Rheology of Reactive Polymer Blends: Separation of Mixing and Reatcion Steps

R. Muller*, M. Bouquey, F. Mauguière, G. Schlatter, C. Serra, J. Terrisse

ECPM – LPMP, Procédés et Matériaux Polymères,
25 rue Becquerel, 67087 Strasbourg Cedex 2, France

Email: MullerR@ecpm.u-strasbg.fr

Abstract:
The crosslinking reaction in various types of polymer blends was followed by rheological measurements. Miscible polymers with controlled glass transition temperature, chain length and number of functional units per chain were synthesized by bulk radical copolymerization. Other experiments were carried out on immiscible systems based on commercial polymers. Blends were either prepared in a batch mixer or directly in the parallel-plate geometry of a rotational rheometer. Due to the low glass transition or melting temperature of most blend components, it was usually possible to separate the mixing step which was carried out at low temperature from the crosslinking reaction which was followed by small amplitude dynamic measurements at higher temperatures. The influence of several parameters on the reaction was studied, in particular : the reaction temperature, the amount of shear during the mixing step (or mixing time), the number of functional units per chain in each blend component and the blend composition. For the miscible blends, a master curve for the dependence of the elastic modulus G' as a function of reaction time could be drawn for different functionalities and blend compositions.

Zusammenfassung:
Die Vernetzungsreaktion für verschiedene Typen von Polymermischungen wurden rheologisch untersucht. Mischbare Polymere mit wohldefinierter Glasübergangstemperatur, Kettenlänge und Anzahl der funktionellen Gruppen pro Kette wurden durch eine Copolymerisation synthetisiert, während nichtmischbare Systeme durch kommerzielle Polymere hergestellt wurden. Die Mischungen wurden entweder im Batch Mixer oder direkt in der Platte-Platte Geometrie des Rotationsrheometers erzeugt. Wegen des niedrigen Glasübergangs- oder Schmelztemperatur der meisten Polymerkomponenten war es grundsätzlich möglich, den Mischvorgang, der bei niedriger Temperatur durchgeführt wurde, von der Vernetzungsreaktion, die unter Oszillationsbeanspruchung bei höherer Temperatur erfolgte, zu trennen. Der Einfluss verschiedener Parameter wie Reaktionstemperatur, Deformation (Scherung pro Zeit), Anzahl der funktionellen Gruppen pro Kette und die Mischungszusammensetzung auf die Vernetzungsreaktion wurde untersucht. Für die mischbaren Polymere unterschiedlicher Funktionalität und Mischungszusammensetzung konnte eine Master Curve für den Speichermodul als Funktion der Reaktionszeit aufgestellt werden.

Résumé:
La réaction de réticulation dans différents types de mélanges de polymères a été étudiée à l'aide de mesures rhéologiques. Des polymères miscibles pour lesquels on a contrôlé la température de transition vitreuse, la longueur des chaînes et le nombre de fonctions réactives par chaîne, ont été synthétisés par copolymérisation radicalaire en masse. D'autres expériences on été réalisées sur des systèmes immiscibles à partir de polymères commerciaux. Les mélanges ont été préparés soit dans un malaxeur interne, soit directement dans la géométrie plan-plan d'un rhéomètre rotationnel. La température de transition vitreuse ou de fusion de la plupart des constituants du mélange étant suffisamment basse, on a en général pu découpler l'étape de mélange, qui a été réalisée à basse température, de la réaction de réticulation qui a été caractérisée par des mesures mécaniques dynamiques de faible amplitude réalisées à haute température. L'influence de différents paramètres sur la réaction a été étudiée et plus particulièrement la température de réaction, la déformation totale en cisaillement pendant l'étape de mélange (ou le temps de mélange), le nombre de fonctions réactives par chaîne dans chaque constituant du mélange et la composition du mélange. Pour les mélanges miscibles, une courbe maîtresse pour la variation du module élastique G' en fonction du temps de réaction a pu être obtenue pour différentes fonctionnalités et compositions du mélange.
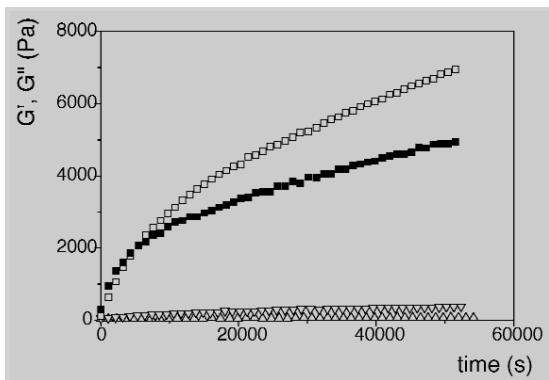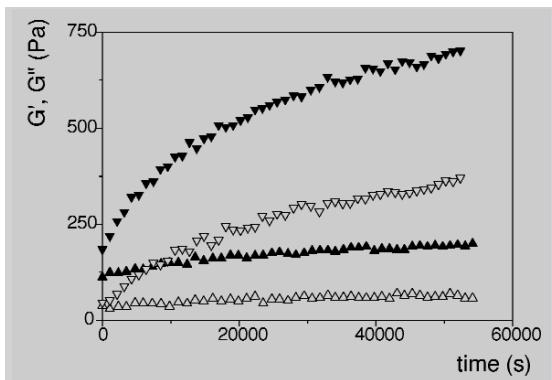
Figure 14 (left): Storage (△, ▲) and loss (▽, ▼) modulus at 0.1 rad/s versus reaction time at 150°C for the diacid (△, ▽) and acid-amine COPA blends.

Figure 15 (right): Storage (△, ▽, □) and loss (■) modulus at 0.1 rad/s versus reaction time at 150°C for the diacid (△), acid-amine (▽) and diamine (□, ■) COPA blends.

4.2 RESULTS

The sample geometry and the blending method are the same as described in Part B. The experimental conditions of the tests are the following: amount of preshear (at the outer rim of the disc) γ_R = 600; temperature of preshear: 85°C; diffusion during 1200s at 85°C and reaction at 150°C. The results for the increase of G' and G'' during reaction for the diacid and acid-amine COPA based blends are shown in Fig. 14. They confirm that the diacid COPA based blend is indeed non reactive since no significant increase in G' is observed at the reaction temperature. For the monofunctional acid-amine COPA, a very small increase is found, indicating that the rheological method is sensitive to an interfacial grafting reaction. Finally, the results for the difunctional diamine COPA based blend are shown in Fig. 15. A more important increase in G' is observed, confirming the assumption on the existence of interfacial crosslinking. However, the values of G' remain smaller by several orders of magnitude to those obtained for the more miscible systems considered in Sections 2 and 3.

5   CONCLUSION

For all investigated systems, the grafting or crosslinking reaction between the two blend components could be characterized by drawing G', taken at a fixed frequency, as a function of reaction time. For the miscible acrylic blends, the components have very low glass transition temperatures compared to the reaction temperature so that the measured values of G' are only due to the crosslinking reaction and not to the relaxation behavior of the blend components. It could be shown for these systems that if the mixing time increases, the G' versus reaction time curve becomes independent of mixing time, which means that the blend are homogeneous when the reaction starts (similar behavior was also observed for the ethylene-acrylic copolymer systems considered in Section 3, indicating that these blends are at least partially miscible). Under these conditions, the storage modulus G' also becomes independent of reaction time for long enough reaction times. From the value of G'

at this plateau, the total reaction time (which exceeded 10 hours even for the most reactive system) as well as the final network structure, like for instance the average molar mass between crosslinking units, can be determined. It was found that the rate of the reaction increases with increasing temperature and chain functionality. A first approach has shown that reduced variables could be defined from the storage modulus G' and the reaction time t using the initial concentration of functional units.

On the other hand, an original yet very simple experimental method has been proposed to characterize via rheological measurements the interfacial reaction in a reactive polymer blend, the two components being directly mixed in the parallel-plate geometry of the rheometer. For the low melting temperature systems investigated in Section 3 of the present study, it was possible to separate the mixing of the two blend components 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 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 for immiscible systems, although the same qualitative behavior is obtained during the interfacial reaction, the levels of G' obtained are lower by several orders of magnitude than for more miscible systems, which is probably due to a much lower value of the volume fraction of the material where the reaction can take place.

REFERENCES

[1] M.Lambla, J.Druz, N.Satyanarayana: Makromol. Chem. 189 (1988) 2703

[2] H. Asthana, K. Jayaraman: Macromolecules 32 (1999) 3412

[3] P.Cassagnau, M.Bert, V.Verney, A.Michel: Pol Eng Sc, 32 (1992) 998

[4] R.E. Riemann, H.J. Cantow, C. Friedrich, Macro-molecules 30 (1997) 5476

[5] B. Ernst, J.F. Koenig, R. Muller, Macromol. Symp. 158 (2000) 43-56

[6] C. Cirman, M. Bouquey, J. Terrisse and R. Muller: Appl. Rheol. 9 (1999) 108

[7] W. Hoffman, W. Fisch: FATIPEC Congress Rev., Wiesbaden 1962, p. 243

[8] U. Sundararaj, C.W. Macosko: Polymer 36 (1995) 1957

[9] N.D.B. Lazo, C.E. Scott, Polymer 40 (1999) 5469

[10] C.E. Scott, C.W. Macosko: 53rd ANTEC 1 (1995) 1135