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Rheological characterization of interfacial crosslinking in blends of reactive copolymers.

Benoit Ernst, Jean-François Koenig, René Muller*

ELF-ATOCHEM, CERDATO-LEM, 27470 Serquigny, France
* ECPM, Polymer Department, 25 rue Becquerel, 67087 Strasbourg Cedex2, France

SUMMARY: The interfacial crosslinking reaction in molten blends of two functionalized ethylene copolymers was followed by rheological measurements. The blends were directly prepared in the rheometer. Due to the low melting temperature of the blend components, it was possible to carry out separately the mixing by steady shearing at low temperature, and the interfacial reaction followed by small amplitude dynamic measurements at higher temperatures. The influence of several parameters on the interfacial reaction was studied: the reaction temperature, the amount of shear during mixing, the blend composition and the compatibility and reactivity of the blend components.

Introduction

Blending of polymers is an important route to the formation of new materials with improved properties. For immiscible systems, the scale of the dispersion can be reduced and the morphology stabilized by reactive blending. The interfacial reaction between the suitably functionalized blend components forms copolymer molecules at the interface which are believed to lower interfacial tension and to reduce coalescence1). Multiple functionality of both blend components may lead to the formation of a crosslinked interface.

Linear viscoelastic properties of a molten blend are sensitive to interfacial tension and morphology and can be described by emulsion models2). Rheological measurements have also been used to characterize the formation of graft copolymer at the interface as well as crosslinking in the molten state3). Linear shear4-6) on dispersed morphologies and extensional measurements7) on multilayered structures were shown to be sensitive to an interfacial grafting or crosslinking reaction.

In this paper we are concerned with the control of the coupling between the generation of interfacial area during mixing and the interfacial grafting or crosslinking reaction between blend components. For this purpose, the chemical system had to be chosen so that the kinetics of the reaction is slow enough compared to the time of blending at a temperature where the

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blend components are above their melting or glass transition temperatures. Rubbery ethylene copolymers, with melting temperatures below 100°C and containing reactive functions like maleic anhydride (MAH) or glycidyl methacrylate (GMA) were used[8)]. The rate of the reaction between the MAH and GMA functions is very slow for temperatures below 140°C, which allows to carry out in a decoupled way the mixing around 100°C, and the reaction at higher temperatures.

Products

The reactive polymers were two statistic terpolymers of ethylene, acrylic ester and maleic anhydride (samples coded as MAH1 and MAH2) and three statistic terpolymers of ethylene, acrylic ester and glycidyl methacrylate (samples coded as GMA1 , GMA2 and GMA3). A copolymer (coded as NR1) with the same nature and content of acrylic comonomer than sample MAH1 but without maleic anhydride functions has also been used to compare the behavior of a reactive blend (MAH1/GMA) to that of a non reactive blend (NR1/GMA). All polymers were produced by a high pressure polymerization process. The nature and content of comonomers are summarized in Table 1.

Table 1. Composition of reactive terpolymers and non reactive copolymer.

Sample	Acrylic Ester	Weight (and molar) fractions of acrylic ester	Weight (and molar) fractions of maleic anhydride	Weight (and molar) fractions of glycidyl methacrylate
MAH1	Butyl Acrylate	0.17 (0.05)	0.03 (0.01)	-
MAH2	Ethyl Acrylate	0.31 (0.11)	0.01 (0.005)	-
GMA1	Methyl Acrylate	0.24 (0.1)	-	0.08 (0.02)
GMA2	Methyl Acrylate	0.24 (0.1)	-	0.03 (0.007)
GMA3	Methyl Acrylate	0.28 (0.11)	-	0.01 (0.002)
NR1	Butyl Acrylate	0.17 (0.05)	-	-

Table 2 shows the molecular weight characteristics and the melting temperature determined by DSC. It is seen that the polymers have broad molecular weight distributions but similar values of the weight average molecular weight. The DSC data show that the melting temperature decreases and the breadth of the melting peak increases with increasing comonomer content. At temperatures higher than 105°C, all samples are in the molten state.

Table 2. Weight average molecular weight and polydispersity index determined by SEC in trichlorobenzene at 145°C. Temperature at the melting peak

Sample	M_w (g/mole)	M_w/M_n	T_m peak (°C)	T_m (upper limit of melting peak) (°C)	Ea (kJ/mole)
MAH1	89 000	5.9	89	100	123
MAH2	96 000	5.5	64	83	78
GMA1	101 000	8.6	61	80	79
GMA2	87 000	5.4	65	84	82
GMA3			64	83	
NR1	86 000	5.2	96	104	68

Therefore, melt-blending of reactive polymer pairs can be carried out at temperatures as low as 105°C. As will be shown below, at this temperature the reaction between the maleic anhydride and the glycidyl methacrylate functions without catalyst is very slow and can be neglected during the time of the blending stage.

Dynamic mechanical measurements on pure polymers

The rheological properties in the melt of all samples were characterized by dynamic mechanical measurements in the parallel plate geometry (diameter 25 mm ; thickness 2 mm) with a Rheometric Scientific RMS-800 mechanical spectrometer. The dynamic moduli were measured in the frequency range [0.1 rad/s - 100 rad/s] at different temperatures (90°C, 120°C and 140°C for MAH2 and GMA, and 120°C, 140°C and 160°C for MAH1 and NR1 samples). The temperature dependence of the shift factors obeys an Arrhenius type equation with the values of the activation energies given in Table 2. With these values of activation energies, master curves were drawn at 105°C which are shown in Fig. 1. We see that in the range [0.5 s^{-1} – 3 s^{-1}] corresponding to the shear rates used for blending, the viscosities of all samples are close. The lowest value is found for the GMA samples with a ratio of about 0.6 compared to the other polymers. The same remarks also hold for the elastic modulus. For the sake of clarity, the curves for sample GMA3 which is very close to those of sample GMA2 are not shown on the figure.

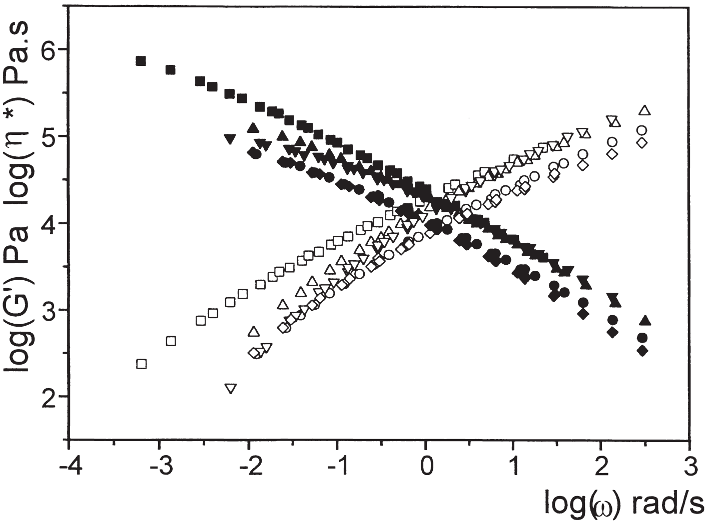

Fig 1: Storage modulus (open symbols) and dynamic viscosity (solid symbols) versus frequency at 105°C for the components : MAH1 (□,■), MAH2 (Δ,▲), GMA1 (O,●), GMA2 (◊,◆), NR1 (∇,▼).

Blending, diffusion and reaction stages

Blending was carried out in the rheometer using the above described parallel plate geometry. We started with specimens formed by two sectors of a disk, one for each blend component, with angles proportional to the desired volume fraction of the blend. For instance, a 50/50 blend was obtained with two adjacent half disks placed between the rheometer plates.

Since the objective was to decouple the blending from the reaction, these specimens were then sheared at a temperature T_0 as low as possible but where both polymers are in the molten state. All over this study, T_0 was equal to 105°C. The total applied shear γ_R, measured in shear units at the outer rim R=12.5 mm of the specimen, was between 500 and 10 000. In order to reduce the blending time, but keeping the normal force within the measuring range of the transducer [0 – 13N], the shear rate was gradually increased. A typical sequence for a total shear of 5000 was : 200s at $0.5s^{-1}$, 300s at $1s^{-1}$, 200s at $2s^{-1}$, 1400s at $3s^{-1}$. Once the total shear strain was reached, the sample was kept at the blending temperature T_0 during a time t_D. During this time, diffusion of the chains at the interface may occur without significant grafting or crosslinking. Finally, after this diffusion stage, the temperature was rapidly increased up to the reaction temperature T_1. The dynamic viscoelastic properties were then measured at this temperature as a function of the reaction time t_r in the frequency range [0.1 rad/s - 100 rad/s]. A typical result is shown in Fig. 2 for γ_R=1000 and T_1=180°C. The curves for the storage modulus G' corresponding to the reacted blends are well above those of the components. A plateau appears at low frequencies, the level of which increases with the reaction time. It can be noticed that the reaction has already started when the thermal equilibration of the sample at 180°C is complete (t_r=0) which takes between 3 and 5 minutes.

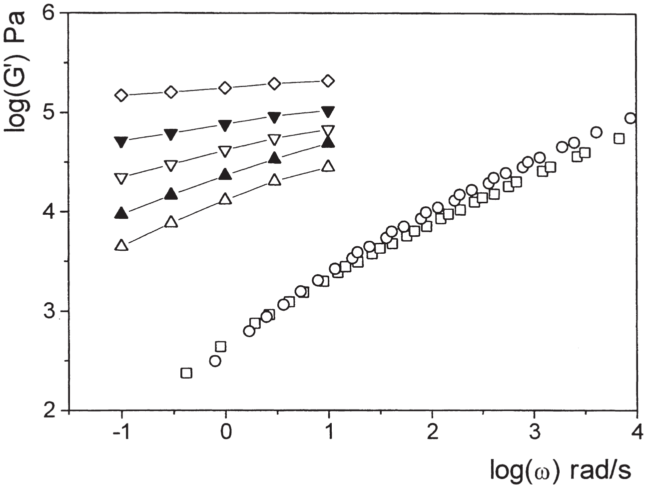

Fig 2: Storage modulus versus frequency at 180°C for MAH1/GMA1 50/50 blend at different reaction times t_r after thermal equilibration and after a preshear of γ_R=1000 at 105°C : t_r=0s (Δ), t_r=600s (▲), t_r=3000s (∇), t_r=10000s (▼), t_r=50000s (◊). Storage moduli of pure components at the same temperature : MAH1 (□), GMA1 (O).

Since the influence of the interfacial reaction is more sensitive at low frequencies, we plotted the value of G' and G'' at the lowest frequency (ω= 0.1 rad/s) as a function of the reaction time. The plots corresponding to the data of Fig. 2 are shown in linear scales in Fig. 3. Whereas the loss modulus reaches an almost constant value after about 10 000 s, the storage modulus continuously increases even after a reaction time of 50 000s and the behavior of the sample becomes mainly elastic.

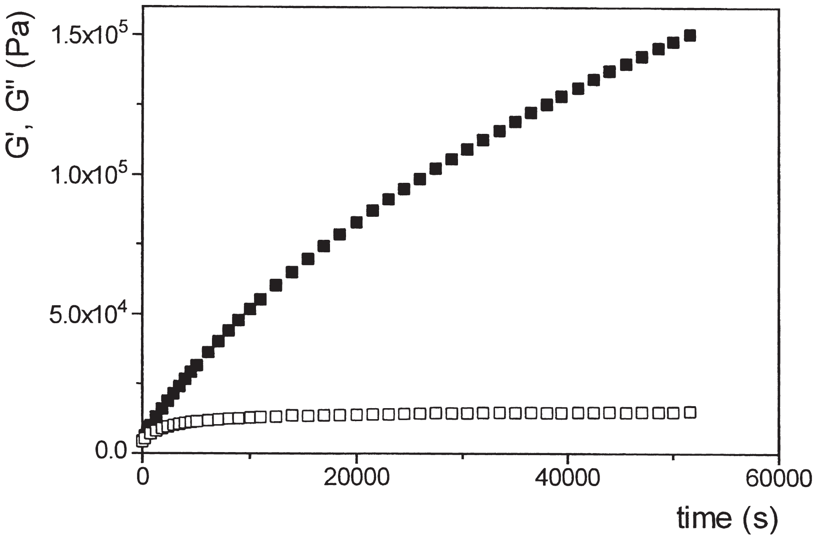

Fig. 3: Storage (■) and loss (□) modulus at 0.1 rad.s^{-1} versus reaction time at 180°C for the experimental conditions of Fig. 2.

Influence of reaction temperature

Several samples of MAH1/GMA1 50/50 blends were mixed at 105°C with the same amount of preshear strain, γ_R=5000, and then reacted at different temperatures in the range [105-200°C]. The results for the evolution of G' as a function of the reaction time are shown in Fig. 4. They confirm that the reaction rate increases with the temperature and that at the mixing temperature of 105°C, almost no reaction occurs within the mixing time (typically 2000s).

As suggested by recent theoretical work$^{9-10)}$ on the kinetics of formation of diblock copolymer at a polymer/polymer interface, which have shown that in a given time range the process is diffusion controlled, we tried to fit a square-root law $G' = A\sqrt{t_r - B}$ of the reaction time on these curves. As shown in Fig. 5 for the lowest reaction temperature, this was only possible in an intermediate time range: at short times, a different mechanism controls the reaction kinetics whereas at long times, the increase of G' is probably slowed down by steric hindrance due to the reacted interfacial layer. For higher reaction temperatures, the time offset B is usually negative, due to some reaction starting during thermal equilibration.

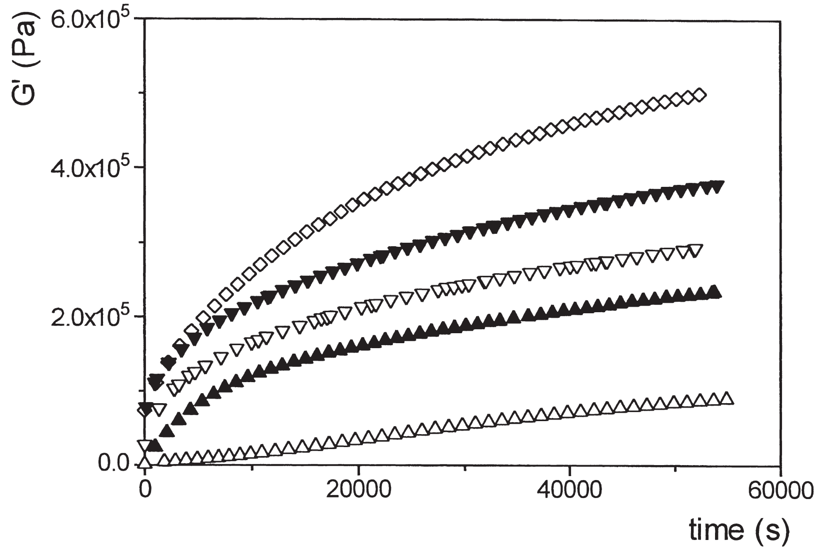

Fig. 4: Storage modulus at 0.1 rad.s^{-1} versus reaction time at different temperatures for MAH1/GMA1 50/50 blend after a preshear of γ_R=5000 at 105°C : 105°C (Δ), 140°C (▲), 160°C (∇), 180°C (▼), 200°C (◊).

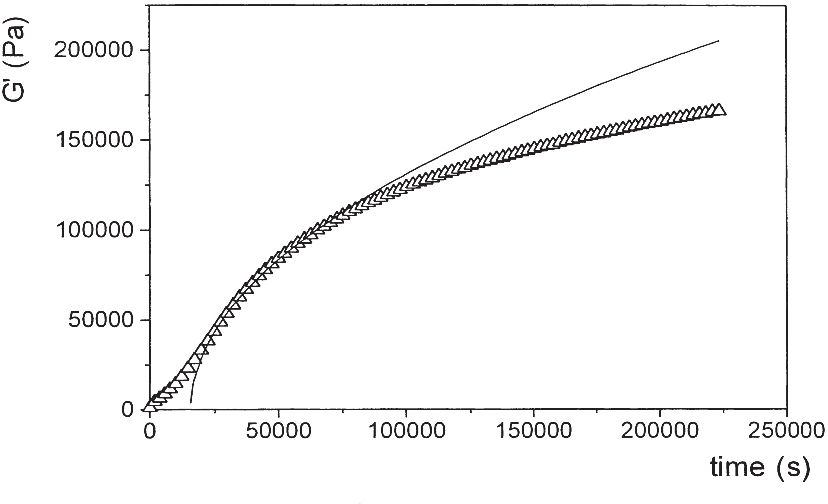

Fig. 5: Storage modulus at 0.1 rad.s^{-1} versus reaction time at 105°C for MAH1/GMA1 50/50 blend (preshear : γ_R =5000) : data (Δ), fit to a square-root law in the intermediate regime (solid line).

Influence of amount of preshear

For these measurements, the reaction temperature was kept constant at 180°C and several samples of MAH1/GMA1 50/50 blend were prepared at 105°C with various amounts of shear strain in the range [500-10 000], leading to different values of the interfacial area per unit volume. The increase in storage modulus at 180°C of these samples is shown in Fig. 6. The results confirm the importance of interfacial area in the blend on the changes in elastic modulus during reaction. Up to γ_R=1000 a linear increase in G' is observed whereas a more pronounced increase with reaction time is found for shear strains above 2000. For strains higher than 5000, the G' versus t_r curve no longer depends on the amount of preshear, indicating that a steady morphology may have been reached during the mixing stage. On the same curve, we also plotted the G'(t_r) curve for the non reactive NR1/GMA1 blend sheared at γ_R=5000. Obviously no measurable increase in G' is found for this blend, confirming that the phenomena observed for the reactive systems are due to the intermolecular chemical reaction at the interfaces.

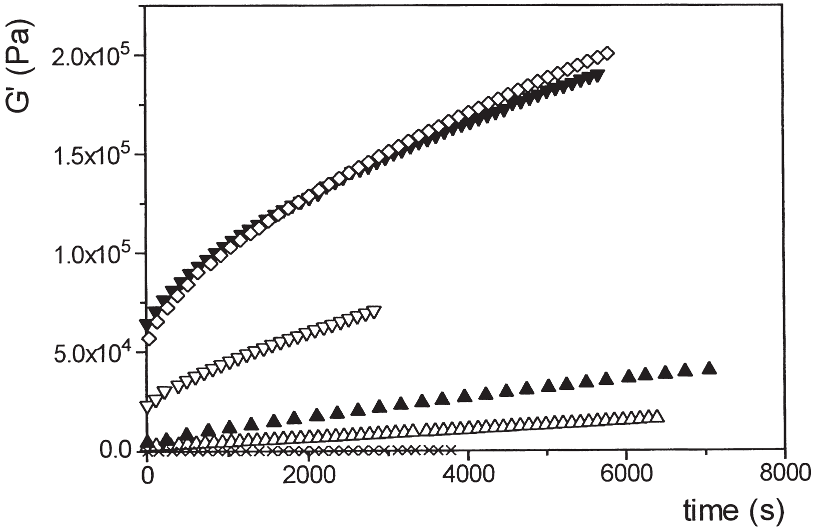

Fig. 6: Storage modulus at 0.1 rad.s^{-1} versus reaction time at 180°C for MAH1/GMA1 50/50 blend and different values of the preshear γ_R at 105°C : 500 (Δ), 1000 (▲), 2000 (∇), 5000 (▼), 10 000 (◊). Same curve for NR1/GMA1 50/50 blend with a preshear of γ_R =5000 at 105°C (×).

To characterize the structure of the reacted samples, solvent extraction experiment were carried out in boiling xylene. They confirmed the rheological data, since for amounts of preshear lower than 1000, the reacted samples eventually peeled off in the solvent, indicating a layered structure[11]. For γ_R higher than 2000 the samples swelled but kept their shape even after 48h in the solvent, indicating a cocotinuous morphology [12] of the blend and resulting in a continuous interface. This in turn gives rise to a sample spanning network structure[13] after reaction, which seems to be directly related with the high values of G' observed.

Influence of blend composition

Here the reaction temperature (180°C) and the amount of preshear (5000) were kept constant and the composition of a series of MAH1/GMA1 blends was varied between 90/10 and 10/90. Composition 66/34 corresponds to stoichiometry of the MAH and GMA groups. The data in Fig. 7 show that the highest increase in G' is obtained for the 50/50 composition, whereas symmetric blend compositions result in similar levels of G'.

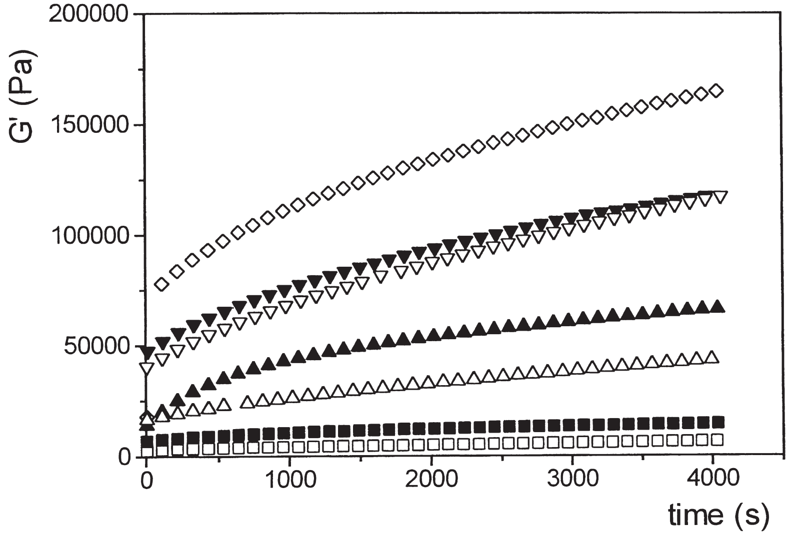

Fig. 7: Storage modulus at 0.1 rad.s^{-1} versus reaction time at 180°C for MAH1/GMA1 blends at different compositions. The preshear was the same for all samples (γ_R =5000) : 50/50 (◊), 66/34 (▽), 34/66 (▼), 80/20 (△), 20/80 (▲), 90/10 (□).

It comes out from these results that the interfacial crosslinking reaction is controlled by the amount of interfacial area produced by the mixing rather than by the stoechiometric ratio of the reactive groups. On the other hand, a minimum concentration of the minor phase of about 20% seems to be required to end up with significant values of G’ in the reacted blend. According to the above assumptions, this concentration would correspond to the formation of a cocontinuous morphology.

Influence of reactivity of the GMA phase

Fig. 8 shows the results obtained for 50/50 blends based on MAH1 and three GMA with different content of reactive comonomer. As seen in Table 1, the nature and concentration of acrylic comonomer are similar for GMA1, GMA2 and GMA3. The results (T_I=180°C, γ_R=5000) confirm that the level of G’ in the reacted blends increase with the reactivity of the GMA phase. To explain the very small values obtained for the MAH1/GMA3 blend, the average number of reactive groups per chain were calculated from the number average molecular weight: we found 3.9, 3 and 0.9 for GMA1, GMA2 and GMA3 respectively. Therefore, there are not enough reactive functions per chain in the GMA3 copolymer to lead to interfacial crosslinking. Only grafted species are formed at the interface which ends up with much lower values of G’.

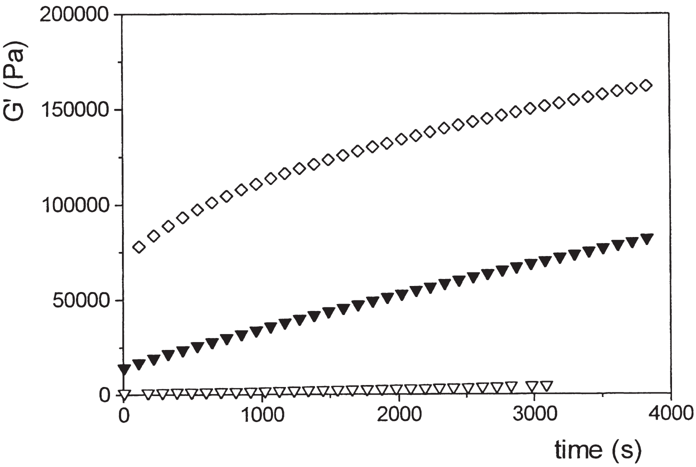

Fig. 8: Storage modulus at 0.1 rad.s^{-1} versus reaction time at 180°C for MAH1/GMA 50/50 blends with different reactivities of the GMA phase. The preshear was the same for all samples (γ_R =5000) : GMA1 (◊),GMA2 (▼), GMA3 (∇).

Influence of blend miscibility and diffusion time

A comparison of MAH1/GMA1 and MAH2/GMA1 50/50 blends is less obvious than in the preceding case. As a matter of fact, for MAH1 and MAH2 both the amount of reactive MAH functions and the nature and concentration of acrylic comonomer differ. The data in Fig. 9 (T_I=180°C, γ_R=5000) obtained after a diffusion time t_D=40 min at 105°C indicate that the highest level in G' is actually obtained for the blend with the less reactive polymer (MAH2). A possible explanation may be the higher compatibility of MAH2 with GMA1, due to the nature of the acrylic comonomers (MA for GMA1, EA for MAH2 vs. BA for MAH1). To confirm this assumption, the same tests were repeated with a diffusion time increased up to 5 hours. The results show that increasing the diffusion time at 105°C before reaction only affects in a significant way the results for the more compatible MAH2/GMA1 blend. This can be qualitatively understood since for the more compatible system, the equilibrium thickness of the interfacial layer is higher and the same holds for the final volume of crosslinked material after diffusion and reaction.

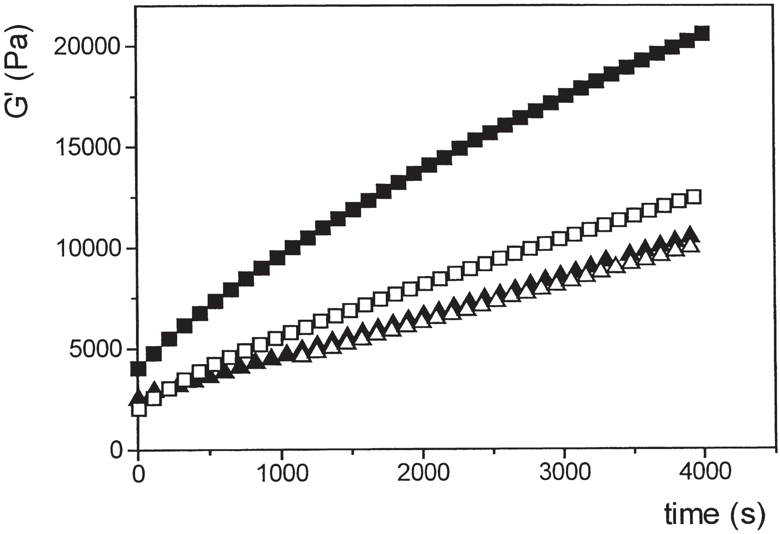

Fig. 9: Storage modulus at 0.1 rad.s^{-1} versus reaction time at 180°C for MAH1/GMA1 50/50 (Δ,▲) and MAH2/GMA1 50/50 (□,■) blends after 40 min (Δ,□) and 5 h (▲,■) diffusion at 105°C (preshear : γ_R =5000).

Influence of coupled mixing and reaction

With the experimental method used in the present study it is easy to carry out an experiment where the mixing and reaction stages are coupled, merely by carrying out the mixing at the same high temperature than the reaction: $T_0=T_1=180°C$. Several tests have been realized under these conditions and for different shear rates in the range [1-10s^{-1}]. It was not possible to further increase the shear rate without overloading the torque transducer. Fig. 10 shows the time evolution of the torque divided by the shear rate in arbitrary units during the premixing stage. It is observed that for the lowest shear rates, the torque increases with time, indicating that for these experimental conditions, the reaction during the mixing can no longer be neglected and affects the viscosity of the blend.

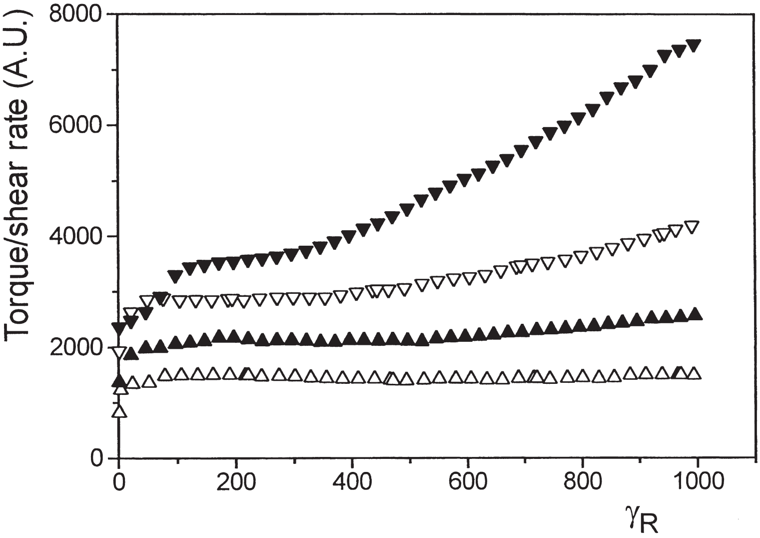

Fig. 10: Torque divided by shear rate during the mixing stage at 180°C of MAH1/GMA1 50/50 blends at different shear rates: (Δ) 1s^{-1} , (▲) 2s^{-1} , (∇) 4s^{-1} , (▼) 10s^{-1} .

The data in Fig. 11, all obtained for the same amount of preshear (γ_R=1000), clearly show that the values of G' for the reacted blends are almost five times higher if the mixing is carried out without reaction at low temperature. This may indicate that if the rate of the interfacial reaction becomes of the same order than the rate of renewal of interface by mixing, the final interfacial area produced by the flow decreases. This is confirmed by the small but reproducible influence of the shear rate during the premix stage on the final G' value: increasing the shear rate during mixing increases the level of the G' curve which becomes closer to the curve for the uncoupled test. This result is in agreement with the above explanation: the higher the shear rate (or rate of interfacial renewal) the closer the test becomes to the uncoupled situation.

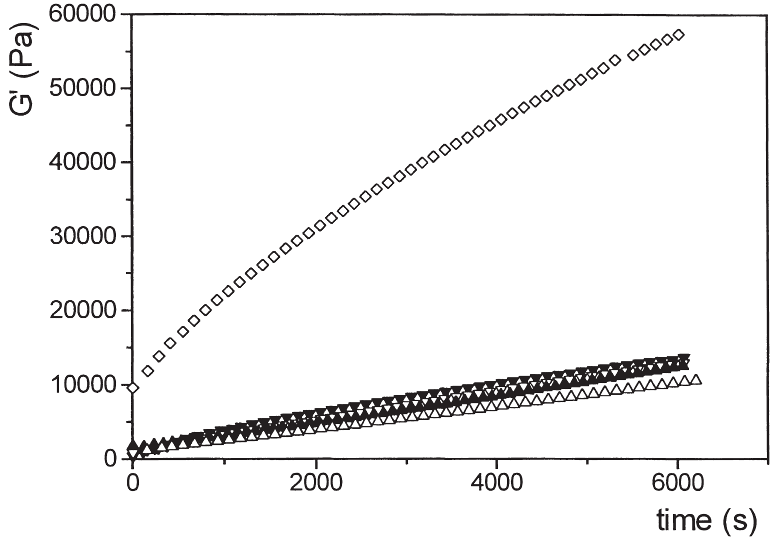

Fig. 11: Storage modulus at 0.1 rad.s^{-1} versus reaction time at 180°C for MAH1/GMA1 50/50 blends premixed either at 105°C (◊) or at 180°C and different shear rates (Δ,▲,∇,▼): (Δ) 1s^{-1} , (▲) 2s^{-1} , (∇) 4s^{-1} , (▼) 10s^{-1} .

Conclusion

An original yet very simple experimental method has been proposed to characterize via rheological measurements the interfacial reaction in a reactive polymer blend. For the low melting temperature systems investigated in the present study, it was possible to separate the mixing of the two blend components in the parallel plate geometry of a rotational rheometer from the interfacial reaction followed on the same specimen after increasing the temperature by using small amplitude dynamic tests.

The storage modulus was measured as a function of time during reaction and was found to be sensitive to several material and blending parameters like for instance: the reaction temperature, the amount of shear during the premix stage, the blend composition, the reactivity and compatibility of the blend components. In particular, it was shown that for systems with low interfacial energy the interfacial reaction is favored if the chains are allowed to diffuse before the reaction takes place. On the other hand, the highest levels of interfacial crosslinking, as measured by the modulus G', are obtained for 50/50 composition blends, which lead to the highest values of interfacial area for nearly isoviscous systems. Finally it was shown that in order to enhance the level of crosslinking in the blend, it is more favorable to carry out the mixing as a first separate step where no interfacial reaction takes place.

Acknowledgments

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