

Viscoelastic and Elastic Behavior of Polypropylene and Ethylene Copolymer Blends

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SYNOPSIS

Thermorheological properties of an incompatible polymer blend of polypropylene inclusions dispersed in a ethylene copolymer matrix were discussed from the emulsion model developed by Palierne. Due to the different rheological behaviors with temperature of the two phases, such a system proved to be a judicious blend in order to consider the special cases of the model applications: (1) the two phases are viscoelastic liquids, (2) the dispersed phase is a solid elastic assimilated to rigid spheres in comparison with viscoelastic liquid behavior of the matrix, and (3) the two phases are elastic solids. At low frequencies, the rheological behavior of the blend was not correctly predicted by the model. So interactions other than hydrodynamics can exist in the intrafacial region, and physical entanglements between the chains of the two constituents leading to topological interactions may be assumed at the interphase. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Mechanical measurements are known to be very useful for the characterization of incompatible polymer blends. The rheological behavior of polymer blends is generally complex, particularly in the case of immiscible blends where the rheological properties depend strongly on composition and viscoelastic properties of the constituents. The linear viscoelastic behavior of incompatible polymer blends has been extensively treated in the literature from experimental and theoretical points of view. One of these models, which has been commonly used in recent publications, is Palierne's model. Starting from the concepts of emulsion rheology, Palierne¹ studied the linear viscoelastic behavior of a dispersion of incompressible viscoelastic materials with interfacial tension. A linear viscoelastic modulus at any concentration and polydispersity of spherical inclusions was derived. The resulting expression of the average modulus includes several results of the literature as special cases: the Kerner² formula for blends of incompressible elastic materials, and Dickie's model³

for a dispersion of viscoelastic material. The development of Palierne's model can be used as the theoretical framework to study the thermorheological behavior $G^*(T)_\omega$ of incompatible polymer blends of polypropylene inclusions dispersed in a ethylene copolymer matrix. Due to the different rheological behaviors with temperature of the two phases, such a system proved to be a judicious blend in order to consider the special cases of the model applications, as illustrated in Figure 1. For example: (1) $T > 175^\circ\text{C}$, the two phases are viscoelastic liquids. The emulsion model with interfacial tension can be applied; (2) $80^\circ\text{C} < T < 155^\circ\text{C}$, the dispersed phase constituted by the polypropylene is a solid elastic assimilated to rigid spheres in comparison with viscoelastic liquid behavior of the ethylene copolymer phase; (3) $T < 65^\circ\text{C}$, the two phases are elastic solids. Kerner's expression for incompressible material is suitable.

THEORETICAL

The rheological model presented by Palierne was developed for incompressible viscoelastic inclusions that are spherical at equilibrium in an incompressible viscoelastic matrix. The model was developed in the linear viscoelastic regime with no affect of

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the imposed deformation either on the morphology of the blend or on the modification of the size. Therefore, this means that the droplet deformation remains small.

From the emulsion model, the complex shear modulus $G^*(\omega)T$ at a given temperature is expressed as a function of the interfacial tension γ_{12} , the complex shear moduli of matrix $G_m^*(\omega)$, and the complex shear moduli of the inclusions $G_i^*(\omega)$ at the same temperature T . A distribution of size and composition of the dispersed phase can be taken into account:

$$G^*(\omega) = G_m^*(\omega) \frac{1 + 3 \sum_i \phi_i H_i(\omega)}{1 - 2 \sum_i \phi_i H_i(\omega)} \quad (1)$$

$H_i(\omega)$

$$= \frac{4(\gamma_{12}/Ri)[2G_m^*(\omega) + 5G_i^*(\omega)] + [G_i^*(\omega) - G_m^*(\omega)][16G_m^*(\omega) + 19G_i^*(\omega)]}{40(\gamma_{12}/Ri)[G_m^*(\omega) + G_i^*(\omega)] + [2G_i^*(\omega) + 3G_m^*(\omega)][16G_m^*(\omega) + 19G_i^*(\omega)]}$$

with ϕ_i the volume fraction of inclusions of radius Ri .

Actually, such an equation was successfully valid,⁴ and it was shown that dynamic shear measurements can be used as a original method for determining the interfacial tension between two polymer melts.

Nevertheless, eq. (1), assuming that the interfacial tension between the matrix and the inclusions is independent of local shear and variation of interfacial area, failed in predicting the effect of copolymers on the dynamic viscosity and the storage modulus of copolymers modified blends.⁵ However, modification of the emulsion model, taking into account the surface dilation and surface shear moduli function, did not lead to significant enhancement of the model.⁶

On the other hand, Graebing et al.⁴ showed that the influence of particle size distribution on the model predictions is not very considerable. Consequently, eq. (1) was treated in this study without polydispersity effect, assuming:

$$\sum_i \phi_i H_i(Ri) = \phi H(R) \quad (2)$$

where R is the volume average radius of the particles.

As previously discussed, eq. (1) predicts the complex moduli of the blend at frequency. Commonly, G^* explains as $G^*(\omega)_T$, and its calculation requires the data of the complex shear moduli of matrix $G_m^*(\omega)_T$ and inclusions $G_i^*(\omega)_T$ at the same frequency and at a constant temperature. However,

thermomechanical measurements of polymer blend in a large range of temperature proved to be useful to the characterization of polymer blend materials. A judicious way is to explicit the complex modulus as a function of the temperature at a constant frequency $G^*(T)_\omega$. Such experiments require the data of the complex shear moduli of matrix $G_m^*(T)_\omega$ and $G_i^*(T)_\omega$ inclusions at the same temperature and at a constant frequency.

Furthermore, eq. (1) includes special models developed in the past in the literature. Indeed, as shown in the introduction about discussions on Figure 1, three ranges of temperatures can be viewed as original cases:

$T > 175^\circ\text{C}$

The two phases are viscoelastic liquids; the emulsion model, which takes into account the interfacial tension between the two phases, can be applied. The complex modulus $G^*(T)_\omega$ may be explained by analogy to eq. (1) as a function of temperature at a constant frequency. However, such an equation requires the variation of the interfacial tension with temperature. On the other hand, for a blend of viscoelastic polymer without interfacial tension between the two phases ($\gamma_{12} = 0$), the expression of Dickie's model³ is found.

The interfacial tension γ_{12} between the polymers blends may be calculated from the surface tensions of their components⁷ by using the thermodynamic work of adhesion between two different solids and assuming that no reaction takes place between the polymers.

With data values of the apolar disperse and the polar components of the surface tension,⁸ the interfacial tension thus obtained is 1.2 mN/m. As mentioned by Wu, a probable error of ± 0.5 mN/m on the value of γ_{12} can be taken into account by this method.

Furthermore, the interfacial tension can be used to calculate the interfacial thickness between the two polymers. For example, according to Wu, the empirical equation results:

$$\gamma_{12} = 7.6L^{-0.86} \quad (3)$$

where γ_{12} is in mN/m and L is nm.

Then, $L = 8.5$ nm.

In addition, the radius giration of a macromolecular chain constituted by N links, each of length b_0 , which obeys a Gaussian statistic conformation, is expressed as:

$$Rg^2 \approx C_\infty N b_0^2 / 6 \quad (4)$$

C_∞ represents the stiffness of the polymer and can be calculated from the local structure of the chains. Values of C_∞ have been reported in the literature.⁹ Values of C_∞ of 7 and 5.8 were reported for polyethylene and polypropylene, respectively.

According to expression (4), the radius of gyration of a chain of two melt polymers is about 18 nm. This value is of the order of magnitude of the value of the interface thickness. This means that the interface of the blend is characterized by high interaction forces between the two polymers other than hydrodynamic ones.

As generally admitted in the literature, the interfacial tension decreases with increasing temperature. This is generally true for liquid-liquid blend systems. Then the temperature can become one of the most influential factors that control the rheological behavior. However, from the literature data⁷ of surface tension, the variation of the interfacial tension with the temperature in the experimental range of 170°C to 220°C is the following:

$$\frac{d\gamma_{12}}{dT} = 4 \times 10^{-3} \text{ mN/m/}^\circ\text{C} \quad (5)$$

This equation means that the interfacial tension increases with increasing temperature. Nevertheless, in view of the error on the determination of γ_{12} , one can assume that the interfacial tension is independent of the temperatures between 170 and 220°C.

80°C < T < 155°C

At these temperatures, the polypropylene is in a partial crystalline state. Therefore, the inclusions of polypropylene can be assumed to be rigid spheres in comparison with viscoelastic liquid behavior of the matrix. Then,

$$G_i^*(T)_\omega \gg G_m^*(T)_\omega \quad (6)$$

$$H(T)_\omega = 0.5 \quad (7)$$

$$G^*(T)_\omega = G_m^*(T)_\omega \left(\frac{1 + 3/2\phi}{1 - \phi} \right) \quad (8)$$

If the matrix is a Newtonian liquid, eq. (8) amounts to Einstein's result on the viscosity of dilute suspension of rigid spheres in a Newtonian liquid.

T < 65°C

As shown in Figure 1, the two phases can be assumed to behave as viscoelastic solids. Therefore, eq. (1)

amounts to results of Uemura and Takayanagi¹⁰ derived for incompressible materials ($\nu = 0.5$)

$$G^*(T) = G_m^*(T) \frac{3G_m^*(T) + 2G_i^*(T) - 3\phi(G_m^*(T) - G_i^*(T))}{3G_m^*(T) + 2G_i^*(T) + 2\phi(G_m^*(T) - G_i^*(T))} \quad (9)$$

This expression has been extended to the viscoelastic case by a corresponding principle from Kerner's expression. Actually, the two phases behave as two elastic solids:

$$G'(T)_\omega \gg G''(T)_\omega$$

consequently:

$$G_m^*(T)_\omega = G'_m(T)_\omega \text{ and } G_i^*(T)_\omega = G'_i(T)_\omega \quad (10)$$

and Kerner's expression (2) is obtained.

EXPERIMENTAL

Materials

PP used was an Appryl 3120 MN1, melt index 12, and molecular weight $M_w \approx 220$ kg/mol and $M_n \approx 80$ kg/mol. EVA and EMA commercial copolymers containing, respectively, in weight 28% of vinyl acetate (Evatane 2803) and 29% of methyl acrylate (Lotryl 29M03) were supplied by Elf Atochem Company. Actually, EVA and EMA copolymers are miscible and were preblended in a twin screw extruder. One must specify that the choice of the EVA-EMA (50-50 in weight) miscible blend rather than a EVA system was only justified by the use of this

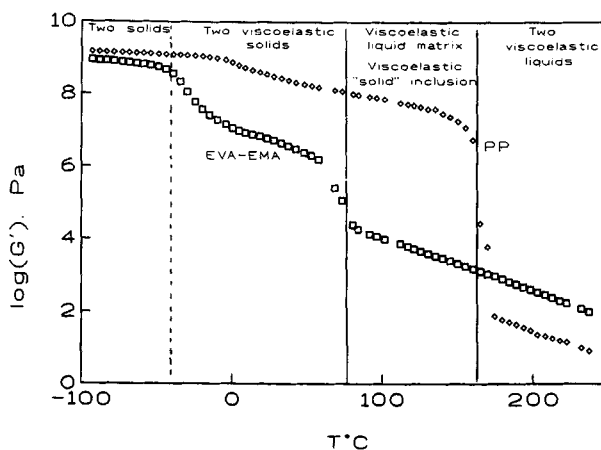


Figure 1 Experimental G' vs. temperature for (EVA-EMA) and PP samples, $\omega = 0.3$ rad/s.

system in previous studies.^{8,11} Then, the respective molecular weights of the EVA-EMA sample are as follows: $M_w = 74$ kg/mol and $M_n = 20.4$ kg/mol.

Moreover, the (EVA-EMA)/PP blend was mixed in twin screw extruder from Leistritz (LSM30-34). Rheological samples were put in shape between two heating plates under a low pressure and at the temperature of 220°C. The fraction volume of polypropylene dispersed phase in EVA-EMA matrix was constant in all the experiments and equal to 0.22.

Morphological Analysis

Dynamic light scattering has been developed in order to determine the particle size distribution of latex particles. Moreover, this technique has been extent to the study of particle size distribution of polymer blends.¹² Experimentally, the (EVA-EMA)/PP blend was dissolved in tetrahydrofuranne (THF) solvent. At room temperature, THF is only solvent of the EVA-EMA phase and does not swell the polypropylene phase, as observed in a previous work.¹¹ Then, inclusions of polypropylene remain in a solid state and behave as a suspension of fine particles of the size of the morphology blend.

On the other hand, the particle size distribution was measured on rheological samples and controlled at the end of the rheological experiments. No deviation on the particle size distribution of the blend was observed. Then, the weight and number average diameters of the PP inclusions were: $R_v = 0.7$ μm and $R_n = 0.65$ μm , respectively, with R_v/R_n the polydispersity of the size inclusions lower than 2.

Rheological Experiments

The frequency and temperature sweep experiments of melt samples were carried out on a Rheometrics RMS800 mechanical spectrometer using a parallel geometry with a radius of 12.5 mm. In all cases, sample response linearity with respect to strain amplitude was verified and nitrogen gas was used to prevent thermal oxidation.

On the other hand, a time sweep experiment at the temperature of 220°C and at 0.3 rad/s was used in order to control the thermal stability of the melt. During 2 h of experiments a constant value of complex moduli was measured. Furthermore, the products of thermal degradation of copolymers (acetic acid), analyzed by thermogravimetry coupled with gas chromatography,¹³ appear for temperatures higher than 290°C.

On the other hand, temperature and frequency sweeps of "solid" samples were carried out on a

RMS800, too. Dimensions of samples are approximately $(2 \times 10 \times 50)$ mm³. Then, Figure 1 presenting (EVA-EMA) and PP samples results in the range of temperature from -100 to 220°C obtained from dynamic plane-plane and torsion rectangular test. A good joining between tests carried out on melt and solid samples was obtained. The temperature was measured with a precision of $\pm 0.5^\circ\text{C}$.

RESULTS AND DISCUSSION

Time-Temperature Superposition

The frequency-dependence complex modulus $G^*(\omega)$ of EVA/EMA and PP samples was measured at a range of temperature of 95–220°C and 175–220°C, respectively. These temperatures curves are shifted onto master curves at the reference temperature of 200°C using the shift factors a_T represented in Figure 2.

This figure shows that the shift factors of the pure constituents obeys an identical Arrhenius' law, with an activation energy of 40 kJ/mol. This value is close to data $E_a = 36$ kJ/mol of the literature.¹⁴

On the other hand, as previously introduced, two different rheological behaviors of the blend can be distinguished from the transition zone of melting temperature ($T \approx 165^\circ\text{C}$) of polypropylene inclusions: at temperatures lower than this critical value, the blend behave as a polymer filled system with rigid reinforcing agents. Then, assuming the validity of eq. (8), the master curve of the matrix and master curve of the blend obey an identical time-temperature principle.

At temperatures above the melting temperature of the PP cristallines, a master curve, within experimental precision, is obtained for the blend. From Palierne's model point of view, assuming that the model is suitable, this result means that the interfacial tension at this range of temperatures is slightly dependent of the temperature, leading to the validity of the equivalency of the forms of the dependences of the viscoelastic function. Moreover, the time-temperature behavior of the blend results of the hydrodynamic interactions of the two phases on each other and would be dissociated from time-temperature of the matrix. Nevertheless, as the two constituents exhibits identical time-temperature behavior, the blend obeys an identical time-temperature law, as shown in Figure 2.

Frequency Sweep

As previously reported, two different rheological behaviors of the blend can be distinguished according

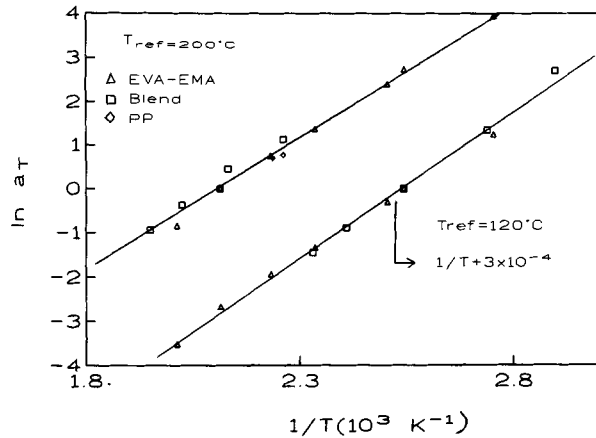


Figure 2 Shift factors a_T from master curves. $T_{ref} = 200^\circ\text{C}$ and $T_{ref} = 120^\circ\text{C}$.

to two different rheological behaviors of the inclusions.

$T > 175^\circ\text{C}$

At this range of temperatures, the two phases behave as viscoelastic liquids. At low frequencies characterized by the long relaxation times, the relaxation mechanisms of the blend are due to geometrical relaxation of the inclusions of melt polypropylene. Then, this system shows elastic properties characterized by a rough shape of a secondary plateau modulus at long relaxation time, as shown in Figure 3. From eq. (1), the value of the interfacial tension can be estimated to 1.3 mN/m as the value leading to the best agreement between experimental data and theoretical curves. This value is close to the value of the interfacial tension ($\gamma_{12} = 1.2$ mN/m) calculated in the thermodynamic adhesion theories. On the other hand, the values of the plateau modulus G_p ($G_p = 460$ Pa) and characteristic relaxation time λ_D ($\lambda_D = 4.6$ s) calculated from the relations derived from the emulsion model by Graebing et al.⁴ are reported in Figure 4. The relaxation time λ_D is the time required for deformed droplet to recover its spherical equilibrium. Although the secondary plateau is not well defined, a good agreement can be observed between theoretical values and experimental data.

However, at very low frequencies, the Palierne's model does not predict correctly the rheological behavior of the blend. Such a result was previously observed^{5,15} for a copolymer-modified immiscible blend in which the interactions at the interphase zone is increased by the addition of compatibilizer copolymers. The study concluded that the predom-

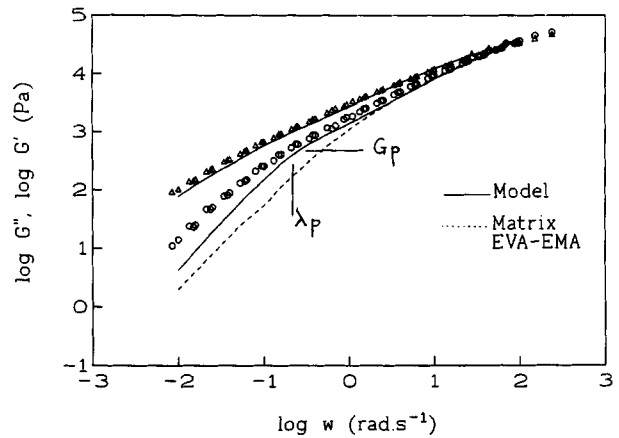


Figure 3 Comparison between experimental data and emulsion model, $T_{ref} = 200^\circ\text{C}$.

inating effect is due to high topological interactions at the interphase that are not take into account in any theoretical models. Therefore, the (EVA-EMA)/PP blend may be viewed as a blend with an interfacial zone where interactions other than hydrodynamic act on the linear viscoelastic response of the blend when any copolymer was added in the blend.

At the opposite, in the case of the PS/PPMA blends in the presence of PS-PMMA diblock copolymers, Graebing et al.⁴ observed that the emulsion model described quantitatively the linear viscoelastic properties of the blend conforing the assumption that the long-time relaxation mechanisms are due to geometrical relaxation of the droplets of the dispersed phase. Note that the polydispersity of PS and PMMA samples was well characterized and the PS PMMA homopolymers can be considered

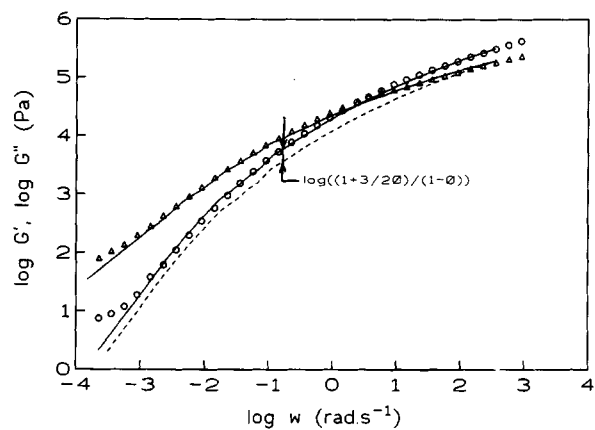


Figure 4 Comparison between experimental data and emulsion model, $T_{ref} = 120^\circ\text{C}$.

as monomolecular ($p \approx 1.05$), whereas the polydispersity of the samples of Germain et al.¹⁵ (Polypropylene/polystyrene blend) Brahim et al.⁵ (Polypropylene/Polyamide blend) studies was not published in their respective articles. However, as polymers provided from industrial developments, it can be expected that these polymers present a broad molecular weight distribution. Furthermore, it was predicted that small chains accumulate slightly at the interface,¹⁶ lowering the interfacial tension. However, the decrease of the interfacial tension with the migration of the shorter chains is valid only at high temperatures.¹⁷ These comments then state the question of the influence of the molecular weight distribution of polymer samples on the rheological behavior of the blend and mainly the contribution of short polymer chains to the interactions in the interfacial zone.

80°C < T < 155°C

In this range of temperatures, the matrix behaves as a viscoelastic liquid, whereas the dispersed phase behaves as a solid elastic ($G' \approx 10^8$ Pa). Then, Figure 4 shows that the eq. (10) can be applied as a predictive relation of the rheological behavior of the blend. A good agreement is obtained in a large frequency range between experimental data and theoretical curve. Indeed, as predicted by the model (relation 8), a vertical shift with the value $\log[(1+3/2\phi)/(1-\phi)]$ is observed between experimental data of the blend and experimental data of the matrix. However, at the low frequencies, the emergence of secondary plateau in G' can be well defined. Obviously, this plateau cannot be attributed to the deformability of the dispersed crystalline polypropylene phase as at the temperature higher than 175°C. On the other hand, such a phenomenon is not accounted for by any rheological models. This plateau

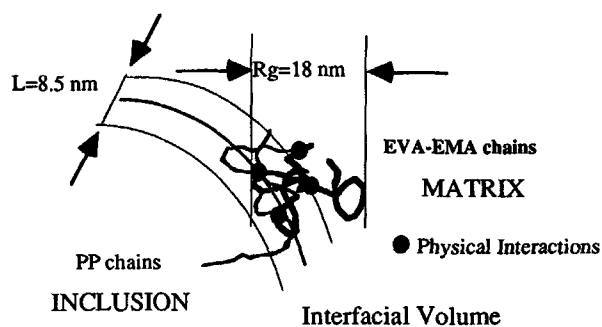


Figure 5 Schematization of the interfacial volume through physical trapping of the entangled polymer chains.

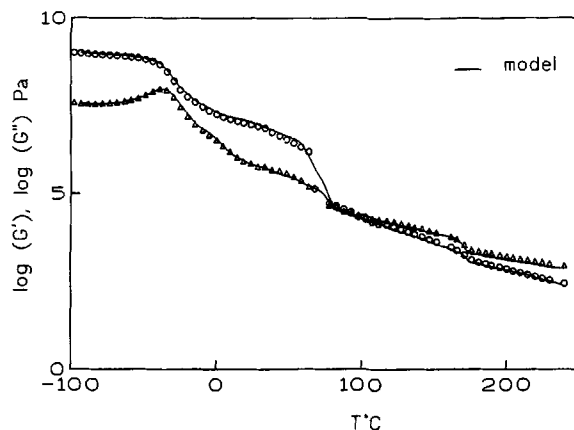


Figure 6 Temperature sweep experiment, $\omega = 0.3$ rad/s. Comparison between experimental data and Paliere's model [eq. (1)].

is probably due to a network-type structure formed by the interconnectivity of the particles, as already observed by Bousmina and Muller¹⁸ in the case of PMMA/rubber particles blends. Actually, the volumic concentration of the dispersed phase is higher than the concentration of percolation ($\phi_p = 0.15$) of monodisperse spheres.¹⁹ This interconnectivity can be attributed to the high interactions at the interphase particle/matrix. At these experimental temperatures, polypropylene inclusions are in a crystalline state. Therefore, the (EVA-EMA) chains in the interfacial volume may be physical trapped by the crystalline network that induces an interconnectivity at the interphase leading to a modification of long relaxation time mechanisms by trapping physical entanglements of the matrix. Such a concept is illustrated in Figure 5.

Temperature Sweep

Such an experiment is an usual way for describing the thermomechanical properties of blends. Temperature sweep experiments were carried out in a large range of temperatures of -150 to 225°C at a constant frequency of 0.3 rad/s. All the special cases, as previously defined, of the Paliere's model applications can be considered in Figure 6. As previously discussed, the interfacial tension was assumed independent of the temperature. Furthermore, the Uemura and Takayanagi model [eq. (9)] is valid for $T < 70^\circ\text{C}$. Therefore, this figure shows that the Paliere's model [eq. (1)] including different rheological models, predicts quite well the thermomechanical properties of the (EVA-EMA)/PP blend. However, the experiment frequency of 0.3 rad/s is

not low enough for detecting the application limits of the model, as previously observed in frequency sweep experiments at the low frequencies.

CONCLUSIONS

The rheological properties obtained for the (EVA-EMA)/PP blend have been used for discussing the predictions of the emulsion model developed by Palierne. On the other hand, such a blend proved to be judicious to consider the previous special cases of the model.

However, at low frequencies, the rheological behavior of the blend is not correctly predict by the model. This result means that interactions other than hydrodynamics can exist at the interfacial region. From the theoretical evaluation of the thickness of the interphase and the radius giration of a macromolecular chain, a concept of interfacial volume was defined. Then, physical entanglements between the chains of the two constituents leading to topological interactions may be assumed at the interphase.

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