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Viscoelastic study of oil diffusion in molten PP and EPDM copolymer

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Abstract

This paper is focused on two important features of the addition of a plasticizer (oil) into a polymer matrix: The influence of its concentration on the viscoelastic properties of the blend, and the diffusion mechanisms that take place during mixing. A rheological approach was chosen for its capacity to support relatively simple modeling.

In the first part of the study, we demonstrate that the incorporation of a plasticizer in a PP matrix results in a reduction of entanglements and a global shift of the relaxation time spectrum. A time-concentration superposition is observed. A dilution model, based on the free volume theory, is implemented and predicts successfully the evolution of viscosity of binary PP/oil blends with oil content. This model appears, however, unsuitable for EPDM, whose relaxation mechanisms do not seem to be modified in the same manner. This suggests the presence of intermolecular interactions in EPDM that are not totally released in spite of oil addition.

In the second part, the transport of the plasticizer in the polymer matrices is followed during viscoelastic testing. The molecular weight of PP in shown to have no influence on the diffusion kinetics, whereas diffusion appears faster in EPDM. The implementation of a model relying on a Fickian description of diffusion leads to satisfactory agreement with experiments for PP only, and allows for the calculation of the oil/polymer mutual diffusion coefficient. Again, a poor quality of fit is achieved with EPDM, suggesting that elastic diffusion is enhanced with this polymer.

Keywords: Plasticized polymers; Diffusion; Modeling

1. Introduction

Thermoplastic vulcanizates (TPVs) have developed for more than a decade and represent a promising alternative to vulcanized elastomers. The particular morphology of TPVs results from selective cross-linking of an elastomer during intensive mixing in a molten thermoplastic phase. This process is generally referred to as dynamic vulcanization. The resulting morphology consists of finely dispersed rubber particles in a thermoplastic matrix. Most commercial TPVs are made from isotactic polypropylene (PP) and ethylene-propylene-diene terpolymer (EPDM).

The quality of mixing is a key issue in achieving a satisfactory microstructure since it governs both the dispersion of the reactive (curing) system and the size of the cross-linked rubber particles. Dynamic cross-linking is generally carried out in combination with the addition of plasticizer (oil) for the production of soft materials with good processability and elastic recovery. Considering the additional incorporation of solid or liquid ingredients like fillers, pigments and stabilizers, TPVs can be seen as very complex multiphase blends. This complexity partially hinders a clear comprehension of all the mechanisms that determine the solid state and flow properties of these materials. Therefore, in the present work, we limited the scope to the incorporation of the plasticizer, viz. paraffinic oil in this case. In the rubbery, i.e. solid state, the oil is generally believed to be predominantly absorbed by the EPDM phase [1], although some of it must be present in the amorphous region of the PP phase [2]. In the melt, the oil is distributed over the EPDM and PP phases. This explains improved processability [1], but the direct quantification of this distribution at processing temperature was undertaken only recently by implementing solid state ^{13}C NMR spectroscopy [3].

This illustrates the complementary contributions of microscopic- and macroscopic-scale techniques for a better understanding of microstructure and properties. However,

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one of the major drawbacks of the former group of techniques is their limited availability to most TPV users. Therefore, rheology appears as a suitable approach for improving comprehension of selected aspects of a TPV elaboration. As a matter of fact, a polymer in its amorphous state, which undergoes mixing with different additives and then the development of chemical cross-links, first displays a modification of its 'liquid' viscoelastic properties prior to being converted into a viscoelastic solid. So, at a macroscopic scale, rheology reveals phenomena that appear at a microscopic scale. Nevertheless, the interpretation of morphology in relation with rheological or mechanical properties is not straightforward. If this type of experimental investigation is chosen, much care has to be taken in separating the different factors of influence. The reduction of the number of variables is of paramount importance. As far as plasticizer mixing is involved, for example, this commands to study at first binary mixtures of plasticizer with every polymer constituent of the TPV, separately. By doing so, Sengers et al. [4] modeled the distribution of oil in PP/EPDM TPVs and showed that oil concentration is all the higher in the elastomer phase as the PP content in the TPV blend is high. This is confirmed by the work of Jayaraman et al. [5], who also implement TEM for additional characterization of the oil distribution.

However, the most interesting issue in both these papers is the confirmation that a time-concentration superposition principle holds for polymer/oil binary blends. Indeed, a shifting procedure was first proposed by Nakajima and Harrel [6], who examined the effect of oil concentration on the dynamic viscosity of elastomers. Two concentration-dependent shift factors were introduced, applied to the viscosity and shear rate, respectively. In the recent papers, this vertical and horizontal shift of rheological curves like those of G' vs. angular frequency [4] or shear viscosity vs. apparent shear rate [5] is successfully implemented and leads to mastercurves. Most interestingly, the shift factors can be modeled as power law relations on the polymer volume fraction in the polymer/oil mixture, in a similar expressions as those established by Graessley and Edwards [7] for a polymer/diluent system.

All these papers develop a 'static' approach of the polymer/oil mixtures, insofar as the mixing process itself is not considered. As mentioned earlier, mixing is a key issue in TPVs elaboration, and the plasticizer incorporation in the polymer phases is an illustration of mixing of fluids with different viscosities. Simple models, like the striation one developed by Tadmor and Gogos in the 70's [8], fail for fluids with very low viscosity ratio. Cassagnau and Fenouillot [9] demonstrated that different mixing modes could be observed according to the value of the viscosity ratio. This requires accounting for diffusion mechanisms. Joubert et al. [10] went more thoroughly into the modeling of diffusion of a low viscosity additive into a molten polymer by implementing calculations of the mutual diffusion coefficient based on the free volume theory ([11–13]). The interest of the rheological approach in the determination of diffusion coefficients is clearly demonstrated in these papers. The key influence of the plasticizer (oil) on the processing properties of a TPV is addressed in this paper through a rheological study relying on well-simplified systems and conditions. Neat polymers and pre-blended polymer/oil binary mixtures were, therefore, tested to support modeling of the evolution of the viscoelastic properties upon oil addition. In a second part, the diffusion process of the plasticizer is demonstrated in the rheometer following a protocole assessed in previous work [10]. The cross-linking process involved in a TPV elaboration is deliberately left aside here and will be the point of a subsequent paper.

2. Experiment

2.1. Materials

Experiments were carried out with bulk polymers (PP or EPDM) and with binary blends of those with various amounts of paraffinic oil (Torilis 7200, TotalFinaElf, France). The specific gravity of this oil is $0.90\ \mathrm{g\cdot cm^{-3}}$ at 20 °C.

The polypropylene used here is an isotactic homopolymer (PPH 3060, Atofina, France) whose molecular characteristics are $\bar{M}_\mathrm{n} = 72{,}000$ g/mol and $\bar{M}_\mathrm{w} = 384{,}000$ g/mol. It has a melting temperature of 162 °C, a melt flow index close to 2 (1.7 g/10 min, at 230 °C, under 2.16 kg) and a specific gravity of $0.905\ \mathrm{g\cdot cm^{-3}}$. It will be denoted PP2 in the following by reference to its MFI. PP2/oil mixtures were prepared at two different oil concentrations by volume, 9 and 23%.

The EPDM used is Vistalon 8800 (ExxonMobil Chemical), a material that comprises a 53.5% ethylene/10% ethylidene norbornene–terpolymer. The following values of molecular weight were measured: $\bar{M}_\mathrm{n} = 170{,}000$ g/mol and $\bar{M}_\mathrm{w} = 310{,}000$ g/mol. This terpolymer, with a specific gravity of $0.86\ \mathrm{g\cdot cm^{-3}}$, is oil-extended with 13% paraffinic oil, what yields a total specific gravity of $0.87\ \mathrm{g\cdot cm^{-3}}$ and a Mooney viscosity $\mathrm{ML}_{(1+4)}$ at 125° of 73. Additional oil was incorporated to Vistalon 8800 with three concentrations: 9, 29 and 36% by volume. These volume fractions do not take into account the 13% oil already present in 'neat' Vistalon 8800, which is the reference material in our tests.

These materials were kindly supplied by Hutchinson (Chalette sur Loing, France). They were used as received from the supplier.

2.2. Sample preparation

The blends were prepared in an internal batch mixer (Haake Rheomix 60 $\mathrm{cm^3}$), at 50 rpm and at a temperature of 200 °C for PP and 120 °C for EPDM. The following protocol was adopted: First, the polymer was introduced into the cavity and sheared by itself for 5 min in order to ensure complete melting (PP) and thermal homogenization. Then, the oil was poured and the two components were mixed for some time, varying between compositions, until a stabilized torque was reached. After dump, all test samples were compression molded into 1 mm-thick sheets at 200 °C for 10 min. The molded samples were stored away from light, at room temperature.

2.3. Viscoelastic measurements

All specimens were tested on a Rheometrics RMS800 rheometer using a 25 mm parallel plate geometry, in the linear viscoelastic regime. A specific protocol was followed for diffusion experiments, as thoroughly described in previous work [10], and is briefly presented here: The polymer disk was placed on the lower plate in the heated oven and allowed for a few minutes for melting or shape relaxation in order to have a plane surface. The plasticizer (oil) was transferred with a syringe between the polymer sample and the upper plate, and the total thickness was measured. For diffusion experiments we used a 50 mm plate geometry.

The evolution of the dynamic moduli G' and G'' and of the complex viscosity η^* during diffusion of the oil in the polymer matrix was followed by time sweep oscillatory shear experiments ($\omega = 10$ rad/s) at a given temperature. The strain amplitude was manually adjusted along the test in order to maintain the torque at a measurable level at the beginning and to remain within the domain of linear viscoelasticity. Furthermore, at the end of the diffusion process, when oil and polymer formed an homogenous medium, a frequency sweep oscillatory shear experiment was performed at the same temperature.

3. Viscoelatic modeling of plasticized PP and EPDM samples

As mentioned in the introduction, the incorporation of oil into a polymer matrix leads to a modification of the viscoelastic properties of the material due to a dilution effect similar to that of a solvent. This influence was successfully taken into account in some recent studies about TPVs ([4,5]) by applying a shifting procedure to the different viscoelastic functions ($G'(\omega)$, $G''(\omega)$, $\eta^*(\omega)$, or $\eta(\dot{\gamma})$) in the same manner as time-temperature superposition. From this 'time-concentration' superposition, shift factors could be determined experimentally, but no theoretical support was given to the interpretation of these factors.

In the present work, we refer to a theoretical framework of the dilution effect which was discussed in detail by Marin et al. [14] and recently extended by Gimenez et al. [15]. The viscoelastic parameters such as zero shear viscosity η_0, plateau modulus G_N^0, and steady state compliance J_e^0 are modified with respect to the bulk polymer parameters and depend on the volume fraction of polymer in the solution.

When considering the entangled regime ($M_w > M_{c_{bulk}} \Phi^{-1.25}$), these modifications can be expressed as follows:

$$[\eta_0] = \eta_{0_{bulk}} \Phi^4 \tag{1}$$

$$G^0_{N_{solution}} = G^0_{N_{bulk}} \Phi^{2.25} \tag{2}$$

$$J^0_{e_{solution}} = J^0_{e_{bulk}} \Phi^{-2.25} \tag{3}$$

where $[\eta_0]$ is the intrinsic viscosity at the same free volume (i.e. at the same distance from T_g).

The zero shear viscosity of the polymer solution, $\eta_{0_{solution}}$, can be deduced from $[\eta_0]$ by introducing a free volume correction a_Φ that accounts for the variation of the glass temperature arising from dilution:

$$\eta_{0_{solution}} = [\eta_0] a_\Phi = \eta_{0_{bulk}} \Phi^4 a_\Phi \tag{4}$$

As discussed by Ferry [16], free volume theories allow the variation of the viscosity of liquids with temperature to be expressed as:

$$\eta_0 = C \exp\left(\frac{1}{f}\right) \tag{5}$$

with f, the fractional free volume, and C a constant depending on the nature of the liquid.

Following the approach by Gimenez et al. [15], Eq. (5) can also be written as:

$$\eta_0 = k \exp\left(\frac{E}{RT}\right) \tag{6}$$

where E is the flow activation energy. Thus, the free volume correction is given by:

$$a_\Phi = \exp\left[-(\frac{1}{f_{bulk}} - \frac{1}{f_{solution}})\right] = \exp\left[-\frac{1}{RT}(E_{bulk} - E_{solution})\right] \tag{7}$$

$E_{solution}$ in Eq. (7) is determined assuming an additive law of the free volume, that yields the following law for flow activation energies:

$$\frac{1}{E_s} = \frac{\Phi}{E_b} + \frac{1-\Phi}{E_{solvent}} \tag{8}$$

The value for the flow activation energy of oil (solvent) was derived from steady shear viscosity measurements at different temperatures: $E_{solvent} = 30.2$ kJ/mol. The determination of E_{bulk} for PP and EPDM will be reported later.

So, the free volume correction can be calculated for any polymer volume fraction Φ with Eqs. (7) and (8). Then, the influence of the dilution on the number average and weight average relaxation times ($\tau_n = \eta_0/G_N^0$ and $\tau_w = \eta_0 J_e^0$), is examined. It is derived from the dilution effect on the terminal viscoelastic parameters as described in Eqs. (2)–(4). Thus, in the entangled regime:

$$\tau_{\mathrm{n}}(\Phi) = \tau_{\mathrm{n_{bulk}}} \Phi^{1.75} a_{\Phi} \tag{9}$$

and

$$\tau_{\mathrm{w}}(\Phi) = \tau_{\mathrm{w_{bulk}}} \Phi^{1.75} a_{\Phi} \tag{10}$$

Finally, assuming the applicability of the Cox–Merz rule ($\dot{\gamma} \equiv \omega$) with the present materials, the complex viscosity of the polymer/oil mixtures can be described by the generalized Yasuda–Carreau equation [17].

$$||\eta^*(\omega)_{\Phi}|| = \frac{\eta_{0_{\mathrm{bulk}}} \Phi^4 a_{\Phi}}{\left[1 + (\tau_{\mathrm{bulk}} \Phi^{1.75} a_{\Phi} \omega)^a\right]^{1-\mathrm{n}/a}} \tag{11}$$

where τ_{bulk} is related to a relaxation time of the neat polymer and characterizes the transition between Newtonian and shear thinning behavior. *n* is the flow index and a is a coefficient that depends on the molecular weight distribution. Both are supposed independent from dilution. In the following, $||\eta^*(\omega)||$ will be noted $\eta^*(\omega)$, for simplification.

Modeling the dynamic moduli G'_{Φ} and G''_{Φ} for the binary blends requires that a model for the relaxation modulus $G(t)$ is formulated, what is out of the scope of the present paper.

4. Modeling of the mutual diffusion coefficient

Plasticizers are commonly used in rubber and TPV formulations, and their mixing into the polymer matrix is affected by molecular transport. Therefore, the study of the diffusion of small molecules into a polymer melt is of great importance for a better understanding of such processing operations. One of the most common models for the diffusion of small molecules (generally considered as the 'solvent') in polymeric matrices is free volume theory. The idea that molecular transport is regulated by free volume was first introduced by Cohen and Turnbull [11] and further extensively developed. The principle can be summarized as follows: If V^* is the minimum hole free volume into which a molecule of solvent can jump, and V_{FH} the average specific free volume, the solvent self-diffusion coefficient can be considered proportional to the probability of finding a hole of V^* or larger:

$$D_1 = A \exp\left(-\frac{\gamma V^*}{V_{\mathrm{FH}}}\right) \tag{12}$$

where γ is a numerical factor between 0.5 and 1 introduced to account for the overlap between free volume elements. *A* is a constant related to the gas kinetic theory. This expression is developed in the form [12]:

$$D_1 = D_0 \exp\left(-\frac{E}{RT}\right) \exp\left(-\frac{\omega_1 V_1^* + \xi \omega_2 V_2^*}{V_{\mathrm{FH}}/\gamma}\right) \tag{13}$$

E is the critical energy necessary for a molecule to overcome attractive forces. ω_1 and ω_2 are the mass volume fractions of the solvent and the polymer, respectively, and V_1^* and V_2^* the specific volumes at 0 K. ξ is the molar volume ratio for the solvent and polymer jumping units. D_0 is a constant, pre-exponential factor.

The Flory–Huggins theory enables to obtain the binary mutual diffusion coefficient D_{12} from the solvent self diffusion coefficient D_1. The expression of the former above the glass temperature is then:

$$D_{12} = D_1 (1 - \Phi_1)^2 (1 - 2\chi \Phi_1) \tag{14}$$

with Φ_1 and χ the volume fraction of the solvent in the polymer and the Flory–Huggins interaction parameter, respectively.

Due to the difficulties in measuring diffusion coefficients at the high temperatures characteristic of most polymer plasticization processes, some recent papers [12,13] provided detailed accounts of the means by which to predict most of the parameters of the theory for the solvent and for the polymer matrix. A more recent study [10] demonstrated how these parameters could be derived from viscoelastic measurements as described in Section 2. In the present work, we transform the expression generally found in the literature, in terms of specific volumes and flow activation energies. For that purpose we assume that flow activation energies E_i (species *i*, plasticizer or polymer), in the range of temperatures investigated, are connected to the free volume fraction:

$$\frac{\gamma}{f_i} \equiv \frac{E_i}{RT} \tag{15}$$

with the following definition of the free volume fraction:

$$f_i = \frac{V_{\mathrm{FH}_i}}{V_i^{\mathrm{g}}} \approx \frac{V_{\mathrm{FH}_i}}{V_i^*} \tag{16}$$

where V_i^{g} is the specific volume at glass temperature. Assuming that the total specific volume at temperature *T*, V_i^T, is expressed as $V_i^T = V_{\mathrm{FH}_i} + V_i^*$, and that free volumes are additive $(V_{\mathrm{FH}}/\gamma = \omega_1 (V_{\mathrm{FH}_1}/\gamma_1) + \omega_2 (V_{\mathrm{FH}_2}/\gamma_2))$, the expression of the diffusion coefficient was derived as follows:

$$D_1 = D_0 \exp\left(-\frac{E}{RT}\right) \exp\left[-\frac{\frac{\omega_1}{1+\frac{RT}{E_1}} V_1^T + \xi \frac{\omega_2}{1+\frac{RT}{E_2}} V_2^T}{\frac{\omega_1}{1+\frac{E_1}{RT}} V_1^T + \frac{\omega_2}{1+\frac{E_2}{RT}} V_2^T}\right] \tag{17}$$

It must be noted that, the γ parameter is assumed to be 1 for the solvent and for the polymer and therefore does not appear in Eq. (17) any more. *E* is generally considered to be zero. All other parameters in this equation can be easily measured or extracted from literature.

Therefore, the pre-exponential factor D_0 and ξ, the molar volume ratio for the solvent and polymer jumping units, are the only two remaining unknowns in Eq. (17).

By implementing a model of the viscoelastic functions

(η^*, G' or G'') in conjunction with the diffusion process (resolution, by a slab method, of Fick's equation during diffusion of oil into the polymer matrix between the plates of the rheometer), the D_0 and ξ parameter can be numerically adjusted to fit the modeled evolution of viscosity with time to the experimental measurements, as described in detail in [10]. These parameters are expected to be constant with respect to temperature and molecular weight since they are characteristic of the solvent and polymer species.

5. Results and discussion

5.1. Bulk polymers

The neat polymers were tested in the linear viscoelastic regime for the determination of the storage and loss moduli, G' and G'' and the complex viscosity η^*. As can be seen by comparing Figs. 1 and 2, the viscoelastic behaviors of the two polymers at 200 °C present very different features.

Polypropylene (PP2) exhibits G' and G'' evolutions with angular frequency that correspond to the pattern most often encountered with polyolefins of moderate molecular weight with linear molecular structure. Time temperature superposition was applied (test temperatures: 180, 200 and 230 °C), but the terminal zone is hardly visible even in this enlarged frequency domain (cf Fig. 1). As a matter of fact, the slope of G'' plot is almost 1 at the lowest angular frequencies, whereas G' slope only tends towards the expected value of 2. However, the terminal region can be assumed to exist below 10^{-2} rad s^{-1}. From the master-curve for complex viscosity, the zero shear viscosity can be determined: $\eta^*_{0\ \mathrm{PP}} = 15,200$ Pa s.

According to data from the literature [18,19] the plateau modulus G^0_N for isotactic PPs with comparable $\bar{M}_\mathrm{w}$ to ours is about 4.5×10^5 Pa, relatively independent on breadth of molecular weight distribution. This value will be retained in the following since our data do not allow determining the plateau value precisely. J^0_e can be derived from the G' and G'' plots in the terminal region, and the terminal relaxation time corresponds to the cross-point between G' and G''. So, the values of the terminal viscoelastic parameters can be easily determined for polypropylene. They are gathered in the first column of Table 1.

The flow activation energy of bulk polypropylene derived from our measurements is $E_\mathrm{PP} = 37$ kJ/mol.

EPDM does not exhibit similar behavior to PP. Time-temperature superposition was also performed successfully, as can be seen in Fig. 2 where the master-curves for G' and G'' at 200 °C are plotted with data obtained at temperatures from 160 to 235 °C. Their slopes and relative positioning clearly indicate a predominantly elastic behavior in the frequency range explored. The flow activation energy was found to be about 48 kJ/mol. In terms of flow properties, the flow index $(1+(d \log \eta^*/d \log \omega))$ calculated in the high frequency domain is 0.35. However, in the frequency region below 1 rad/s, the slope of the viscosity curve does not show any trend towards a decrease as frequency decreases. It can be concluded that the terminal zone, if it exists, is located at frequencies far below 10^{-2} rad/s. Consequently, the terminal relaxation time would be several orders of magnitude larger than that of PP.

5.2. Binary polymer/plasticizer mixtures

Fig. 3(a) (symbols) illustrates the influence of oil on the viscosity of polypropylene/oil mixtures. The incorporation of moderate quantities of oil (9 and 23%) into the PP matrix reduces considerably the zero shear viscosity, for example by a factor 5 approximately from 0 to 23%. In addition, it somewhat enlarges the Newtonian domain and affects the flow index. This clearly expresses the influence of the plasticizer in decreasing relaxation times.

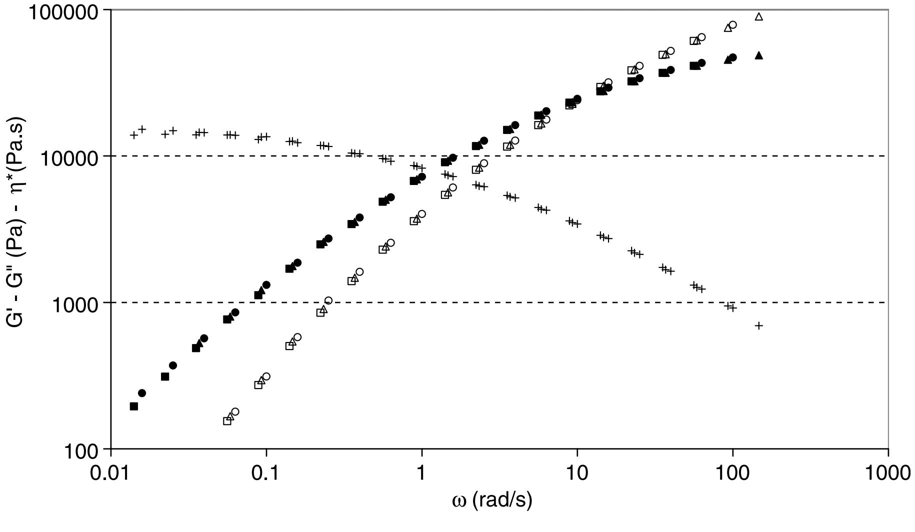

Fig. 1. Viscoelastic behavior of PP2 at 200 °C. Master-curves for G' (open symbols), G'' (closed symbols) and η^* (+).

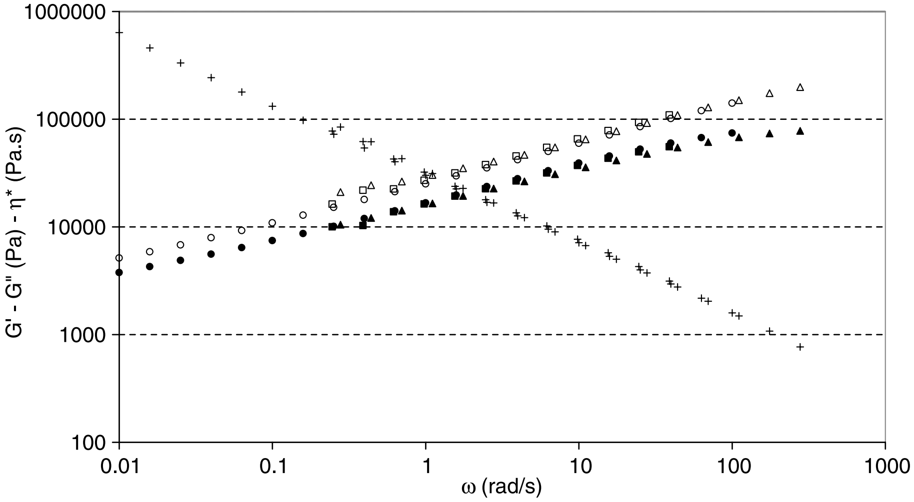

Fig. 2. Viscoelastic behaviour of EPDM at 200 °C. Master-curves for G' (open symbols), G'' (closed symbols) and η^* (+).

Fig. 3(b) shows the evolution of G' and G'' with increasing oil content. As anticipated, the moduli are decreased significantly and, as indicated by the shift of the G'–G'' cross-point towards higher frequencies, relaxation times are decreased, too. The values of the terminal relaxation parameters measured with these binary PP/oil blends can be found in Table 1.

Plasticizers (oils) are of common use with most EPDMs at relatively high weight fractions, therefore the properties of EPDM/oil blends are reported in Fig. 4(a) and (b) for oil contents up to 37.5%. For these binary mixtures, the shape of viscosity plots (Fig. 4(a)) is very similar to that of pure EPDM, but the viscosity values are significantly decreased (about a decade, a little more at low angular frequency). The flow index slightly increases with increasing oil content, reaching ca. 0.41 for the most plasticized sample. This reduction of the shear sensitivity of the bulk due to the presence of small molecules again expresses the decrease of relaxation times. The shape of these viscosity profiles is quite complex. Indeed, the evolution of curvature of the plot, already noticed for the raw material, is emphasized for its blends with plasticizer: the concavity of the plot changes between the low and high frequency regions and an inflexion point appears in the 0.1–1 rad/s interval, approximately. However, the curves do not remain just 'translated' from one another, but tend to be 'parallel' in the low frequency domain and to get closer at high frequencies.

This is illustrated in a different manner in Fig. 4(b), where the storage and loss moduli are plotted for the three binary blends ($\Phi_{\mathrm{EPDM}}=0.91$, 0.71 and 0.64): All these present a cross-point between G' and G'' whereas the neat EPDM does not (cf Fig. 2). Consequently, the observation of Fig. 4(a) and (b) enables one to predict that a time-concentration superposition is not possible with EPDM/oil blends.

Modeling the effect of oil on PP2/oil blend viscosity requires first the free volume correction a_Φ to be calculated from the flow activation energies E_{PP} and E_{solvent}. The values of a_Φ are reported in Table 1. As shown from the more detailed results reported in Table 1, this model provides values of the steady-state compliance J_e^0 and relaxation time τ_w that are in reasonable agreement with measured values. As expected, all relaxation times decrease as polymer volume fraction decreases. The computed relaxation time τ_n $(=\eta_{0_{\mathrm{calc}}}/G^0_{\mathrm{N_{calc}}})$ compares well with measurements of the relaxation time τ_0 from G'–G'' cross-point. The plateau modulus G_N^0 cannot be validated due to lack of experimental data.

The results for the complex viscosity η^* are plotted in solid lines in Fig. 3(a). According to Eqs. (4) and (9), shift factors of $\Phi^4 a_\Phi$ and $\Phi^{-1.75}/a_\Phi$ were applied on the

Table 1
Terminal viscoelastic parameters of polypropylene and polypropylene/oil binary mixtures at $T=200$ °C

PP/oil composition (w/w)	100/0	100/10 ($\Phi=0.91$; $a_\Phi=0.86$)		100/30 ($\Phi=0.77$; $a_\Phi=0.68$)	
		Measured	Calculated	Measured	Calculated
η_0 (Pa s)	1.5×10^4	6.4×10^3	8.9×10^3	2.8×10^3	3.6×10^3
J_e^0 (Pa^{-1})	3.6×10^{-4}	3.8×10^{-4}	4.5×10^{-4}	5.5×10^{-4}	6.5×10^{-4}
G_N^0 (Pa)	4.5×10^5	–	3.6×10^5	–	2.5×10^5
τ_0 cross-point (s)	1×10^{-1}	4×10^{-2}	–	2.5×10^{-2}	–
τ_n (s)	3.4×10^{-2}	–	2.5×10^{-2}	–	1.4×10^{-2}
τ_w (s)	5.5	2.4	4.0	1.5	2.3

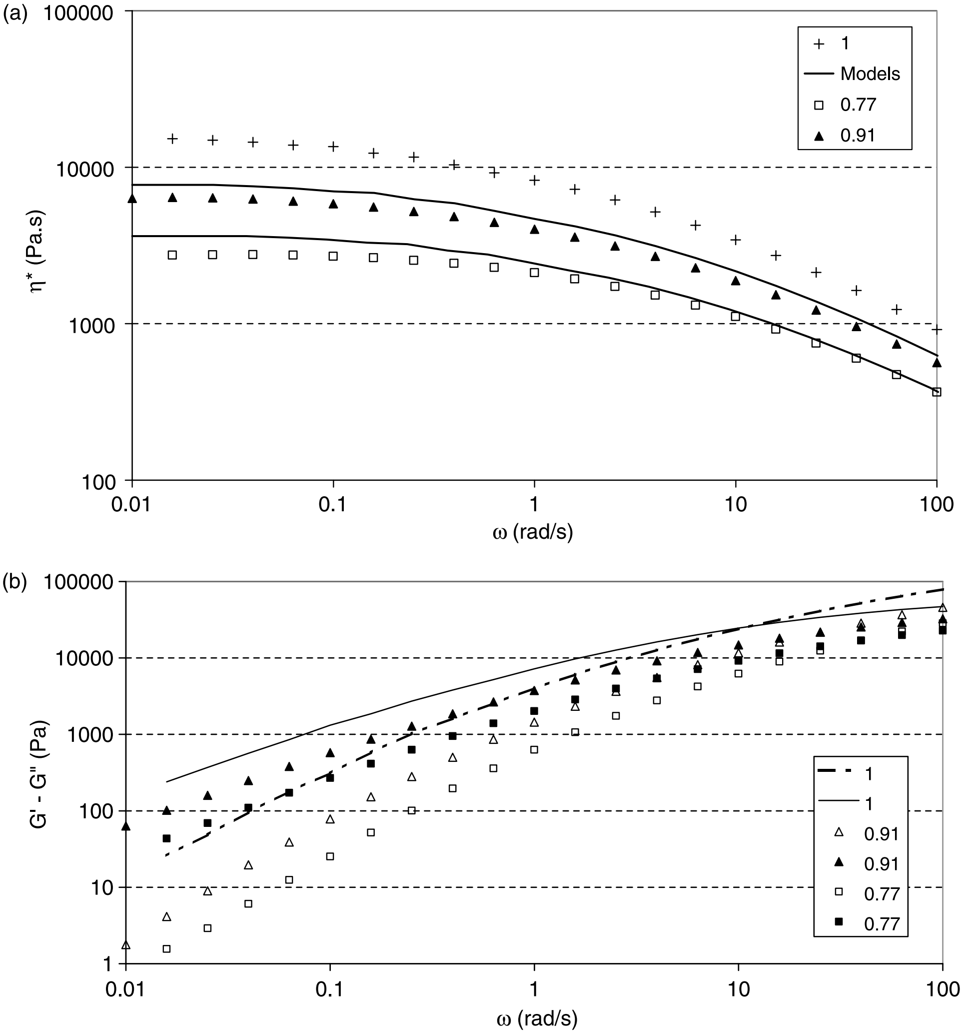

Fig. 3. (a) Complex viscosity vs. ω at 200 °C for different PP2 volume fractions: (+) pure PP2, (▲) $\phi=0.77$, (□) $\phi=0.91$. Solid lines correspond to the model which describes viscosity at $\phi=0.77$ and $\phi=0.91$. (b) Viscoelastic behavior of PP2 at 200 °C with several polymer volume fractions. Solid line: G'' of pure PP2 and dashed line: G' of pure PP2. Open and closed symbols for G' and G'', respectively, at $\phi=0.77$ and $\phi=0.91$.

viscosities and frequencies, respectively. The agreement between experiment and model is very satisfactory, despite a slight over-prediction of zero shear viscosity (Table 1). Consequently, it can be said that a dilution model is suitable to predict the modification produced on viscosity by the presence of the plasticizer, whatever the frequency. This is consistent with the fact that molten PP comprises entangled macromolecules whose topologic interactions with neighboring molecules, and therefore relaxation mechanisms, are homogenous in nature. According to the theory by De Gennes about solvent osmotic pressure in a polymer medium, the presence of the plasticizer induces a reduction of entanglements, leading to an overall shift of the relaxation time spectrum with oil content.

As anticipated, the dilution model fails in fitting experimental data with EPDM/oil blends, whatever the volume fraction of polymer. For clarity purposes, only the $\Phi_{\mathrm{EPDM}}=0.64$ blend is represented in Fig. 5, but the trends for other compositions are exactly same. The viscosity curve shifted from neat EPDM, by application of similar shift factors as for PP, clearly diverges from experimental data both in the low and in the high frequency domains. Data are over-predicted by the model at low frequencies, and under-predicted in the high frequency region. This demonstrates that relaxation mechanisms are not modified in the same way in the presence of the plastifier, and therefore suggests structural heterogeneities in EPDM. High frequency under-prediction may be due to the presence of intermolecular interactions that are not totally released in spite of the plasticizer. Why the model fails in predicting low frequency behavior is not clear yet.

It can be noted that the paper by Sengers et al. [4] presented ‘time-concentration’ superposition of dynamic moduli of EPDM/oil binary mixtures. However, in the

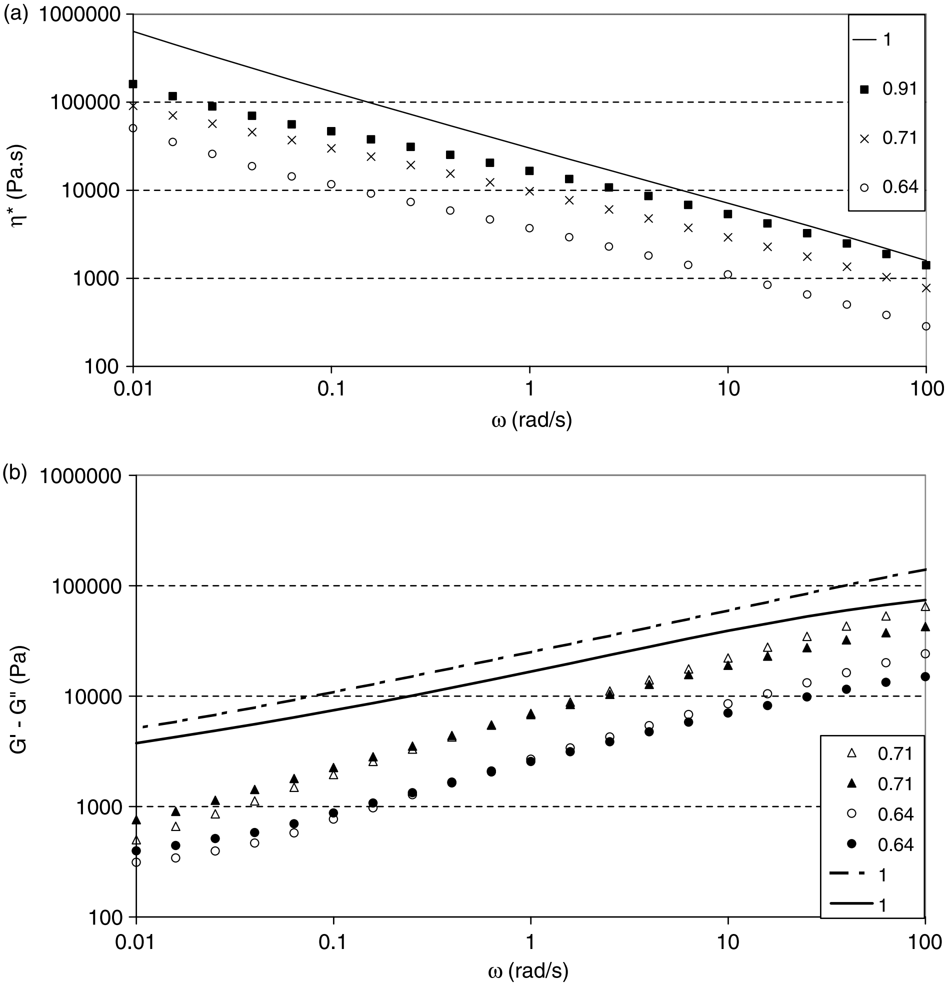

Fig. 4. (a) Complex viscosity vs. ω at 200 °C for several EPDM volume fractions: (■) $\phi=0.91$, (×) $\phi=0.71$, (○) $\phi=0.64$. Solid line corresponds to neat EPDM. (b) Viscoelastic behaviour of EPDM at 200 °C with several polymer volume fractions. Solid line: G'' of neat EPDM; dashed line: G' of neat EPDM. Open and closed symbols for G' and G'', respectively, at $\phi=0.71$ and $\phi=0.64$.

frequency domain explored in that study, the behavior of the blends was predominantly elastic (G' exhibited a clear plateau at lower frequencies and was two decades higher than G''), and terminal flow was definitely not observed. Therefore, the success of the time-concentration superposition on G' (and its relative failure with G'' in the paper in question) cannot be discussed only with respect to reduction of entanglements.

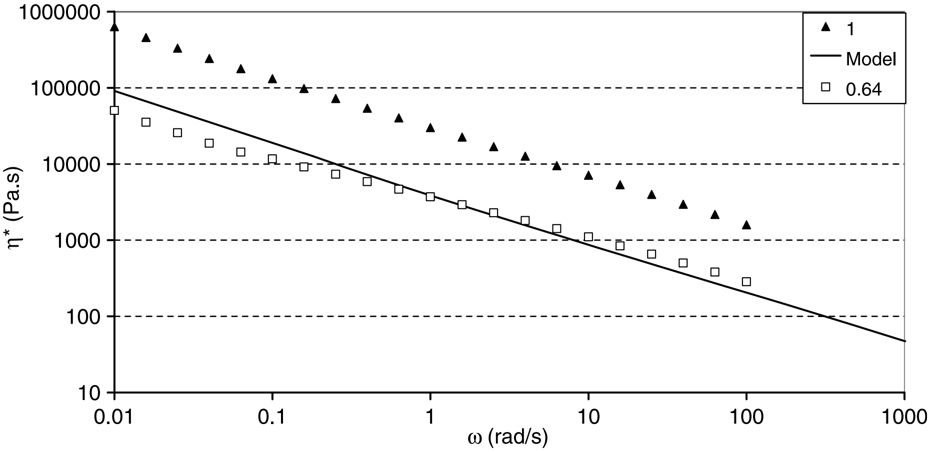

Fig. 5. Complex viscosity vs. ω at 200 °C for neat EPDM (▲) and for $\phi_{\mathrm{EPDM}}=0.64$ (□). Solid line corresponds to the model.

5.3. Diffusion of the plasticizer

The transport of the plasticizer in the polymer matrices in molten or rubbery state was followed via viscoelastic measurements. In that purpose, the dynamic moduli were recorded during the diffusion of oil into the polymer. Prior to comparing the diffusion kinetics of oil between PP and EPDM, the experiments were carried out with two grades of PP, differentiated by their average molecular weights and therefore by their melt indexes. PP2 is the one used in all characterizations presented up to now, and PP12 is the same homopolymer with lower molecular weight ($\bar{M}_w = 220,000$ g/mol), resulting in a melt index of 12. The zero shear viscosity of PP12 at $T=200$ °C is $\eta_0=2300$ Pa s. So, in this comparison, only the effect of molecular weight is involved.

Fig. 6 shows the evolution of complex viscosity η^* for both polypropylenes at 200 °C. Interestingly, the initial pattern of the recordings is similar for PP2 and PP12. Then the plots diverge from each other after some time, estimated around 1200s from the graph, to tend towards plateaus. The superposition of the initial parts of the plots for both PP grades indicates that the kinetics of oil diffusion does not depend on PP molecular weight. Moreover, the time for reaching the stabilized values of viscosity is equivalent with both grades. Only the value of the final viscosity varies between the two polymer/oil mixtures, as a consequence of the difference in molecular weights.

PP12 was tested during oil diffusion at three temperatures: 180, 200 and 230 °C. The viscosity recordings are displayed in Fig. 7, where the influence of temperature is clearly illustrated on the initial slope of the plot. The diffusion rate is obviously enhanced by increasing temperature.

Oil diffusion is compared in our reference PP (PP2) and in EPDM, as shown in Fig. 8 through the evolution of viscosity with time at 200 °C. Relative superposition of the plots is observed in the first 500s or so. Then the slope of the curve towards the plateau is steeper with EPDM, and the stabilization of viscosity occurs more rapidly than with PP. This simply demonstrates that the oil diffusion kinetics is faster in EPDM.

The slight change of slope that can be noticed with both polymer matrices around 1000s, may be attributed to the moment when the oil layer vanishes and a single (but not yet homogenous) phase of oil-extended polymer is formed. Within this time interval, and considering the very large relaxation times assumed for EPDM, the diffusion process is most likely to be elastic in nature rather than Fickian, i.e. the plasticizer diffuses and swells this polymer without inducing disentanglement. The curve pattern with PP is different since the much shorter relaxation times of this matrix allow for some disentanglement and polymer diffusion to occur towards the oil layer.

The subsequent part of the plots results from the evolution of the concentration gradient in the polymer towards homogenization, and this process appears much faster for EPDM than for PP, supposedly for the same reasons as mentioned above.

Modeling was performed with PP12 at 200 °C, and the result is compared with experiment in Fig. 9. The values of the two parameters D_0 and ξ derived from adjustment of computation to experimental data are 0.03 m^2/s and 3.2, respectively. It can be seen that the model mainly captures the initial and final features of the experimental plot, whereas the actual global kinetics of diffusion is slower than modeled. Of course, some reasons can be suggested for this. First, some limits of the free volume diffusion models can be put forward, as it was done by different authors ([21,13]). In particular, the polymer self-diffusion coefficient is neglected here, and the Flory–Huggins thermodynamic model may not be adequately describing the polymer/solvent interactions in the present case. Next, the critical energy E is presently set equal to zero, whereas the model was shown to be very

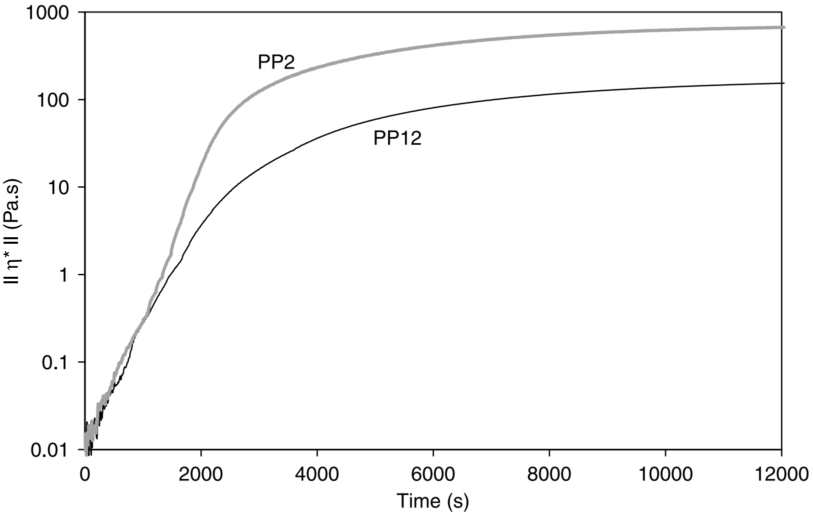

Fig. 6. Evolution of viscosity of polypropylene during diffusion of oil ($T=200$ °C, $\omega=10$ rad/s).

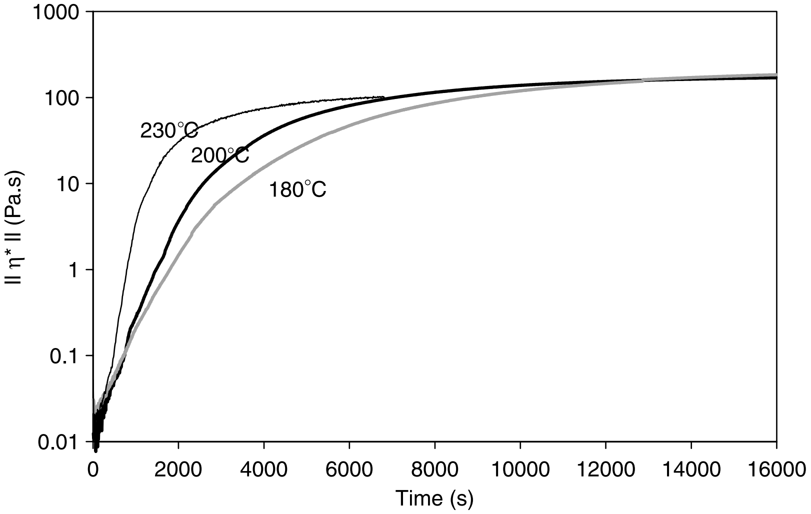

Fig. 7. Evolution of viscosity of PP12 during oil diffusion at different temperatures ($\omega = 10$ rad/s).

sensitive to its value [13]. Similarly, ξ, which is the ratio of the molar volume of a solvent jumping unit to the molar volume of a polymer jumping unit, has been known for long as a key parameter in free volume diffusion models. It has a strong influence on the magnitude of the resulting diffusion coefficients prediction ([10,21]). However, in theoretical approaches aimed at predicting all free volume parameters, ξ is among those being predicted with least accuracy.

In spite of these reservations, the physical significance of the calculated D_0 and ξ is demonstrated here by the fact that equally satisfactory, or even better prediction can be achieved at different temperatures while keeping the values of these parameters constant, as expected. For clarity purpose, this is illustrated in Fig. 9 at 230 °C only: The experimental and computed plots are in better agreement than those at 200 °C. This is consistent with the fact that energy effects are all the more dominant over free-volume effects as temperature increases [21]. Indeed, in the present study, we developed an energy formulation for the solvent self-diffusion coefficient.

Further validation of D_0 and ξ was carried out by implementing the model with the 0.03 and 3.2 values for PP2 at 200 °C, as represented in Fig. 10. Again, it can be seen that the general pattern of the model plot differs substantially from experiment in the region where viscosity changes dramatically, but that the model acceptably fits the first few minutes of diffusion as well as the final viscosity. Considering the preceding remarks about free-volume diffusion models, this result is encouraging.

Finally, once the D_0 and ξ parameters have been determined by modeling the experimental curves, the binary mutual diffusion coefficient D_{12} can be calculated via Eqs. (14) and (17). Consequently, the evolution of D_{12} with the solvent (oil) weight fraction ω_1 can be plotted with respect to temperature, as presented here in Fig. 11 for PP12. A quite simple general expression for $D_{12}(T,\omega_1)$ could then be

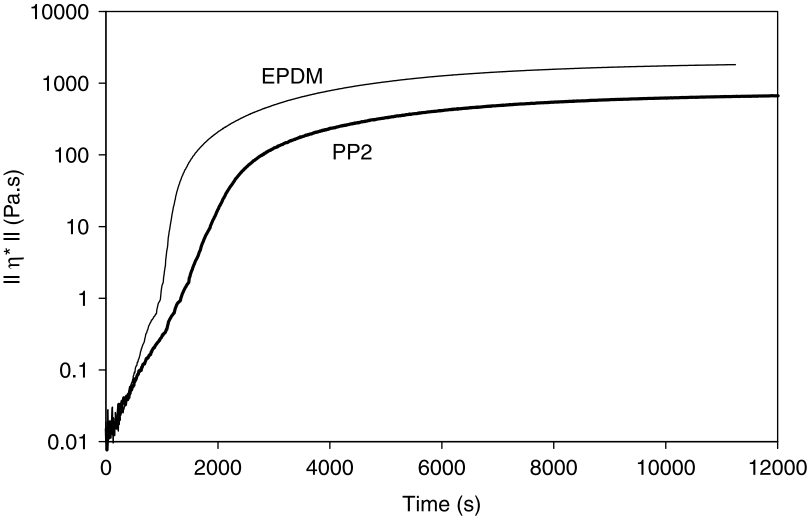

Fig. 8. Comparison of the viscosity response during oil diffusion (at $T = 200$ °C, $\omega = 10$ rad/s) in PP2 and EPDM.

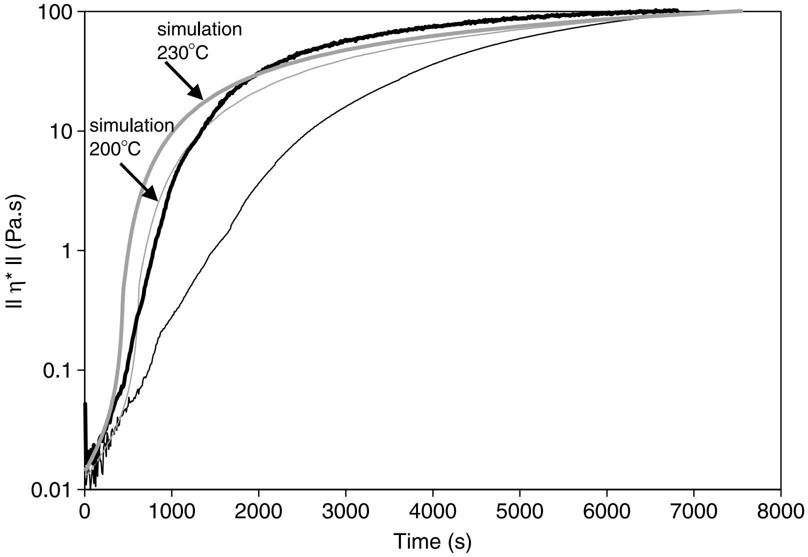

Fig. 9. Influence of temperature on oil diffusion in PP12 ($\omega = 10$ rad/s). Comparison between experimental data (black lines) and model (grey lines). (○) and solid line: 200 °C; (—) and dashed line: 230 °C.

derived for implementation in further diffusion/rheology coupled modeling.

From our results, in terms of relaxation time and diffusion coefficient, the validity of the assumption for Fickian diffusion can be evaluated for PP. Indeed, the diffusion process is characterized by a dimensionless group called the Deborah diffusion number (Db), which is defined as the ratio of the characteristic time λ_m of the fluid to the characteristic time θ_D of the diffusion process [20]:

$$\mathrm{Db} = \frac{\lambda_m}{\theta_D} \tag{18}$$

If the Deborah number is large, the mass transport is called elastic diffusion. If the Deborah number is small, both the polymer and solvent behave like purely viscous fluid. When the Deborah number approaches one, the molecular relaxation and diffusion transport processes occur in comparable time scales. The diffusion transport is then denoted as viscoelastic diffusion and does not follow a Fickian law.

The characteristic relaxation time of the polymer chain is the reptation time. In the present case $\lambda_m = \tau_0$ ($\tau_0 = 0.1$ s for PP, Table 1) and θ_D can be defined as follows: $\theta_D = L^2/D_{12}$ with L the initial thickness of the polymer sample. Considering $L \approx 10^{-3}$ m and $D_{12} \approx 7\times10^{-11}$ m^2/s from our data ($\Phi_{PP} = 0.5$ and $T = 200$ °C) we finally find $\mathrm{Db} \approx 7\times10^{-6}$. This result proves that we can reasonably consider a Fickian diffusion process of the oil in molten PP polymer.

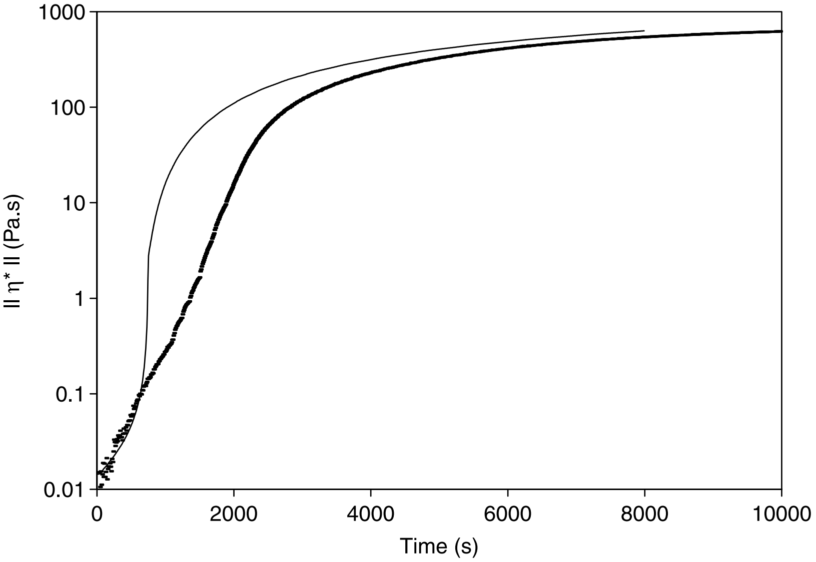

Fig. 10. Evolution of the viscosity during diffusion of oil for PP2 ($T = 200$ °C, $\omega = 10$ rad/s). Comparison between experimental data (symbols) and model (line).

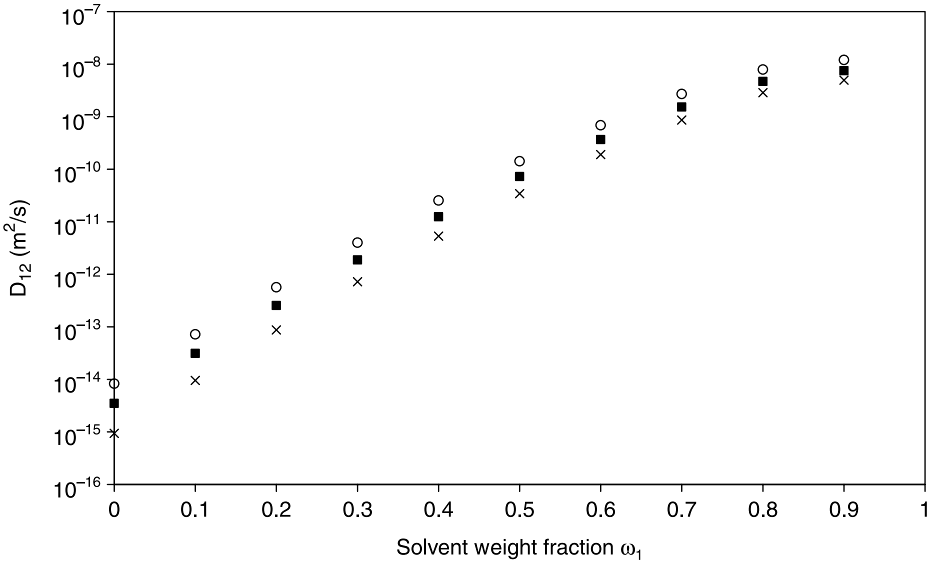

Fig. 11. Evolution of the PP12/oil mutual diffusion coefficient with oil concentration and temperature. D_{12} was computed according to Eq. (17), with D_0 = 0.03 m^2/s and $\xi = 3.2$ at all temperatures. (×), 180 °C; (■), 200 °C; (○): 230 °C.

In the case of EPDM the situation is quite different due to the microstructure of this polymer. Indeed a terminal relaxation time does not exist anymore as it tends to infinite. This has two consequences with respect to modeling. The first one is the unavailability of the zero shear viscosity, that would have to be compensated by the calculation of an additional correction factor to take into account the effect of dilution on the non-Newtonian viscosity ($\eta_{\mathrm{solution}}(\omega) = \eta_{\mathrm{bulk}}(\omega)\Phi^{4+1.75(n_{\mathrm{bulk}}-1)}a_{\Phi}^{n_{\mathrm{bulk}}}$, where n_{bulk} is the flow index of the bulk polymer at frequency ω). The second one is that an infinite relaxation time leads to an elastic diffusion process. This is likely to be the major reason for the poor quality of fit achieved when modeling the diffusion of oil in EPDM in the framework of Fick's equation.

6. Conclusion

In this paper, we demonstrate that a dilution model based on the free volume theory is able to predict the rheological properties of binary polymer/plasticizer mixtures as long as the relaxation mechanisms in the polymer matrix are homogenous in nature. The model used here proves very suitable for molten polypropylene, because the reduction of entanglements is the prevailing phenomenon taking place with this material upon mixing with a plasticizer. In the case of EPDM, a global shift of the relaxation time spectrum is not sufficient to model the evolution of viscoelastic properties with oil addition. Therefore, the presence of structural heterogeneities can be suspected, inducing different relaxation processes in this polymer matrix.

A proper description of the evolution of viscosity with the polymer volume fraction in the blend is necessary for modeling the diffusion process in such a rheological experiment as presented here. As demonstrated with PP, fitting a model of Fickian diffusion to our rheological measurements enables to estimate the binary mutual diffusion coefficient of the polymer/plasticizer system. This is a key issue in further prospects of predicting the evolution of viscoelastic properties of a polymer in presence of a plasticizer or a solvent, and consequently during mixing operations.

The polymer systems presented in this study are the basic components of a TPV. TPV processing is a combination of mechanical mixing, diffusion and chemical reaction (cross-linking). The latter, taking place in the elastomer phase (EPDM), is more specifically addressed in a subsequent paper.

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References

[1] Gessler AM, Kresge EN, Exxon Research and Engineering Co. US Patent, 4,132,698, 1979.
[2] Abdou-Sabet S, Puydak RC, Rader CP. Rubber Chem Technol 1996; 69:476.
[3] Winters R, Lugtenburg J, Litvinov VM, van Duin M, de Groot HJM. Polymer 2001;42:9745.
[4] Sengers WFG, Sengupta P, Noordermeer JWM, Picken SJ, Gotsis AD. Polymer 2004;45:8881.

[5] Jayaraman K, Kolli VG, Kang SY, Kumar S, Ellul MD. J Appl Polym Sci 2004;93:113.

[6] Nakajima N, Harrell ER. J Rheol 1982;26:427.

[7] Graessley WW, Edwards SF. Polymer 1981;22:1329.

[8] Tadmor Z, Gogos G. Principles of polymer processing. New York: Wiley; 1979. p. 426.

[9] Cassagnau P, Fenouillot F. Polymer 2004;45:8019.

[10] Joubert C, Cassagnau P, Choplin L, Michel A. J Rheol 2002;46(3): 629.

[11] Cohen MH, Turnbull D. J Chem Phys 1959;31:1164.

[12] Vrentas JS, Vrentas CM. Eur Polym J 1998;34(5/6):797.

[13] Tonge MP, Gilbert RG. Polymer 2001;42:1393.

[14] Marin G, Menezes E, Raju VR, Graessley WW. Rheol Acta 1980;19: 462.

[15] Gimenez J, Cassagnau P, Michel A. J Rheol 2000;44(3):527.

[16] Ferry JD. Viscoelastic properties of polymers. New York: Wiley; 1980. p. 280.

[17] Yasuda KY, Armstrong RC, Cohen RE. Rheol Acta 1981;20:163.

[18] Fetters LJ, Lohse DJ, Graessley WW. J Polym Sci, Part B: Polym Phys 1999;37:1023.

[19] Fulchiron R, Verney V, Marin G. J Non Newt Fluid Mech 1993;48:49.

[20] Vrentas JS, Duda JL. Polym Sci, Polym Phys Ed 1977;15:441.

[21] Zielinski JM, Duda JL. AIChE J 1992;38:405.