highly grafted and branched structure, which prevented any further diffusion. As a result, the diffusion was no longer possible before the end of the apparent induction period, and the calculated value was strongly overestimated.

Moreover, we could conclude from Figure 14 that the higher the amount of preshear was, the thinner were the layers and the more pronounced was the increase in G' . On the other hand, we find that for e 's lower than 1000 R_g , the G' versus reaction time curves no longer depended on the amount of preshear because the 1000 R_g curve was well superimposed with the curve of a a5g5 blend prepared in the batch mixer that is known to generate a homogeneous blend.

In a first attempt to interpret these results, a simple model of multilayer structure can be proposed, as shown in Figure 15. The initial structure was com-

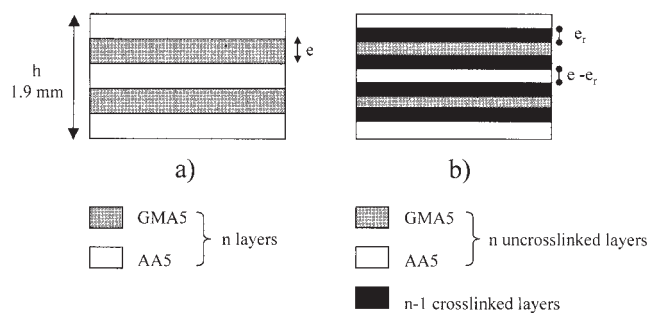


Figure 15 Structure of the multilayer generated (a) during the mixing step and (b) after the reaction.

posed of pure, alternated terpolymer layers. As the reaction proceeded, a crosslinked layer appeared at each interface, and the structure became an assembly of alternated pure terpolymer and crosslinked layers.

We estimated, from the experimental G' , the thickness of the crosslinked layers (e_r) and, thus, the crosslinked fraction in the following way.

For a layer in the parallel plate geometry, the complex strain (γ^*) and complex torque (C^*) are given by the following relations:

$$\gamma^* = \frac{R\alpha^*}{h} \quad (17)$$

$$\alpha^* = \alpha_0 e^{i\omega t} \quad (18)$$

$$C^* = \frac{\pi\alpha_0 R^4}{2h} G^*(\omega) e^{i\omega t} = \frac{\pi R^4}{2h} \alpha^* G^*(\omega) \quad (19)$$

where G^* is the complex modulus, α^* is the complex angle, and ω is the frequency.

For a multilayer sample, with the simple model shown in Figure 15, C^* is the same in each layer ($C^* = C_i^*$), whereas the resulting α^* is the sum of all angles (α_i^* 's) of each layer number i .

$$C^* = \frac{\pi R^4}{2e_i} \alpha_i^* G_i^*(\omega) \quad (20)$$

$$\alpha^* = \sum_1^{2n-1} \alpha_i^* = \frac{2C^*}{\pi R^4} \sum_1^{2n-1} \frac{e_i}{G_i^*(\omega)} \quad (21)$$

where G_i^* and e_i are, the complex modulus and the thickness, respectively, of layer i . By identification of eqs. (19) and (21), the experimental G^* of the entire sample was related to e and to G^* of the different layers of the multilayer sample by the following relation:

$$G^*(\omega) = \frac{h}{\sum_1^{2n-1} \frac{e_i}{G_i^*(\omega)}} \quad (22)$$

In the same way, with the same simple model, we could also express the experimental complex compliance (J^*) of the entire sample as a function of e_i and the complex compliances of the different layers (J_i^* 's):

$$J^*(\omega) = \frac{\sum_1^{2n-1} e_i J_i^*(\omega)}{h} \quad (23)$$

TABLE IV
Gel Fraction e_r/e (%) Calculated from the Experimental G' According to Eq. (22) Compared with Experimental Crosslinked Fractions

ω (rad · s ⁻¹)	10,000 R_g (%)	5,000 R_g (%)	2,000 R_g (%)
100	70.5	75.9	86.1
50	82.3	85.0	92.4
10	94.9	96.1	98.2
5	97.1	97.9	99.0
1	99.3	100.0	99.0
Experimental	82.2	N/A	86.3

N/A = not applicable.

As schematically represented in Figure 15, as the crosslinking reaction proceeds, e_r appeared at the interface between the two pure layers of GMA5 and AA5 terpolymers. As a result, the multilayer sample was a successive assembly of n e 's ($e - e_r$; GMA5 or AA5, which have not yet reacted) and of $(n - 1)$ e_r 's.

G' and G'' of the n uncrosslinked layers were known. They were indeed deduced from the data obtained at 150°C to draw the master curves of the pure terpolymers. For $n - 1$ crosslinked layers, as the reaction time was long enough, we could make the following assumption: $G_r^* \approx G_r'$ are respectively the complex and storage modulus of a crosslinked layer. G' of the crosslinked layers was known at certain reaction times, as extracted from the data measured for the homogeneous blends either prepared in an internal mixer or obtained after a preshear of 1000 $R_{g,r}$, where we could consider that the whole thickness was crosslinked.

As a result, we could calculate the thickness of the crosslinked layers, and therefore, the crosslinked fraction, from eq. (22) and compare it with the crosslinked fraction obtained by chemical extraction. The results are summarized in Table IV for a reaction time of 16,000 s. As expected, the higher the amount of preshear was, the higher the crosslinked fraction was. We also observed a ω dependence: the lower the ω was, the higher the crosslinked fraction was. This could be explained simply by the ω dependence of the G'' and G' values of the uncrosslinked layer conversely to the crosslinked layer for which a plateau value was rapidly reached.¹⁶ As ω decreased, the uncrosslinked layer moduli decreased, whereas the crosslinked layer moduli remained at a constant value; the use of eq. (22) led, therefore, to an apparent increase in the crosslinked fraction.

Kinetics of the reaction in heterogeneous blends: Influence of ω . In the low- ω range, G' was strongly dependent on ω in the uncrosslinked polymers, whereas for the crosslinked polymers, G' reached a plateau value.^{12,14-16,20} For a long enough reaction time and for homogeneous samples, we indeed observed that G' was independent (or weakly dependent) on ω .

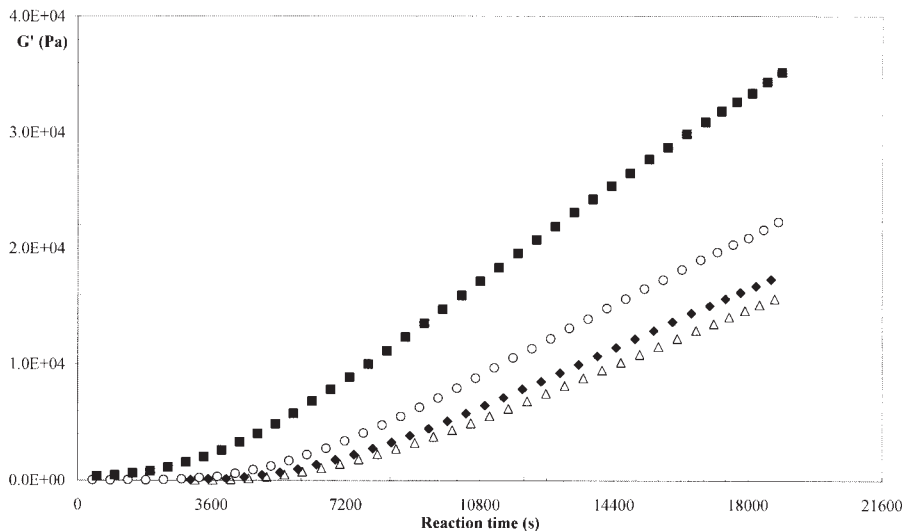


Figure 16 G' versus reaction time as a function of ω for $e = 10,000 R_g$: (■) 100, (○) 10, (◆) 1, and (△) 0.1 rad/s.

However, for the multilayer samples, we expected a strong ω dependence because these samples were an assembly of uncrosslinked layers, which were strongly dependent on ω , and crosslinked layers, which were weakly dependent on ω . Experiments were performed to explore the effect of the amount of shear generated during the mixing step on the ω dependence of G' . The results are shown in Figures 16 and 17. As clearly shown, the thicker the layers were, the lower the crosslinked fraction was, as demonstrated previously, and the greater was the ω dependence.

Kinetics of the reaction in heterogeneous blends: Influence of t_D . As discussed in the Blend Preparation section, preparing the samples directly in the parallel plate geometry of the mechanical spectrometer allowed us

to introduce an additional step into the process: a t_D or annealing time. Three t_D 's or annealing times were investigated: 1 h 30 min, 5 h 0 min, and 15 h 0 min. We first expected that the longer the t_D was, the greater would be the increase in G' . As shown in Figure 18, we observed just the opposite behavior.

G' was also found to increase as a function of t_D during this step (Fig. 19). Contrary to our previous assumptions, the crosslinking reaction may have already occurred at 60°C. We could explain this behavior by considering that the estimated apparent E_a of the reaction for a 5g5 blend was about 63 kJ/mol, whereas the E_a of self-diffusion was about 100 kJ/mol. As a result, the reaction was favored at low temperature with regard to the polymer chain diffusion, and a thin crosslinked layer was formed at the polymer in-

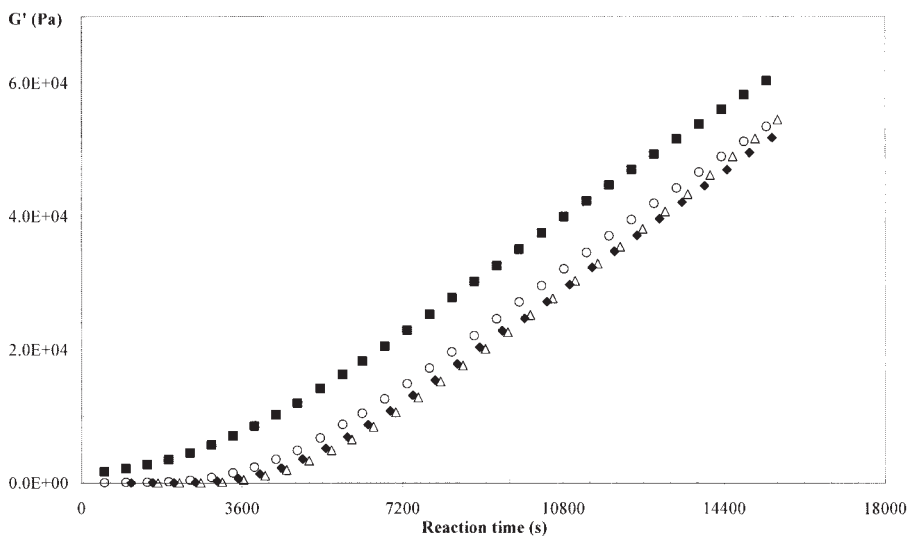


Figure 17 G' versus reaction time as a function of ω for $e = 2000 R_g$: (■) 100, (○) 10, (◆) 1, and (△) 0.1 rad/s.

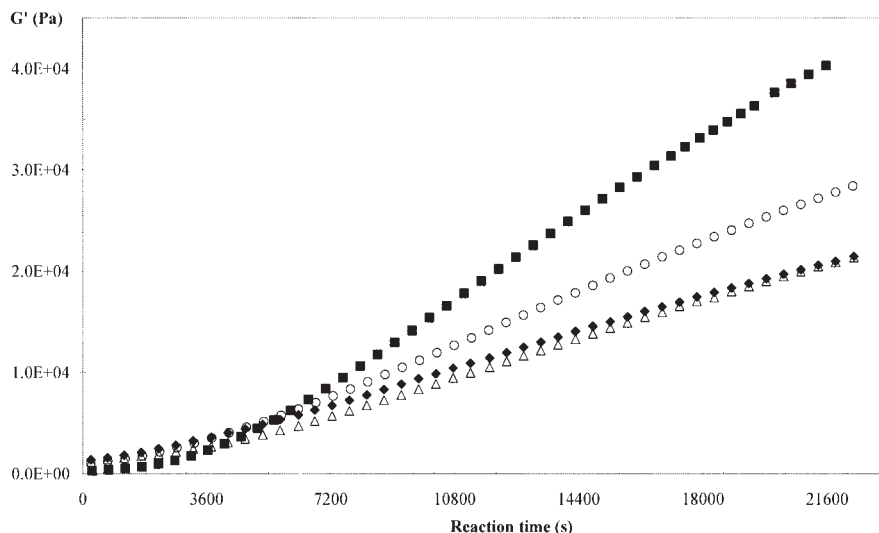


Figure 18 G' versus reaction time as a function of t_D at 100 rad/s for $e = 10,000 R_g$: $t_D = (\blacksquare)$ 0, (\circ) 1 h 30 min, (\triangle) 5 h 0 min, and (\blacklozenge) 15 h 0 min. $t = 0$ corresponds to the end of the annealing step.

terface. After an annealing time of about 6 h, G tended toward a plateau value, as the thin crosslinked layer prevented further chain diffusion and, thus, further crosslinking (Fig. 19). This was confirmed by experiments because the curves obtained during the reaction step after, respectively, 5 and 15 h of annealing time were superimposed (Fig. 18).

Because the crosslinking reaction began during this additional step, the interfaces were already fixed when the temperature was increased up to 150°C. As a result, the longer the annealing step was, the thinner were the crosslinked layers and the smaller was the final G' .

CONCLUSIONS

We investigated crosslinking reactions at the interphase of two multifunctional polymers bearing epoxy

and carboxylic acid units in the melt by following either the torque of an internal mixer or the increase of G' at a fixed ω , both as a function of the reaction time. The chemical components were chosen in such a way that the mixing step could be carried out independently of the reaction step.

IR spectrometry measurements were conducted to explore the potential reactions of the epoxy units in such a chemical system and allowed us to conclude that the main reaction was the crosslinking reaction between the epoxy and carboxylic acid units. We found also that the mixing step performed in the batch mixer did not allow the obtention of partially mixed blends. This mixing process indeed produced homogeneous samples. However, when the mixing step was conducted directly between the parallel plates of a dynamic rheometer, we obtained multilayer morphologies, as clearly shown by

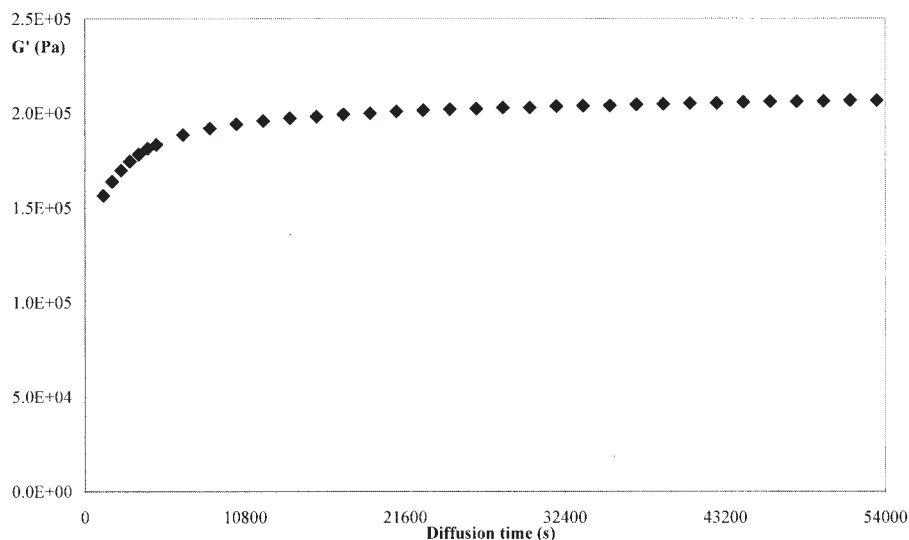


Figure 19 G' versus t_D at 100 rad/s for $e = 10,000 R_g$. $t = 0$ corresponds to the end of the mixing step.

X-ray microtomography. This mixing process allowed us to access intermediate mixing states and, therefore, nonhomogeneous blends.

With samples prepared from samples taken from the batch mixer operating at 120 rpm, we studied the influence of other parameters, such as the reaction temperature and the blend composition, on samples with a homogeneous morphology. Under these conditions, G' also became independent of the reaction time for long enough reaction times. From the value of G' at this plateau, the total reaction time (which exceeded 10 h even for the most reactive system) and the final network structure, for instance, Mf_{exp} , were determined. The rate of the reaction increased with increasing temperature and chain functionality. A first approach showed that reduced variables could be defined from G' and the reaction time with the initial concentration of functional units to obtain a master curve independent of the species concentration.

When the blend was prepared directly in the dynamic rheometer, the influence of the amount of shear generated was investigated. The higher the amount of preshear was, the thinner the layers were and the more pronounced the increase in G' , which was directly correlated to the reaction rate, was. From the variation in G' , a first attempt was made to calculate the crosslinked fraction. We used a simple model, which considered the reacted blend as a succession of crosslinked and uncrosslinked layers. The former layers were supposed to be as homogeneous crosslinked blends as those obtained in an internal mixer. The results were qualitatively in good agreement with the crosslinked fractions obtained by chemical extraction. Another study dealt with a further step introduced into the process: an annealing time after the mixing step at 60°C. The crosslinking reaction appeared to begin during this step. We concluded that the chosen chemical system allowed us to separate the mixing step but not the diffusion step from the crosslinking reaction.

In a further study, increasing the average molar mass or modifying the architecture of the terpolymer should allow us to slow down or accelerate chain diffusion independently from chemical reactivity and thus allow us to separate diffusion and reaction in the system. Also, we will make attempts to characterize the multilayer morphologies generated during the mixing step by taking into account a crosslinking gradient at the interface of the two polymers.

NOMENCLATURE

$a_{T \rightarrow T_0}$	shift factor from T to T_0
α	angle (rad)
C	torque ($\text{N} \cdot \text{m}$) or functional unit concentration (AA or GMA) (mol/L)

D	diffusion constant (m^2/s)
e	layer thickness (m)
E_a	activation energy (kJ/mol)
G	elastic modulus (Pa)
G'	storage modulus (Pa)
G''	loss modulus (Pa)
G^*	complex modulus (Pa)
γ	strain
$\dot{\gamma}$	shear rate (s^{-1})
h	sample disk height (m)
J	compliance (Pa^{-1})
k	crosslinking kinetics constant ($\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$)
k_b	Boltzmann constant (J/K)
λ	relaxation time (s)
Mf	number-average molecular mass between two consecutive functional groups (g/mol)
n	number of layers
N_A	Avogadro's number (mol^{-1})
ν_e	number of elastic strands per unit volume (m^{-3})
ω	frequency (rad/s)
ω_c	frequency crossover of the storage modulus and loss modulus curves (rad/s)
Φ	volume fraction
q	order of the crosslinking reaction with respect to the concentration of acrylic acid units
R	molar gas constant ($\text{J mol}^{-1} \text{K}^{-1}$) or sample disc radius (m)
R_g	radius of gyration (m)
ρ	density (kg/m^3)
T	temperature ($^{\circ}\text{C}$)
t	time (s)
T_g	glass-transition temperature ($^{\circ}\text{C}$)
x	diffusion distance (m)

Subscripts

0	initial (time) or reference (temperature)
1	mixing step
1'	annealing step
2	reaction step
D	diffusion step
exp	experimental
R	chemical reaction
r	crosslinked layer
real	real time
reduced	reduced variable
set	internal mixer programmed temperature
th	theoretical

Acronyms

AA	acrylic acid
AAy	terpolymer of butyl acrylate and methyl methacrylate with a number-average molecular mass between two consecutive acrylic acid groups of $y10^3$ g/mol
BA	butyl acrylate
GMA	glycidyl methacrylate

GMAx terpolymer of butyl acrylate and methyl methacrylate with a number-average molecular mass between two consecutive glycidyl methacrylate groups of $\times 10^3$ g/mol
MMA methyl methacrylate

References

1. Stewart, M. E.; George, S. E.; Miller, R. L.; Paul, D. R. *Polym Eng Sci* 1993, 33, 675.
2. Dagli, S.; Kamdar, K. M. *Polym Eng Sci* 1994, 34, 1709.
3. Guégan, P.; Macosko, C. W.; Ishizone, T.; Hirao, A.; Nakahama, S. *Macromolecules* 1994, 27, 993.
4. Kalfoglou, N. K.; Skafidas, D. S.; Kallitsis, J. K.; Lambert, J.-C.; van der Stappen, L. *Polymer* 1995, 36, 4453.
5. Kim, J. K.; Lee, H. *Polymer* 1996, 37, 305.
6. Sun, Y.-J.; Hu, G.-H.; Lambla, M.; Kotlar, H. K. *Polymer* 1996, 37, 4119.
7. Kim, S.; Kim, J. K.; Park, C. E. *Polymer* 1997, 38, 1809.
8. Jeon, H. K.; Kim, J. K. *Polymer* 1998, 39, 6227.
9. Kim, J. K.; Yi, D. K.; Jeon, H. K.; Park, C. E. *Polymer* 1999, 40, 2737.
10. Hale, W.; Keskkula, H.; Paul, D. R. *Polymer* 1999, 40, 365.
11. Martin, P.; Devaux, J.; Legras, R.; van Gurp, M.; van Duin, M. *Polymer* 2001, 42, 2463.
12. Lambla, M.; Druz, J.; Satyanarayana, N. *Makromol Chem* 1988, 189, 2703.
13. Legros, A.; Carreau, P. J.; Favis, B. D.; Michel, A. *Polymer* 1994, 35, 758.
14. Cirman, C.; Bouquey, M.; Terrisse, J.; Muller, R. *Appl Rheol* 1999, 9, 108.
15. Ernst, B.; Koenig, J.-F.; Muller, R. *Macromol Symp* 2000, 158, 43.
16. Muller, R.; Bouquey, M.; Mauguère, F.; Schlatter, G.; Serra, C.; Terrisse, J. *Appl Rheol* 2001, 11, 141.
17. Mussati, F. G.; Macosko, C. W. *Polym Eng Sci* 1973, 13, 236.
18. Harran, D.; Laudouard, A. *Rheol Acta* 1985, 24, 596.
19. Winter, H. H.; Morganelli, P.; Chambon, F. *Macromolecules* 1988, 21, 532.
20. Cassagnau, P.; Bert, M.; Verney, V.; Michel, A. *Polym Eng Sci* 1992, 32, 998.
21. Chiou, B.-S.; Khan, S. A. *Macromolecules* 1997, 30, 7322.
22. Asthana, H.; Jayaraman, K. *Macromolecules* 1999, 32, 3412.
23. Martin, J. S.; Laza, J. M.; Morrás, M. L.; Rodríguez, M.; León, L. M. *Polymer* 2000, 41, 4203.
24. Hoffman, W.; Fisch, W. *FATIPEC Cong Rev* 1962, 243.
25. Muller, R.; Picot, C.; Zang, Y. H.; Froelich, D. *Macromolecules* 1990, 23, 2577.
26. Picot, C.; Duplessix, R.; Decker, D.; Benoit, H.; Boué, F.; Cotton, J. P.; Daoud, M.; Farnoux, B.; Jannink, G.; Nierlich, M.; de Vries, A. J.; Pincus, P. *Macromolecules* 1977, 10, 436.