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Rheological characterization of interfacial reaction in reactive polymer blends

Michel Bouquey(✉), René Muller, Guy Schlatter, Christophe Serra

ECPM – Laboratoire d'Ingénierie des Polymères pour les Hautes Technologies
25, rue Becquerel, 67087 Strasbourg cedex 2, France

E-mail: bouqueym@ecpm.u-strasbg.fr

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Summary

An original method has been developped which allows to study the influence of chain diffusion on the reaction kinetics in reactive polymer blends. Blends with controlled multilayer morphologies were directly prepared in a rotational rheometer and time-dependent dynamic mechanical measurements allowed to follow the progress of the reaction. Model miscible copolymers with different acrylic monomers were prepared for this study by controlling the composition, molecular weight and average number of reactive groups per chain. Reduced variables for the modulus and the reaction time were introduced to compare the results obtained for different concentrations of reactive groups. In comparison to homogeneous blends, the normalized results for the multilayered structures show that the extent of the reaction depends directly on the chain length and is thus controlled by chain diffusion.

Introduction

Polymer blends are of growing importance in industry [1]. They offer the possibility to create new materials by combining the main characteristics of the blend components, which is economically more attractive than developping new polymers. However, the mechanical properties of these systems are generally poor and depend on the compatibility between the polymers. One way to improve this situation consists in modifying the chemical structure of the blend components with reactive groups allowing to generate grafted copolymers or even a crosslinked interphase during further processing steps [2-6].

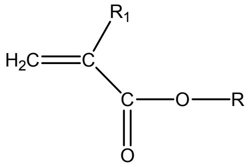
Although such modified polymers are available commercially and used in industry, many fundamental aspects are not really understood today, in particular the contribution of the kinetics of diffusion of the polymer chains at the blend interphase. This problem was considered by several groups in recent years [7,8]. In the present work, model random copolymers synthesized by radical polymerization were used: the system should allow to separate the creation of interfaces by shearing from the chemical reaction. For this purpose, the glass transition temperature of the polymers should be well below the temperature at which the kinetics of the interchain grafting reaction becomes significant. The ratio between comonomers was fixed in function of the desired glass transition temperature. On the other hand, the number of functional units per chain was controlled by the concentration of a third reactive comonomer. The functional groups carried by these reactive comonomers were chosen such as an interchain condensation reaction can occur between the two blend components. Finally, the chain lengths were adjusted by the concentration of initiator and transfert agent.

The first step of this work consisted in characterizing the reactive copolymers by different methods. The second part of the present study is devoted to compare the rheological measurements carried out on reactive blends before and during the crosslinking reaction. As will be shown, several parameters, like the reaction temperature, the mixing time, the blend composition or the chain length, influence the results. The final aim of this work is to etablish some fundamental rules allowing to predict the reactivity and the morphology of reactive polymer blends.

Experimental

The commercially available reactive polymers did not satisfy the requested conditions for our study. For this reason, copolymers have been synthesized with acrylic (R_1=H scheme 1) and methacrylic (R_1=CH_3 scheme 1) monomers. A large variety of such monomers with different lateral groups R carried by the ester function (scheme 1), are commercially available. Thus it is possible by selecting various comonomers, to adjust physical (glass transition temperature) and chemical (nature and number of reactive groups per chain) properties of the synthesized materials. In the frame of this study, the reactive groups are either R=epoxy or R=acid. For each reactive copolymer, a similar synthesis was carried out without the reactive comonomer.

For all copolymer compositions (reactive and non reactive), different chain lengths in a desired range were obtained.



Scheme 1: Chemical structure of monomers used to synthesize the different copolymers

Products

The chemical nature of the chain backbone was the same for both blend components. Butyl acrylate (BuA), (R_1=H, R=C_4H_9) and methyl methacrylate (MMA), (R_1=CH_3, R= CH_3) have been chosen as comonomers. Acrylic acid (AcA), (R_1=H, R=COOH) and glycidyl methacrylate (GMA), (R_1= CH_3, R=C_3H_5O) are the reactive comonomers used for the synthezis of reactive copolymers. Except for AcA, all monomers were destabilized by passing through an aluminia column (Alumina B, 1CN).

Synthesis conditions

The copolymers were produced by a bulk polymerization process at 80°C. Azo-bis-isobutyronitrile (AiBN) was used as an initiatior and the reaction was thermally activated. The number average molar masses have been controlled by the ratio AIBN/BuSH (butanethiol, transfert agent) and the quantity of comonomers. All reagents were introduced into small polypropylene (PP) tubes with a diameter of 2 cm which were immersed in water. In these conditions, the process allowed a good dissipation of the reaction heat and could be considered as nearly isothermal. The overall conversion was determined by weighting a given amount of the obtained copolymer before and after degasing under vaccum for 24 hours. Its value was always found to be between 96 and 97 %.

Instruments

Gel permeation chromatography (GPC) analysis was performed on a Waters Liquid Chromatograph system using six microstyragel columns having various porosities (10^6, mixture, 10^5, 10^4, 10^3 and 500Å), equipped with a Waters differential refractometer 401 using THF as eluent. Calibration was conducted with polymethylmethacrylate standards.

The rheological properties of all samples were characterized by dynamic mechanical measurements at small strains in the parallel plate geometry (diameter 25 mm ; thickness 2 mm) of a mechanical spectrometer (ARES ; Rheometric Scientific). The samples were shaped in the form of small 25 mm diameter discs and put in the parallel plate geometry of the rheometer. The dynamic moduli were measured in the frequency range [0.1 rad/s - 100 rad/s] at different temperatures in the range [30°C - 150°C]. The temperature dependence of the shift factors obeys an Arrhenius-type equation with the same activation energy (around 110 kJ/mole) for all copolymers.

Glass transition temperatures were measured by differential scanning calorimetry (DSC 131 ; Setaram) between –70°C and +150°C with a fixed heating rate (10°C/min).

Blend preparation

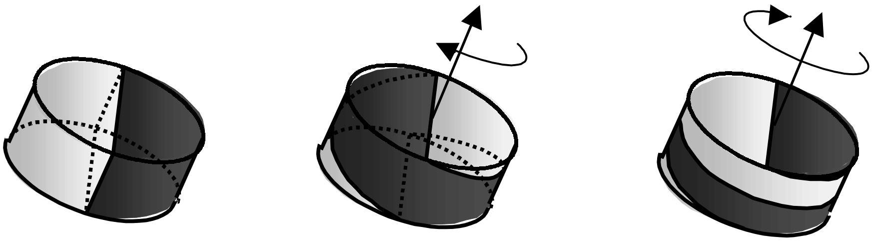
Blends of two mutually reactive copolymers (one of them carrying AcA - , the other one GMA functions) were prepared by three ways:

- In the first case, both polymers were dissolved in methylene chloride and dried under vaccum as described in a previous paper [9].
- The second method consisted in melt-blending in a batch mixer (Haake - Rheocord 9000). When the mixer was operated at 30 rpm during five minutes, the blends could be considered as homogeneous at a molecular level. This has been verified by heating up the blends after mixing to allow the condensation reaction between blend components. This reaction was followed by measuring the complex modulus as a function of reaction time at 150°C. No difference for the complex modulus curves could be observed with respect to the corresponding curves obtained for homogeneous solvent – blended samples [9].
- In the third method, the blends were directly obtained in the parallel plate geometry of a rotational rheometer [9]. Each reactive copolymer was first compression molded separately in the form of 25mm diameter discs. To obtain a 50/50 blend composition, these discs were cut in two parts along a diameter and two semi-discs (one of each component) were placed side by side between the plates of the rheometer (Figure 1a). Before shearing, the thickness of the sample was reduced to 1,9 mm, to make sure that the whole gap between the plates is filled with polymer.

The mixing was carried out by a steady rotation of one plate of the rheometer, which leads to a multilayer morphology [10] in which the thickness of the layers (e) is easily controlled by the amount of applied shear (Figures 1b and 1c). For high shear deformations the morphology of the sample can be considered as a multilayer structure. The layer thickness can be estimated from relation (2):

$$e = \frac{\pi . r}{\dot{\gamma}(r) . t} \qquad (2)$$

where $\dot{\gamma}$ **(r)** is the shear rate at radius r and **t** the shearing time. Since the shear rate in the parallel plate geometry is a linear function of the radius, the layer thickness is the same in the whole sample. The choice of the shear rate and mixing temperature T1 had to satisfy two conditions : a/ avoid interchain reaction during the mixing step, b/ torque and normal force during shearing should be kept low enough to stay in the measuring range of the transducer. These conditions were met by taking T1 = 50°C and shear rate at the outer rim of the discs = 0,5 s^{-1}.



1a 1b 1c

Figure 1: Preparation of the multilayer samples. 1a: initial position; 1b: after half a turn; 1c: after one turn. ■ AcA terpolymer □ GMA terpolymer

Characterization of blends components

Since the main objective of the present study was to separate the mixing and diffusion steps from the crosslinking reaction, it was necessary to control the structure of the copolymers. Different methods including DSC, GPC and viscoelastic measurements were used to characterize the synthezised copolymers and to choose the most adapted system.

Choice of backbone composition

It has been previously shown [11] that the reaction between an acid and an epoxy function without catalyst becomes significant above 100°C. For this reason, the blend preparation was carried out around 50°C to avoid any reaction during this step. Since the synthesized copolymers are amorphous, their viscosity in the molten state is mainly depending on the molecular weight and on the temperature gap with respect to Tg. For the typical range of molecular weight used in this study, it was found that the mixing temperature had to be at least 50°C above the glass transition temperature so that the viscosity was low enough to allow the mixing. On the other hand, it was important for practicle reasons to handle the samples at room temperature, which implies a low values of Tg. It appears therefore that the most appropriate value of Tg for our copolymers is around 0°C.

Supposing that the comonomers are randomly distributed along the chains, Fox' relation gives a single glass transition temperature for a given ratio between BuA and MMA comonomers. Several poly (BuA- co-MMA) copolymers were synthesized with different compositions by bulk radical polymerization. The expected number average molar masses (about 50 000 g/mol) were the same for each copolymer as seen in Table 1. The results for Tg values obtained by DSC for different compositions are given in Table 2 and compared to the calculated values according to Fox' relation. A good overall agreement is observed, which confirms the random structure of the synthesized copolymers.

Table 2 shows that the Tg value of the sample obtained with a BuA/MMA 60/40 weight ratio is very close to the desired value of 0°C. Therefore, all samples studied below were synthesized with this composition.

Table 1: Typical characterization of random copolymers prepared through radical bulk copolymerization of Butylacrylate and methylmethacrylate. Experimental conditions of entry are : [AIBN] = 1.12E-3 mol/L ; reaction time 14h at 80°C. a: $\overline{M}_n^{\textit{théo}}$ calculated from the initial concentrations of initiator, transfert agent and comonomers ; b: $\overline{M}_n^{\exp}$ calculated from SEC analysis; see experimental part ; c: $\overline{M}_w^{\exp}$ calculated from SEC analysis coupled with SALS apparatus

Reference	***[BuSH] mol.L^{-1}***	***[BuA] mol.L^{-1}***	***[MMA] mol.L^{-1}***	$\overline{M}_n^{\textit{théo}}$ *(a)*	$\overline{M}_n^{\exp}$ *(b)*	$\overline{M}_w^{\exp}$ (c)	$I = \frac{\overline{M}_w}{\overline{M}_n}$
306040	9.26E-2	4.28	3.65	33000	28000	55000	1.96
506040	5.36E-2	4.28	3.65	52000	50000	158000	3.16
706040	3.69E-2	4.28	3.65	68500	62000	178000	2.87
503070	5.36E-2	6.42	2.22	59500	55200	94400	1.71
505050	2.27E-2	4.58	3.58	36800	31000	62000	2.00

Choice of the molecular mass

Since the reactivity of the functional groups carried by the chains is independent of their composition and molecular mass, control of the total chain length provides a convenient way to study the influence of diffusion kinetics on the interchain condensation reaction. Only masses above the critical molecular mass Mc were considered. For the pure BuA and MMA homopolymers, the values of Mc are respectively 30 000 g/mol and 27 000 g/mole [12]. For our copolymers, we took therefore molar masses above 30 000 g/mole. A broad enough range for the values of chain length was necessary to obtain a significant effect on the diffusion kinetics. On the other hand the melt viscosity and therefore the molar mass of the chains had to be kept low enough to allow convenient mixing of the blends at 50°C. Therefore the investigated range of molecular masses was between 30 000 and 70 000 g/mole.

Table 2: Theorical values (calculated by Fox' relation) and experimental values determined by DSC (setaram DSC 131 ; - 70°C to + 150°C ; rate = 10°C / min) of glass transition temperatures for different ratios BuA/MMA in the copolymers (M_n about 50 000 g/mol)

Weight fraction BuA %	Weight fraction MMA %	Weight fraction AcA% or GMA% in the copolymer	$T_g^{theo,Fox}$ (°C)	$T_g^{\exp,DSC}$ (°C)
100	0	0	-45	-50
60	40	0	-6	3
60	40	1	-6	3
60	40	2	-6	4
50	50	0	7	15
40	60	0	28	36
30	70	0	37	42
0	100	0	110	94

Three poly(BuA-co-MMA) copolymer samples with molecular masses in this range were synthezised as described in the experimental section. The results of SEC analysis are reported in Table 1 and compared with those obtained by light scattering. A good correlation between experimental and expected values of molecular masses is observed, even if the polydispersity index is always higher than 2.

Dynamic mechanical measurements were carried out at different temperatures and master curves at 90°C were obtained for all samples. The results for the storage modulus G' are shown in Figure 2. The curves confirm the existence of a plateau zone which extends to low frequencies for increasing molecular mass. At higher frequencies close to the glass transition zone, the behavior should depend only on the copolymer composition and become independent of chain length, as confirmed by the curves in Figure 2.

Choice of number of reactive functions per chain

For each value of molecular mass, two reactive copolymers were synthezised by adding into the batch reactor a small amount (of the order of a few %) of either acrylic acid (AcA) or glycidyl methacrylate (GMA). It has been checked that this low amount of reactive comonomer does not significantly affect the value of Tg (see Table 2), the molar mass distribution and the viscoelastic behaviour in the melt.

For each molecular mass (30 000, 50 000 and 70 000) and for each kind (AcA or GMA) of reactive comonomer, three samples with different amounts of reactive comonomer were synthezised: The functionnality of a given terpolymer will be expressed by the number average molar mass M_f between two adjacent functionnal units on the same chain. The concentration of reactive comonomer was adjusted in order to obtain the following values of M_f : 2 000, 5 000 and 8 000 g/mol. It was assumed that the synthesized terpolymers are fully random. The characteristics of all sythezised reactive terpolymers are summarized in Table 3. In the following, these samples will be called according to the references given in the same table.

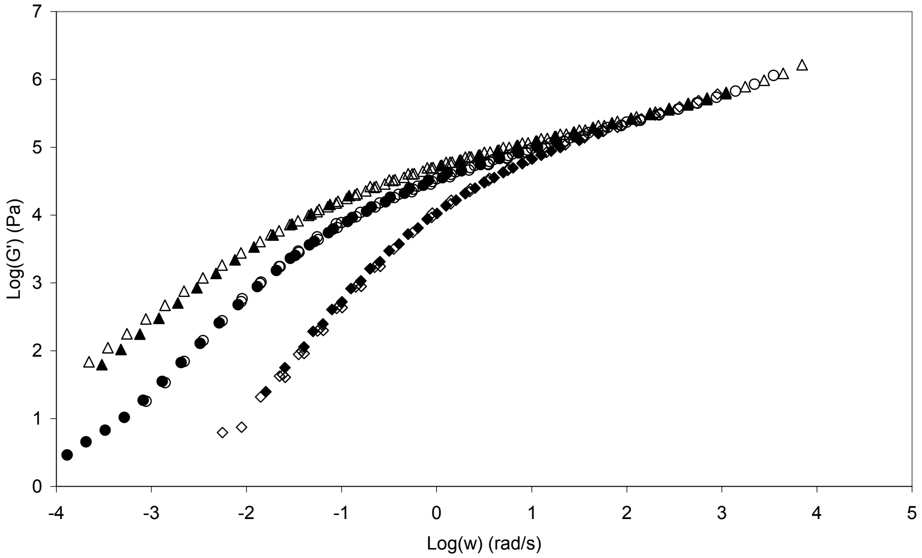


Figure 2: Master curves for G' at 90°C for non reactive polymers: △, ▲ 706040 ; ○,● 506040; ◇,◆ 306040 (see Table 1)

Results and discussion

Six different blends with three values of molar mass and two functionalities were prepared in the parallel plate geometry of the rheometer as described above: $30AcA_2/30GMA_2$, $30AcA_5/30GMA_5$, $50AcA_2/50GMA_2$, $50AcA_5/50GMA_5$, $70AcA_2/70GMA_2$ and $70AcA_5/70GMA_5$. The striation thickness for both phases of the obtained multilayer structure was fixed to 10µm by controlling the total applied shear.

For each blend, the temperature was increased to 150°C to start the condensation reaction and the storage modulus was continuously measured as a function of the reaction time. The results for all blends are shown in Figure 3.

As expected, the results confirm that the higher the concentration of reactive comonomer, the higher the values of G' for a given chain length and reaction time. On the other hand, we observe that for a given concentration of reactive comonomers, the highest increase of modulus is found for the shortest chains. As will be pointed out below, this effect is probably due to the diffusion rate of the chains which decreases with increasing chain length.

For homogeneous blends obtained in a batch mixer, and assuming that the reaction is of the first order, it was shown in a previous paper [9] that the curves of G' vs reaction time t could be normalized for different initial concentrations C_0 of reactive functions by dividing the values of G' by C_0 and by multiplying the reaction time t by C_0^2. A master curve could be obtained by this procedure thus confirming the assumption on the order of the reaction, and showing that for homogeneous blends the reaction is only controlled by the concentration of reactive groups in the blend.

Table 3: Composition of terpolymers poly(BuA-co-MMA-co-AcA) and terpolymers poly(BuA-co-MMA-co-GMA) synthesized with different molar masses and different functionalities in acrylic acid (AcA) and glycidylmethacrylate (GMA) but with the same initial ratio BuA/MMA=60/40 in weight. *(a)*: $\overline{M}_n^{th\acute{e}o}$ calculated from the initial concentrations of initiator, transfert agent and comonomers; *(b)*: $\overline{M}_n^{\exp}$ calculated from SEC analysis; see experimental part. Mf(AcA) and Mf(GMA) represent the average molar mass between two functional AcA or GMA units

(a) // (b)	**33 000 // 28 000**			**52 000 // 50 000**			**68 500 // 62 000**		
M_f (AcA)	2000	5000	8000	2000	5000	8000	2000	5000	8000
Samples	30 AcA$_2$	30 AcA$_5$	30 AcA$_8$	50 AcA$_2$	50 AcA$_5$	50 AcA$_8$	70 AcA$_2$	70 AcA$_5$	70 AcA$_8$
M_f (GMA)	2000	5000	8000	2000	5000	8000	2000	5000	8000
Samples	30 GMA$_2$	30 GMA$_5$	30 GMA$_8$	50 GMA$_2$	50 GMA$_5$	50 GMA$_8$	70 GMA$_2$	70 GMA$_5$	70 GMA$_8$

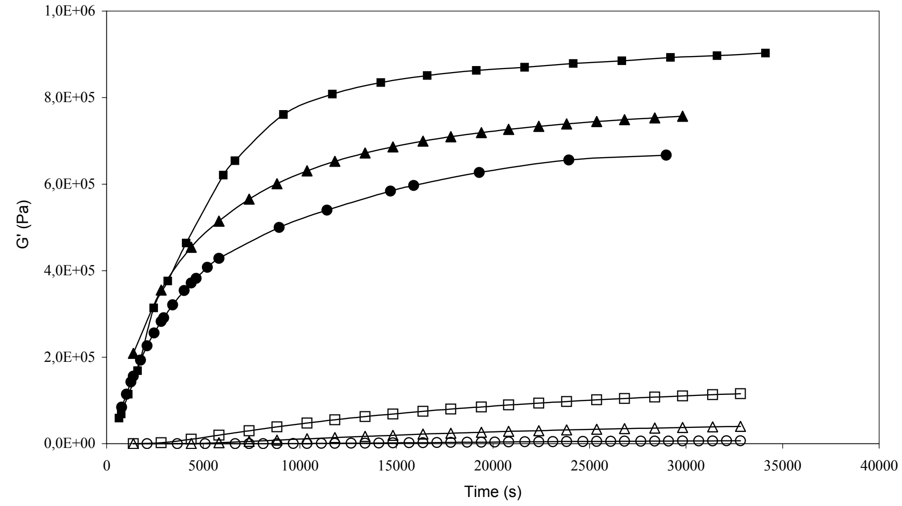


Figure 3: Elastic modulus as a function of reaction time for different blends with three values of molar mass and two functionalities ■30AcA$_2$/30GMA$_2$; □30AcA$_5$/30GMA$_5$; ▲50AcA$_2$/ 50GMA$_2$, △50AcA$_5$/50GMA$_5$; ●70AcA$_2$/70GMA$_2$; ○70AcA$_5$/70GMA$_5$

The same normalization procedure has been applied to the G' data obtained for the non homogeneous blends of the present study and the results are shown in Figure 4. The full line in this figure corresponds to the master curve obtained at the same temperature for homogeneous blends at different concentrations of reactive functions and for a chain length of 50 000 g/mole [9]. All data have been reduced to the highest concentration of reactive functions corresponding to the AcA$_2$/GMA$_2$ blend.

For all investigated systems, it is observed that the moduli of non homogeneous blends are below that of homogeneous blends at equivalent reaction time. As a consequence, it is not possible to apply the above described normalization procedure to non homogeneous blends which indicates that the reaction kinetics depends not only on the average concentration of reactive functions, but is also controlled by chain diffusion which slows down the reaction rate. The difference between the G’ curve for a non homogeneous blend and the master curve for homogeneous systems could therefore provide a way of characterizing the influence of chain diffusion on the reaction kinetics of reactive polymer blends.

Influence of chain length at a given concentration of reactive functions

As seen in Figure 4, the modulus at a given reaction time is a decreasing function of chain length, both for the AcA$_2$/GMA$_2$ and for the AcA$_5$/GMA$_5$ blends. This confirms the above assumption on the influence of diffusion on the reaction kinetics, since the diffusion rate is the lowest for the chains with the highest molar masses. Moreover, for the AcA$_2$/GMA$_2$ blends, a plateau value for G’ seems to be reached for reaction times of the order of 30 000 to 40 000 s, whereas the value of G’ still increases for homogeneous blends. This seems to indicate that the diffusion rate of free chains is further limited by the crosslinking density at the blend interfaces. It is not clear from the data of this study whether the same effect would also be observed for the AcA$_5$/GMA$_5$ blends. As a matter of fact, it was not possible to increase the reduced reaction time up to the same value than for the AcA$_2$/GMA$_2$ blends without thermal degradation of the polymers.

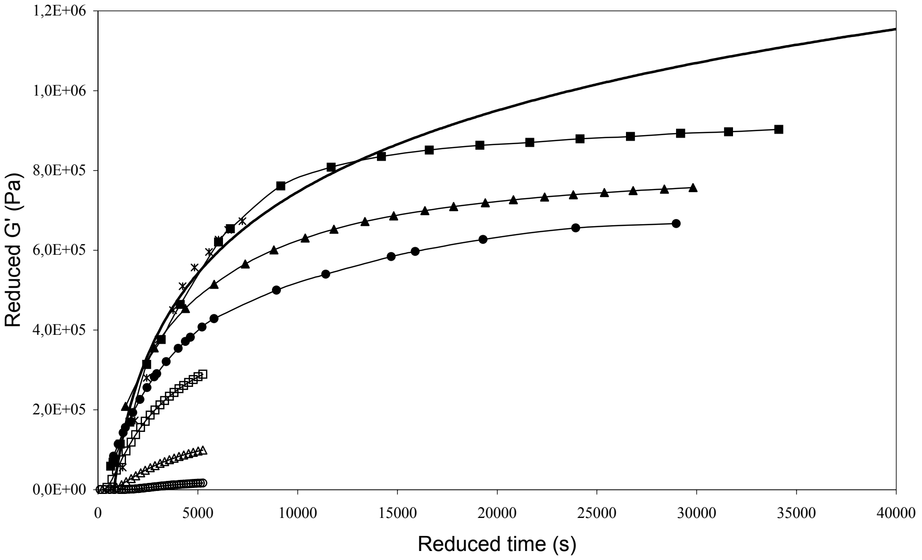


Figure 4: Reduced elastic modulus as a function of reduced time for different blends with three values of molar mass and two functionalities ■30AcA$_2$/30GMA$_2$; ●70AcA$_2$/70GMA$_2$; ▲50AcA$_2$/50GMA$_2$; □30AcA$_5$/30GMA$_5$ Normalized ; ○70AcA$_5$/70GMA$_5$ Normalized ; △50AcA$_5$/50GMA$_5$ Normalized ; ✱homogeneous blend 50AcA$_2$/50GMA$_2$ (A2G2) ; — Master curve for homogeneous blend 50AcA$_2$/50GMA$_2$ (A2G2)

Influence of concentration of reactive functions at a given chain length

In the beginning, the diffusion kinetics is only function of chain length and is progressivly slowed down when interchain grafting starts to increase the molar mass of the reacting species. Therefore it could have been expected that the slowing down of the reaction kinetics was more important for the chains with the highest amount of reactive functions. As a consequence, it could have been expected that the curves for the more reactive systems were below those for the less reactive blends, when normalized by the average concentration of reactive functions. The experimental results clearly demonstrate the opposite behavior: Figure 4 shows that for a fixed chain length, the G' curves corresponding to the lower concentration of reactive functions (AcA_5/GMA_5 blends) lie below those of the more reactive AcA_2/GMA_2 systems. Moreover, the difference between the two curves (AcA_5/GMA_5 and AcA_2/GMA_2) for a given chain length is an increasing function of chain length.

Conclusion

The reaction kinetics of reactive polymer blends depends both on creation of interface by shearing and on diffusion of the reactive chains, which occur simultaneously during industrial processing. The methodology developped in this study allowed to quantify the influence of these two effects. One of the main results of the paper is the observed deviation of normalized curves obtained for multilayered blends with respect to the master curve corresponding to homogeneous blends. This gap depends in an expected way on the chain length which determines the diffusion coefficient. On the other hand, there is still a strong influence of the average concentration of reactive groups which cannot be explained in the frame of our normalization method used for homogeneous blends.

The next step of this work will consist in simulating the reaction/diffusion process in a multilayered reactive blend. This will require the development of a diffusion model which will be assessed by comparing the simulation to the experimental results obtained with the above metodology for different values of layer thickness, chain length and concentration of reactive functions.

Finally, the method could be extended to immiscible blends by changing the composition of one of the blend components.

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