Transient Rheological Behaviour of PA6/EPM/EPM-g-MA Blends

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Abstract

In this work the transient shear behaviour, in terms of both flow and stress relaxation, were measured for several blends of PA6/EPM/EPM-g-MA. The results indicate that there is a competition between slip at the interface due to the non-compatibility between the PA6 and the EPM and the action of the compatibilizer. In flow experiments, at low total strains it was observed that the behaviour is characteristic of immiscible polymer blends and gradually changes to that typical of compatible blends. This suggests that initially the action of the compatibilizer (especially for low compatibilizer contents) is not enough to prevent the lower viscosity PA matrix from slipping around the high viscosity EPM droplets. However, as the droplets are deformed and oriented, the increase in interfacial area enhances the performance of the compatibilizer, thus resulting in a much better interaction between the two phases across the interface.

Introduction

The flow properties and microstrutural characteristics of blends of immiscible polymers is of interest in many fields of science and technology and especially so with regard to the Physics of processed polymer blends. The rheology of blends of two Newtonian fluids is reasonably well understood. However, most polymers show non-Newtonian behaviour, such as a shear rate dependent viscosity and normal stress difference and the rheology of blends of viscoelastic components is still not well understood. There is a large number of available studies on the effect of droplet elasticity on its deformations in a Newtonian matrix (see, for example, refs. [1-5]): in general, droplet elasticity leads to less deformed droplets as compared to the Newtonian case. Similarly, there are other studies on the deformation of Newtonian droplets in a viscoelastic matrix (refs.[6,7]). In these cases, the elasticity of matrix tends to deform and destabilize the droplets. When the two phases are viscoelastic additional effects appear and the behaviour of the blend is not predictive. The use of compatibilizers to improve the properties of immiscible polymer blends has become common practice in the polymer industry. The rheological properties of compatibilized polymer blends, namely on the understanding of how compatibilizers change the interfacial proprieties and, consequently, the rheological behaviour of the materials is a very important issue about which there are relatively few studies available. However, it can safely be said that, in this case, the technological capability is more advanced that the scientific knowledge, with only a few studies being available in the open literature (Van Hemelrijck, Van Puyvelde et al. [8]; Iza, Bousmina, et al. [9]; Riemann, Cantow, et al. [10] are amongst the few existing ones). Riemann, Cantow, et al. showed that the addiction of $\mathrm{P(S}-b-\mathrm{MMA)}$ and $\mathrm{P(CHMA}-b-\mathrm{MMA)}$ block copolymers changes the interfacial proprieties of a PS/PMMA blends. The study of Van Hemelrijck, Van Puyvelde et al. on PDMS/PI blend with different amounts of PDMS/PI diblock, observed differences in the dynamics of interfaces. Iza, Bousmina, et al. demonstrated that the amount of compatibilizer as well as its structure drastically affect the rheological response to a sudden imposition of a shear rate. The present work aims at complementing those above and contribute to a better knowledge of the effect of the amount of compatibilizer on the transient rheological behaviour of compatibilized polymer blends.

Materials and methods

Several blends of a commercial polyamide-6 (PA-6 Akulon® K123), an ethene-propene rubber (EPM Keltan® 740) and an ethene-propene rubber modified with maleic anhydride (EPM-g-MA ExxelorVA 1801, containing 0.49wt% of MA, as determined by FT-IR) were prepared in a twin screw extruder, under the same process conditions. The PA-6 content was kept constant in all blends, but the amount of modified rubber was varied in order to have different amounts of maleic anhydride in each blend and thus various amounts of compatibilizer at the interface. The chemical and morphological characterizations were performed in a previous work [11], some data is summarized in Table 1. The volume (R_v) and number (R_n) average radii were calculated using the Eqs. (1) and (2):

$$R_v = \frac{\sum_i n_i R_i^4}{\sum_i n_i R_i^3} \tag{1}$$

$$R_n = \frac{\sum_i n_i R_i}{\sum_i n_i} \tag{2}$$

where n_i = number of the droplets having radius R_i.

Blend (w/w/w)	EPM-g-MA (wt%) [a]	MA content of rubber phase (wt%)	$R_v (\mu\,\mathrm{m})$	$R_n (\mu\,\mathrm{m})$	R_v / R_n
80/20/0	0	0	17.6	5.6	3.1
80/15/5	5	0.13	8.25	1.28	6.5
80/10/10	10	0.25	2.35	1.18	2.0

80/5/15	15	0.37	1.78	1.11	1.6
80/0/20	20	0.49	0.36	0.20	1.8

Table 1 - Composition, MA content of the rubber phase and particle size of the various PA-6/EPM/EPM-g-MA blends.

The rheological measurements of the five blends were performed on a Paar Physica MCR 300 rheometer, using a plate-plate geometry (diameter = 25 mm) with a 1.000 mm gap. All measurements were carried out at 240 °C. Samples were vacuum dried at 80°C during 12 h before the corresponding rheological experiments. The start-up shear rate experiments were performed with a shear rate of $0.1\ s^{-1}$. In the stress relaxation experiments was applied a shear rate of $0.1\ s^{-1}$ during 250 s and it was measured the shear stress after cessation of flow.

Results and discussion

Figures 1 and 2 show the dynamic modulii for the non-compatibilized blend, the blend with the highest amount of compatibilizer and initial components (PA-6, EPM, EPM-g-MA).

For compatibilised blends, i.e., blends that have the copolymer formed at the interface as a result of the reaction between maleic anhydride groups of the rubber and amine groups of the polyamide (see [11]), the values of dynamic modulii are intermediate between the PA-6 dynamic modulii (lower) and the EPM or EPM-g-MA dynamic modulii (higher), at all frequencies. The non-compatibilized blend shows a negative deviation behaviour (NDB), i.e., it shows values of dynamic modulii lower than that of either one of the components, at all frequencies. Since there is no interaction between the two polymers, this behaviour has previously been attributed to slip at the interface [12]. The transient rheological measurements showed significant differences among the several blends in the start-up and cessation of flow experiments. In start-up, all blends showed an overshoot at low total strains (Fig. 3), followed by an undershoot before reaching equilibrium, with the exception of non-compatibilised blend. In fact, while the other blends continue to increase their transient stresses, before reaching steady-state, the non-compatibilized reaches a stationary state for short times. This suggests that, initially the action of the compatibilizer (especially for low compatibilizer contents) is not enough to prevent the lower viscosity PA matrix from slipping around the higher viscosity EPM droplets. However, as the droplets are deformed and oriented, the increase of interfacial area enhances the performance of the compatibilizer, thus resulting in a better interaction between the two phases across the interface. Despite a better adhesion between the phases, in the compatibilized blends, break-up should not occur, since the critical number is very large for $p > 10$ [13]. Shear stress relaxation measurements, on the other hand, illustrated that all blends relax in two steps: a) a fast initial relaxation followed by b) a slower one (Fig. 4). The first step should be related with the relaxation of the PA6 matrix and second step is due to relaxation of EPM and/or interfaces. In this case the particle size and the interfacial adhesion play a determinant role in the shear stress relaxation function. For the compatibilised blends, the second relaxation time increases with the increasing amount of compatibilizer which indicates that the increase of relaxation time is related with a better adhesion between the interfaces. An interesting feature of Fig. 4 is that the second relaxation time of the 80/15/5 blend is shorter than that of the non-compatibilised blend, which indicates that low compatibilizer amounts are enough to decrease significantly the droplets average size but not to prevent the slip between the phases.

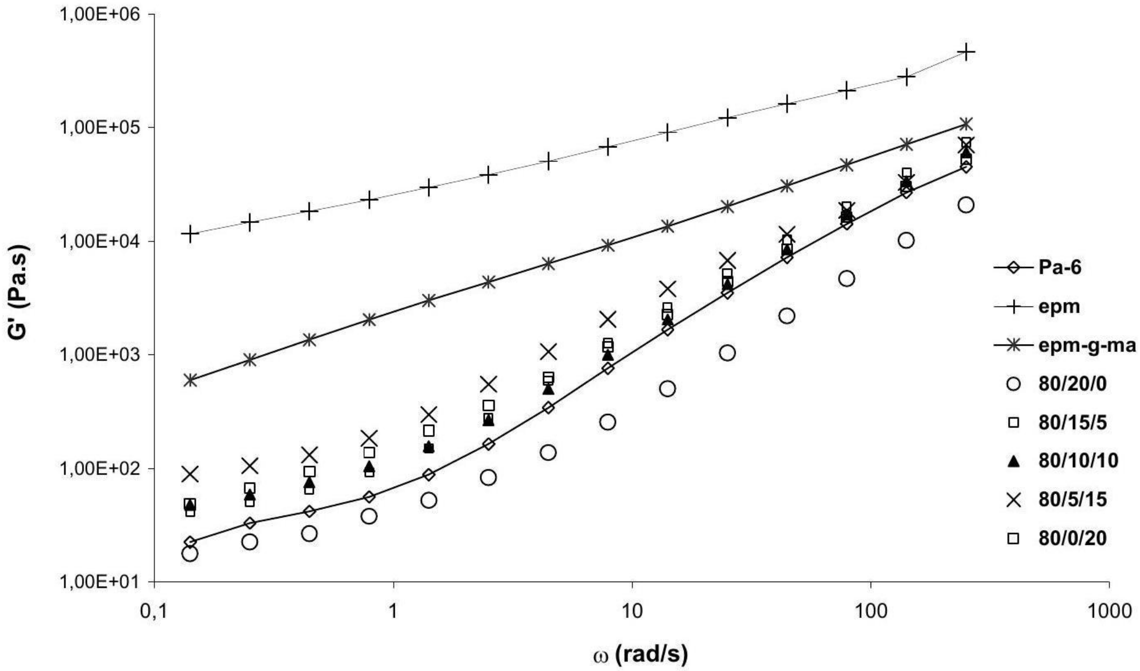

Fig. 1 - Storage modulus, $G(\omega)$, for Pa-6 and EPM and two blends.

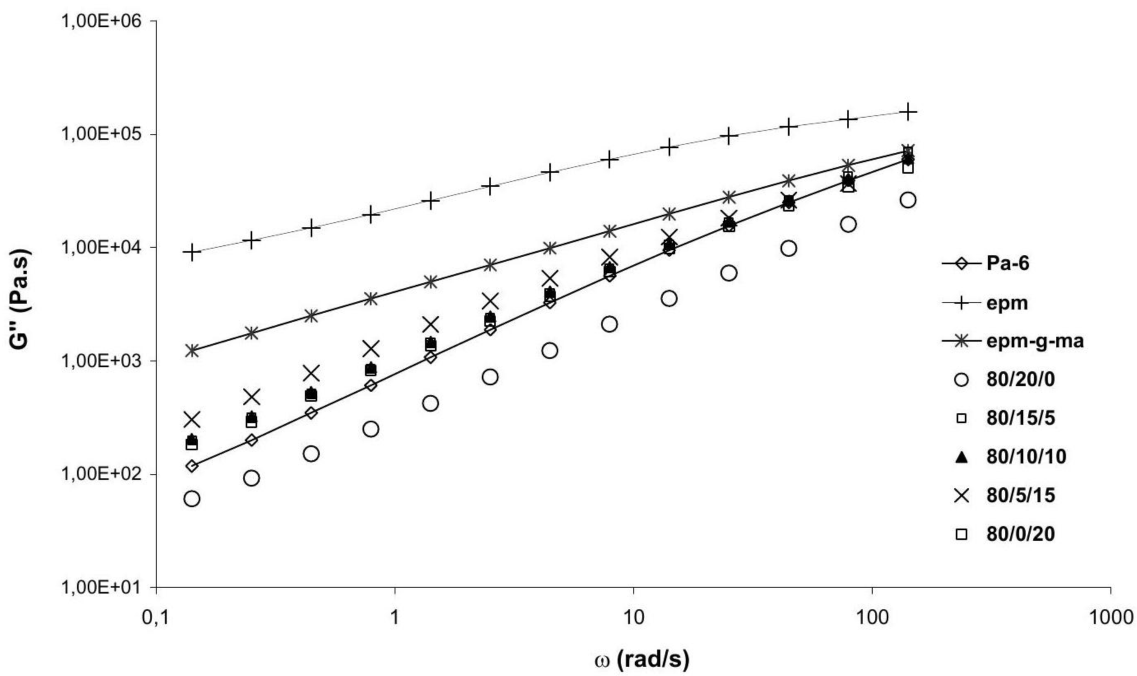

Fig. 2 - Dissipative modulus, G'' (ω), for Pa-6 and EPM and two blends.

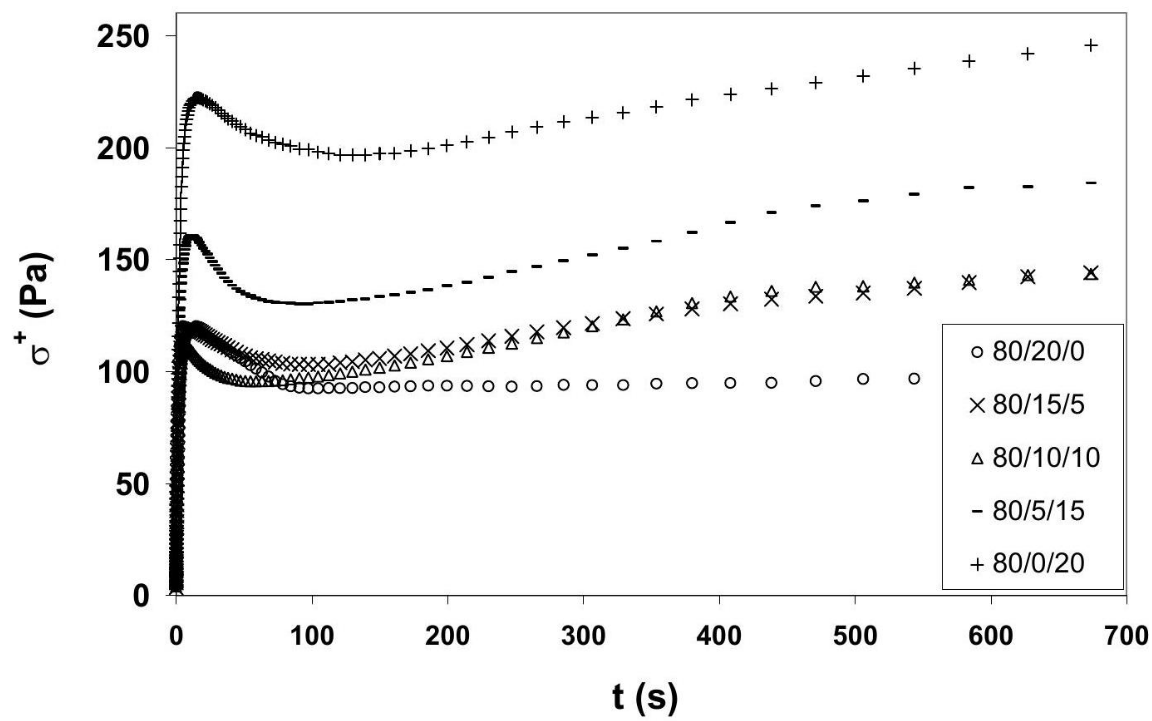

Fig. 3 - Shear stress growth function, $\sigma^+(t, \dot{\gamma})$, for several blends of PA6/EPM/EPM-g-MA. Test shear rate of $0.1\ s^{-1}$.

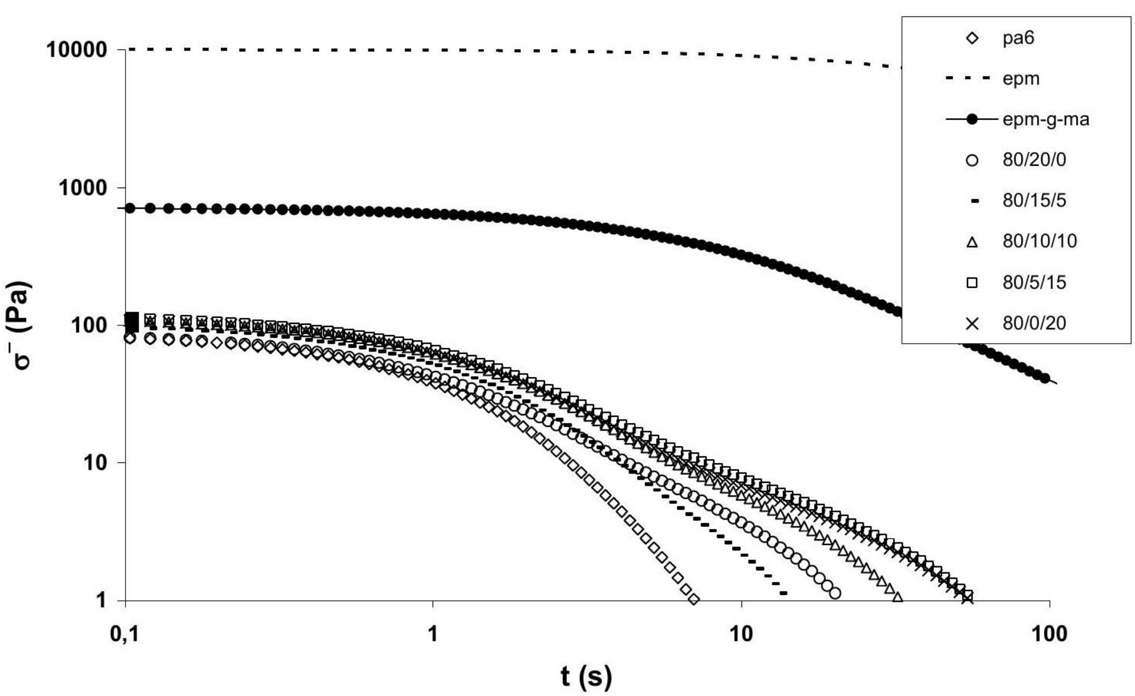

Fig. 4 - Shear stress relaxation function, $\sigma^{-}(t,\dot{\gamma})$, for the components and blends PA6/EPM/EPM-g-MA. Experiments after a cessation of flow of 0.1 s^{-1} during 250s.

Conclusions and future work

This was an initial and qualitative work of the role of particle size and interfacial adhesion on the transient function. It was possible to conclude that a large amount of compatibilizer promotes a better adhesion between the phases and consequently has a significant effect on relaxation at the interface. In the future and in order to implement a quantitative model, experiments of stress relaxation on extension will be realized and the orientation and the deformation of a droplet of EPM in a PA-6 matrix with and without compatibilizer subject to different flows will be measured.

References

[1] H. B. Chin, C. D. Han: Journal of Rheology Vol. 23 (1979), p. 557
[2] W. J. Milliken, L. G. Leal: Journal of Non-Newtonian Fluid Mechanics Vol. 40 (1991), p. 355
[3] F. Mighri, A. Ajji et al.: Journal of Rheology Vol. 41 (1997), p. 1183
[4] F. Mighri, P. J. Carreau et al.: Journal of Rheology Vol. 42 (1998), p. 1477
[5] F. Mighri,M. A. Huneault: Canadian Journal of Chemical Engineering Vol. 80 (2002), p. 1028
[6] W. Lerdwijitjarud, A. Sirivat et al.: Polymer Engineering and Science Vol. 42 (2002), p. 798
[7] W. Lerdwijitjarud, R. G. Larson et al.: Journal of Rheology Vol. 47 (2003), p. 37
[8] Van Hemelrijck, P. Van Puyvelde et al.: Journal of Rheology Vol. 48 (2004), p. 143
[9] M. Iza, M. Bousmina et al.: Rheologica Acta Vol. 40 (2001), p. 10
[10] R. E. Riemann, H. J. Cantow et al.: Macromolecules Vol. 30 (1997), p. 5476
[11] A. V. Machado, J. A. Covas et al.: Journal of Polymer Science Part a-Polymer Chemistry Vol. 37 (1999), p. 1311
[12] L. A. Utracki: Polymer Engineering Science Vol. 23 (1983), p. 602.
[13] P. Van Puyvelde: Flow-induced morphology changes in immiscible polymer blends: a rheooptical study (PhD. Thesis, K. U. Leuven 1999).