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Polymer Vol. 37 No. 14, pp. 2939-2947, 1996

0032-3861/96/$15.00+0.00

Properties of PETG/EVA blends: 1. Viscoelastic, morphological and interfacial properties

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(Received 6 February 1995; revised 4 November 1995)

The linear viscoelastic properties of molten polyethylene terephthalate glycol/polyester–ethylene vinylacetate (PETG/EVA) immiscible blends were measured as a function of frequency for different compositions and temperatures. The morphology of the blends was determined by scanning electron microscopy and the rheological behaviour of the blends is described by the Palierne emulsion model. The behaviour is typical of homogeneous molten polymers except for the appearance of a shoulder in the storage modulus data at low frequencies. This corresponds to an increase in elasticity in the terminal zone and longer relaxation time compared to the matrix. The model describes correctly the experimental data, and the model predictions are used to determine the interfacial tension between PETG and EVA. The interfacial tension is shown to vary between 4.5 mN m^{-1} and 7 mN m^{-1}, depending on composition and temperature. These values are in the range of interfacial tension values determined for other similar polymer systems. No comparison with literature data was possible and an attempt to use the breaking thread method to verify the interfacial tension value for this system was not successful. Copyright © 1996 Elsevier Science Ltd.

(Keywords: blends; morphology; linear viscoelasticity)

INTRODUCTION

Polymer blends consist of mixtures of either homopolymers or copolymers, which are generally thermodynamically immiscible. The development of blends of better and specified properties is related to the control of the interfacial chemistry. A typical binary blend generally demonstrates a two-phase morphology with poor physical/mechanical properties due to weak adhesion at the interface.

Compatibilization and enhancement of the adhesion at the interface can be achieved by various methods. Functionalization of the blend constituents before blending or the addition of a copolymer during blending promotes, in most cases, the compatibilization in multiphase systems. Compatibilization through *in situ* reactions during melt-blending is also becoming very important[1] and may result in the formation of copolymers primarily located at the interface[2]. Among reactions of this category, we note ester exchange reactions, favoured by the presence of dibutyltin (Bu_2SnO). These reactions have been used to synthesize polyester–ethylene vinyl acetate (EVA) copolymers and also to crosslink elastomeric phases in polypropylene/elastomer blends[3–5]. In fact, this organometallic compound initiates the formation of a dimeric distannoxane structure[6,7]. This intermediate has proved to be efficient in the redistributive transesterification phenomena. Quite often, organometallic compounds are used as catalysts which enhance significantly the ester exchange reaction[8]. Partial miscibility reported in the literature for blends such as polyethylene terephthalate (PET)/polycarbonate (PC) and polyester/polyarylate may result from transesterification reactions induced by catalytic residuals. Interchange reactions are believed to enhance the miscibility of the blend components by the formation of a copolymer in contrast to other types of reaction which lead to cross-linking or degradation[9–13].

The blends investigated in this study consisted of an amorphous copolyester polyethylene terephthalate glycol (PETG) and an EVA copolymer. A previous study has shown the effectiveness of adding Bu_2SnO, as a catalyst, to this PETG/EVA system[14]. The addition of Bu_2SnO leads either to the formation of a PETG-*g*-EVA copolymer or to the co-cross-linking of both PETG and EVA[14].

The increase in adhesion is one of the criteria used to evaluate the effects of compatibilization. Determining the interfacial tension value before and after treatment is also a successful method[15] for evaluating the physical or chemical modifications at the interface. The interfacial

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tension is related to the degree of interactions in a polymer mixture. Compatibilization can be achieved largely by reducing the interfacial tension[16] between components of multiphase systems.

The blend morphologies are strongly dependent on the rheological properties of the components and may be affected by the addition of a copolymer[15,17,18]. Rheological properties are useful for understanding the processing of blends and can provide powerful information for elucidating chemical phenomena. The rheological behaviour of polymer blends is, however, very complex. In the case of immiscible blends, the rheological properties depend on composition and properties of the components as well as on the morphology and interactions between phases, characterized by the interfacial tension.

The ultimate objective of this work is the compatibilization of immiscible PETG/EVA blends. In this first article, we analyse the linear viscoelastic properties of PETG/EVA blends and use the Palierne[19] model for determining the interfacial tension. No data in the literature are available for the PETG/EVA system. The determination of the interfacial tension by capillary thread instabilities[20] was also undertaken. This method, however, did not work for the PETG/EVA system. The influence of the interfacial tension and the effect of composition and temperature on the dynamic moduli of the blends are also discussed. In a second article, we report on the effect of adding dibutyltin oxide using n.m.r. spectroscopy and rheological methods. Reactions between model esters and Bu_2SnO were carried out in solution in order to support the observed rheological properties of the PETG/EVA blend in the presence of the catalyst. The resulting products of the model reactions were analysed by ^1H, ^{13}C and ^{119}Sn n.m.r. spectroscopy, with the scope of interpreting the rheological properties of the immiscible PETG/EVA system in the light of chemical mechanisms occurring during the reactive compatibilization step.

EXPERIMENTAL

Commercial polymers were used for preparing the blends. The PETG, from Eastman Kodak Chemical Company (PETG 6763), is a copolyester synthesized from a mixture of terephthalic acid, ethylene glycol and cyclohexane 1,4 hydroxymethyl. Its molecular weight is 26000 g mol^{-1}. It is essentially amorphous and has a glass transition temperature around 80°C[14]. The EVA, supplied by A. T. Plastics Inc. (AT 2803M), contains 28% vinyl acetate by weight and its number average molecular weight is approximately equal to 30000 g mol^{-1}.

Blend preparation

Before each blending, the copolyester was dried under vacuum at a temperature between 80°C and 95°C for at least 24 h. Blending of 25 g samples was carried out using a 30 ml Brabender Plasticorder chamber. The pellets were first dry-blended and melted in the Brabender chamber at 210°C at a rotor speed of 20 rev min^{-1}. Then the speed was increased to 40 rev min^{-1} and the components were mixed for 200 s, time necessary to reach a constant torque value. The melt processing was carried out under a nitrogen atmosphere. Samples for rheological measurements were prepared by compression moulding at 210°C for 7 min, using the molten blend extracted from the Brabender chamber. The pressure load applied to close the heating press was progressively increased from 0.75 to 4 tons. The samples were then cooled down to room temperature under pressure. PETG/EVA blends with compositions of 90%/10% and 80%/20% by weight were studied. For the 90/10 PETG/EVA blend, 1.2 wt% Bu_2SnO was added as a transesterification catalyst. Blending conditions were exactly the same, both with and without catalyst. The complementary compositions (10/90 and 20/80) were not be studied because of the very poor homogeneity of these blends when adding Bu_2SnO.

Scanning electron microscopy

Blend morphologies were examined using a Jeol JSM-820 scanning electron microscope. The samples were fractured in liquid nitrogen and coated with 50/50 gold/palladium to avoid charging. The morphological stability was assessed by comparing samples after mixing and, for the compression moulded samples, after curing. The number and volume average diameters, d_n and d_v respectively, were determined using a digitalizing device and by analysing the surface of some 300–600 particles. The Schwartz–Saltikov correction[21] has been applied for the determination of d_n and d_v.

Rheological measurements

The linear viscoelastic properties of molten PETG/EVA blends were measured as a function of frequency using a Bohlin CSM rheometer with a concentric disc geometry with a diameter of 25 mm and a gap of about 1.5 mm. The samples were pre-dried under vacuum during 12 h and the measurements were carried out under a nitrogen atmosphere in a temperature range of 180–210°C. The frequency ranged from 0.01 Hz to 20 Hz. Depending on frequency and temperature, the stress was adjusted to keep the experiment within the linear viscoelastic domain, that is: the strain response was maintained between 0.03 and 0.20. The morphologies of samples after rheological measurements under small deformation were found to be very similar to those of samples in parallel curing tests at the same temperature for the same time.

Breaking thread method

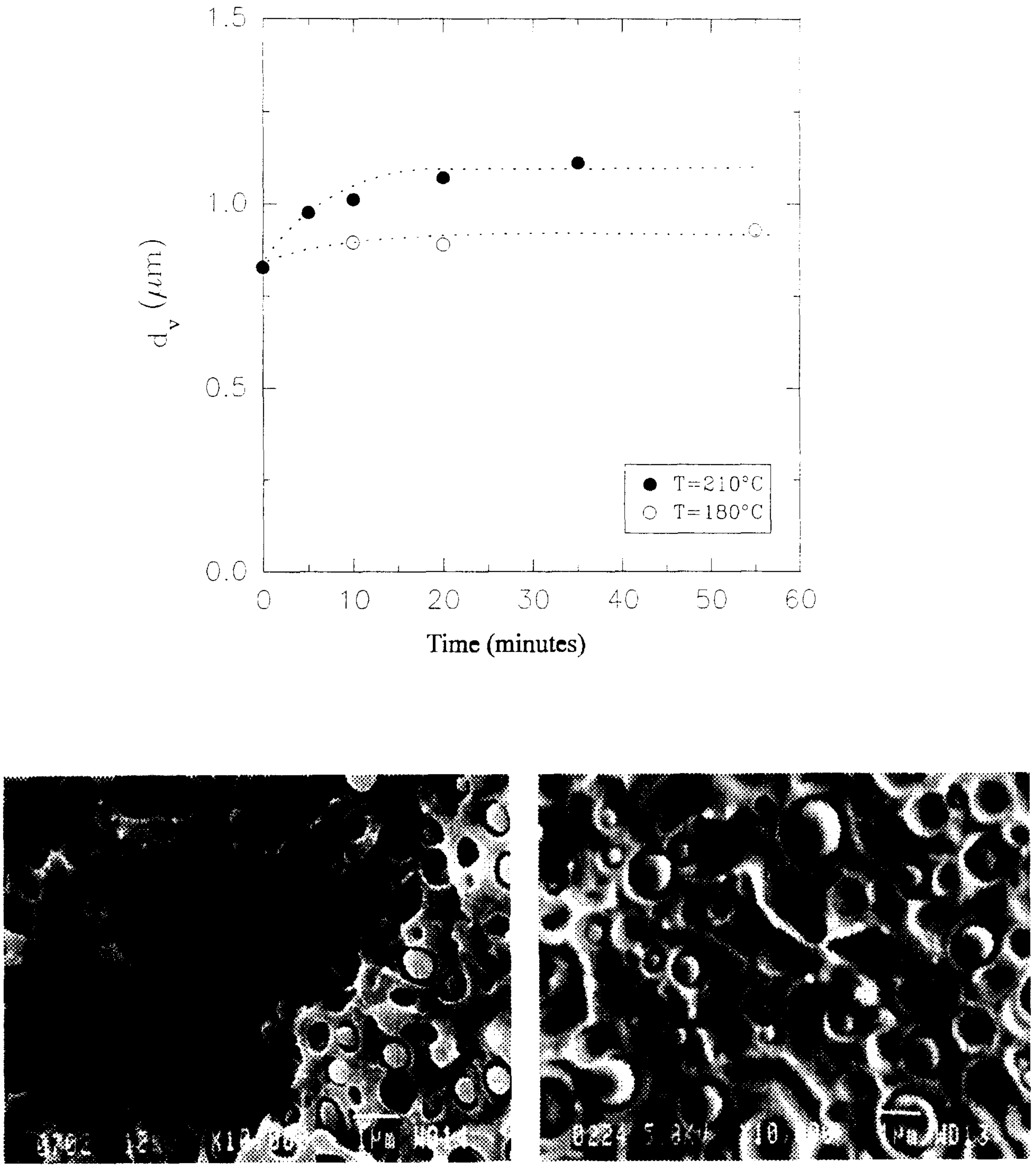
A PETG thread obtained by drawing molten granules, dried at least during 24 h under vacuum at a temperature between 80°C and 95°C, was placed between two EVA films maintained by two glass plates. The whole sandwich was positioned under a Nikon optical microscope in a Mettler FP82HT hot stage. The temperature was fixed at 210°C. The growth rate of disturbances was determined from the photographs in order to calculate the interfacial tension.

RESULTS AND DISCUSSION

Morphology

The rheological as well as other physical properties of polymer blends are closely related to the state of the dispersion and the distribution of the droplets of the minor phase. It is, therefore, essential to determine the sizes of the droplets and their distribution in the blend in order to interpret the rheological data and to assess rheological models. It was impossible to obtain homogeneous blends rich in EVA in presence of Bu_2SnO. Therefore, only

PETG rich blends are examined for the two compositions: 90/10 and 80/20 wt% PETG/EVA with or without 1.2 wt% of Bu_2SnO. The morphological stability of the blend extracted from the Brabender Plasticorder was examined and compared to that of moulded samples from the press at 210°C. No differences in the volume average diameter, d_v, and in the number average, d_n, were observed between moulded samples and blends extracted from the Brabender. In a second step, samples were cured at 180°C and 210°C (temperatures used for the rheological measurements) and changes in d_v with time are reported in *Figure 1* for the 90/10 PETG/EVA blend, and in *Figure 2* for the 80/20 PETG/EVA blend (the variations of d_n are not reported). The corresponding micrographs are shown in *Figures 1a*, *1b*, *2a* and *2b*. In the case of 90/10 PETG/EVA blend, the initial values were determined to be 0.83 μm and 0.56 μm for d_v and d_n respectively. Changes in diameter during curing at 180°C were negligible and within the experimental error. During curing at 210°C, both values increased slightly with time. An equilibrium value of 1.1 μm for d_v was reached while the equilibrium value for d_n was approximately equal to 0.64 μm. Hence, the polydispersity increased with time as shown by the micrographs of



(a) (b)

Figure 1 Variation of d_v with curing time, 90/10 PETG/EVA. Scanning electron micrographs: (a) before curing; (b) after 20 min curing, T = 210°C

Figures 1a and *1b*. The particle size increase with time was more pronounced for the 80/20 PETG/EVA blend, as reported in *Figure 2*. The increases in diameter occurred in the first 5 min. After mixing in the Brabender at 210°C, the diameter of the droplets was approximately equal to 1.56 μm for d_v and 1.00 μm for d_n. During curing at 180°C, d_n stayed at a value of 1.00 μm, but d_v increased to 2.20 μm. During curing at 210°C, the d_v value increased to 2.46 μm while the d_n value was stable at about 0.95 μm. Hence, as shown also by the micrographs of *Figures 2a* and *2b*, polydispersity in diameter and coalescence are enhanced by curing at 210°C.

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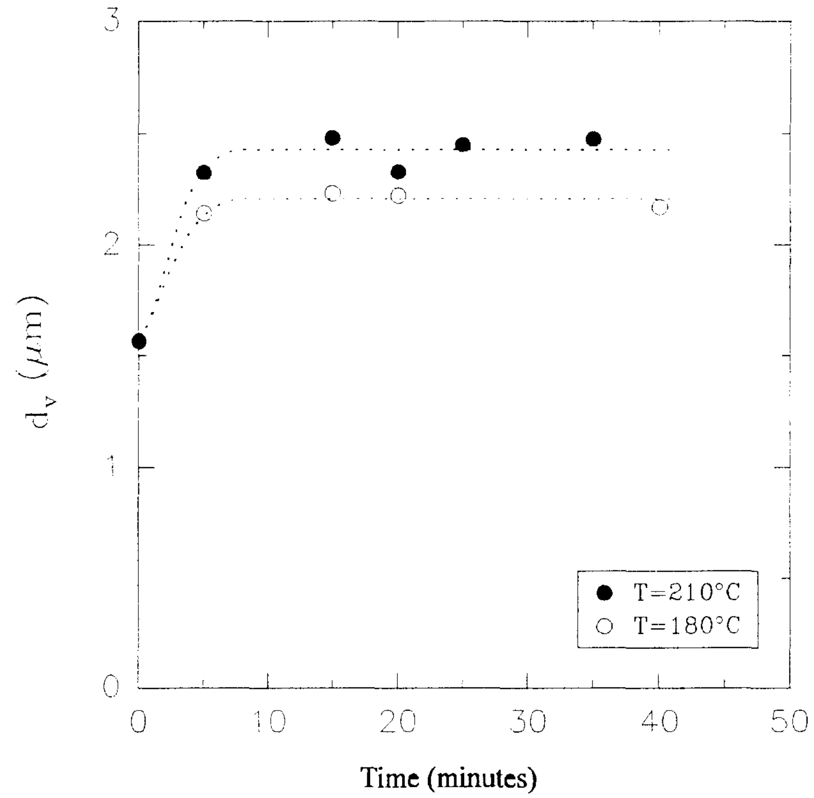
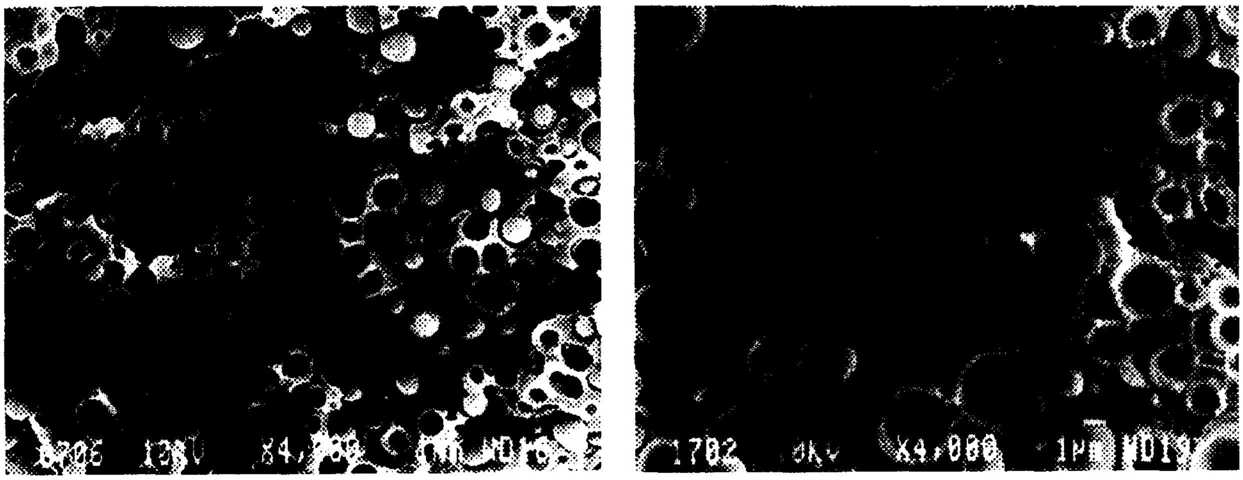
No significant reduction in the particle size was observed after mixing with 1.2 wt% Bu_2SnO (transesterification catalyst), and this for both 90/10 and 80/20 compositions. Generally, compatibilization results in a decrease of both the interfacial tension and the particle size. For the 90/10 PETG/EVA blend, modified by adding 1.2 wt% Bu_2SnO, the values of d_v and d_n were found to be 0.77 μm and 0.48 μm respectively. In the case of the blend containing 20% EVA as the dispersed phase,





(a)

(b)

Figure 2 Variation of d_v with curing time, 80/20 PETG/EVA. Scanning electron micrographs: (a) before curing; (b) after 35 min curing, $T = 210°C$

d_v and d_n were determined to be 1.85 μm and 1.06 μm respectively after extraction from the Brabender. The blend morphology is known to be related to the capillary number which expresses the ratio between the viscous and the interfacial forces. In the presence of Bu_2SnO, a decrease of the interfacial tension concurrently with a decrease of the matrix viscosity could potentially result in no significant particle size reduction[15]. As will be shown in the second article, the presence of Bu_2SnO leads to significant decreases of the dynamic moduli of the blends. A reaction mechanism will be proposed in order to explain the viscosity decrease. Such decreases have already have reported in the literature[14].

Rheology

In this section we use the emulsion model proposed by Palierne[19] to determine from linear viscoelastic data the interfacial tension between the blend components. The model describes the complex modulus, G^*, of molten blends taking into account the particle size distribution and the interfacial tension. The complex modulus of the blend is a function of the complex moduli of both phases (G^*_M for the matrix and G^*_I for the inclusions) and of the ratio of the interfacial tension and the droplet size and size distribution, as follows:

$$G^*(\omega) = G^*_M(\omega)\frac{1 + 3\sum_i \Phi_i H_i(\omega)}{1 - 2\sum_i \Phi_i H_i(\omega)} \tag{1}$$

with $H_i(\omega)$ given by

$$H_i(\omega) = \frac{4(\alpha/R_i)[2G^*_M(\omega) + 5G^*_I(\omega)] + [G^*_I(\omega) - G^*_M(\omega)][16G^*_M(\omega) + 19G^*_I(\omega)]}{40(\alpha/R_i)[G^*_M(\omega) + G^*_I(\omega)] + [2G^*_I(\omega) + 3G^*_M(\omega)][16G^*_M(\omega) + 19G^*_I(\omega)]} \tag{2}$$

where α is the interfacial tension and Φ_i is the volume fraction of droplets with radius R_i.

The general Palierne model formulation also contains parameters related to the interface: $\beta'(\omega)$ due to the change of interfacial area and $\beta''(\omega)$ related to the local shear. Since these parameters are virtually impossible to determine experimentally, they are usually set equal to zero[22]. It is interesting to note that the model contains no empirical parameters and one can predict the linear viscoelastic properties of the blend from the knowledge of the complex moduli of both phases, the particle size and size distribution, the volume fraction of inclusions and the interfacial tension. All of the required data for using the model are experimentally accessible. If the interfacial tension is unknown, the model can be used to determine its value by fitting model predictions to experimental data. The error on the determined value is then directly related to the error incurred in estimating the particle size (term α/R_i in equation (2)). In order to apply the Palierne model, rheological data should be obtained in the linear regime in which the particle deformation remains small (these are the conditions of linear viscoelasticity, i.e. small amplitude oscillatory flow). The morphology must also be stable during the measurements and particles have to be spherical at equilibrium.

In the case of a constant interfacial tension and for a uniform particle size, the Palierne model and the Oldroyd model[23] expressions are similar although the two approaches are different. The Oldroyd model is restricted to dilute emulsions of Newtonian phases[23,24] while the Palierne model is formulated for an undiluted suspension of viscoelastic droplets in a viscoelastic fluid. Since the volume average diameter, d_v, is known to take into account most of the particle size distribution effects[15], we will assume uniform particles and all the model predictions will be calculated using d_v as the characteristic dimension. Under this assumption, the storage and loss moduli of the blends can be expressed explicitly in terms of the moduli of both components[15]:

$$G' = \frac{1}{D}[G'_M(B_1B_2 + B_3B_4) - G''_M(B_4B_1 - B_2B_3)] \tag{3}$$

and:

$$G'' = \frac{1}{D}[G'_M(B_1B_4 - B_2B_3) + G''_M(B_1B_2 + B_3B_4)] \tag{4}$$

where the constants are expressed by:

$$B_1 = C_1 - 2\Phi C_3 \tag{5}$$

$$B_2 = C_1 + 3\Phi C_3 \tag{6}$$

$$B_3 = C_2 - 2\Phi C_4 \tag{7}$$

$$B_4 = C_2 + 3\Phi C_4 \tag{8}$$

$$D = (C_2 - 2\Phi C_4)^2 + (C_1 - 2\Phi C_3)^2 \tag{9}$$

with

$$\begin{aligned} C_1 = {} & 40\frac{\alpha}{R_v}(G'_M + G'_I) + 38(G'^2_I - G''^2_I) \\ & + 48(G'^2_M - G''^2_M) + 89(G'_M G'_I - G''_M G''_I) \end{aligned} \tag{10}$$

$$\begin{aligned} C_2 = {} & 40\frac{\alpha}{R_v}(G''_M + G''_I) + 96G'_M G''_M + 76G'_I G''_I \\ & + 89(G''_M G'_I + G'_M G''_I) \end{aligned} \tag{11}$$

$$\begin{aligned} C_3 = {} & 4\frac{\alpha}{R_v}(2G'_M + 5G'_I) - 16(G'^2_M - G''^2_M) \\ & + 19(G'^2_I - G''^2_I) - 3(G'_M G'_I - G''_M G''_I) \end{aligned} \tag{12}$$

$$\begin{aligned} C_4 = {} & 4\frac{\alpha}{R_v}(2G''_M + 5G''_I) - 32G'_M G''_M + 38G'_I G''_I \\ & - 3(G''_M G'_I + G'_M G''_I) \end{aligned} \tag{13}$$

The Palierne model predictions are in good agreement with the experimental results of viscoelastic emulsions but fails as expected in the case of strong particle–particle interactions or agglomerated particles[17,25–27]. Failures are also reported for systems in which a high concentration of a copolymer has been added[28]. This is not surprising since these systems containing a compatibilizing agent are no longer simple suspensions with possibly thick interphases of a totally different rheological behaviour. Hopefully, the more complete Palierne model could cope with such interphase effects[19].

Rheological characteristics of the components are shown in *Figure 3*. Both the storage and loss moduli of the PETG and the EVA exhibit classical viscoelastic behaviour which can be described by a multimode Maxwell model. At low frequencies, the storage and loss moduli are proportional to ω^2 and to ω respectively. The time–temperature principle was applied to the

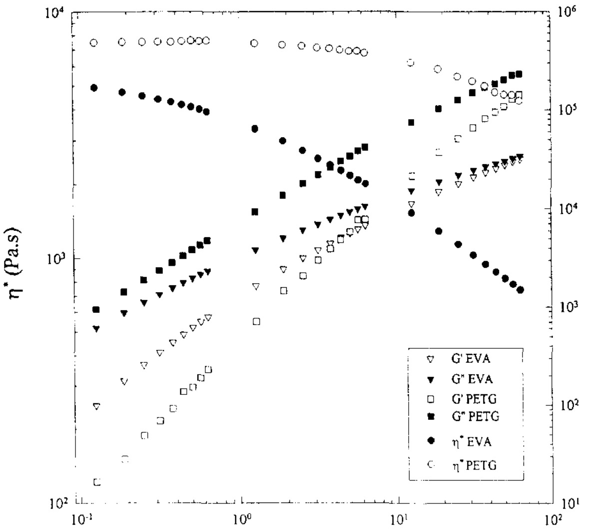


Figure 3 Complex viscosity η^* and dynamic moduli G', G'', of unblended PETG and EVA at 210°C

Table 1 Shifts factors for the dynamic moduli of the components and the blends using the time–temperature superposition. The reference temperature is 210°C

T°(C)	PETG (Loga_T)	EVA (Loga_T)	PETG/EVA 90/10 (Loga_T)	PETG/EVA 80/20 (Loga_T)
210	0	0	0	0
195	0.354	0.175	0.320	0.360
180	0.659	0.394	0.650	0.800

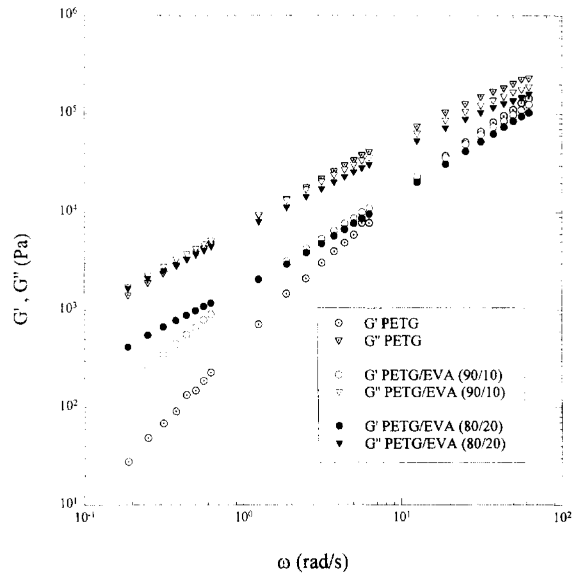


Figure 4 Comparison between dynamic moduli G', G'' of the 90/10 and 80/20 PETG/EVA blends and the PETG matrix, $T = 210$°C

Table 2 Rheological parameters of the terminal zone for the components and the blends at $T_0 = 210$°C

	η_0 (Pa s)	J_e^0 (1/Pa)	λ_w (s)
PETG	7.753×10^3	2.27×10^{-6}	1.76×10^{-2}
EVA	5.55×10^3	1.012×10^{-4}	5.62×10^{-1}
90/10	1.007×10^4	8.254×10^{-6}	8.31×10^{-2}
80/20	1.445×10^4	9.997×10^{-5}	1.444

components and to the blends. Rheological characteristics for a material at a temperature T can be obtained from the knowledge of the properties of the same material at a reference temperature T_0. Both G' and G'' are then related by a shift factor a_T[29]. The curves obtained at three different temperatures were superimposed on master curves (not shown here), using 210°C as the reference temperature. The time–temperature superposition principle was verified for the components as well as for the blends. The shift factor values are reported in *Table 1*. The shift factors for the blends are close to the values obtained for the matrix. Because of differences in the morphology observed after curing at different temperatures, we prefer to analyse the rheological properties for each temperature.

The storage and loss moduli at 210°C of the PETG/EVA blends (10% and 20% of EVA) are compared to those of the matrix in *Figure 4*. The loss modulus of the blends coincides almost with that of the matrix, but the blends exhibit much higher values of the storage modulus in the terminal (low frequency) zone of the matrix. This enhancement of elasticity at low frequencies, generally observed for multiphase systems, has been attributed to the dispersed phase particle deformability[15,17,22,25–27]. *Table 2* reports the parameter values for the terminal zone: the steady-state compliance J_e^0, the zero-shear viscosity η_0 and the terminal relaxation time λ_w, defined as follows:

$$J_e^0 = \lim_{\omega \to 0} \frac{G'}{G''^2} \tag{14}$$

$$\eta_0 = \lim_{\omega \to 0} |\eta^*(\omega)| = \lim_{\omega \to 0} \eta'(\omega) \tag{15}$$

$$\lambda_w = J_e^0 \eta_0 \tag{16}$$

Notice that the zero-shear viscosity ratio $\eta_{0\mathrm{EVA}}/\eta_{0\mathrm{PETG}}$ is lower than 1 for each temperature studied; At 210°C, the viscosity ratio is equal to 0.715. The resulting effect of the droplet deformability is a shift of the terminal zone in the blends towards lower frequencies and longer relaxation times λ_w, as shown in *Table 2*. Notice also that the zero-shear viscosities of the blends are larger than those of the unblended components.

In order to compare the predictions to experimental data, known values of G' and G'' for the matrix and the dispersed phase have to be used. The rheological data of the unblended components were described by a generalized (multimode) Maxwell model and the model was used for calculating the predictions of the Palierne model. The sensitivity of the Palierne model predictions to the interfacial tension is shown in *Figure 5*, which reports predictions for a 80/20 PETG/EVA blend at 210°C for different values of the interfacial tension keeping the radius of particles constant ($d_v = 2.46\,\mu$m). Only the G' values are represented, because G'' is not sensitive to droplet deformation. The data for the blend are shown by the solid line and the predictions have been intentionally calculated for lower frequencies. It is clearly seen that the appearance of a shoulder at low frequency is directly related to the interfacial tension (for example curve 1 corresponding to $\alpha = 1\,\mathrm{mN\,m^{-1}}$). Two limiting cases are also presented in *Figure 5*: the first case with $\alpha = 0\,\mathrm{mN\,m^{-1}}$ and the second case with $\alpha = \infty$. The

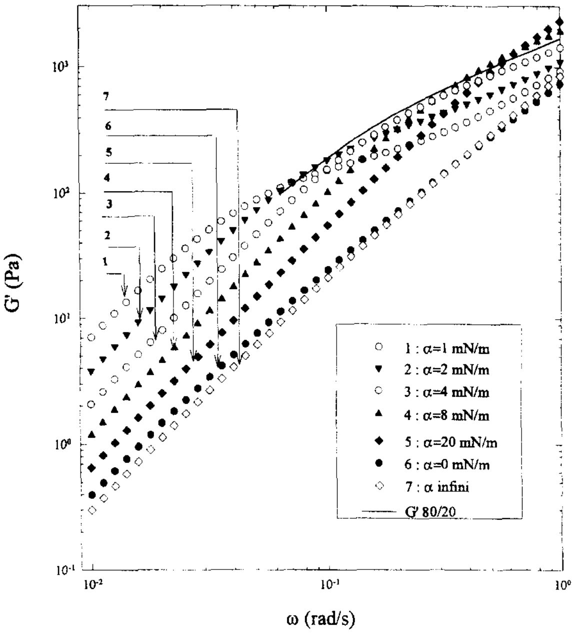


Figure 5 Simulations illustrating the influence of the interfacial tension on the storage modulus predicted by the Palierne model. The solid line represents the experimental data for the 80/20 PETG/EVA blend; $T = 210°C$, $d_v = 2.46\,\mu m$

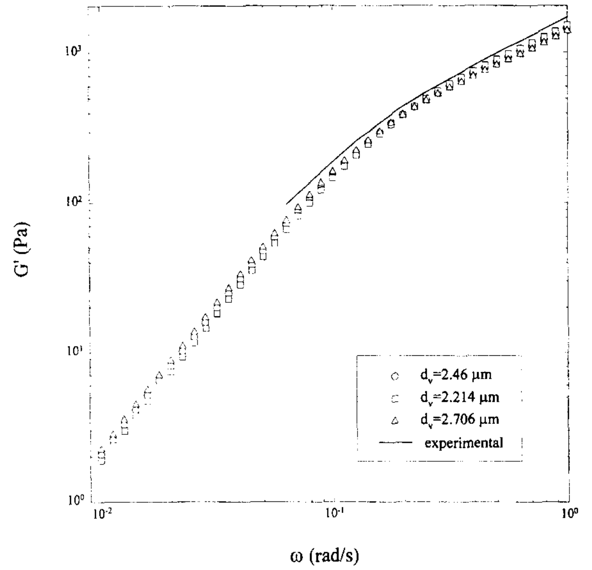


Figure 6 Simulations illustrating the influence of the particle size on G' predicted by the Palierne model. The solid line represents the experimental data for the 80/20 PETG/EVA blend; $T = 210°C$, $\alpha = 4$ mN m^{-1}, $d_v = 2.46\,\mu m$ is the experimentally determined value

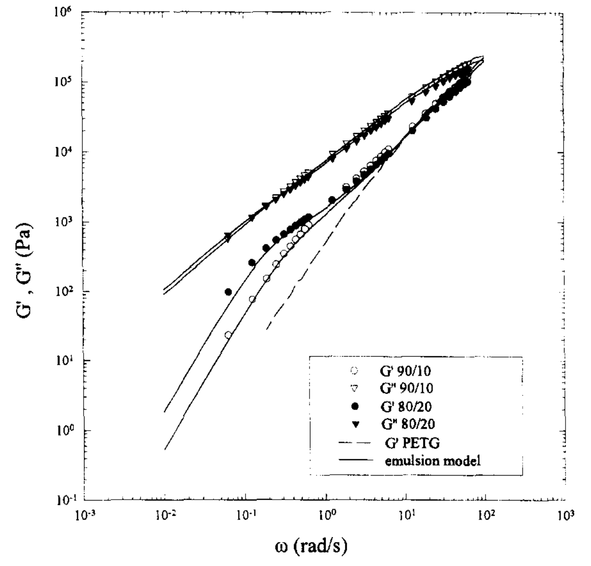


Figure 7 Comparison between experimental data and the Palierne emulsion model predictions for the 90/10 and 80/20 PETG/EVA blends; $T = 210°C$

magnitudes of G' at extremely high or low values of interfacial tension are sensibly equivalent. This steams from the fact that the sensibility of G' of the blend at low frequencies is related to the capability of the dispersed particles to store or not elastic energy. If the interfacial tension is high enough ($\alpha = \infty$), the droplets do not deform, and no extra elastic energy is stored; the emulsion in this case is described by a simple Taylor model. On the other hand for homogeneous blends (negligible interfacial tension), the dispersed droplets take part in the blend elasticity through its storage modulus with no extra contribution due to the interfacial tension. Therefore in an emulsion containing 20% of minor component, the viscoelastic behaviour of the blend will be dominated by the properties of the matrix. Obviously, depending on the rheological properties of both phases, small differences in the storage modulus of the blend will be predicted, compared to that of the matrix. For both cases, if the complex modulus of the particles is much larger than that of the matrix, $H_i(\omega) = 0.5$ and the model simplifies to:

$$G^*(\omega) = G^*_M(\omega)\left(\frac{1 + 3/2\Phi}{1 - \Phi}\right) \tag{17}$$

For a very dilute suspension in a Newtonian matrix, equation (17) reduces to Einstein's result. *Figure 5* shows also that an increase in α results in a decrease of the width and eventually the vanishing of the shoulder. As mentioned previously, the sensitivity of the model in estimating the interfacial tension value is related to the particle size determination. *Figure 6* illustrates the effect of 10% error in diameter for the 80/20 PETG/EVA blend at 210°C with α fixed at 4 mN m^{-1}. The differences are negligible especially in the range of the experimental data. An approximate expression for the relaxation time of the deformed droplets can be used to explain the shift towards the low frequency region for the terminal zone of the emulsion with increasing concentration of the minor phase[15,24].

The morphology was found to be stable during rheological measurements after 5 min (see *Figures 1* and *2*). Comparisons between experimental data and the Palierne model predictions are shown in *Figure 7* for the 90/10 and 80/20 PETG/EVA blends. At 210°C, the droplet volume average radius R_v is 0.55 μm for the 90/10 PETG/EVA blend, and the interfacial tension α, is determined to be 3.9 mN m^{-1}. For the two other temperatures, 180°C and 195°C, α is found to be in the interval of 3.5 to 4.0 mN m^{-1} corresponding to R_v equals to 0.42 μm. Using the same approach for the 80/20 PETG/EVA blend, at a temperature of 210°C, R_v was determined to be 1.23 μm and α is in the interval of 4–5 mN m^{-1}. At 180°C, α is between 6 mN m^{-1} and 8 mN m^{-1} for R_v equal to 1.1 μm. With these values, the model satisfactorily describes the behaviour of the blends for the two compositions over the entire frequency range. *Figure 8* shows the comparison between the experimental data and the emulsion model predictions at the various temperatures for both blends. All the curves show a very similar increase in elasticity in the terminal zone of the matrix, although the droplets are much larger at higher temperatures. The rheological behaviour over the whole frequency range as well as the increase in elasticity is well predicted by the emulsion model. The agreement is shown to be excellent for both blends. As mentioned previously, the enhancement of elasticity is attributed to the deformability and the relaxation of the EVA droplets suspended in the PETG matrix. Measurements have to be carried out at low frequencies in order to observe phenomena associated with droplet deformation.

In all cases, the results are thermodynamically sound as they predict a decrease of the interfacial tension with increasing temperature. It is well known that the interfacial tension displays a low temperature coefficient[16]. The temperature is shown to have no significant influence on the interfacial tension for the 90/10 PETG/EVA blend. In the case of the 80/20 PETG/EVA blend, the interfacial tension decreases from around 7 mN m^{-1} at 180°C to 4.5 mN m^{-1} at 210°C. This change is significantly larger than normally expected and is potentially due to important changes in the morphology, not accounted by using the volume average diameter. *Figures 2a* and *b* reveal an important increase in the particle diameter polydispersity during curing at 210°C.

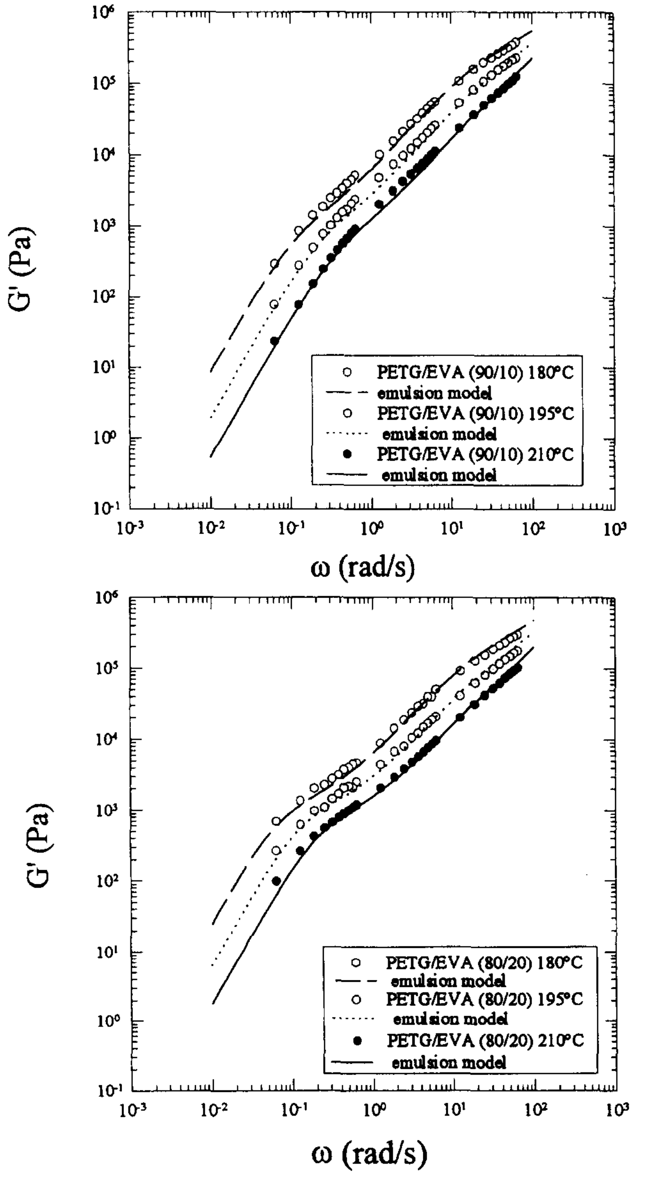


Figure 8 Comparison between experimental data and the Palierne emulsion model predictions at various temperatures for both blends

Breaking thread results

The breaking thread method is based on the growth of an instability along a cylindrical thread embedded in a molten matrix. The sinusoidal distortions along the thread will grow exponentially when the wavelength of the distortions is larger than the circumference of the thread. In Tomotika's theory[30], the rate of distortions, q, is related to the interfacial tension as follows:

$$q = \frac{\alpha \Omega(\lambda, k)}{2\eta_M R_0} \tag{18}$$

where $\Omega(\lambda, \mathrm{k})$ is a tabulated function of the wave length, λ, and of the viscosity ratio k. R_0 is the initial radius of the thread. The values of $\Omega(\lambda, \mathrm{k})$ are reported by Tomotika[30]. From the plot of $\ln(a/R_0)$ vs. t, a being the distortion amplitude, it is possible to determine the interfacial tension. Results for the determination of the interfacial tension by the breaking thread method are reported in *Table 3*. The wave number, X, was estimated to be 0.57 from Tomotika's analysis, and only some results which were close to this theoretical value are reported. Unfortunately, it was impossible to observe reproducible instabilities driven by the interfacial forces for a PETG thread embedded in an EVA matrix at a temperature of 210°C. We note from *Table 3* that the values of α vary between 8.2 mN m^{-1} and 16.0 mN m^{-1} for the repeated experiments. These variations are clearly unacceptable. Note these values are much larger than the interfacial tension obtained by rheometry. The PETG, like all polyesters in general, is very sensitive to moisture. Measurements in our hot stage equipment could not be carried out under nitrogen atmosphere. It is suspected that, with the long experimental time required, polyester degradation occurs and modifies the interface with the EVA matrix. It would be of considerable interest to confirm the results obtained by rheology using the breaking thread experiment carried out under a nitrogen atmosphere. This is what we intend to do in a near future. As far as we know, there is no interfacial tension value reported in the literature for the PETG/EVA system.

Table 3 Interfacial tension between PETG and EVA at 210°C using the breaking thread method

R (μm)	α (mN m^{-1})	X_{exp}
14.77	10.0; 11.0; 9.1; 11.5	0.54
14.33	8.2; 12.3; 12.4	0.53
40.67	13.9; 13.7	0.60
12.44	8.8	0.47
15.65	10.8; 13.3	0.54
26.21	8.5	0.55
9.64	16.0; 15.1	0.59

CONCLUSION

The linear viscoelastic properties of molten PETG/EVA blends have been determined and analysed for two compositions and three temperatures. An increase in elasticity in the low frequency region characterizes the blends. The Palierne emulsion model is shown to describe the data very well. The model predictions are used for determining the interfacial tension between PETG and EVA, which is found to vary between 4.5 mN m^{-1} and 7 mN m^{-1}. It decreases with increasing temperature as thermodynamically expected. These values are in the range of interfacial tension reported in the literature for similar polymer blends (no value is available for PETG/EVA blends). The rheologically determined interfacial tension is lower than that determined using the breaking thread method. Due to experimental difficulties encountered with the PETG/EVA blends, the breaking thread method did not yield reproducible results.

ACKNOWLEDGEMENT

We gratefully acknowledge financial support received from the FCAR program of the Province of Quebec.

REFERENCES

1 Xanthos, M. and Dagli, S. S. *Polym. Eng. Sci.*, 1991, **31**, 929

2 Fayt, R., Jérôme, R. and Teyssié, Ph. *J. Polym. Sci. Lett. Edn* 1986, **24**, 25

3 Cassagnau, P., Bert, M., Verney, V. and Michel, A. *Polym. Eng. Sci.* 1992, **32**, 15, 998

4 Cassagnau, P., Bert, M., Verney, V. and Michel, A. *Polymer* 1993, **34**, 124

5 De Loor, A., Cassagnau, P., Michel, A. and Vergnes, B. *J. Appl. Polym. Sci.* 1994, **53**, 1675

6 Bonetti, J., Gondard, C., Petiaud, R., Llauro, M. F. and Michel, A. *J. Organomet. Chem.* 1994, **481**, 7

7 Espinasse, I., Pétiaud, R., Llauro, M. F. and Michel, A. *Int. J. Polym. Anal. Charact.* 1995, **1**, 137

8 Stewart, M. E., Cox, A. J. and Naylor, D. M. *Polymer* 1993, **34**, 4060

9 Wang, L. H., Huang, Z. and Hong, T. *J. Macromol. Sci.-Phys B.* 1990, **29**, 2&3, 155

10 Porter, R. S., Jonza, J. M., Kimura, M., Desper, C. R. and George, E. R. *Polym. Appl. Sci.* 1989, **29**, 55

11 Godard, P., Dekoninck, J. M., Devlesaver, V. and Devaux, J. *J. Polym. Sci.: Part A: Polym. Chem.* 1986, **24**, 3315

12 Pilati, F. *Polym. Eng. Sci.* 1983, **23**, 13, 750

13 Pilati, F., Marianucci, E. and Berti, C. *J. Appl. Polym. Sci.* 1985, **30**, 1267

14 Legros, A., Carreau, P. J., Favis, B. D. and Michel, A. *Polymer* 1994, **35**, 758

15 Bousmina, M., Bataille, P., Sapieha, S. and Schreiber, H. P. *J. Rheol.* 1995, **39**, 3, 499

16 Wu, S. 'Polymer Interface and Adhesion', Dekker, New York, 1982

17 Carreau, P. J., Bousmina, M. and Ajji, A. in 'Progress in Pacific Polymer Science 3' (Ed. K. P. Ghiggin), Springer-Verlag, New York, 1994, p. 25

18 Germain, Y., Ernst, B., Genelot, O. and Dhamani, L. *J. Rheol.* 1994, **38**, 681

19 Palierne, J. F. *Rheol. Acta* 1990, **29**, 204

20 Elemans, P. H. M., Janssen, J. M. H. and Meijer, H. E. H. *J. Rheol.* 1990, **34**, 1311

21 Lavallée, C. National Council of Research Canada, IMI, Boucherville, QC, Canada, 1990, personal communication

22 Bousmina, M. and Muller, R. *J. Rheol.* 1993, **37**, 663

23 Oldroyd, J. G. *Proc. Roy. Soc., A* 1953, **218**, 122

24 Scholz, P., Frölich, D. and Muller, R. *J. Rheol.* 1989, **33**, 481

25 Graebling, D. and Muller, R. *J. Rheol.* 1990, **34**, 193

26 Bousmina, M. and Carreau, P. J. in 'Linear Viscoelastic Properties of Molten Blends' (Ed. L. A. Utracki), Polyblends-93, Boucherville, Canada, 1993

27 Graebling, D., Muller, R. and Palierne, J. F. *Macromolecules* 1993, **26**, 320

28 Brahimi, B., Ait-Kadi, A., Ajji, A., Jérôme, R. and Fayt, R. *J. Rheol.* 1991, **35**, 6, 1069

29 Ferry, J. D. 'Viscoelastic Properties of Polymers', John Wiley & Sons, New York, 1980

30 Tomotika, S. *Proc. Roy. Soc., A* 1935, **150**, 322