Mutual entanglements in poly(vinyl acetate)/poly(methyl acrylate) interpenetrating polymer networks

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An equation has been derived for the equilibrium swelling of sequential interpenetrating polymer networks (IPNs), which exhibit a single glass transition temperature and the two components are considered to be compatible. The properties of the equilibrium swelling and elastic modulus of sequential poly(vinyl acetate)/poly(methyl acrylate) IPNs have been discussed according to the derived equation and the Siegfried–Thomas–Sperling formula of the elastic modulus for homo IPNs. In both fully swollen and bulk states, there was favourable evidence for added physical crosslinks in poly(vinyl acetate)/poly(methyl acrylate) IPNs. The Binder–Frisch theory is also discussed.

(Keywords: interpenetrating networks; entanglements; crosslinking)

INTRODUCTION

Important advances in the theory of rubber elasticity have been made. These include the introduction of the phantom network by Flory[1] and a two-network model for crosslinks and trapped entanglements by Ferry *et al.*[2,3]. The physical entanglements, which act as crosslinking loci, are designated as Buche–Mullin trap, Ferry trap, and Langley trap by Kramer[4] and Graessley[5]. Although these theories have made great progress, it is difficult for research workers who are interested in using them directly to interpret the mutual entanglements between the two networks in interpenetrating polymer networks (IPNs). Fortunately, Binder and Frisch[6] have recently suggested a theory on the thermodynamic aspect of IPNs, which gives a more morphological interpretation of mutual entanglements in IPN systems.

The study of mutual entanglements or added physical crosslinks in IPNs is of special interest for modern network theories, but the experimental results are inconclusive in the literature[7]. For this reason Sperling *et al.* derived two special relationships between the elastic modulus and swelling properties of homo IPNs to re-examine the data from different laboratories.

As with most polymer blends, the phases of the IPNs usually separate even for polystyrene/polystyrene IPNs, but the extent of phase separation is restricted because of the presence of mutual entanglements between the two networks. It is believed that the morphology of most IPN systems has dual phase continuity. When two polymer networks are interpenetrating in three dimensions, obviously, the molecular chains of different networks must be mutually entangled. These internetwork entanglements can be thought of as a type of 'Ferry trap', which could not be disentangled physically without destruction of the networks[5].

We have reported the forced compatibility of poly(vinyl acetate)/poly(methyl acrylate) (PVAc/PMA) IPNs[8], which is ascribed to the interlocks between the two networks. In this paper, a swelling equation for general homo IPNs will be derived, and the results of the equilibrium swelling and modulus of PVAc/PMA IPNs discussed according to it and the modulus theory. The experimental results are further interpreted using the Binder–Frisch analysis.

EXPERIMENTAL

A series of PVAc/PMA IPNs with different compositions and crosslinking densities were prepared sequentially. The details of the synthesis can be found elsewhere[9].

The measurement of equilibrium swelling degree was accomplished by the increase in weight when placed in acetone at 25°C. The interaction parameters between PVAc and acetone, χ_{I}, PMA and acetone, χ_{II}, and PVAc and PMA, $\chi_{\mathrm{I,II}}$, are 0.46, 0.48 and 0.015, respectively[10].

The moduli were measured using a Rheovibron DDV-II-EA. The measurements were carried out at 3.5 Hz from −25°C to 150°C with a heating rate of 2°C min^{-1}. The values of rubbery moduli at 100°C were selected as the data used in the following discussion.

The characteristics of the PVAc/PMA IPN samples are given in *Table 1*.

DEVELOPMENT OF THEORY

The Flory–Rehner[11] swelling equation has served to characterize the properties of single networks for many

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Table 1 Characterization of the IPN samples

Samples	Volume composition (PVAc/PMA)	$\bar{M}_{C,I}$ ($\times 10^{-4}$)	$\bar{M}_{C,II}$ ($\times 10^{-4}$)	Polymerization temperature (°C)
IPN-1-10B	17/83	1.50	3.82–0.32	80
IPN-1-10C	28/72	0.67	3.82–0.32	80
IPN-1-6D	39/61	3.55–0.19	2.77	80
IPN-1-6E	39/61	3.55–0.19	1.05	80

years. Thiele and Cohen[12] derived a corresponding equation for homo IPNs, in which networks I and II are chemically identical except for their crosslinking level. However neither the Flory–Rehner nor Thiele–Cohen equations contain the thermoelastic front factor to account for the internal energy change of network I swelled by network II. For this reason, Siegfried *et al.*[7] modified the Thiele–Cohen swelling equation.

When swelled by a solvent, a homo IPN can be regarded as a two-component (polymer/solvent) system. However, ordinary IPNs swelled in a solvent correspond to three-component systems of polymer I/polymer II/solvent. In order to analyse properly the swelling behaviour of general compatible IPNs in which only one glass transition temperature is observed, we derived the following:

$$\begin{aligned}\mu_1 - \mu_1^{o} = RT\Big[\Phi - \ln(1-\Phi) + \Phi(\chi_I\Phi_I + \chi_{II}\Phi_{II}) \\ - \chi_{I,II}\Phi_I\Phi_{II} + \frac{\rho_I v_1}{\bar{M}_{C,I}}\left(1 - \frac{2\bar{M}_{C,I}}{\bar{M}_r}\right) \\ \times (\Phi_I^{o})^{-2/3}\left(\Phi_I^{1/3} - \frac{\Phi_I}{2}\right) + \frac{\rho_{II} v_1}{\bar{M}_{C,II}} \\ \times \left(1 - \frac{2\bar{M}_{C,II}}{\bar{M}_{II}}\right)\left([\Phi_{II}^{o}]^{2/3}\Phi_{II}^{1/3} - \frac{\Phi_{II}}{2}\right)\Big] \quad (1)\end{aligned}$$

where the superscript o refers to the dry state of IPNs, Φ, Φ_I and Φ_{II} represent the volume fraction of a whole sample and its two-component networks, with $\Phi_I + \Phi_{II} = \Phi = \lambda^{-1}$ where λ is the degree of swelling, χ_I, χ_{II} and $\chi_{I,II}$ denote the interaction parameters of polymer I/solvent, polymer II/solvent and polymer I/polymer II, ρ is the polymer density, v_1 is the molar volume of the solvent, and $\bar{M}$ and $\bar{M}_c$ represent the molecular weights of polymer chains consisting of the network and that between two adjoining crosslinking loci, respectively. For homo IPNs, the two networks are the same chemically, i.e. $\chi_I = \chi_{II}$, $\chi_{I,II} = 0$, then equation (1) reduces to the modified Thiele–Cohen swelling equation.

In the calculation, both networks were presumed to be ideal, i.e. $\bar{M}_I$, $\bar{M}_{II} \rightarrow \infty$. This makes the theoretical value of the volume fraction a little larger, especially when the crosslinking density is low. Besides, the microphase heterogeneity of PVAc/PMA IPNs (domain size $\leqslant$ 100 Å) was not considered.

In calculating the modulus of PVAc/PMA IPNs, the equation derived by Siegfried *et al.*[7] was used. The Young's modulus, $E_{R,IPN}$, of a sequential IPN in the rubber state is

$$E_{R,IPN} = 3RT(\Phi_I^{1/3}n_I + \Phi_{II}n_{II})$$

or (2)

$$E_{R,IPN} = \Phi_I^{1/3}E_{R,I}^{o} + \Phi_{II}E_{R,II}^{o}$$

where n_I and n_{II} represent the number of moles of chains of networks I and II per cm^3, Φ_I and Φ_{II} are the volume fraction of the two networks, and $E_{R,I}^{o}$ and $E_{R,II}^{o}$ refer to the Young's modulus of homopolymer networks I and II, respectively.

In all cases, a sequential model of synthesis is assumed where network I was swelled by network II, and the two networks are continuous in the whole sample space and elastically independent.

Neither equation (1) nor equation (2) considered the contribution of mutual entanglements or added physical crosslinks. If they do exist in IPNs, the experimental values should be larger than the theoretical ones of Φ calculated from equation (1) and E from equation (2).

Binder and Frisch[6] recently studied the stability of IPNs theoretically, and derived a formula that could be used to estimate the entropy change caused by the mutual entanglement number per unit volume as

$$\Delta S_{ent,IPN} \propto \Phi_I^{-2/3}(1-\Phi_I)^{1/3}\bar{M}_{C,I}^{-1}\bar{M}_{C,II}^{-1/2}\sigma_I^{-2}\sigma_{II}^{-1} \quad (3)$$

where σ_I and σ_{II} are the parameters related to polymers I and II, respectively. It is believed that when $\bar{M}_{C,I} \rightarrow 1$, $\bar{M}_{C,II}$ is large, and Φ_I is near unity, the entropy change caused by mutual entanglements between the two networks would be more important than that of elasticity of the networks in IPNs.

RESULTS AND DISCUSSION

Equilibrium swelling

In *Figures 1* and *2*, the volume fraction (Φ) calculated from equation (1) is plotted *versus* Φ determined from equilibrium swelling experiments. As mentioned above, if physical crosslinks arising from IPN entanglements are added the swelling data would be expected to shift to the right-hand side of the theoretical line. This clearly is the case in *Figure 1*. As the crosslinking density of network I increases, the deviation is regularly enhanced, indicating the existence of mutual entanglements. The extent of added physical crosslink depends on $\bar{M}_{C,I}$ principally and linearly. All the data lies on the same line, no matter

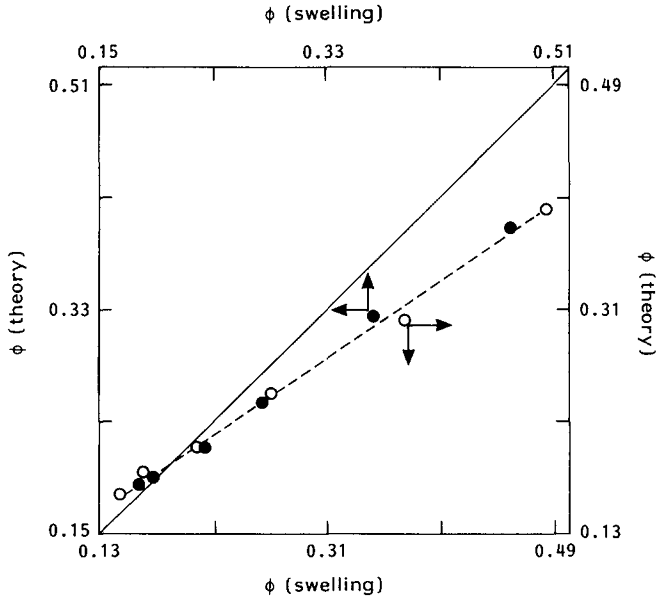

Figure 1 Plot of volume fraction (Φ) at equilibrium swelling predicted from theory *versus* Φ measured in experiments for D(○) and E(●) series of IPNs

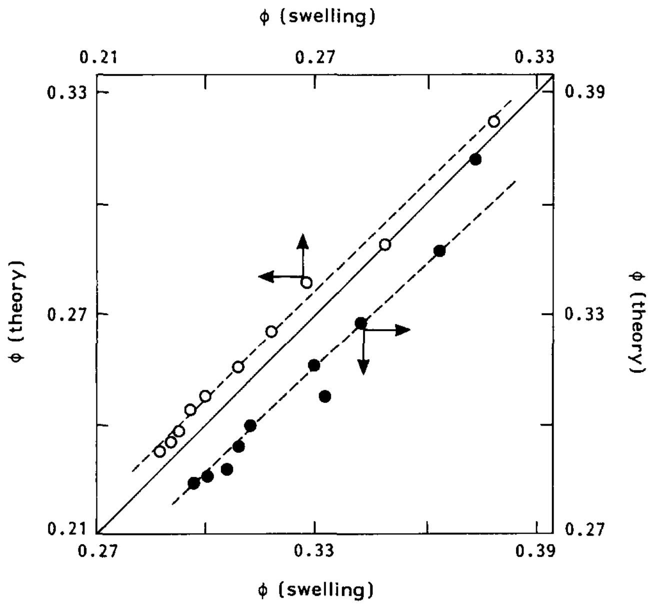

Figure 2 Plot of volume fraction (Φ) at equilibrium swelling predicted from theory *versus* Φ measured in experiments for B(○) and C(●) series of IPNs

how high the value of $\bar{M}_{\mathrm{C,II}}$. Domination of network I is another important implication of the results. Changing $\bar{M}_{\mathrm{C,II}}$ does not change the slope of the experimental data. It is almost identical to that of the theoretical line in *Figure 2*, indicating that the contribution of $\bar{M}_{\mathrm{C,II}}$ to the added physical crosslinks is hardly detectable. The added physical crosslinks are exhibited only when $\bar{M}_{\mathrm{C,I}}$ is below a certain value ($\sim 1.3 \times 10^4$).

If $\bar{M}_{\mathrm{C,I}}$ is well below this value, the data points shift to the right-hand side of the theoretical line even though the crosslinking density of network II is rather low ($\bar{M}_{\mathrm{C,II}}$ is high). When the crosslinking density of network I is relatively low, $\bar{M}_{\mathrm{C,I}} > 1.3 \times 10^4$, the swelling data are close to the theoretical line and shifted to the left-hand side. This may be due to there being less IPN entanglements and to the assumption of the networks being both ideal.

Elastic modulus

Since the contribution of physical crosslinks and defects, etc. in single networks has already been included in the measurements of $E^0_{\mathrm{R,I}}$ and $E^0_{\mathrm{R,II}}$, the effect of added physical crosslinks on the modulus of the IPNs should be similar to that of equilibrium swelling behaviour. So there could be a similar analysis for the moduli data in *Figures 3* and *4*.

The changing tendency of the modulus is satisfactorily consistent with that of swelling. Comparing the data in *Figures 1* and *3*, the same conclusions are reached, i.e. the presence of added physical crosslinks introduced by IPN entanglements. Network I dominates the properties of swelling and modulus in a very similar way except in the slope of the broken line of *Figure 3*, which is a little smaller than that of swelling in *Figure 1*. It now seems possible to characterize the extent of mutual entanglements in IPNs quantitatively.

The main points indicated by the data in *Figure 4* are also similar to those shown in *Figure 2*, with the exception of the linearity and the deviations from the theoretical line. In the studies of polystyrene/polystyrene IPNs, while only the modulus data of Shibayama and Suzuki[13] indicated the presence of added physical crosslinks, the evidence of the domination of network I was found from all the modulus data[7].

In our opinion, the inconsistency in the data of polystyrene/polystyrene IPNs on added physical crosslinks in the literature is probably due to the difference in sample preparation procedure and variations in crosslinking density. In fact, both the swelling and modulus data given by Shibayama and Suzuki tend towards the presence of added physical crosslinks in IPNs, especially for the samples with higher crosslink density.

Binder–Frisch theory

Binder and Frisch[6] have pointed out that the outstanding basic problems in IPNs reflect our ignorance of the basic molecular structure, microphase structure

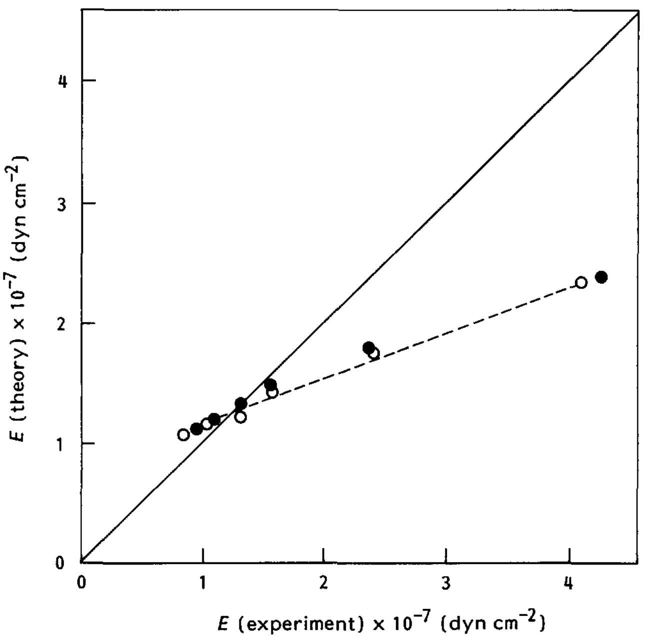

Figure 3 Plot of Young's modulus (E) predicted from theory *versus* E measured in experiments for D(○) and E(●) series of IPNs

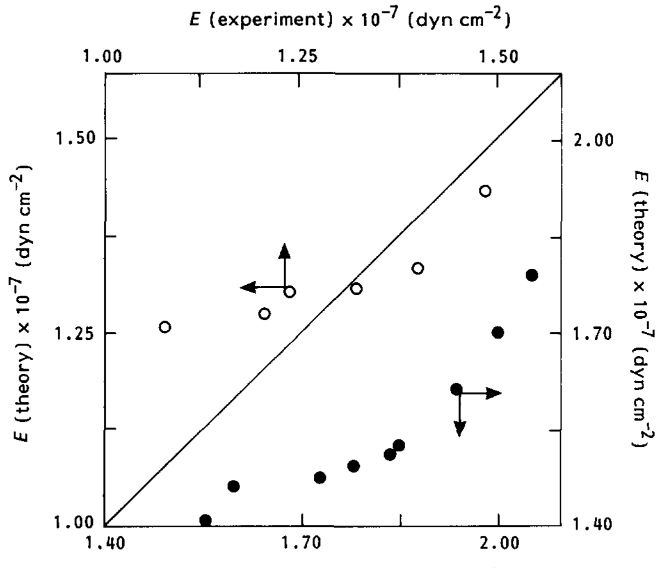

Figure 4 Plot of Young's modulus (E) predicted from theory *versus* E measured for B(○) and C(●) series of IPNs

and a lack of knowledge of property–structure correlation. All these problems are directly related to the mutual entanglement of the networks in IPNs.

Why are there added physical crosslinks in IPNs, and why does network I dominate the properties of IPNs? The Binder–Frisch consideration can give us a qualitative answer. According to the theory, the change in elastic entropy of IPNs during deformation can be simplified to:

$$\Delta S_{\mathrm{el,IPN}} = \Delta S_{\mathrm{el,I}} + \Delta S_{\mathrm{el,II}} = C_{\mathrm{I}} M_{\mathrm{C,I}}^{-1} + C_{\mathrm{II}} M_{\mathrm{C,II}}^{-1} \tag{4}$$

and the entropy change of IPNs introduced by mutual entanglements between the networks [equation (3)] can be simplified to:

$$\Delta S_{\mathrm{ent,IPN}} = C M_{\mathrm{C,I}}^{-1} M_{\mathrm{C,II}}^{-1/2} \tag{5}$$

where the subscripts I and II refer to networks I and II, respectively, M_{C} is the molecular weight between two neighbouring crosslinking loci, and C refers to the parameter related to the network structure.

From equations (4) and (5) the following deductions can be obtained.

When $\bar{M}_{\mathrm{C,I}} \rightarrow 1$, and $\bar{M}_{\mathrm{C,II}} \gg 1$, the changes of entropy are

$$\Delta S_{\mathrm{el,IPN}} \sim M_{\mathrm{C,II}}^{-1} \tag{6}$$

$$\Delta S_{\mathrm{ent,IPN}} \sim M_{\mathrm{C,II}}^{-1/2} \tag{7}$$

Comparing equations (6) and (7), we see that mutual entanglements should have a relatively stronger contribution to the properties related to the entropy thermodynamically, such as equilibrium swelling and modulus.

When $\bar{M}_{\mathrm{C,I}} = \bar{M}_{\mathrm{C,II}} = \bar{M}_{\mathrm{C}} \gg 1$, equations (4) and (5) can be reduced to

$$\Delta S_{\mathrm{el,IPN}} \sim M_{\mathrm{C}}^{-1} \tag{8}$$

$$\Delta S_{\mathrm{ent,IPN}} \sim M_{\mathrm{C}}^{-3/2} \tag{9}$$

In this case, the contribution of mutual entanglements can be ignored.

In equation (5), the absolute value of the power of $\bar{M}_{\mathrm{C,I}}$ is larger than that of $\bar{M}_{\mathrm{C,II}}$. This means that network I plays a dominant role in the properties of IPNs compared to network II. Besides, the deductions represented by equations (6), (7), (8) and (9) also hide the same meaning.

All this is qualitatively consistent with the results of equilibrium swelling and modulus experiments. Although the modulus experiments were aimed at the problem of added physical crosslinks and they have yielded positive results, we think that much more still remains to be examined both experimentally and theoretically to understand this interesting problem of mutual entanglements or added physical crosslinks in IPNs.

CONCLUSIONS

It is apparent that added physical crosslinks are presented in PVAc/PMA IPNs, which are introduced by mutual entanglements between the networks, and may be enhanced linearly as $\bar{M}_{\mathrm{C,I}}$ decreases. The domination of network I is also inherent in IPNs. The Binder–Frisch theory can be used qualitatively to interpret the experimental results.

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