

Rheological Quantification of Molecular Parameters: Application to a Hydrogen Bond Forming Blend

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Received 25 July 2003; accepted 18 February 2004

DOI 10.1002/app.20613

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The component dynamics and molecular parameters were investigated for miscible poly(4-vinyl phenol)/poly(ethylene oxide) (PVPh/PEO) blends. Global values of molecular weight between entanglements (M_e) were first estimated for the blends and were compared with existing athermal model predictions. Global interchain friction coefficients (ξ) of the blends were deduced from the zero-shear viscosity. A maximum was observed at a composition of 20–30 wt % of PEO. Chain dimensions of this phase are estimated by using a relationship between the plateau mod-

ulus and a packing length (i.e., number of individual chains present in a given small volume of the melt). A slight increase in M_e is observed at low PEO weight fraction (before 0.20), followed by a sharp decrease in M_e values after this concentration. Values of ξ in PVPh/PEO blends show a maximum value at 20–30 wt % of PEO. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1623–1630, 2004

Key words: poly(4-vinyl phenol) blend; rheology; hydrogen bonds; orientation

INTRODUCTION

When applying an external force on a polymer, the following two concurrent phenomena occur: deformation-induced orientation and relaxation, which both contribute to the final observed orientation and properties of the material under study. It is well accepted^{1,2} that molecular weight between entanglements (M_e) and interchain friction coefficients (ξ) significantly affect relaxation and, therefore, final orientation. Consequently, to better understand the processes leading to orientation, determination of M_e and ξ is important. For pure polymers, these can be conveniently extracted from rheological data. For miscible polymer blends, this still poses a considerable challenge.

The molecular weight between entanglements is related to topological constraints and can be calculated from the rubbery plateau modulus,³ G_N^0 ,

$$M_e = \frac{\rho RT}{G_N^0} \quad (1)$$

where R is the gas constant and ρ is the density of the polymer at the absolute temperature T . The use of this

equation results, for miscible blends, in a global value for all chain entanglements. The significance of this global value is, however, not clear, and its usefulness is limited, as it is well known that the two components of a polymer blend often do not orient (and therefore relax) in the same way. Different relaxation times can only be explained on the basis of different entanglements or different chain friction coefficients. Global values can nevertheless be used for comparative purposes with results from athermal models, for instance, and may serve to enlighten the effect of interactions on a specific blend.

Interchain friction, which is estimated by using the friction coefficient ξ , is thought to originate from interchain interactions⁴ and represents the resistance encountered by a submolecule junction when moving through its surroundings.

Quantitative evaluation of ξ is even more challenging. Even the calculation of a global value is not straightforward. Various blending rules were reported for the viscoelasticity of homogeneous blends, including a molecular theory developed by Han and Kim,⁵ Tsenoglou's blending rules,^{6,7} and the modified Doi and Edwards equation proposed by Wu.⁴ Problems with respect to quantification of ξ arise from mathematical difficulties in calculating or measuring the self-diffusion coefficient, relaxation times, effective bond lengths, and mean square end-to-end distance ($\langle R^2 \rangle$) of blends, depending on the model selected. Among these, the most straightforward variable to determine appears to be $\langle R^2 \rangle$.

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* Deceased December 3, 2001.

Contract grant sponsor: Natural Science and Engineering Research Council of Canada (NSERC).

Contract grant sponsor: Fonds pour l'Aide à la Recherche (FCAR).

Wu⁴ proposed, based on the Doi and Edwards theory, that ξ_r , the Rouse friction coefficient, can be related to zero-shear viscosity (η_0) and $\langle R^2 \rangle$ by using the equation:

$$\eta_0 = (5/48)\rho N_0(M_w/M_e)^2 \xi_r (\langle R^2 \rangle / M_w) \exp\{2.26[1 - (2M_e/M_w)^{0.5}]\} \quad (2)$$

where N_0 is the Avogadro number, M_w is the weight-average molecular weight, and M_e is the entanglement molecular weight. This equation is based on the assumption of a Rouse chain and on the tube leakage effect⁸ (i.e., the wriggling motion of a Rouse chain which induces the chain to leak out of the tube ends).

To use this equation, one must derive η_0 values for the pure polymers and the blends. Wu proposed a blending rule for zero-shear viscosity:

$$\log \eta_{0b} = \phi_1 \log \eta_{01} + \phi_2 \log \eta_{02} + \phi_1 \phi_2 \log \lambda \quad (3)$$

where η_{0i} and ϕ_i are the zero-shear viscosity and the volume fraction of pure component i , respectively, and λ is a constant for a blend system.

Wu's model predictions for zero-shear viscosity was found to correctly predict data for various systems,^{5,9} but was found unsuitable in other cases.^{10,11} In the present work, a different blending rule for η_0 was therefore used.

To use eq. (2), one also needs to derive chain dimensions, $\langle R^2 \rangle / M_w$, for the pure polymers and the blends. Wu⁴ proposed that the $\langle R^2 \rangle / M_w$ for pure polymers could be derived from the characteristic ratio (C_∞) values that can be found for most polymers in the literature. For a blend, C_∞ can be obtained from interpolation by using the relationship $C_\infty \propto N_e^{0.5}$, where N_e is the number of repeat units in an entanglement strand. Although Aharoni's chain stiffness parameters and M_e 's of a large number of polymers support this relationship,⁹ it was shown later by Fetters et al.¹² that the relation $C_\infty \propto N_e^{0.5}$ is imprecise because N_e increases with temperature while C_∞ can either remain constant, decrease, or increase. Various polymer entanglement models were reviewed by Heymans,¹³ who demonstrated that the Fetters¹² and the Colby-Rubinstern¹⁴ models are applicable.

In the present work, the Fetters model, which relates plateau modulus to packing length, from which $\langle R^2 \rangle / M_w$ can be estimated, will be preferred for its ease of use.

Global M_e and ξ values, while being useful for comparison purposes, do not address the question of how each polymer chain is affected by the presence of specific interchain interactions. To gain information on this specific point, one would like to separate the parameters experienced by the different polymers, which are related to the formation of three types of

chains contacts (i.e., 1-1, 2-2, and 1-2 chain contacts). Unfortunately, it is difficult to assess the contribution of each contact type to M_e and ξ , the 1-2 chain contacts being notably difficult to unravel.¹⁵ Early classification of entanglements are described as localized points, or temporary crosslinks such as knots, winding loops, or local interactions. A topological classification of entanglements was proposed more recently and expresses itself through a variety of values of M_e obtained from the plateau modulus.¹³ A way to look at things is to extract directly M_{e1} and M_{e2} , the molecular weights between entanglements of polymers 1 and 2 of the blends, for which Tsenoglou proposed an approach.⁶ The equivalent is, however, not possible at this time for ξ .

In the present article, we will use rubber plateau modulus G_N^0 and zero-shear viscosity η_0 previously extracted from rheological data of poly(4-vinyl phenol)/poly(ethylene oxide) (PVPh/PEO) blends,¹⁶ to investigate how global M_e and ξ can be derived. The PVPh/PEO blend was chosen to address the effect of specific interchain interactions on the blend behavior. The hydroxyl functionality in PVPh can exist under three forms in PVPh/PEO blends: free hydroxyls, hydroxyl-hydroxyl-specific interactions (intraassociation or intrachain hydrogen bond formation, occurring between two OH groups of PVPh chains), and interchain hydrogen bonding interactions between PVPh and PEO (interassociation of interchain hydrogen bond formation, occurring between an hydroxyl of PVPh and an oxygen atom of PEO), as depicted in Figure 1. For this blend, a discontinuity in a_T , G_N^0 , and η_0 was observed around 20–30 wt % PEO blend composition.¹⁶ Orientation was found to reach a sharp maximum near this concentration.¹⁷ Further, quantitative information on the hydrogen bond interactions are available for this system.¹⁸ Our major objective is to qualitatively correlate global M_e , global ξ , and M_{ei} ($i = 1$ or 2) proposed by Tsenoglou,⁶ with the previously reported orientation behavior of this system.

EXPERIMENTAL

Polymer and rheological data discussed in the present article were reported previously.¹⁶

Room-temperature densities of PVPh, PEO, and their blends were determined by using a hydrometer in a 25°C water bath.¹⁹ Melt densities (ρ) of PVPh/PEO blends were approached by using PVT relatives [i.e., $\rho = f(P, T)$]. A Gnomix PVT apparatus was used to measure the changes in density as a function of temperature and pressure. Experiments were performed in the isobaric mode at 10, 60, and 120 MPa. The sample cell used mercury as a confining fluid and could hold about 1 g of polymer. The minimum pressure to prevent mercury from evaporating at high temperatures was 10 MPa. The sample was heated to

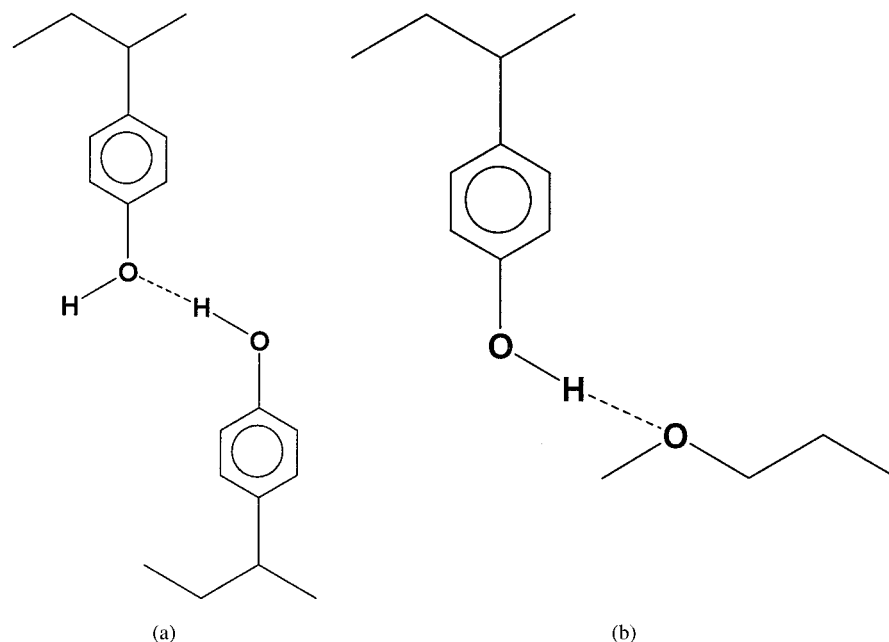


Figure 1 Schematic representation of hydrogen bond types: (a) PVPh-PVPh intrachain; (b) PVPh-PEO interchain.

$\sim 100^\circ\text{C}$ for PEO (Sigma-Aldrich Canada Ltd., Oakville, Ontario, Canada) and $\sim 200^\circ\text{C}$ for PVPh (Triquest, Corpus Christi, TX) and then cooled down to room temperature. The data were taken upon cooling and then extrapolated to 1 atm to give the density.

RESULTS AND DISCUSSION

Determination of global M_e

As reported in a previous article,¹⁶ the single-phase rheology of PVPh/PEO was studied through oscillatory shear measurements. It was found that these blends were thermorheologically simple because master curves of G' , G'' , and $\tan \delta$ could be constructed by using the time-temperature superposition principle.

The key parameters for determining M_e for pure polymers are the rubbery plateau modulus (G_N^0) and

the density of the polymer melt. A similar approach will be used to determine a global M_e value for the blends. G_N^0 values of the blends were determined in the previous article, whereas the densities of the polymer melts are reported in Table I. M_e depends slightly on temperatures and melt density, and G_N^0 is slightly affected by these variables and could be treated as an instantaneous modulus characterized by the storage modulus at the minimum of $\tan \delta$.^{20,21} The molecular weight between entanglements of pure PVPh can be calculated by using eq. (1) and yields a value of $29,300 \pm 1200$ g/mol at 192°C . To our knowledge, no M_e value for PVPh was reported by other groups. This value is slightly higher than the M_e value of polystyrene (PS), for which we calculate a value of $23,200 \pm 1800$ g/mol at 192°C by using previously published data.¹⁶ In the literature, the M_e value of PS is reported

TABLE I
Values of M_w , T_g , ρ , η_{0b} , and G_N^0 for PVPh/PEO Blends

Sample ID	mol % of PEO	M_w (g/mol)	T_g ($^\circ\text{C}$)	ρ at $T_g + 15$ (g/cm^3)	η_{0b} @ $T_g + 15$ (Pa.s)
PVPh	0	78,900	177	1.079	6.33E+06
PVPh/PEO(95/5 wt)	13	75,200	154	1.087	3.56E+07
PVPh/PEO(85/15 wt)	32	68,100	131	1.096	4.17E+07
PVPh/PEO(80/20 wt)	41	64,400	115	1.101	1.70E+08
PVPh/PEO(75/25 wt)	48	60,800	92	1.109	1.50E+07
PVPh/PEO(70/30 wt)	54	57,200	88	1.111	2.12E+07
PVPh/PEO(65/35 wt)	59	53,600	67	1.118	6.72E+07
PVPh/PEO(60/40 wt)	65	50,000	33	1.130	1.10E+08
PEO	100	6600	-61	1.200 ^a	—

^a Taken at 25°C rather than $T_g + 15$ (-46°C).

as 18,700–28,800 g/mol, depending on isotacticity of PS.²² Based on the M_e values and the molecular weight of a repeat unit (M_0), the number of repeat units between entanglements ($N_e = M_e/M_0$) of PVPh can be determined as 244 ± 10 , whereas that of PS is 223 ± 17 , indicating that the higher M_e value of PVPh can be explained on the basis of difference in molecular weight of repeat unit. Intraassociated hydrogen bonds in PVPh therefore exert a limited influence on chain entanglements. This comes in disagreement with the suggestion by Wu⁴ that specific interchain interactions tend to align the chain segments and locally stiffen the chains, leading to decreased chain entanglements. Rigidity of the aromatic cycle and packing requirements largely dominate the behavior of PVPh, and in this specific case, hydrogen bonds may occur between hydroxyl groups attached to the same chain, thereby stabilizing helixlike conformations, as suggested by the observation that, in near-FTIR spectroscopy, the absorbance of a O—H vibration related to PVPh–PVPh hydrogen bonds does not vary significantly upon addition of PEO.¹⁸

Wu,⁴ Lomellini,²⁰ and Tsenoglou⁶ studied the effect of molecular interactions on entanglement probability. Wu⁴ proposed a blending rule for several miscible blends that can be written as:

$$G_{Nb}^0 = \phi_1 G_{N1}^0 + \phi_2 G_{N2}^0 + \phi_1 \phi_2 (\lambda_e - 1) (G_{N1}^0 + G_{N2}^0) \quad (4)$$

where G_{Nj}^0 is the plateau modulus of the blend ($j = b$) or the constituent ($j = 1$ or 2), and ϕ_i ($i = 1$ or 2) is the volume fraction. λ_e is normally a constant for a given system. However, it was shown, for the weakly interacting poly(methyl methacrylate) (PMMA)/poly(styrene-*co*-acrylonitrile) (SAN) system,¹⁰ that λ_e varies with molecular weights of the pure polymers. This effect, however, vanishes when molecular weights of the polymers in the blends are chosen to have the same number of entanglements, $n_e = M_w/M_e$, in their pure form. In the present PVPh-PEO study, care was taken in the selection of molecular weights: n_e is 2.7 for PVPh and 2.6 for PEO. Therefore, λ_e should be constant for all compositions.

When $\lambda_e = 1$, eq. (4) reduces to a linear mixing rule, for instance,

$$G_{Nb}^0 = \phi_1 G_{N1}^0 + \phi_2 G_{N2}^0 \quad (5)$$

In this case, corresponding to Wu's athermal-blending rule, specific interchain interactions exert little influence on entanglement probability, which is unperturbed with respect to individual components. When $\lambda_e < 1$, the G_{Nb}^0 value is lower than that of the athermal case, meaning that there is a repulsive effect of interchain interactions on the entanglement probability.

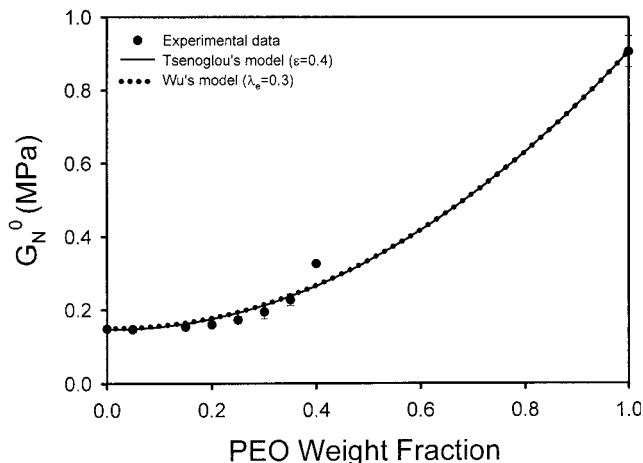


Figure 2 G_N^0 values of PVPh/PEO blends.

The opposite case ($\lambda_e > 1$) corresponds to an attractive effect on the entanglement probability.

Tsenoglou,^{6,7} on the other hand, proposed a random formation of chain entanglement between dissimilar chains of the two components in a miscible blend. The blending rule is then given by

$$\begin{aligned} \sqrt{G_{Nb}^0} = & \phi_1 \sqrt{G_{N1}^0} [1 + \varepsilon (\phi_2 \sqrt{G_{N2}^0} / \phi_1 \sqrt{G_{N1}^0})]^{n=\pm 1/2} \\ & + \phi_2 \sqrt{G_{N2}^0} [1 + \varepsilon (\phi_1 \sqrt{G_{N1}^0} / \phi_2 \sqrt{G_{N2}^0})]^{n=\pm 1/2} \quad (6) \end{aligned}$$

where the sign of the exponent (n) depends on the presence of attractive or repulsive interactions between dissimilar species ($n = +1/2$ for attraction, $-1/2$ for repulsion) and ε represents the relative strength of these interactions.

When $\varepsilon = 0$, eq. (6) reduces to Tsenoglou's athermal case, for instance,

$$(G_{Nb}^0)^{1/2} = \phi_1 (G_{N1}^0)^{1/2} + \phi_2 (G_{N2}^0)^{1/2} \quad (7)$$

which is based on the fact that entanglement probability between dissimilar chains is proportional to the geometric average of the entanglement probability between similar chains. An athermal case blending rule was proposed to be valid in cases where interactions do not modify the entanglement probability.

It is shown in Figure 2 that experimental G_N^0 values for the blends are in good agreement with both Wu's model predictions ($\lambda_e = 0.3$) and Tsenoglou's model predictions ($\varepsilon = 0.4$, $n = +1/2$). However, for the 0.4 PEO weight fraction, a slight but significant deviation is noted. This is tentatively attributed to a change in network type, which could be fitted with different interaction parameters. This was, however, not performed here due to the limited experimental window studied. Therefore, both Wu's model and Tsenoglou's model are applicable to the PVPh/PEO system if us-

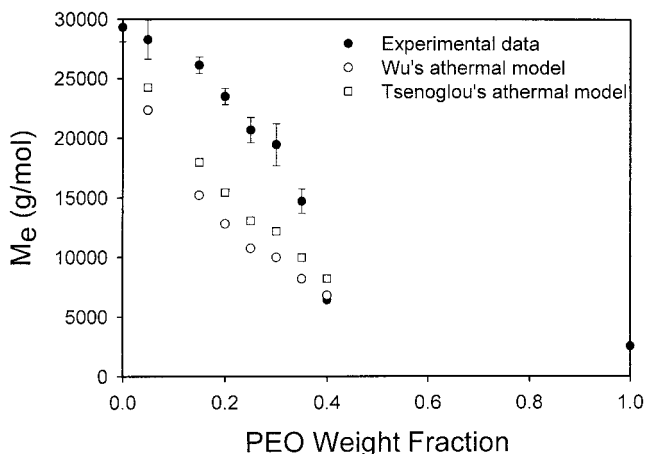


Figure 3 M_e values of PVPh/PEO blends at $T_g + 15$.

ing suitable λ_e or ε values. The λ_e value obtained for Wu's model (0.3) is indicative of reduced entanglement probabilities in the blend with respect to the case of the pure polymers,^{4,20} in agreement with the $\varepsilon = 0.4$ value of the Tsenoglou's model, which indicates the presence of strong interactions between dissimilar species compared to those of weakly interacting blends.⁶ Alternatively, both models can be used to predict what would have been the G_{Nb}^0 values in an athermal case [eqs. (5) and (7)].

From the G_N^0 experimental and athermal case values, using eq. (1), it is possible to derive for each blend composition a global M_e , as reported in Figure 3. A reference temperature of $T_g + x$ ($T_g + 15$ in this case) was used, as is customary in orientation studies. As can be seen, experimental global M_e values rapidly decrease upon addition of PEO. At a 0.40 weight fraction, M_e has almost reached the value observed for pure PEO. It must, however, be stressed that this M_e value was taken at a reference temperature of 130°C, as it was not possible to assess G_N^0 at $T_g + 15$ (−46°C). PEO can crystallize below its melting point (around 60°C) and causes G_N^0 to be located above the upper frequency limit and could not be measured. Nevertheless, G_N^0 is only slightly affected by temperature, and therefore, this gives a reasonable reference point for the behavior of the pure polymer.

These global values are of limited use, as they are the result of averages over the different polymer chains forming the blends. As mentioned earlier, they are mostly useful for comparing with athermal models, and in this way, to explore the effect of interactions on the specific aspect of chain entanglement in a blend. As can be seen in Figure 3, predictions using both athermal models yield lower global M_e values than those derived from experimental G_N^0 values up to 0.4 PEO weight fraction, clearly indicating the presence of hydrogen bond forming interactions modifies the entanglement probability. It is concluded that spe-

cific interactions in PVPh/PEO blends lead to a decrease in the number of chain entanglements as compared to the mathematical average. At a concentration of 0.4 PEO weight fraction, however, the blends behave as an athermal blend. This may indicate a change in the entanglement regime or network type for this concentration.

Determination of global ξ

Rheological measurements being global, for a blend, determination of a global ξ should have been relatively straightforward. It is, however, not the case, and a number of approximations must be made, which limit the precision with which one can determine ξ for a blend. Further, as in the case for M_e , the meaning of such a global parameter is not evident. Therefore, it is proposed here as a means of comparing the behavior with respect to composition and to interaction formation. PVPh-PEO blends are particularly well suited for this purpose, as the characterization of the number of interchain interactions is possible via determination of the number of hydrogen bonds by infrared spectroscopy. Such a quantification was already performed for the present blend system¹⁸ and can serve to verify the validity of the conclusions drawn from derivation of friction coefficients from rheological measurements. On the other hand, limitations in the width of the rheological window for the PVPh-PEO system result in high uncertainties in the ξ determination. This must also be taken in consideration in the present case.

Various researchers^{10,23,24} reported that interchain friction coefficients of the individual components have distinct compositional dependence at constant $T - T_g$. ξ_A/ξ_B can vary by orders of magnitude across the composition range, even at a fixed temperature interval above the composition-dependent glass transition temperature (T_g). As seen in eq. (2), to estimate global ξ , it is essential to determine zero-shear viscosity (η_0) and the chain dimensions of the PVPh/PEO blend. As shown in the first article of this series, η_0 can be deduced from a relaxation spectrum determined by neural network models. The η_{0b} values of the blends at $T_g + 15$ are reported in Table I. It must be recalled that, because of experimental limitations, the experimental window was limited for this blend, and η_0 values were estimated via extrapolation of the relaxation spectrum to minimize the error. Nevertheless, this procedure introduces uncertainties on the order of 10–20%, depending on the width of the rheological window, without taking into account other errors associated with rheological measurements.

Due to the incorrectness of the relation $C_\infty \propto N_e^{0.5}$ as mentioned earlier, an alternative is proposed in the present work to estimate chain dimensions $\langle R^2 \rangle / M_w$ in polymer blends by using the concept of packing length.¹² The packing length P is defined as

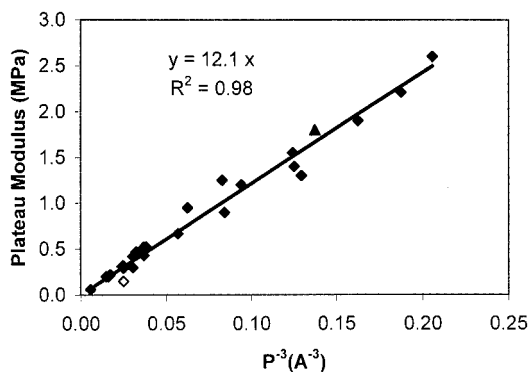


Figure 4 Relationship between plateau modulus and packing length for various polymers; data taken from ref. ¹² for all polymers except PVPh, for which data are taken from refs. ¹⁶ and ²⁵ (Open symbol: PVPh; triangle: PEO).

$$P = \frac{M_w}{\rho N_0 \langle R^2 \rangle} \quad (8)$$

denoting the number of individual chains present in a given small volume of the melt. It has been shown by Fetters et al.¹² that G_N^0 versus P^{-3} yields a linear relationship for about 30 polymers for which it was tested, including polymers that form hydrogen bonds such as nylon 6. It is therefore proposed here that an average packing length for a miscible blend can be estimated through interpolation by the relation $P^{-3} \propto G_N^0$.

To realize the interpolation, P values for pure polymers and a linear relationship between P^{-3} and G_N^0 are used. The G_N^0 values for individual polymers and polymer blends were determined by rheological measurements. Normally, G_N^0 is only slightly affected by temperature. Therefore, its use to deduce chain dimensions in a blend seems to be a reasonable approximation. Once P is determined, chain dimensions $\langle R^2 \rangle / M_w$ in a polymer blend can be obtained by the relation

$$\langle R^2 \rangle / M_w = \frac{1}{\rho P N_0} \quad (9)$$

For a miscible PVPh/PEO blend, the plateau modulus values (G_N^0) for PVPh, PEO, and the blend have to be determined via rheological measurements. By using the above relation, P in a PVPh/PEO blend is deduced from the values of G_N^0 , and chain dimensions $\langle R^2 \rangle / M_w$ can be estimated by eq. (9).

As shown in Figure 4, the relationship $G_N^0 = 12.1 P^{-3}$ is formulated by using the literature data.¹² Chain dimensions of PVPh used here are taken from an atomistic molecular modeling simulation for this polymer performed by Gestoso and Brisson,²⁵ and those of PEO are taken from the literature. Data for pure PVPh are shown as an open symbol and are in reasonable

agreement considering that chain dimensions were derived from modeling. P values for PVPh/PEO blends were assessed by using the obtained G_N^0 values, and $\langle R^2 \rangle / M_w$ can be derived from eq. (9). The results are listed in Table II.

Alternatively, chain dimensions of the pure polymers can be used to calculate an average chain dimension of the blend, following

$$\langle R^2 \rangle / M_w = f_{\text{PEO}} (\langle R^2 \rangle / M_w)_{\text{PEO}} + f_{\text{PVPh}} (\langle R^2 \rangle / M_w)_{\text{PVPh}} \quad (10)$$

This, however, supposes that specific interactions do not affect chain dimensions, and therefore, the approach, using a global packing length derived from the experimental plateau modulus, is preferred.

Once all global parameters related to the blend have been determined (e.g., η_{0b} , M_w , M_v , and $\langle R^2 \rangle / M_w$), global friction coefficients ξ can be evaluated by using the modified Doi–Edwards eq. (2). The global ξ values for the blends estimated in this way are reported in Figure 5 with respect to blend composition for both types of calculations of chain dimensions. As can be seen, both give the same evolution as a function of composition, the values using the individual values for the pure polymers giving systematically higher values than those derived from the modulus of the blend. This, however, can allow estimation of the error associated with chain dimensions as being around 5%. Therefore, although the absolute values of ξ rely on accurate determination of chain parameters, they would therefore require more thorough evaluation. Evolution with composition does not appear affected by the method used to determine chain dimensions.

The most prominent feature of this figure is the presence of a maximum in ξ at ~ 0.2 PEO weight fraction (i.e., at 0.4–0.5 PEO mole fractions). Both before and after this maximum, ξ values are almost constant within estimated error and tend to be larger for the higher percentage of PVPh, although this may not be significant in view of the various error sources in the calculation. The 20 wt % data point was repeated several times more than the other composi-

TABLE II
Chain Dimensions for Blends

Sample ID	P (Å)	$\langle R^2 \rangle / M_w$ ($\text{m}^2 \text{mol g}^{-1}$)
Pure PVPh	1.94	7.94E–21
PVPh/PEO(95/5 wt)	3.38	4.40E–21
PVPh/PEO(85/15 wt)	3.37	4.41E–21
PVPh/PEO(80/20 wt)	3.52	4.22E–21
PVPh/PEO(75/25 wt)	3.40	4.37E–21
PVPh/PEO(70/30 wt)	3.22	4.61E–21
PVPh/PEO(65/35 wt)	3.65	4.93E–21
PVPh/PEO(60/40 wt)	2.28	6.51E–21
Pure PEO	3.42	4.05E–21

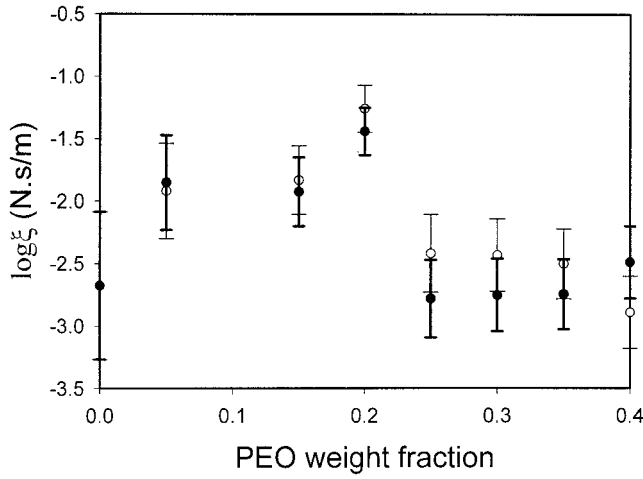


Figure 5 Global friction coefficients ξ for PVPh/PEO blends at $T_g + 15$ (Open symbol and thin error bars: chain dimensions retrieved from packing length of blend. Filled symbol and thick error bars: chain dimensions averaged using values for pure polymers).

tions, hence its lower estimated error. It is interesting to note that a broader, more flattened maximum was observed for the number of hydrogen bonds using near-FTIR spectroscopy.¹⁸ Although hydrogen bonds are not expected to be the sole interaction contributing to the chain friction coefficient, this similarity does confirm that the observed maximum in the global friction coefficient can be correlated to a maximum in interactions in the blend.

Determination of individual molecular parameters

As each polymer orients differently in a blend, for each is needed an individual molecular weight between entanglements and a chain friction coefficient.

The latter is difficult to assess, and this will not be attempted here. However, Tsenoglou proposed an approach to derive M_{e1} and M_{e2} in blends.⁶ In the framework of Tsenoglou's model for a blend composed of m different polymer species, M_{eij} and M_{eii} are deduced from the equations:

$$\frac{1}{M_{eij}} = \phi_2 \left(\frac{\rho_j / \rho_i}{M_{ei0} M_{ej0}} \right)^{1/2} \left\{ \left[1 + \varepsilon \left(\frac{\phi_j^2 \rho_j M_{ei0}}{\phi_i^2 \rho_i M_{ej0}} \right)^{1/2} \right] \left[1 + \varepsilon \left(\frac{\phi_i^2 \rho_i M_{ej0}}{\phi_j^2 \rho_j M_{ei0}} \right)^{1/2} \right] \right\}^{\pm 1/2} \quad (11)$$

$$\frac{1}{M_{eii}} = \frac{\phi_i}{M_{ei0}} \left[1 + \varepsilon \left(\frac{\phi_j^2 \rho_j M_{ei0}}{\phi_i^2 \rho_i M_{ej0}} \right)^{1/2} \right]^{\pm 1} \quad (12)$$

where M_{eij} (i or $j = 1, 2, \dots, m, i \neq j$) is the average molecular weight with respect to a segment lying on an i polymer chain and is confined by two successive

entanglements with j polymer, and M_{ei0} is the molecular weight between entanglements of the i th component in the pure state.

The total number of entanglement for the i th component in the blend (N_i) is given by the equation

$$N_i = \sum_{j=1}^m N_{ij} \cong \sum_{j=1}^m \frac{M_i}{M_{eij}} \quad (13)$$

where M_i is the molecular weight of the i th component.

Therefore, M_e of the i th component in the blend can be determined by

$$M_{ei} = \frac{M_i}{N_i} \quad (14)$$

Tsenoglou's model required that M_{e10} and M_{e20} be known at the temperature where calculations are performed. In the framework of orientation, the temperature sought is $T_g + 15$. Unfortunately, for the PVPh/PEO system, $T_g + 15$ of the blends is below T_g of pure PVPh; G_N^0 of PVPh cannot be directly measured under these conditions. To deduce M_{e1} (related to PVPh) and M_{e2} (related to PEO) in the blends by using this model, G_N^0 of PVPh has to be assumed to vary only slightly with temperature, whereas this assumption is not included in Wu's model as it uses G_N^0 , which is measured at a constant T for the blend and pure polymers. In the present work, both these models were used and compared. Figure 6 shows the compositional dependence of M_{e1} and M_{e2} at $T_g + 15$ by using Tsenoglou's model. At any blend composition, M_{e1} of PVPh $\gg M_{e2}$ of PEO, indicating that the flexible chains of PEO entangled much more easily than those of PVPh. Both M_{e1} and M_{e2} decrease with the addition of PEO up to 0.4 PEO weight

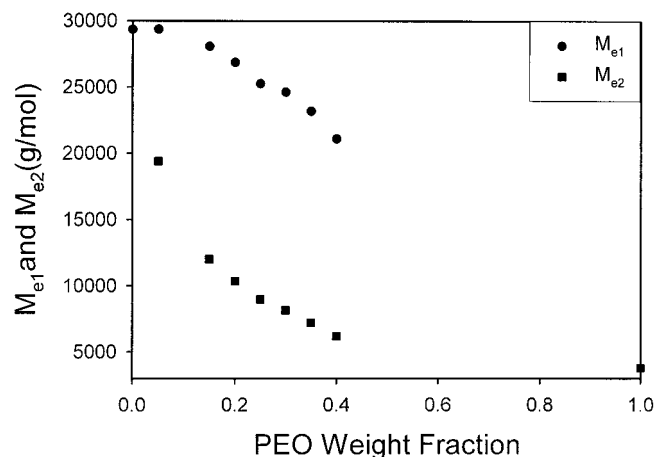


Figure 6 M_{e1} (related to PVPh) and M_{e2} (related to PEO) for PVPh/PEO blends at $T_g + 15$.

fraction. In all cases, both components of the blends are dominated by the chain rigidity of PVPh.

Comparison with orientation behaviors

According to the Doi and Edwards theory,²⁶ the evolution of orientation with time after stretching will tend toward an isotropic state because the tube is affinely deformed and the polymer chain tends to go back to the random coil conformation. The chain relaxation after a sudden deformation is usually described as three different processes with relaxation times τ_A , τ_B , and τ_C . Chain entanglement and inter-chain friction are viewed as the two key parameters that influence the orientation behavior.²

Abtal and Prud'homme²⁷ proposed that the orientation factor was sensitive to experimental measurements only when the relaxation time was limited to a given time range (e.g., 10^2 to 10^4 s). Outside of this range, the relaxation process was either too fast or too slow to be detected in the orientation measurements. Therefore, for PVPh/PEO blends, it is rationalized that orientation behavior may be mainly dominated by τ_A and τ_B . Intermolecular interactions, which contribute to miscibility in binary mixtures, can also hinder the convolution of polymer chains and obstruct the orientation relaxation. This results in a higher observed orientation.² On the other hand, intermolecular interactions, which tend to align the chain segments and to locally stiffen the segments, could cause a decrease in entanglement and an increase in M_e and N_e , thus allowing faster relaxation and resulting in a decrease in observed orientation. These two opposing effects on the orientation process in miscible blends are therefore complex.

As mentioned earlier in the introduction, the PVPh/PEO system exhibits a maximum in the orientation of the PEO component at 0.3 PEO weight fraction.¹⁷ It is worth noting that there is a transition ranging from 0.30 to 0.40 PEO weight fraction in M_e 's for PVPh/PEO blends. The region before 0.3 PEO weight fraction could be attributed to a PVPh dominating major network phase, while another region after 0.30 PEO weight fraction could be attributed to the PEO dominating one. The maximum in the orientation may occur at the transition between these two networks.

Evaluation of friction coefficients is also needed for better understanding of orientation behavior. ξ values show a maximum with blend compositions at $T_g + 15$, respectively, quite different from the behavior of M_e where a simple discontinuity occurs. Although errors are relatively large when evaluating ξ , this observation is corroborated by the occurrence of a broad maximum in the number of hydrogen bonds, as previously measured by using near-FTIR spectroscopy.¹⁸ Therefore, the maximum in orientation could be correlated both to a maximum in interactions and to a change in the entanglement network.

CONCLUSION

Calculations of M_{e1} , M_{e2} , global M_e , and ξ were conducted. Approximations being more important in the case of ξ , this parameter should be viewed with caution, and more emphasis was placed on M_e , M_{e1} , and M_{e2} . A sharp transition occurring at 0.3–0.4 PEO weight fraction for M_e at $T_g + 15$. For ξ at $T_g + 15$, a maximum occurs, in agreement with the presence of a broad maximum in the number of hydrogen bonds for a composition of ~ 0.4 weight fraction PEO, as reported elsewhere from near-FTIR spectroscopy measurements.¹⁸ The previously observed maximum in orientation function therefore occurs in a network transition region (i.e., 0.3–0.4 PEO mole fraction) and is therefore affected both by a rapid change in entanglement and by a hydrogen bond formation.

This work was financially supported by the Natural Science and Engineering Research Council of Canada (NSERC) and the Fonds pour l'Aide à la Recherche (FCAR). Thanks are sincerely given to Ky Nguyen, of the Industrial Materials Institute (IMI), Canada for measuring density values of polymer melts. The technical assistance of Marlene Rousseau of the CERSIM is also acknowledged.

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