Structure and properties of an interpenetrating polymer network-like system consisting of polystyrene–polyethylene: 1. Synthesis, elastomeric and thermoanalytical characterization

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A polystyrene–polyethylene (PS–PE) interpenetrating polymer network (IPN)-like system was prepared by synthesis *in situ*. The system differs from 'pure' IPN systems in that the PS network is partially grafted onto the PE network. The mean molar mass of the polymer chain between two junction points ($\bar{M}_c$) was calculated from the values of uniaxial compression modulus. Differential scanning calorimetry and thermomechanical analysis measurements pointed to a considerable decrease of the crystalline phase in PE with increasing PS content. The melting temperature enhancement of the crystalline phase of PE is discussed.

(Keywords: polystyrene–polyethylene; interpenetrating network; synthesis)

INTRODUCTION

Interpenetrating polymer networks (IPNs) are generally characterized as polymer blends composed of crosslinked polymers. They are more or less intimate mixtures of two or more distinct crosslinked polymer networks with no covalent bonds between the polymer of each component[1,2].

We used synthesis *in situ* to prepare an IPN system of polystyrene–polyethylene (PS–PE). Dynamic mechanical measurements[3] indicate that it is not possible to prevent the PE radicals generated in the styrene solution from forming a PE–PS graft structure as well as the desired crosslinked PE network. For this reason, we describe these materials as an IPN-like system. As will be shown later, in spite of some interconnection of both polymer networks, the system shows properties similar to those observed in 'pure' IPN systems. On the other hand, this procedure for the preparation of a PS–PE IPN system can be used as a way to produce an intimate blend of the two immiscible polymers. In analogy with other IPN systems composed of two immiscible polymers, we expect that each polymer will create a discontinuous phase throughout the whole volume of the IPN. IPNs generally display different degrees of phase separation, and this depends primarily on the compatibility of the components. The phase regions may vary in size from several micrometres (incompatible systems[4]) to several tens of nanometres (intermediate[5]) up to homogeneous systems (without domain structure). These structures specifically affect mechanical behaviour.

Pozniak and Trochimczuk[6,7] used IPN systems containing PE and PS networks for preparing anion exchange membranes. However, they used a procedure consisting of film swelling of the low-pressure PE using a mixture of styrene, divinylbenzene and benzoyl peroxide followed by thermal polymerization.

This paper follows a previous article[3] which dealt with the mechanical behaviour of the IPN-like system, PS–PE. Attention is devoted to the examination of the structure of the IPN-like systems by measuring their uniaxial compression modulus and subjecting them to differential scanning calorimetry (d.s.c.) measurements.

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Table 1 Physical parameters calculated according to equations (1) and (2) on the basis of the compression modulus measurement of IPN samples with various ratios of PS to PE

Sample nos[a]	PS/PE[b] (molar ratio)	v (10^{-4} mol cm^{-3})	G_c (10^6 Pa)
1	0.6	3.59	1.26
2	1	2.73	0.96
3	1.67	2.19	0.77
4	2	1.99	0.70
5	3	1.47	0.52
6	0.6	4.09	1.44
7	1	2.87	1.01
8	1.67	2.13	0.75
9	2	2.19	0.77
10	3	1.13	0.75

Measurement temperature, $T_m = 150°C$; v = network density; G_c = shear modulus

[a] Samples 1–5 were prepared in the presence of 3% di-*tert*-butyl peroxide; samples 6–10 were prepared in the presence of 3% 2,5-di-methyl-2,5-di-(*tert*-butylperoxy)hexane

[b] Divinylbenzene (0.5%) was used as a crosslinking agent in the preparation of all samples

EXPERIMENTAL

Sample preparation

Polyethylene (Bralen RA 2-19 type with a flow index of 1.7–2.3 g/10 min) was dissolved in styrene with various molar ratios of PS to PE (*Table 1*). For samples 1 to 5, 3% di-*tert*-butyl peroxide (DTBP) and for samples 6 to 10, Luperox 101 (2,5-dimethyl-2.5-di-(*tert*-butylperoxy)hexane, were used as initiators. Divinylbenzene (DVB) (0.5 wt%) was used as a crosslinking agent in all samples. A small amount of inhibitor (benzoquinone) was also used to prevent thermal polymerization for about 20 min while dissolving PE in S. The crosslinking polymerization of S solution of PE was carried out between two glass plates sealed with PVC tubing. Curing took place at 120°C for 5 h followed by 1 h at 160°C. We assume that the crosslinking polymerization of S occurred first. In the last stages of the reactions mainly PE network is formed.

Gel content determination in samples

The gel content of the polymer network was determined in all samples listed in *Table 1* as well as in the samples used for examining the relationship between gel formation and reaction time. The gel content in individual samples was determined by extraction of the soluble (uncrosslinked) polymer in boiling xylene for 14 h. The mass gel fraction, w_g, was assessed from the mass of the sample before and after extraction.

Measurement of uniaxial compression modulus

The density of crosslinks, v, and the mean molar mass of the polymer chain between two junction points, $\bar{M}_c$, was calculated from the shear modulus (uniaxial compression modulus) of the dry network (height 4 mm and diameter 6 mm) in uniaxial compression, G_c. For the uniaxial compression of unswollen test specimens[8,9], the following relationship applies for a small deformation at low strain, according to the statistical theory of rubber elasticity[10]:

$$\sigma = f/A_0 = G_c(\lambda^{-2} - \lambda) \quad (1)$$

where σ is compressive stress, f is force of compression, A_0 is area of test specimen in the unswollen and unloaded state, λ is ratio of compression and $\lambda = (h - \Delta h)/h$ where Δh is change of initial height, h, in the compressed state.

The shear modulus (the slope in *Figure 1*) is given by:

$$G_c = AvRT = A\bar{M}_c^{-1}\rho RT \quad (2)$$

where A is the front factor ($A = 1$ for small deformation at small strain), $v = \rho/\bar{M}_c$ where ρ is the density of the dry network; R is the gas constant and T is the temperature (K). G_c was determined according to ref. 11 using a device developed in this laboratory, equipped with a measuring gauge with 0.01 or 0.001 mm gradation[9], in combination with a modified gas chromatograph GCHF 18.3-4 (Fa. Chromatron, Berlin, Germany) for annealing (*Figure 2*).

For test specimens thicker than 1 mm, a specially constructed apparatus employing a displacement transducer and a digital voltmeter to measure displacement was used[12]. It was sensitive to displacements of 10^{-4} mm.

The uniaxial compression was measured at a temperature of T_{extr} (on *Figure 4*) + 20–40°C, that is, at a constant working temperature T_w of 150°C and this temperature guaranteed that $T_w > T_m$ of the PE network and $T_w > T_g$ of the PS network. Therefore it is possible to calculate with the help of equations (1) and (2) for rubber-like

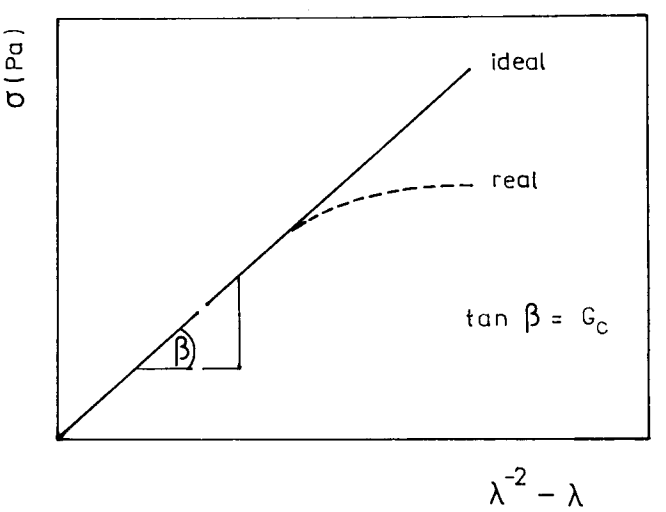

Figure 1 Dependence of compressive stress σ on $\lambda^{-2} - \lambda$

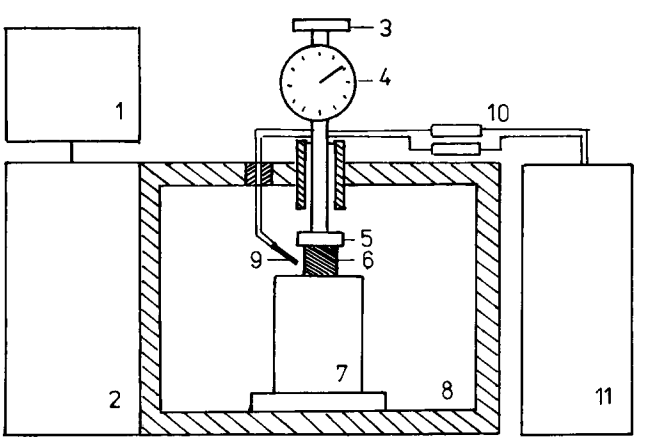

Figure 2 Measuring device for uniaxial compression: 1, temperature programmer; 2, control device; 3, plate for weights; 4, dial gauge; 5, stamp; 6, sample; 7, fitting for sample; 8, air thermostat; 9, Pt-thermometer; 10, 5Ω resistors; 11, chart recorder

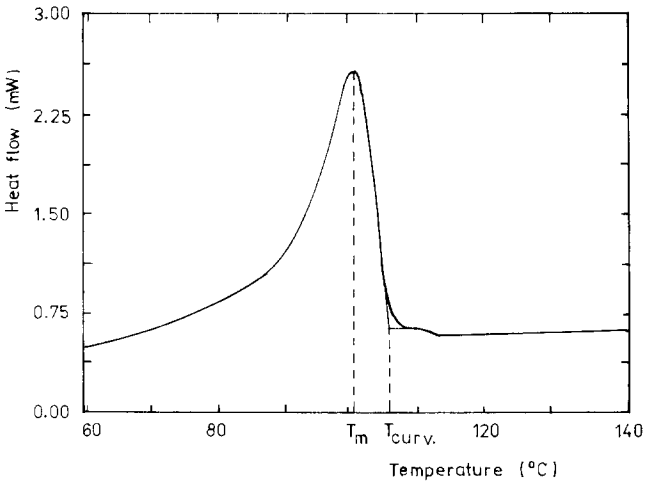

Figure 3 Method for determining T_m and T_{curv} on d.s.c. curves

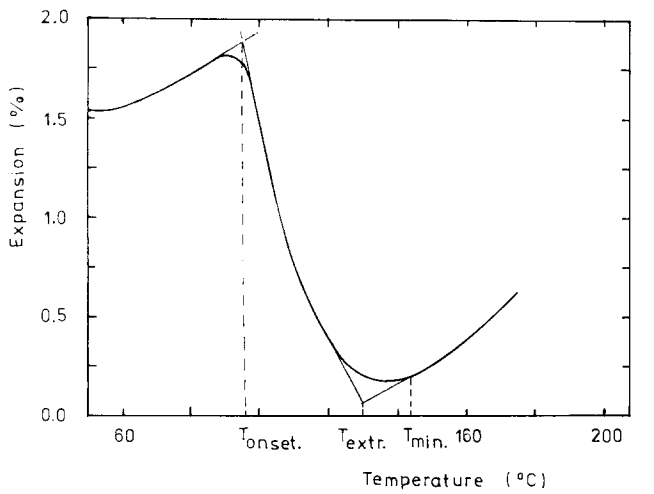

Figure 4 Method for determining T_{onset}, T_{extr} and T_{min} on t.m.a. curves

networks from the G_c (equation (1)) of the IPN-like network a network density ν or a M_c value (equation (2)). These values consist of the ν and M_c values of both the networks in the IPN-like network.

Every sample was maintained at the working temperature (150°C) for 0.5 h before measurement to attain T_w in the whole sample. A preload of 50 g causes the stamp (5 in *Figure 2*) to contact the specimen (the sample 6 in *Figure 2*) directly; the dial gauge (4 in *Figure 2*) is set to zero after 30 min. Then a weight of 25 g is added to the plate for weights and after 5 min the compression is read. After the sample has been relaxed for 5 min, the compression is repeated with a weight of 50 g.

The loading of weights was performed in this way in the range between 50 and 500 g in steps of 25 g until the compression Δh deviated by 10% from the initial height h of the sample. *Table 1* contains the results obtained using these conditions. The compression signal was plotted using a chart recorder.

Thermoanalytical characterization

Thermal analysis allows the measurement of changes in a polymer network's physical and chemical properties as a function of temperature. There is still no complete knowledge of the influence of the chemical composition of the reaction mixture and the degree of crosslinking on the physical properties and the supermolecular structure of the IPN. However, thermoanalytical studies on partial crystalline networks[13] have shown that the regions of the glass transition, crystallization and melting and the crystallization and melting enthalpy change with the degree of crosslinking.

Therefore a Perkin–Elmer DSC 7 differential scanning calorimeter, and a Perkin–Elmer TMA7 thermomechanical analyser were used for thermoanalytical examination of crosslinked samples at between 30 and 200°C. The thermograms (*Figures 3* and *4*) were recorded in air at heating rates of 5 and 10°C min^{-1}. For the d.s.c. measurements, samples with a weight of 10 mg were used, and for the t.m.a. method the samples had a diameter of 6 mm and a thickness of 2 mm. In the t.m.a. measurements the samples were loaded with a constant force of 10 mN. An empty sample pan was used as a reference in d.s.c. measurements.

Measurements were made on the two series of samples having an equally varying ratio between PS and PE. Both series only differed in the type of crosslinking initiator: 3 wt% of DTBP and 3 wt% Luperox 101, respectively. *Tables 2* and *3* show the results obtained by using d.s.c. (T_m and T_{curv} in *Figure 3*) and t.m.a. (T_{onset}, T_{extr}, T_{min} in *Figure 4*).

Table 2 Results of thermomechanical analysis of IPN samples with various ratios of PS to PE

Sample nos[a]	PS/PE (molar ratio)	T_{onset} (°C)	T_{min} (°C)	T_{extr} (°C)
1	0.6	97.2	115.1	111.4
2	1	96.1	125.4	-
3	1.67	96.4	126.4	114.0
4	2	95.2	130.2	-
5	3	96.9	122.1	111.9
6	0.6	98.4	123.3	113.7
7	1	97.2	122.6	114.4
8	1.67	95.9	131.0	119.2
9	2	94.2	152.3	120.8
10	3	94.2	(152.8)	133.9

[a] For conditions of sample preparation see *Table 1* and Experimental section

Table 3 Results of d.s.c. measurements of IPN samples with various ratios of PS to PE

Sample nos[a]	PS/PE (molar ratio)	T_m (°C)	T_{curv} (°C)	ΔH (J g^{-1})
1	0.6	95.8	101.9	18.50
2	1	99.8	109.5	13.00
3	1.67	101.3	108.2	10.10
4	2	100.93	110.06	7.42
5	3	108.7	116.4	8.90
6	0.6	99.95	106.4	17.58
7	1	100.06	116.7	15.55
8	1.67	95.13	115.5	9.35
9	2	98.00	-	6.72
10	3	105.8	114.0	6.79

[a] For conditions of sample preparation see *Table 1* and Experimental section

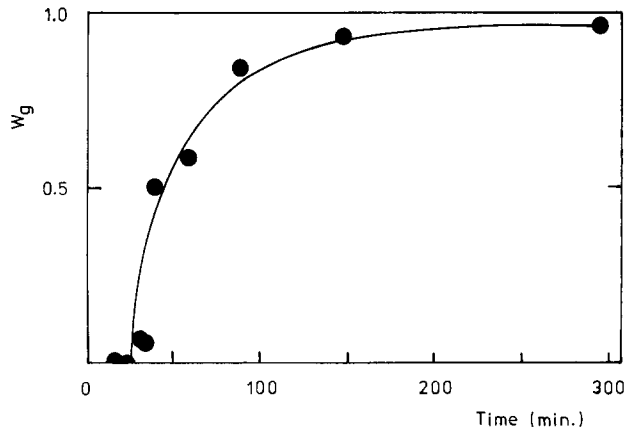

Figure 5 Dependence of the weight fraction of the gel, w_g, on the reaction time at 120°C (after 14 h extraction in boiling xylene)

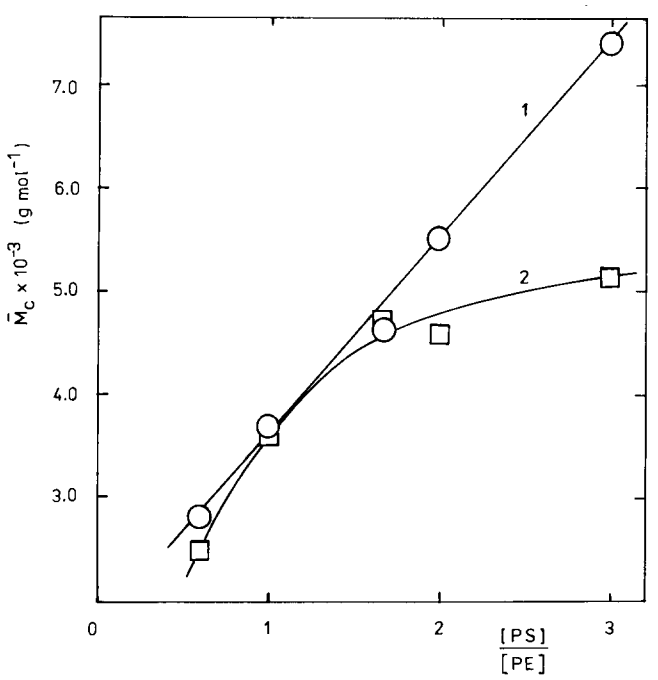

Figure 6 Dependence of the mean molar mass of the polymer chain between two junction points, $\bar{M}_c$, on the ratios of polystyrene to polyethylene (PS/PE): curve 1, samples 1–5; curve 2, samples 6–10

RESULTS AND DISCUSSION

Gel content and network density determination

Examination of the formation of insoluble gel in the preparation of an IPN sample at a 1:1 molar ratio of PS to PE as a function of the reaction time (*Figure 5*) shows that at reaction time $t > 150$ min and reaction temperature of 120°C the gel contwnt w_g is ~ 0.95.

The measurement of uniaxial compression modulus of IPN PS–PE samples having various ratios of PS to PE gave an unambiguous dependence of the mean molar mass $\bar{M}_c$ of the polymer chain between two junction points calculated from equations (1) and (2) (*Table 1*). As the PS content increases, the network density, v, decreases and the value of $\bar{M}_c$ increases (*Figure 6*) in both sample series. It has to be mentioned here that the values obtained for the average molecular masses between two crosslinks are the mean values of $\bar{M}_c$ of both polymer networks, i.e. PS and PE networks. Since grafting of the system onto PE is also assumed to some extent[3], the indicated value of $\bar{M}_c$ includes the chains between the PS and PE networks as well.

The dependence observed is in agreement with the reaction conditions under which both series of samples were prepared. With increasing content of styrene relative to DVB, the number of crosslinks is reduced in the PS network. This also lowers the overall value of network density, which in turn will be reflected in the increase of the $\bar{M}_c$ values.

When using DTBP as an initiator for the crosslinking polymerization of styrene/DVB and for the crosslinking of PE, the values of $\bar{M}_c$ in the IPN system formed rise almost proportionally with increasing PS content (*Figure 6*, curve 1). For initiation by Luperox 101, the increase in the values of $\bar{M}_c$ with the increase of styrene content is remarkably slower. The samples with higher content of PS prepared with DTBP are consequently less crosslinked than those prepared in the presence of Luperox 101. The latter initiator is bifunctional and may to some extent exert a similar effect to DVB during PS crosslinking. Its bifunctionality can also be seen in higher efficiency in PE crosslinking.

D.s.c. and t.m.a. measurements

Characteristic curves for melting obtained in the examination of the PS–PE networks (*Figure 7*) were in the range 50–130°C (similar to the d.s.c. analysis of crosslinked PE[14]). They indicate the melting in the

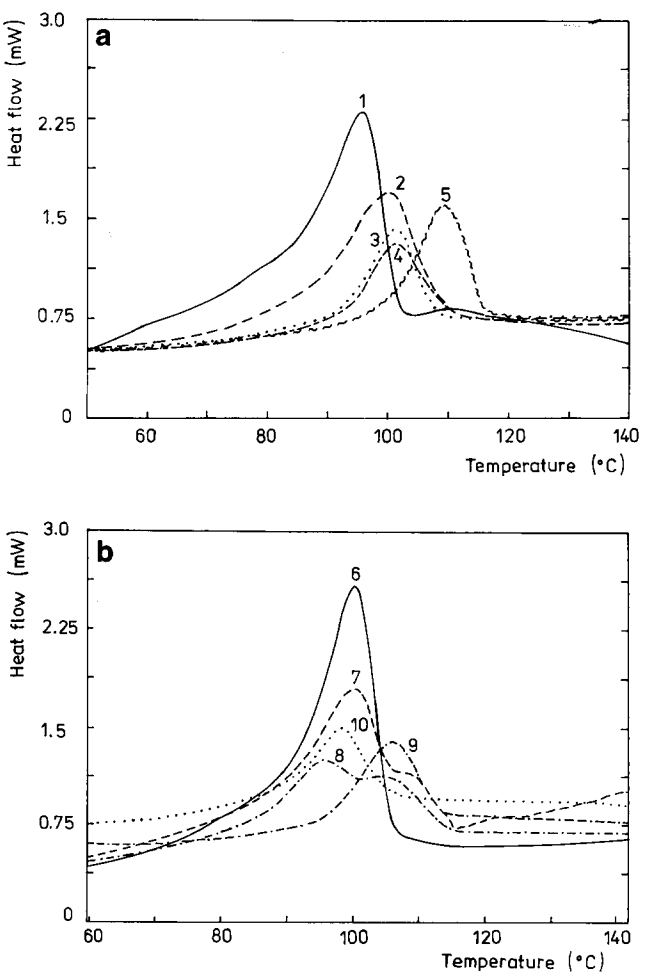

Figure 7 D.s.c. curves of IPN samples PS–PE; scanning rate, 10.0°C min^{-1}. (a) Samples 1–5; (b) samples 6–10

crystalline regions of PE networks. A decrease in the melting enthalpy calculated from the peak of melting relative to the indium standard was observed as a function of the increasing amount of PS in a sample (*Table 2* and *Figure 8*). Even at a relatively low ratio (PS/PE = 0.6), ΔH of pure PE decreases from 106 J g^{-1} to <20 J g^{-1} in both sample series (i.e. samples 1–5 and 6–10). At the maximum content of PS in PS–PE network (PS/PE = 3), these values decrease to 6–7 J g^{-1}. It was found that when DTBP is used for crosslinking, the ΔH curve (curve 1 in *Figure 8*) in the region of higher contents of PS decreases more steeply than in the presence of Luperox 101 (*Figure 8*). The rapid decrease of ΔH in the presence of Luperox 101 can be ascribed to higher network density, which follows from the measurements of uniaxial compression modulus (*Table 1*, *Figure 6*). As reported earlier[15], ΔH_m decreases with increasing network density, which in fact means a decrease in the crystalline content within the PE network.

Melting temperatures T_m and T_{curv} of networks prepared using DTBP (determined from d.s.c. dependence in the manner shown in *Figure 3*) are also unambiguously dependent on network density (*Table 2*). With increasing styrene content and hence decreasing network density, higher values of T_m and T_{curv} were obtained (*Table 3*). This can only be attributed to an increase in the order of the polymer because upon raising the PE crosslinking accompanied by the lowering of the crystalline portion, a decrease in T_m and T_{curv} values is expected. The electron-microscopic investigation of these systems[16] shows that crystalline portion residues of PE are located between the domains of PS. The sizes of the PS domains were in the region of several hundreds of nanometres and they depend on the ratio of PS/PE[16]. A limited mobility of the PE matrix is then expected, which can, to some extent, account for the melting temperature enhancement.

No similar dependence was observed in d.s.c. measurements of networks prepared in the presence of Luperox 101 (see also d.s.c. curves 6 to 9 in *Figure 7*). The final vaue of T_{curv} of 116°C is already observable at the ratio PS/PE = 1.

Transition temperatures T_{onset}, T_{min}, T_{extr} obtained by t.m.a. measurement (*Figures 9a* and *9b*), corresponding to *Figure 4*, are affected (as is seen in *Figure 10*) by T_g of

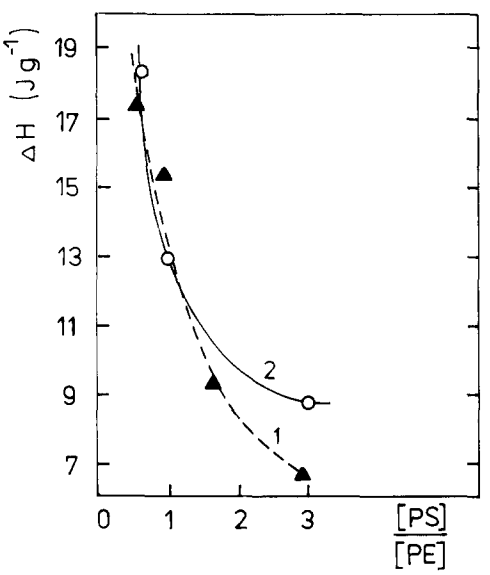

Figure 8 Dependences of the melting enthalpy of the crystalline portion of PE on the ratio PS/PE in IPN system prepared in the presence of the two different free radical initiators (DVB content = 0.5 wt% = const.); 1–3 wt% DTBP; 2–3 wt% Luperox 101

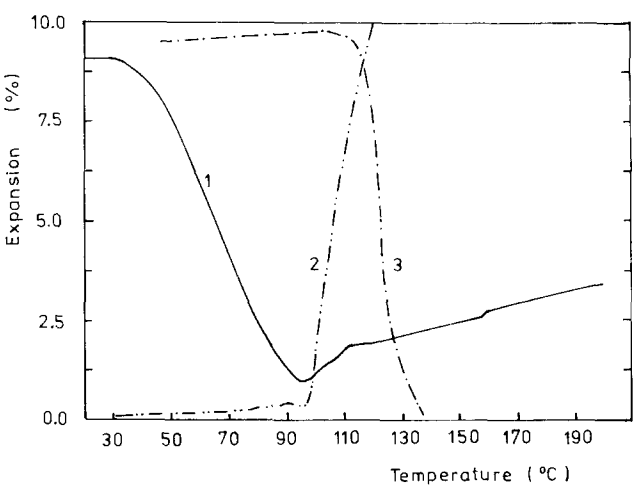

Figure 10 Comparison of t.m.a. curves of an IPN sample (sample 1, PS:PE = 0.75:1.25, curve 1) with a pure PS (curve 2) and PE (curve 3) sample at a scanning rate of 5.0°C min^{-1} and force of 10 mN

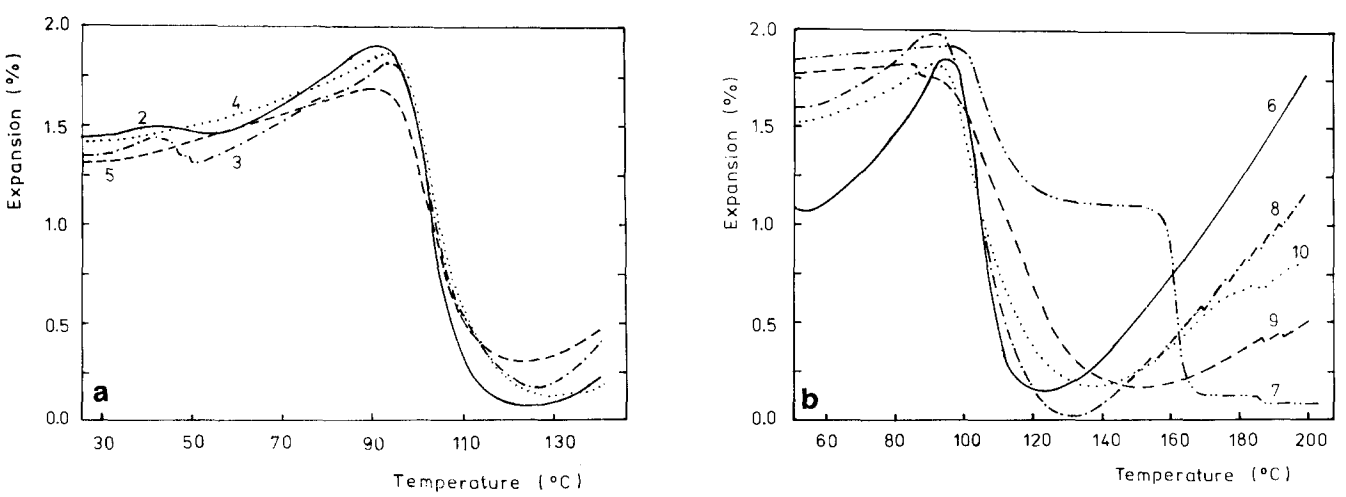

Figure 9 T.m.a. curves of IPN samples PS–PE; scanning rate, 5.0°C min^{-1}, force, 10 mN. (a) Samples 2–5; (b) samples 6–10

PS as well as by T_m of PE. These measurements present, with the exception of T_{onset} and T_{extr} in the DTBP system, an increase in the values of T_{min} and T_{extr} as a function of the increasing PS content as observed in the d.s.c. measurements.

CONCLUSIONS

By measuring the uniaxial compression modulus the values of mean molar mass, $\bar{M}_c$, between two junction points of polymer networks in IPN of PS and PE were determined. The increase of $\bar{M}_c$ was inversely proportional to the concentration of crosslinking agent (DVB), which indicates that crosslinking agent increases the mean network density in the whole volume of the sample. As it appears that crosslinking agent particularly affects the network density in the PS network, one can consider this as evidence of interpenetration of PE and PS networks.

D.s.c. study of IPN revealed that crystallinity of the PE network decreases with increasing network density. This indicates that the PE network also contributes to the increase of the mean network density.

The surprising increase of T_m and T_{curv} for the crystalline component of PE with increasing content of PS and hence decreasing network density can be ascribed only to a limited mobility of the PE matrix located between the domains of PS.

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