

RHEOLOGICAL STUDY OF THE INTERFACIAL CROSSLINKING REACTION IN REACTIVE POLYMER BLENDS

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ABSTRACT

Two reactive methacrylic polymers were synthesized by copolymerization of isobutylmethacrylate with a small amount of either methacrylic acid or glycidyl methacrylate. In a molten blend, the condensation reaction between the acid and epoxy groups leads to crosslinking at the interface between the domains formed by the two polymers. This reaction was followed by dynamic mechanical measurements in the melt. Blends were prepared by compression molding a mixture of pellets of controlled size and then by shearing these samples in a cone and plate rheometer up to different values of total shear strain, thus achieving different values of interfacial area per unit volume. Since the two copolymers are miscible, a homogeneous blend could be obtained by coprecipitation and was considered as a limiting case for high values of interfacial area. The glass transition temperature of the polymers was well below the temperature at which the kinetics of the condensation reaction becomes significant. It was therefore possible to separate the creation of interface by shearing from the interfacial crosslinking reaction, which was induced by increasing the temperature. For the blends with the highest values of interfacial area, the viscoelastic properties in the melt after reaction revealed a low frequency plateau for the storage modulus G' , whose level increases almost linearly with the amount of applied shear strain.

KURZFASSUNG

Zwei reaktive Methacrylat-Polymere wurden mittels Copolymerisation von Isobutylmethacrylate mit einem kleinen Anteil Methacrylsäure bzw. Glycidil-Methacrylat synthetisiert. In aufgeschmolzenem Zustand führt die Kondensationsreaktion zwischen der Säure und der Epoxidgruppe zur Vernetzung an der Grenzfläche zwischen den Domänen der beiden Polymere. Diese Reaktion wurde mittels dynamisch-mechanische Messungen in der Schmelze verfolgt. Die Mischungen wurden mit Hilfe des Kompressionsformens aus Pellets mit definierter Größe hergestellt und anschließend durch Scherung in einem Kegel-Platte-Rheometer bei verschiedenen Schereinheiten geschert, um unterschiedliche Größen der Grenzfläche pro Volumeneinheit zu erzielen. Da die beiden Copolymere mischbar sind, erzielte man bei gleichzeitiger Fällung der Polymere eine homogene Mischung, die als Grenzfall für die hohen Werte der Grenzflächenbereiche angenommen wurde. Die Glasübergangstemperatur der Polymere lag deutlich unter der Temperatur, bei der die Kinetik der Kondensationsreaktion signifikant wird. Es war deshalb möglich, die scherinduzierte Ausbildung der Grenzfläche, wie auch die Vernetzungsreaktion an dieser Grenzfläche – die durch den Temperaturanstieg induziert wurde – zu separieren. Für Mischungen mit dem höchsten Grenzflächenwert zeigte sich bei den viskoelastischen Stoffwertfunktionen ein niedrig-frequenter Plateau-Bereich im Speichermodul, dessen Niveau mit dem Betrag der Scheramplitude linear ansteigt.

RÉSUMÉ

Deux polymères réactifs ont été synthétisés par copolymérisation du méthacrylate d'isobutyle avec une faible quantité d'acide méthacrylique ou de méthacrylate de glycidyle. Dans un mélange à l'état fondu, la réaction de condensation entre les groupes acides et époxydes conduit à la réticulation aux interfaces des domaines formés par les deux polymères. Cette réaction a été suivie par mesures mécaniques dynamiques à l'état fondu. Les mélanges ont été préparés en moulant sous vide des granules de taille contrôlée des deux copolymères, puis en cisailant ces échantillons dans un rhéomètre cône-plan jusqu'à différentes valeurs de déformation correspondant à différentes valeurs d'aire interfaciale. Comme les polymères sont miscibles, un mélange homogène peut être obtenu par coprécipitation et a été considéré comme un cas limite pour les valeurs élevées de l'aire interfaciale. La température de transition vitreuse des polymères est inférieure à la température à laquelle la cinétique de la réaction de condensation devient significative. Il a été par conséquent possible de séparer la création d'interface par cisaillement de la réaction de réticulation interfaciale qui a été déclenchée par élévation de température. Pour les mélanges d'aire interfaciale élevée, les propriétés viscoélastiques à l'état fondu après réaction révèlent un plateau aux basses fréquences pour le module élastique G' , dont le niveau augmente quasi linéairement avec la quantité de déformation appliquée.

KEY WORDS:

Rheology, polymer blends, interfacial reaction

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Figure 6 (left): $G'(0.01)/G_e$ as a function of Φ (average).

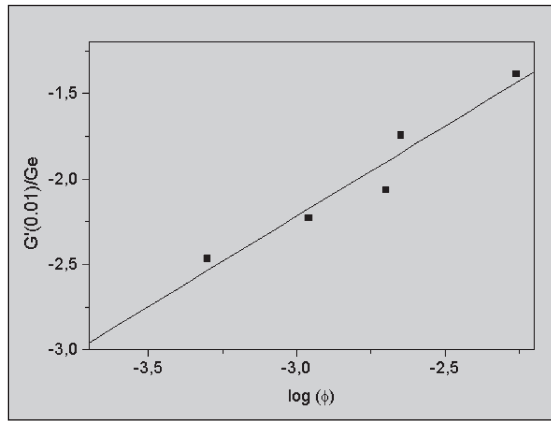


Table 4 (right): Interfacial area per unit volume and estimated volumic fraction of the crosslinked phase as a function of applied deformation.

Deformation γ	A_{int}/V (1/m)	Φ	$G'(0.01 \text{ rad/s})/G_e$
200	$1 \cdot 10^5$	$5 \cdot 10^{-4}$	$3.4 \cdot 10^{-3}$
450	$2.25 \cdot 10^5$	$1.1 \cdot 10^{-3}$	$5.9 \cdot 10^{-3}$
788	$3.9 \cdot 10^5$	$2 \cdot 10^{-3}$	$8.6 \cdot 10^{-3}$
1100	$5.5 \cdot 10^5$	$2.25 \cdot 10^{-3}$	$1.8 \cdot 10^{-2}$
2170	$1.1 \cdot 10^6$	$5.5 \cdot 10^{-3}$	$4.1 \cdot 10^{-2}$

In order to compare the different blends, we arbitrarily chose to take the value of G' at 160°C and for the lowest accessible frequency ($\omega = 0.01 \text{ rad/s}$). The highest and lowest values are respectively obtained for the homogeneous blend ($G_e = 2.9 \cdot 10^5 \text{ Pa}$) and for the heterogeneous blend without pre-shearing ($G_o = 500 \text{ Pa}$). The equilibrium value of G_e for the homogeneous blend is reached after annealing the sample at 160°C during 9 hours. If this value is compared to the upper limit calculated from the functionality of the chains, it appears that in the average only one among 8 reactive functions have indeed reacted.

In Figure 4, the curve corresponding to the heterogeneous blend without pre-shear (\blacklozenge) is compared to those obtained for the pure copolymers iBMA-co-MA (\square), iBMA-co-GMA (\circ) and for the homopolymer iBMA (\bullet) at the same temperature. G_o of the unsheared heterogeneous blend is slightly higher than in the case of the homopolymer and one of the copolymers (iBMA-co-GMA) ($G_o = 150 \text{ Pa}$), probably due to partial crosslinking; but it is almost equal to that in the case of the second copolymer (iBMA-co-MA) ($G_o = 400 \text{ Pa}$). Taking into account the experimental error for such small values of G' , all values can be considered to be relatively close to each other and indicate that all copolymers have nearly the same molecular weight.

3.4 INFLUENCE OF DEFORMATION

As mentioned before, blends with different morphologies were obtained by applying various shear strains at 125°C at the same shear rate to samples molded from pellets. The total time spent at 125°C was kept constant for all samples, independently of the total applied shear strain: it was the time to apply the highest shear strain ($\gamma = 2170$), i.e. four hours. Samples with lower shear strains were first annealed at 125°C before being sheared, so that the total time spent at that temperature always represented four hours.

In Figure 6 we have plotted the variations of G' as a function of frequency for blends sheared

up to various deformations between 200 and 2170 and after a reaction time of 10 min at 160°C . Whereas the high frequency part of the G' curves is almost not affected by the interfacial crosslinking, the value of G' at 0.01 rad/s is an increasing function of applied shear strain, i.e. of interfacial area. For all blends, this values lies as expected between G_o and G_e .

With a simple assumption we have tried to estimate the interfacial area per unit volume and the volume fraction of the crosslinked interphase: we considered an initial morphology of cubic domains of size $d = 2 \text{ mm}$ affinely deformed by the shear strain. The surface area of such a domain sheared by an amount γ is then:

$$A = 2\left(2d^2 + d^2\sqrt{1+\gamma^2}\right) \quad (3)$$

which for large strains amounts to $2\gamma d^2$. For a blend with a 50/50% composition, the interfacial area per unit volume is:

$$\frac{A_{int}}{V} = \frac{A}{2d^3} = \frac{\gamma}{d} \quad (4)$$

The volume fraction Φ of crosslinked interphase is then simply obtained by multiplying Equation 4 by the thickness of the interfacial layer on which the crosslinking takes place. It can be assumed that the lower limit for this value is close to the radius of gyration of a chain of mass Me , Me being the molecular weight between entanglements. This amounts to consider that mutual diffusion of the two miscible copolymers does not occur, since the samples are heated up to 160°C immediately after shearing and that diffusion is rapidly inhibited by interfacial crosslinking. The modulus at the rubbery plateau for iBMA at 160°C is close to 10^5 Pa , and from the density $\rho = 1.045 \text{ g/ml}$, we find $Me = 38000 \text{ g/mol}$. Due to the lack of data for the relation between molecular weight and radius of gyration of iBMA, the corresponding relationship for PMMA [31] will be used:

$$R_g^2 = 0.096 M_w^{0.98} \quad (5)$$

where the radius of gyration is expressed in Å and the molecular weight in g/mol. With M_w equal to $3.8 \cdot 10^4$ g/mol, the radius of gyration is close to about 5nm. To compute the volume fraction of the crosslinked phase, this value is multiplied by the interfacial area per unit volume. The data are given in Table 4.

Experimentally, we found a plateau modulus $G_e = 2.9 \cdot 10^5$ Pa for the homogeneous blend, which corresponds to the upper limit of homogeneous crosslinking in the bulk ($\phi = 1$). Assuming that G' at 0.01 rad/s is simply proportional to the amount of crosslinked material, ϕ for a given shear strain can be estimated as the ratio $G'(0.01\text{rad/s})/G_e$. The data are also given in Table 4. We notice that the values of ϕ obtained from the interfacial area are lower than the values of the same parameter obtained from the values of G' . This could be due to the arbitrary estimation of the interfacial thickness. However, the two sets of values are almost proportional as shown in Figure 5 where $G'(0.01\text{rad/s})/G_e$ has been plotted on logarithmic scales as a function of ϕ obtained from the interfacial area.

4 CONCLUSION

The main result of this study is that bulk viscoelastic measurements in the melt are sensitive to interfacial crosslinking in a reactive polymer blend. A low frequency plateau in G' appears after reaction for the blends with the highest values of interfacial area. Moreover, the value of G' at an arbitrarily chosen frequency is nearly proportional to the shear applied during the mixing step carried out at low temperature. The absolute value of the volume fraction of crosslinked interphase estimated from the interfacial area is lower by a factor of about 5 to 10 to the value deduced from a comparison between the modulus of the blend and that of a homogeneous blend. Several assumptions may be at the origin of this discrepancy: in particular, the influence of the miscibility and chain diffusion on the interfacial thickness should be more thoroughly investigated.

This will be the purpose of a forthcoming study, where the thickness of the crosslinked interphase will be controlled by the annealing time after pre-shearing and at the same low temperature where the crosslinking reaction is slow.

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