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Entanglements in interpenetrating polymer networks evidenced by simple physicochemical investigations

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Abstract

A series of in situ sequential interpenetrating polymer networks (IPNs) of polyurethane (PU) and polystyrene (PS) were prepared at room temperature. The PU network was made from oligomeric polypropylene oxide, end-linked with an aliphatic triisocyanate. The PS network results from free radical photocopolymerization of styrene with a small amount of divinylbenzene. During synthesis, the homogeneous initial mixture segregates into co-continuous phases with no chemical bonds between them. However, the samples exhibit high optical transparency. The measurements of refractive index and equilibrium swelling in ethyl acetate gave the evidence of interpenetration, i.e. additional entanglements between unlike network chains.

Keywords: Interpenetrating polymer networks; Entanglements; Swelling

1. Introduction

In recent years, blending of existing polymers gained importance because of the expensive development costs of new polymers, and because it is an interesting way to prepare novel materials with tailor made properties. Mechanical blending is the oldest and simplest way to combine two or more polymers. Multicomponent materials often exhibit phase separation, and the end-use performance strongly depends, in part, upon their phase morphology.

One attractive approach for reducing the degree of phase separation and combining the properties of different polymers is to form interpenetrating polymer networks (IPNs). IPNs are defined [1] as a more or less intimate combination of crosslinked polymers, held together by their mutual entanglements resulting from their specific synthesis techniques. However, up to now, evidence of more entanglements in IPNs has been shown for homo-IPNs [1] only, which are combination of two identical networks, namely polystyrene/polystyrene. The pioneer work of Millar [2] was analyzed by Shibayama and Suzuki [3], Siegfried et al. [4] and Thiele and Cohen [5]. The presence of trapped entanglements in IPNs was deduced from Young's modulus measurements and use of rubber elasticity theory, after comparison with the sum of the modulus of the component networks [6]. Later, Gent et al. [7] have evidenced additional physical crosslinks for homo-IPNs based on model polydimethylsiloxane networks prepared by end-linking. These conclusions are still controversial since they concern miscible sequential IPNs only, obtained by swelling a preformed polymeric network with his monomer and subsequent polymerization. Also, the calculations based on the Thiele–Cohen equation [5] or modified Thiele–Cohen equation [4] involve parameters not being experimentally accessible or dependent on conditions (pressure, temperature), like the interaction parameter, χ, between the swelling solvent and the elastic chains of the network.

The present work reports on classical physico-chemical investigations made in view of clarifying the concept of additional physical entanglements and chain interlocking in actual IPNs, i.e. based on incompatible components. Experiments concern swelling and refractive index measurements on in situ sequential polyurethane/polystyrene (PU/PS) IPNs of various crosslink density and composition.

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2. Theoretical background

2.1. Refractive index

The molar refraction, R, is a characteristic physical value of a molecule. The Lorentz–Lorenz equation [8] expresses the relationship between R, the density, ρ and the refraction index, n

$$R=\frac{n^2-1}{n^2+2}\frac{M}{\rho} \tag{1}$$

where M is the molar mass of the polymer. Since the molar refraction is an additive term (ΣR_i), where R_i is the molar refraction of the polymer repeating unit, the specific refraction, R', which equals R divided by M, of each network is given by:

$$R'=\frac{R}{M}=\frac{n^2-1}{(n^2+2)\rho} \tag{2}$$

For a mixture of networks, one obtains

$$R'_{12}=x_1R'_1+x_2R'_2 \tag{3}$$

where x_1 and x_2 are the volume fraction of networks 1 and 2, respectively.

From R'_{12} and experimental refractive index, the density of the IPNs can be calculated using Eq. (2). If that calculated value is higher than the calculated value from relative additivity of the density of the individual networks, densification would have occurred when forming IPNs, thus indicating the presence of additional physical crosslinks. It is worth noting that this argument counts for IPNs made from incompatible polymer pairs only with no chemical or physical interaction among themselves.

2.2. Equilibrium swelling

It is assumed that the IPN swelling solvent is a good swelling agent for both networks.

In case a, considering two networks 1 and 2, being spacelly independent, the swelling degree, ${}^{a}Q$ of the mixture a can be written as

$${}^{a}Q\ =w_1{}^{1}Q+w_2{}^{2}Q \tag{4}$$

where w_1 and w_2 are the weight fraction of each network in the dry state, and ${}^{1}Q$ and ${}^{2}Q$ are the swelling degree of the individual networks, respectively.

In case b, network 1 and network 2 are mixed in IPN form with two co-continuous pure phases. In the presence of the swelling solvent, both networks swell mutually. Thus, the IPN fraction in the swollen state, $1/{}^{b}Q$, is obtained from the individual network fraction, $1/{}^{1}Q$ and $1/{}^{2}Q$, respectively, by the relation:

$$\frac{1}{{}^{b}Q}=\frac{w_1}{{}^{1}Q}+\frac{w_2}{{}^{2}Q} \tag{5}$$

The theoretical swelling degree of the IPN can be calculated from the swelling data of the individual networks, using the swelling degree by weight, rather than by volume, because of weight-conservation between individual polymers and polymers in IPN form. However, network 1 is formed in solution (in monomer 2) and its topology depends on dilution on the time of formation [9], which will correspond to the composition, w_1/w_2, of the IPN. On the other hand, network 2 is formed within polymer matrix 1, which in deed cannot be considered as a molecular swelling solvent. Therefore, the swelling degree of network 2 is taken as the swelling degree of the network synthesized in bulk. By taking the conditions of network formation into consideration, Eqs. (4) and (5) can be re-written:

$${}^{a}Q_{w_1/w_2}=W_1{}^{1}Q_{w_1/w_2}+w_2{}^{2}Q_{\mathrm{bulk}} \tag{6}$$

and

$$\frac{1}{{}^{b}Q}=\frac{w_1}{{}^{1}Q_{w_1/w_2}}+\frac{w_2}{{}^{2}Q_{\mathrm{bulk}}} \tag{7}$$

These equations do not involve any kind of physical crosslinks or mutual entanglements. Hence, if molecular interpenetration would exist for IPNs, the experimental swelling value would be lower than the value calculated from Eq. (7). This is only true if there is no possibility of chemical grafting between the networks. Note also that the contribution of the polymeric species to the swelling of one network can be neglected with regard to the swelling behaviour of the molecular solvent.

3. Experimental

PU/PS IPNs were prepared at room temperature, either by a two-step method (sequential IPNs), or by a one-shot process (in situ IPNs). For the sequential IPNs, the first step was the formation of crosslinked PU, by end-linking 1 equiv. of polypropylene oxide, average molar mass: 1000, 2000 and 4000 g/mol, respectively, with 1.07 equiv. [10] of tris(6-isocyanato hexyl)isocyanurate in a given amount (typically 50 wt%) of ethyl acetate, in the presence of 1.5 wt% of dibutyltin dilaurate as catalyst. The solvent was subsequently removed under vacuum and, in the second step, samples (approximately $20\times20\times0.7$ mm^3) of the dry PU network were immersed in a definite amount of styrene–divinylbenzene monomers, containing 1.5 wt% benzoin, and allowed to swell for 48 h in the dark. After homogenization, styrene was photopolymerized to its maximum conversion. Unreacted materials were removed under vacuum at 80 °C.

In situ IPNs were prepared likely from the same precursors, except that ethyl acetate was replaced by a styrene–divinylbenzene–benzoin mixture. Photopolymerization of the vinyl monomers was initiated after completion of the step polymerization (monitored by FTIR spectroscopy [11]).

Refractive index measurements were made using a digital Abbe refractometer. A circulating water bath was employed to maintain the temperature at a constant value ± 0.1 °C. The refractive index, n was accurately determined to the fourth decimal place with respect to the average sodium D line (wavelength 589.3 nm) at 25 °C.

The density was measured at 25 °C, using a picnometer, four times for each sample, and averaged. A run begins with the weighing of the dry calibrated picnometer. A given amount of the solid sample was placed into the picnometer, which was then filled with distilled water and tapped to release air bubbles and weighed again. The density, ρ, of the sample is determined by $\rho = (m_f - m_e)/V$ where m_f is the mass of the filled picnometer, m_e is the mass of the empty picnometer and V is the volume of the picnometer. The experimental uncertainty was about 1%.

To measure the equilibrium swelling degree, preweighed dry samples were immersed in ethyl acetate, a common solvent for both polymers. From time to time, the samples were removed from the solvent and rapidly weighed after removal of excessive surface solvent with filter paper. The procedure, carried out at 25 °C, was repeated until there was no further weight increase (average duration 4 days). The swelling ratio, Q was calculated by $Q = W_s/W_d$ where W_s is the weight of the swollen sample and W_d is the weight of the dry sample. Three specimens of each sample were taken, and the average value reported. The experimental uncertainty was less than 2%.

4. Results and discussion

As described in the experimental part, PU/PS IPNs with various compositions have been prepared sequentially, i.e. the PU network is first formed in solution. These IPNs exhibit a microheterogeneous structure and/or a dual-phase co-continuity (in situ sequential IPNs), without any chemical link between the networks.

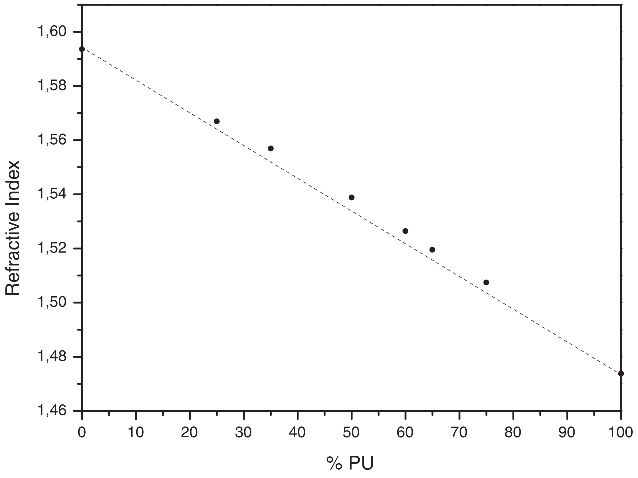

Fig. 1. Variation of refractive index of in situ sequential PU/PS IPNs with composition. The dotted line is the additivity line based on the refractive index of the individual networks.

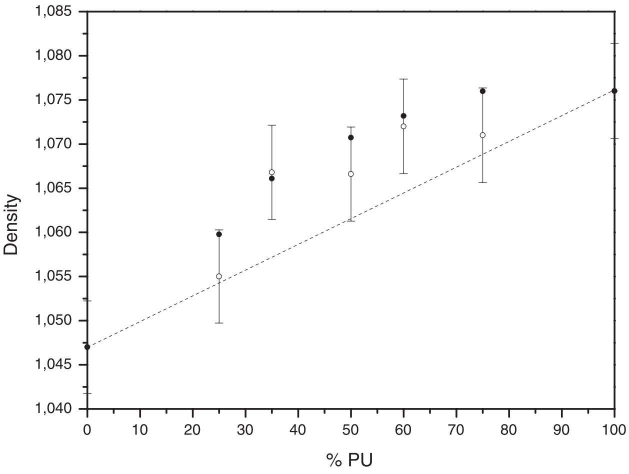

Fig. 2. Variation of density of in situ sequential PU/PS IPNs with composition. Calculated density (○) from refractive index measurements; measured density (●) by picnometry. The dotted line is the additivity line based on the density of the individual networks.

4.1. Refractive index measurements

The variation of the refractive index with IPNs composition is shown in Fig. 1. As expected from the index of the individual networks, the refractive index decreases with increasing PU content. However, within the composition range considered, the experimental values are located above the additivity line joining the refractive index of the individual networks. Deviation from additivity seems to be maximum for mid-range composition. Fig. 2 compares the measured densities with the calculated densities (Table 1) as a function of composition. Densification for IPN samples appears clearly, thus suggesting the presence of additional physical crosslinks. Figs. 3 and 4 show that the refractive index deviates less from simple additivity when decreasing the crosslink density. Consequently, the number of additional physical crosslinks is reduced. It is important to point out that entanglements, loops, trapped chains, increase with increasing the molecular weight between

Table 1
Refractive index, n, specific refraction, R', and calculated density, d_{calc}, of IPNs at 25 °C

Composition (PU/PS)	N	R'	d_{calc}
0/100	1.5936	0.323	1.047
25/75	1.5669	0.308	1.059
35/65	1.5569	0.302	1.065
50/50	1.5388	0.292	1.070
60/40	1.5264	0.286	1.072
75/25	1.5074	0.277	1.075
100/0	1.4737	0.261	1.076

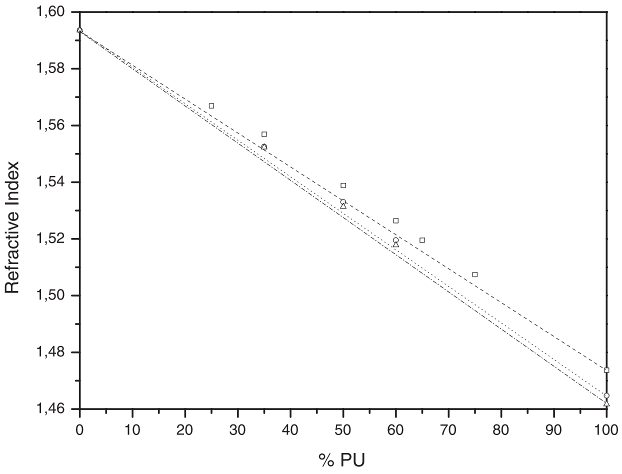

Fig. 3. Variation of refractive index of in situ sequential PU/PS IPNs with composition. Influence of the crosslink density of the PU network. Molar mass between crosslinks, M_c, was 4000 g/mol (△), 2000 g/mol (○) and 1000 g/mol (□).

crosslinks, i.e. reducing the crosslink density, but this counts for individual networks, and not for the combination of two networks in IPN form, where the physical crosslinks considered here are inter-network entanglements, not intramolecular entanglements. Hence, from a very practical point of view, simple measurements of the refractive index show the existence of entanglements between the chemically different networks of an IPN.

4.2. Swelling experiments

The dependence of the equilibrium swelling degree of IPNs on its composition is shown in Fig. 5. As previously reported by other authors for another incompatible polymer pair [12], the IPN swells more than the individual networks. The explanation proposed at that time was a lower than expected crosslink density of the polymers in IPN form. However, when taking into account the conditions of dilution at the time of network formation (see Table 2), a parabolic profile of the swelling degree of IPNs vs. composition is obtained, assuming co-continuity of the networks, and calculated values are close to the

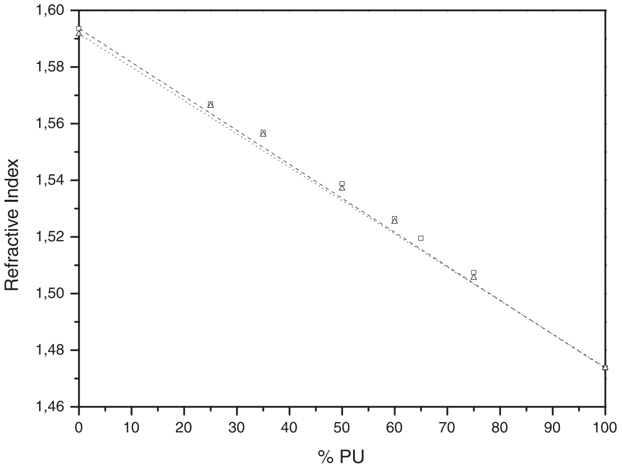

Fig. 4. Variation of refractive index of in situ sequential PU/PS IPNs with composition. Influence of the crosslink density of the PS network. DVB = 5% (□), DVB = 0% (△).

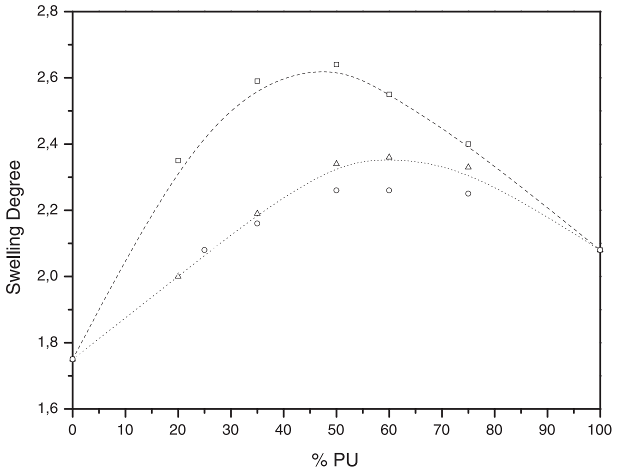

Fig. 5. Equilibrium swelling degree vs. composition for in situ sequential PU/PS IPNs. Experimental data (○), calculated data according to ${}^{a}Q_{w1/w2}$ (□) and ${}^{b}Q_{w1/w2}$ (△), respectively.

Table 2
Calculated swelling degrees of in situ PU/PS IPNs according to Eqs. (6) and (7), and experimental swelling degree of individual PU networks in ethyl acetate

Composition (PU/PS)	${}^{PU}Q_{w1/w2}$	${}^{a}Q_{w1/w2}$	${}^{b}Q_{w1/w2}$
0/100	–	1.75	1.75
20/80	4.76	2.35	2.00
35/65	4.15	2.59	2.19
50/50	3.54	2.64	2.34
60/40	3.09	2.55	2.36
75/25	2.62	2.40	2.33
100/0	2.08	2.08	2.08

${}^{PS}Q_{bulk} = 1.75$.

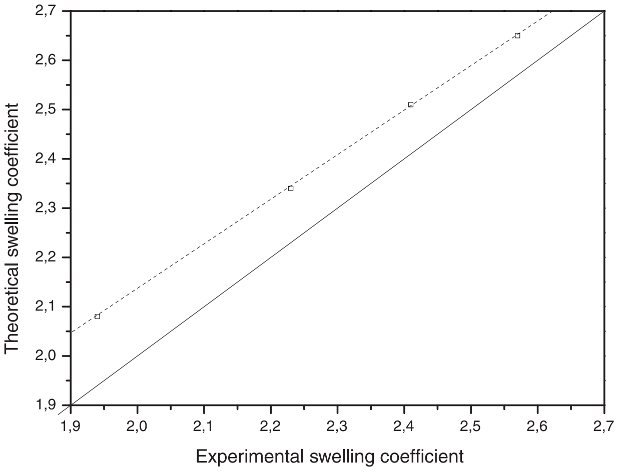

Fig. 6. Calculated swelling degree, ${}^{b}Q$, vs. experimental swelling degree, Q, for 50/50 in situ sequential PU/PS IPNs with various PU crosslink densities.

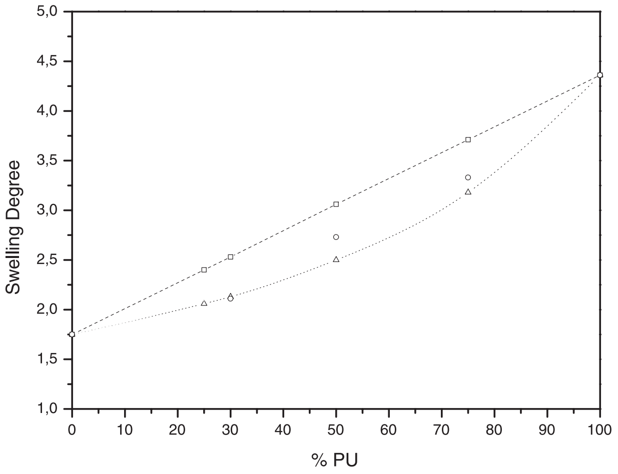

Fig. 7. Equilibrium swelling degree vs. composition for sequential PU/PS IPNs. Experimental data (○), calculated data according to $^aQ_{w1/w2}$ (□) and $^bQ_{w1/w2}$ (△), respectively.

experimental data, but the latter are systematically located under those calculated. This demonstrates the presence of additional physical crosslinks for IPNs. The maximum of entanglements is achieved for a 50/50 IPN composition as previously shown by the results of refractive index measurements.

For a fixed 50/50 IPN composition, the crosslink density of the primary PU network was varied by the use of macrodiols with different molar masses, and the calculated swelling degree ^bQ from Eq. (7) is plotted, Fig. 6, vs. the experimental swelling degree. The observed positive deviation from the theoretical line indicates the presence of added physical crosslinks.

Compared to the in situ sequential IPNs considered until now, the swelling behaviour of sequential PU/PS IPNs is quite different. By definition [1], sequential IPNs are obtained by a two-step process, consisting in the diffusion of monomers into a preformed network, with a heterogeneous swelling of the primary network, likely leading not to phase co-continuity after polymerization. The swelling degree of sequential PU/PS IPNs vs. composition is shown Fig. 7. The experimental values are found to be between the calculated curves, assuming simple additivity or phase co-continuity (Table 3). Therefore, certainty of the presence of additional entanglements cannot be given in that case.

Table 3
Calculated swelling degrees of sequential PU/PS from the swelling degree of the individual networks

Composition (PU/PS)	$^aQ_{w1/w2}$	$^bQ_{w1/w2}$
0/100	1.75	1.75
25/75	2.40	2.06
35/65	2.53	2.13
50/50	3.06	2.50
75/25	3.71	3.18
100/0	4.36	4.36

Primary PU formed in 50% ethyl acetate.

5. Conclusion

The difference between the experimental and the calculated values of refractive index and swelling degree of in situ PU/PS IPNs emphasizes the presence of additional physical crosslinks for that combination. It appears also that interpenetration increases with increasing the crosslink density of the primary PU network, and that the number of mutual entanglements is maximum in the mid-range composition.

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