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IPN-like systems based on polyethylene and methacrylates

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Interpenetrating polymer networks (IPNs) based on polyethylene (PE) and poly(methacrylate)s were prepared by *in situ* polymerization. A co-continuous phase morphology was obtained. The use of dodecyl methacrylate produces good compatibility between PE and poly(methacrylate)s. The degree of PE crosslinking in IPNs has been estimated by comparison of the melting temperatures of PE crystallites in pure crosslinked PE with those in IPNs.

(Keywords: polyethylene; poly(methacrylate)s; interpenetrating networks)

INTRODUCTION

Interpenetrating polymer networks (IPNs) are characterized by a mixture of two or more polymer networks having partial or total physical interlocking with one another. They are a special kind of polymer blend offering the chance to combine thermodynamically incompatible polymer systems with a high degree of dispersion of the component polymer domains. For IPNs comprising thermodynamically incompatible polymers, this dispersion is preserved as microphase separation.

IPNs based on polyethylene (PE) with polystyrene (PS) as second component have been previously reported[1–5], with different methods being described for their synthesis. In refs 1–3 PE was swollen with a mixture of styrene and divinyl benzene, these monomers were then polymerized and crosslinked inside the swollen PE. In refs 4 and 5 PE was dissolved in a styrene/divinyl benzene mixture, the monomers being polymerized and simultaneously crosslinked at temperatures above the melting temperature of the PE. The latter method (*in situ* polymerization above the melting point) allowed better interlocking of both components, at least in the beginning of methacrylate polymerization[5], than the swelling method below the melting point of PE.

In the present study we used *in situ* synthesis to prepare IPN-like systems based on PE and methacrylic polymers or copolymers. With this kind of synthesis it is not possible to prevent the PE radicals generated in the monomer solution from forming PE–poly(methacrylate) graft structures. Therefore, we describe these materials as IPN-like systems.

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EXPERIMENTAL

Materials

Materials used for synthesis are listed in *Table 1*. Methyl methacrylate (MMA), dodecyl methacrylate (DMA) and butanediol dimethacrylate (BDDM) were freed from inhibitor and dried. MMA was distilled under reduced pressure in a dry nitrogen atmosphere shortly before use. Polyethylene (non-stabilized) and the peroxide Luperox 101 were used as received.

Synthesis of the individual networks

For PE crosslinking, 20 g of PE powder was impregnated with a solution of 0.4 g Luperox 101 in 50 cm^3 chloroform. The mash-like mixture was kept in a dark bottle for 24 h. The PE mixture was dried to constant weight at 40°C under vacuum. Then the peroxide-containing PE was crosslinked in a heated press at 160°C for 1 h, forming a plate ~2 mm thick.

Poly(dodecyl methacrylate) (PDMA) and methyl methacrylate–dodecyl methacrylate copolymer (MMA-*co*-DMA) were prepared by polymerization of the respective monomers in various molar ratios initiated with Luperox 101 (see *Table 2*). The polymerization was carried out between two glass plates sealed with silicone tubing. To ensure crosslinking, different amounts of BDDM were added to the monomer composition before starting the polymerization.

Synthesis of IPN-like materials

IPN-like materials based on PE/PDMA and PE/MMA-*co*-DMA were prepared by the *in situ* method[5]. PE was dissolved in the monomers at elevated temperature. Then BDDM was added as the crosslinking agent of the methacrylates and Luperox 101 was added as initiator. Curing was carried out under the

Table 1 Materials used for synthesis

Material	Description	Supplier
Polyethylene (LDPE)	Bralen RA 2-19	Slovnaft
DMA	Dodecyl methacrylate for synthesis (70%)	Merck
MMA	Methyl methacrylate	Považske chemicke zavody
BDDM	Butanediol dimethacrylate (95%)	Aldrich
Luperox 101	2,5-Dimethyl-di(tert-butylperoxy)-hexane	BASF

Table 2 Sample compositions and gel contents

Sample	Molar ratio	Molar ratio	BDDM (mol%)	Gel content (wt%)
	PE:DMA			
D-7	1:1		1	86.2
D-7[a]	1:1		0	84.2
D-8	1:1		2	88.8
D-9	1:1		4	89.6
D-10	2:1		2	81.3
D-11	2.5:1		2	87.4
	PE:DMA/MMA	DMA:MMA		
D-17	1:1	1:1	4	91.6
D-18	1:1	1:2	4	[b]
D-19	1:1	1:3	4	88.5
D-20	1:1	1:4	4	[b]
D-21	1:1	1:5	4	[b]
D-22	1:1	1:6	4	86.4
D-23	1:1	1:6	1	87.7
D-24	1:1	1:6	2	85.8
D-24[a]	1:1	1:6	0	85.5
	Pure components			
D-12	PE	-		0.0
D-13	PE, crosslinked	-		92.1
D-15	PDMA	1:0	0	85.4
D-16	PDMA, crosslinked	1:0	4	87.7

[a] Without crosslinker for methacrylate
[b] Not determined

following conditions: 105°C, 6 h and 160°C, 1 h for PE/PDMA; and 115°C, 6 h and 160°C, 1 h for PE/MMA-*co*-DMA. In the first step, at either 105 or 115°C, free radical polymerization or copolymerization, respectively, occurs. Peroxidic crosslinking of the PE prevails in the last stage of the IPN preparation at 160°C.

In all syntheses, Luperox 101 was used at a concentration of 3 wt%.

Methods

Solvent extraction. The gel content of the polymer network was determined by Soxhlet extraction (system HT6, Tecator) in boiling xylene for 25 h.

Electron microscopy. Transmission electron microscopy (TEM) was performed using a Tesla BS 540 transmission electron microscope, operating at 80 keV. Prior to examination, cryofractured ultra-thin sections (prepared at 200 K) were stained in OsO_4 vapour for 24 h. Scanning electron microscopy (SEM) was carried out using a Tesla BS 340 scanning electron microscope. Cryofractures were prepared at 77 K.

Differential scanning calorimetry (d.s.c.). A Perkin–Elmer DSC-7 calorimeter was employed. Samples were subjected to a cycle of first heating, cooling and second heating, (heating rate = 10 K min^{-1}, cooling rate = 80 K min^{-1}) over a temperature range −60 to 150°C. The melting behaviour was determined in the first heating, while the glass transition temperatures (T_g) were determined in the second heating using the half-step method.

The maximum temperature of the melting peak T_m depends on the crystallinity of the sample[6]. To compare T_m values for pure PE and PE-containing IPNs, a correction was necessary. The values of T_m were corrected to zero weight to account for thermal lag, using the equation[6]:

$$\Delta T_m = T_m - T_m(m_{PE} \rightarrow 0) = K(m_{PE} \times dT/dt)^{1/2} \quad (1)$$

To a first approximation ΔT_m was estimated at $K = 0.332$ (K min/mg)$^{1/2}$, which was determined by Pompe *et al.*[7] for the same d.s.c. device using other materials, with $m_{PE} = c_{PE} m_s$. Here, m_s is the weight of sample (in mg), c_{PE} the concentration of PE in the sample, m_{PE} the weight of PE in the sample (in mg) and dT/dt the heating rate (in K min^{-1}).

Dynamic mechanical analysis (d.m.a.). Samples of dimensions 50 × 10 × 2 mm were analysed using an Explexor 150N instrument (GABO Qualimeter) in the temperature range −90 to 90°C. The heating rate was 2 K min^{-1} and frequency 1 Hz.

RESULTS AND DISCUSSION

Synthesis

For the preparation of IPN systems based on PE and methacrylates, *in situ* synthesis was a suitable method. The principle involved the preparation of a PE solution in a monomer (or mixture of monomers) before synthesis of the IPNs at elevated temperature[4].

Dodecyl methacrylate and methyl methacrylate were chosen as methacrylic components. However, PE is insoluble in pure MMA, even at the boiling temperature of the MMA. But methacrylates with longer aliphatic ester groups like butyl methacrylate[4] or dodecyl methacrylate are good solvents for PE. Therefore, addition of DMA to MMA has been used to achieve solubility of PE in this monomer mixture at elevated temperatures.

From the point of view of mechanical properties, the prepared IPNs based on PE and PDMA were rather soft materials with poor strength. We therefore tried to produce IPNs with the highest possible content of MMA incorporated in the polymer, to improve the disadvantageous mechanical properties. *Table 2* gives the compositions of the synthesized materials.

Solvent extraction

By means of solvent extraction it was not possible to extract PDMA completely from either the PE/PDMA semi-IPN or from pure PDMA (both synthesized without the methacrylate crosslinker BDDM at reaction conditions used for preparation of the IPNs). The gel contents were 85.4 and 84.2 wt% for pure PDMA and for the semi-IPN, respectively. This means that the long aliphatic ester groups in PDMA were significantly

involved in peroxide-initiated crosslinking at the reaction conditions used (*Table 2*). The presence of the crosslinker BDDM at a concentration of 4 mol% increased the gel content in pure PDMA by ~2 wt% and that in PE/PDMA semi-IPN by ~5 wt%. It was noted that linear chain molecules were not completely extracted from polymer networks due to entanglements, if their molecular weights are higher than M_c of the crosslinked polymer[8]. This fact may have some influence on the values obtained.

On the other hand, at small contents of DMA in PE/DMA/MMA reaction systems (DMA : MMA = 1 : 6) without BDDM, the gel content is almost the same as in pure PDMA (*Table 2*). It is remarkable that the gel content does not correlate with the BDDM content in IPNs based on a molar ratio of DMA : MMA of 1 : 6.

Electron microscopy

The morphology was studied by electron microscopy; in TEM micrographs PE is the dark and methacrylate the light phase. An increasing PE content results in a finer distribution of both components, the distribution indicating a co-continuous phase morphology. The diffuse nature of the phase boundaries in the electron micrographs of both IPN systems (*Figure 1*) suggests that substituents with long aliphatic chains in the ester group of the methacrylates produce increased compatibility of the methacrylates and PE. This hypothesis is corroborated by SEM micrographs (*Figure 2*): at the fractured surface sharply edged particles are not detectable.

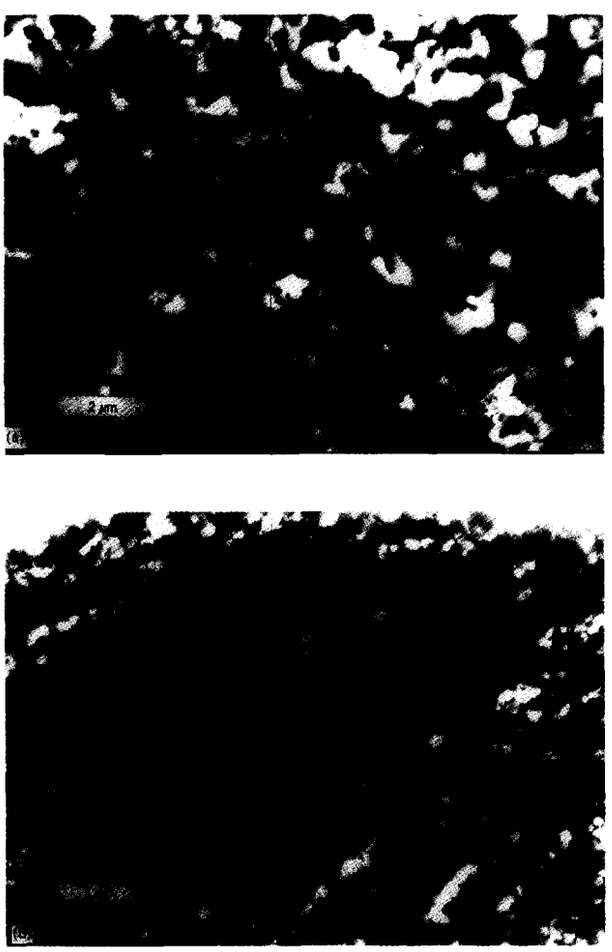

Figure 1 TEM micrographs of IPN-like material, PE/PDMA and PE/DMA-*co*-MMA, BDDM content 2 and 4 mol%, respectively

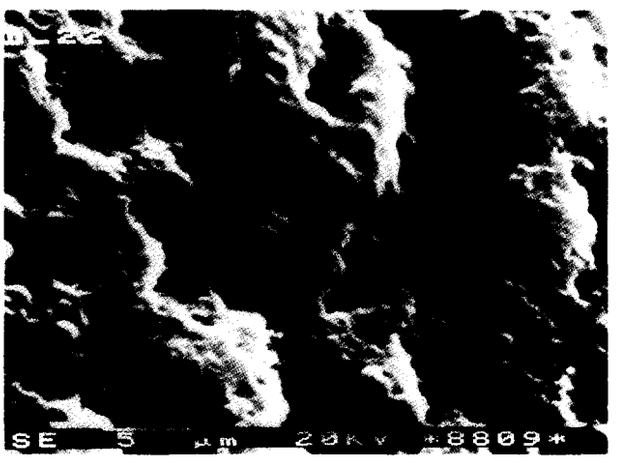

Figure 2 SEM micrograph of a fractured surface of IPN-like material, PE/DMA-*co*-MMA, BDDM content 4 mol%

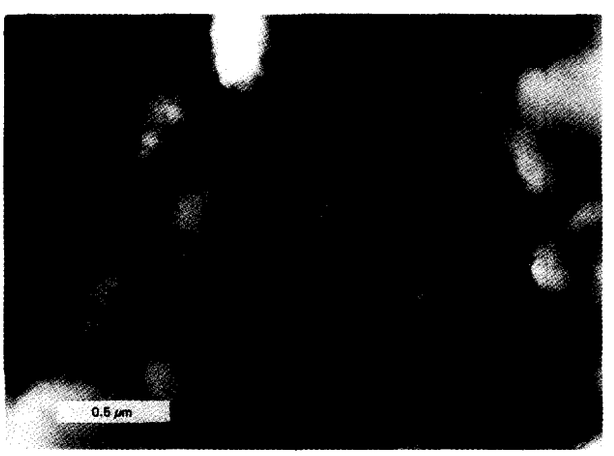

Figure 3 TEM micrograph of IPN-like material, PE/DMA-*co*-MMA, BDDM content 4 mol%, extracted with ethyl acetate

Fine dark lines observed within the poly(methacrylate) phase were first considered as unreacted monomers (*Figure 3*). However, these lines were still visible after extraction with ethyl acetate and therefore they must be interpreted as fine PE layers of thickness 10 to 50 nm.

D.s.c. measurements

The melting behaviour of PE in the IPNs is discussed for the PE/PDMA system. The crystallinity of the PE phase of the IPNs is not influenced by the degree of crosslinking of the second component. Using the value for the heat of fusion of a perfect PE crystal[9], $\Delta H_0 = 293\,J\,g^{-1}$, the crystallinity of PE could be calculated to $\alpha_{PE} \approx 36\%$. The lack of change in crystallinity of the PE phase with the degree of crosslinking of the second component is in contrast to the results obtained for PE/PS IPNs[2]. In these IPNs, the T_g of PS is in the same range as the melting peak of PE and, therefore, the mutual influence is stronger.

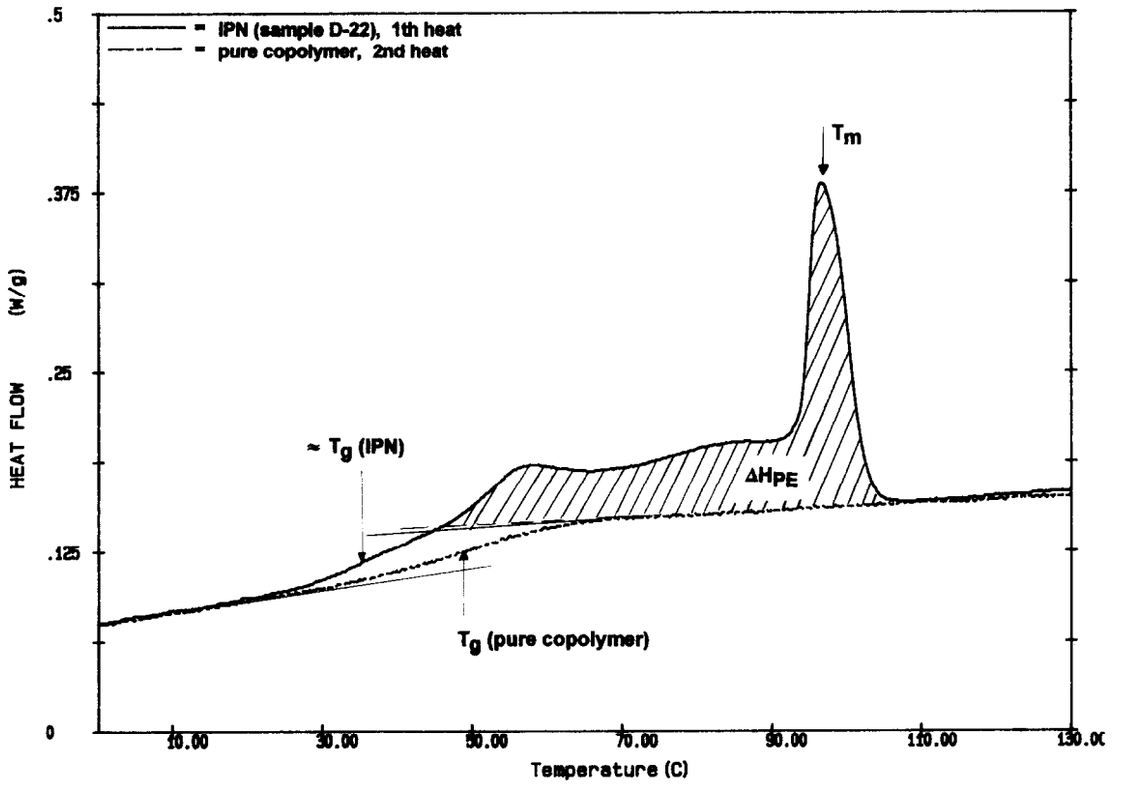

Figure 4 D.s.c. thermograms of IPN-like material, PE/DMA-*co*-MMA, BDDM content 4 mol%, and corresponding copolymer

Table 3 D.m.a. and d.s.c. results from PE/DMA-*co*-MMA IPNs and the corresponding copolymers

Sample [a]	MMA content (wt%)	T_g (°C) d.s.c.	T_g (°C) d.m.a.	T_g (in the IPN) (°C) d.m.a
		DMA-*co*-MMA		PE/DMA-*co*-MMA
D-17	28	5	10	6
D-18	44	12.5	26	21
D-19	54	25	42	37
D-22	70	47	61	59

[a] IPN-like material or respective copolymer

Table 4 Melting temperatures of PE crystallites and estimated degrees of PE crosslinking (gel contents) in IPNs

Sample	Melting temperature of PE crystallites T_m ($m_{PE} \rightarrow 0$) (°C)	Degree of crosslinking of PE estimated from T_m (wt%)
D-7	99.8	86.4
D-8	99.9	85.9
D-9	98.0	90.7
D-10	99.3	87.5
D-11	98.9	88.5
D-17	98.8	88.7
D-18	98.7	88.9
D-19	97.3	91.9
D-20	96.3	95.5
D-22	96.0	96.3
D-23	95.0	(98)
D-24	98.0	90.7

An estimation of the glass transition temperature was attempted. This was complicated, because exact separation of the glass transition range of the methacrylic copolymers and the melting range of PE was not possible (*Figure 4*). *Table 3* compares the estimated T_g values of pure copolymers with the results of d.m.a. investigations.

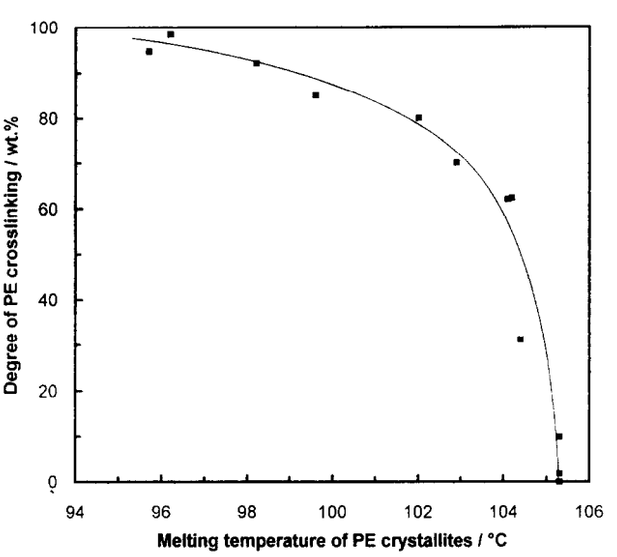

Figure 5 Correlation between the melting temperature of uncrosslinked and crosslinked pure PE and gel content

The degree of crosslinking of one component of a blend based on polymer networks cannot be determined with methods commonly used for pure components, such as the compression modulus. Therefore, the maximum temperature of the PE melting peak, T_m, was analysed for an estimation of the degree of crosslinking of PE in the IPNs. Bolder and Meier[10] found, for simple networks

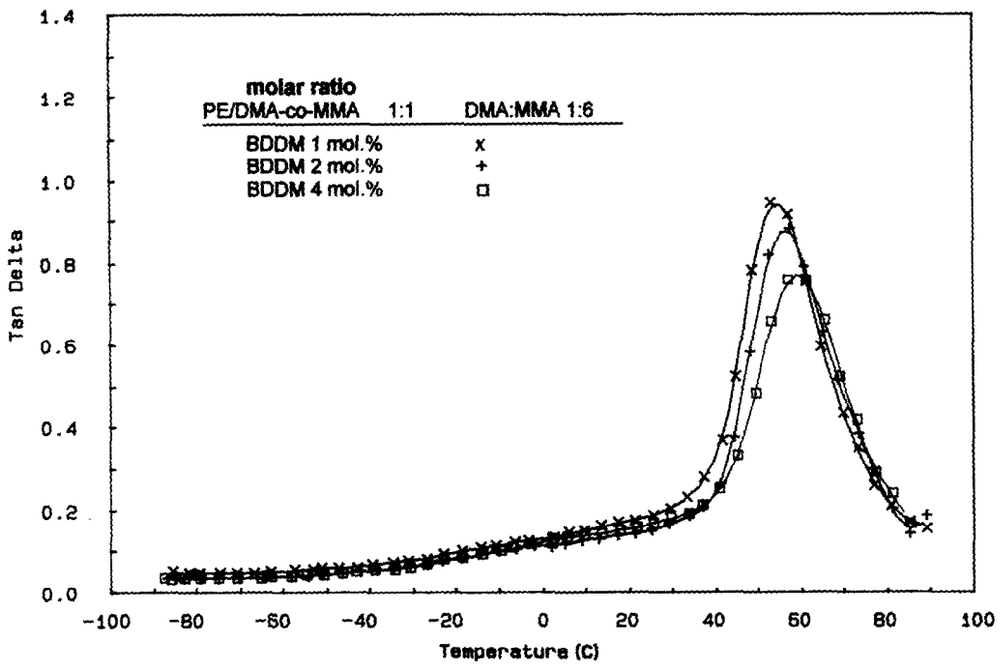

Figure 6 Dynamic mechanical behaviour of IPN-like materials as a function of crosslinker content

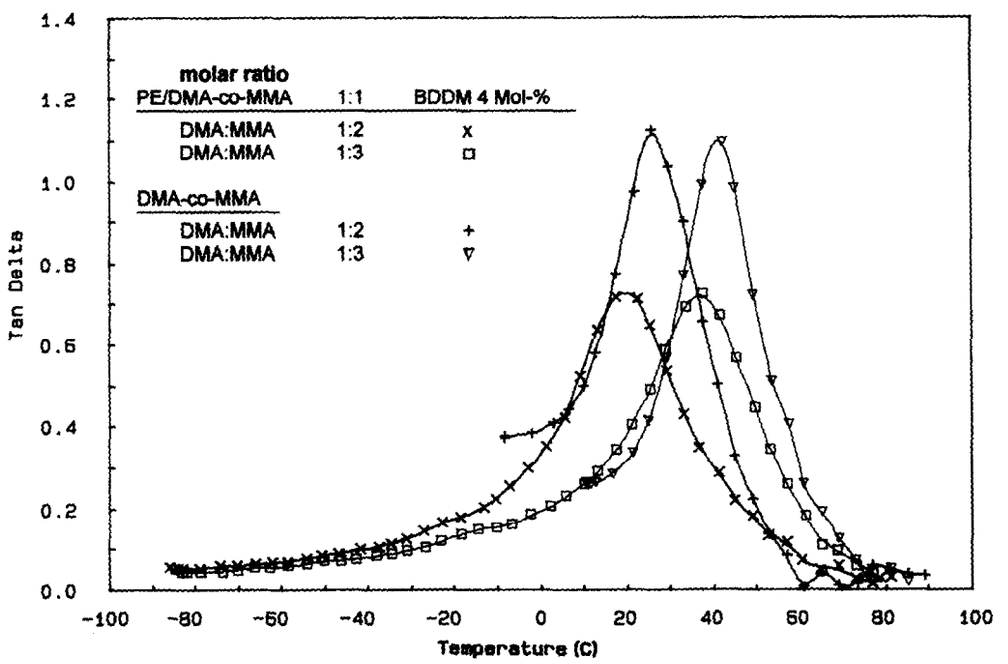

Figure 7 Dynamic mechanical behaviour of IPN-like materials and corresponding copolymers

of pure PE, a correlation between T_m and the gel content as a measure for the degree of PE crosslinking. *Figure 5* shows our values of T_m *versus* the gel content of uncrosslinked and crosslinked PE. All T_m values were corrected according to equation (1). Using the correlation of *Figure 5*, the degree of PE crosslinking in the different networks could be estimated to be about 86 to 96 wt% (*Table 4*). It is interesting that for the IPNs the dependence of the degree of PE crosslinking on BDDM content shows the same tendency as found for the overall gel content of the IPNs by solvent extraction. The highest degrees of PE crosslinking were found in IPNs with high MMA contents.

Dynamic mechanical properties

As expected, the T_g of the methacrylate copolymer phase, which is reflected by the tan δ maximum of the α-relaxation, depends strongly on composition for both the pure copolymers and the IPNs. For copolymers with the same content of BDDM crosslinking agent, T_g is shifted to higher temperatures with increased MMA content (*Table 3*). This tendency agrees with the d.s.c. results.

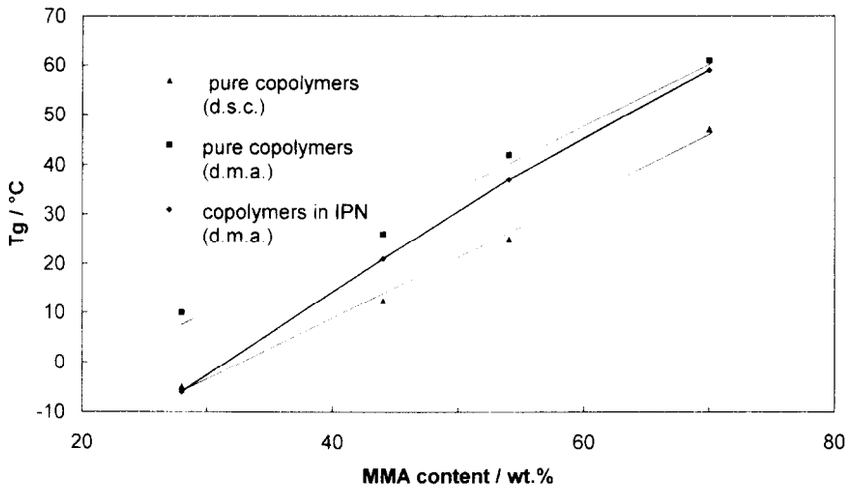

Figure 8 T_g of methacrylate copolymers in IPN and of the corresponding pure copolymers *versus* composition determined by d.m.a. and d.s.c.

The influence of crosslinking agent (BDDM) on the dynamic mechanical behaviour of the IPNs is shown in *Figure 6*. With increasing BDDM content the T_g of the methacrylate copolymer phase is enhanced and the intensity of tan δ decreased due to reduced mobility of the copolymer chain.

The T_g of the methacrylate copolymer phase in the IPN is lower than that of the corresponding pure copolymer (*Figure 7*). The reduced glass transition temperature in the IPN, especially for copolymers with high DMA contents, is explained by the compatibility between the two networks (*Figure 8* and *Table 3*), and is in agreement with both the observed solution behaviour during the synthesis and the results of electron microscopy.

Changes in the T_g of the PE phase (≈ -30°C) cannot be detected due to their overlapping with the β-relaxation of the methacrylate copolymers.

SUMMARY

A series of IPN-like materials, based on PE and methacrylate copolymers and which differ in composition, has been synthesized using a special *in situ* method. The prepared IPN-like materials have a co-continuous phase morphology. Methacrylates with long aliphatic side chains produce increased compatibility between the methacrylic and PE phases, as shown for DMA. It is possible to estimate the degree of PE crosslinking in the IPN using a relation between the melting temperature of the PE crystallites and the gel content of the PE, which was determined by solvent extraction of pure PE. The degree of PE crosslinking in the IPNs varied from 86 to ~96 wt%. In IPNs based on PE and methacrylate copolymers with high MMA contents, high degrees of PE crosslinking were realized. The crystallinity of the PE phase is not influenced by the second IPN component. Dynamic mechanical analysis shows a strong dependence of the T_g of the pure methacrylate copolymers on their composition, which agrees with d.s.c. results. The T_g of the copolymers in the IPN is shifted to lower temperature compared with that of the corresponding pure materials, especially if the methacrylate copolymers contain high concentrations of DMA. It seems that grafting of methacrylates on PE plays a positive role in the compatibility of both polymers in the IPNs.

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