PII: S0032-3861(97)00366-2

Polymer Vol. 39 Nos. 6–7, pp. 1289–1297, 1998
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0032-3861/97/\$17.00+0.00

IPN-like systems based on polyethylene and methacrylates: 2. Polyethylene–butyl methacrylate copolymer IPNs

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(Received 31 October 1996; revised 22 April 1997)

IPN-like materials based on polyethylene and butyl methacrylate copolymers were prepared by *in situ* polymerization above the melting point of PE. A co-continuous phase morphology was observed. The use of butyl methacrylate-*co*-methyl methacrylate and a low content of methacrylate crosslinker resulted in a fine dispersion of the IPN components in one another. Grafting reactions during the synthesis of the IPN-like materials between PE and methacrylates were demonstrated. A decrease in the chain length of the substituent at the ester group of the methacrylate comonomer, in the order dodecyl methacrylate (DMA) > 2-ethylhexyl methacrylate (EHMA) > butyl methacrylate (BMA), is advantageous to the mechanical properties of the IPNs. © 1997 Elsevier Science Ltd. All rights reserved.

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

INTRODUCTION

The formation of interpenetrating polymer networks (IPNs) is practically the only way to combine two or more crosslinked polymers in fine dispersion[1,2].

In Part 1[3] the synthesis and characterization of IPN-like systems based on polyethylene and poly(dodecyl methacrylate) (PEPDMA) or poly(dodecyl methacrylate-*co*-methyl methacrylate) (PEDMA-*co*-MMA) were described. At temperatures above the melting temperature of PE the methacrylate monomer solution was polymerized and simultaneously crosslinked using a bifunctional monomer as a crosslinker. This method, *in situ* synthesis, allows better interlocking of both components, at least at the beginning of methacrylate polymerization[4], than the swelling method below the melting temperature of PE[5–7].

The IPN-like system PEDMA-*co*-MMA exhibits poor mechanical properties[3]. With the experience in synthesis of these systems it was desirable to increase the mechanical strength of the IPNs. To achieve this aim the copolymers poly(butyl methacrylate-*co*-methyl methacrylate) (BMA-*co*-MMA) and poly(butyl methacrylate-*co*-ethyl methacrylate) (BMA-*co*-EMA) were chosen as the methacrylate component of the IPN-like system. To study the influence of the structure of the aliphatic side group in the comonomer on the thermal and mechanical properties of the IPNs and on side reactions during their synthesis, an analogous IPN based on PE, MMA and 2-ethylhexyl methacrylate was synthesized (PEEHMA-*co*-MMA).

In addition, model compounds of IPNs and methacrylate copolymers without divinyl crosslinker were synthesized to investigate crosslinking and grafting reactions. Finally, the results of the BMA copolymer-based IPNs were compared with those of the DMA copolymer-based IPNs[3].

In this work, IPN-like systems were also prepared by *in situ* synthesis. With this kind of synthesis it is impossible to prevent grafting of methacrylates onto PE. Ideal IPNs do not contain grafted structures. Therefore we describe these materials as IPN-like systems[4].

EXPERIMENTAL

Materials

The materials for synthesis are listed in *Table 1*.

Methyl methacrylate (MMA), butyl methacrylate (BMA), ethyl methacrylate (EMA), 2-ethylhexyl methacrylate (EHMA) and butanediol dimethacrylate (BDDM) were freed from inhibitor and dried. MMA was distilled under reduced pressure in dry nitrogen atmosphere immediately before use. Polyethylene (non-stabilized) and 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane (Luperox 101) were used as received.

Synthesis

Since PE is insoluble in MMA even at the MMA boiling point[3], the presence of a comonomer with longer aliphatic side groups is necessary for the *in situ* synthesis of PEmethacrylate IPN-like structures. In a mixture of the short side-chain methacrylates MMA or EMA with the longer side-chain monomers BMA or EHMA the PE is soluble, and therefore PEBMA-*co*-MMA and PEBMA-*co*-EMA are accessible by *in situ* synthesis of IPNs analogously to the synthesis of PEDMA-*co*-MMA[3,8].

PE was dissolved in the methacrylate monomer mixture at elevated temperature. Then BDDM as crosslinking agent for the methacrylate phase and Luperox 101 as peroxide

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Table 1 Materials

Material	Description	Supplier
Polyethylene	Bralen RA 2-19	Slovnaft
(LDPE)	(MFI = 1.7 ... 2.3 g (10 min)$^{-1}$	
BMA	Butyl methacrylate	Aldrich
EMA	Ethyl methacrylate	Merck
EHMA	2-Ethylhexyl methacrylate	Aldrich
MMA	Methyl methacrylate	Povazske chemicke zavody
BDDM	Butanediol dimethacrylate (95%)	Aldrich
Luperox 101	2,5-Dimethyl-2,5-di(*tert*-butylperoxy)hexane	BASF

Table 2 Sample compositions of the synthesized IPNs[a]

Sample	Molar ratio	Molar ratio	BDDM (mol%)
	PE:BMA-*co*-MMA	BMA:MMA	
D-331	1:1	1:0	4
D-341[b]	1:1	0.6:1.4	3
D-34	1:1	0.8:1.2	3
D-35[b]	1:1	1:1	3
D-351	1:1	1:1	2.5
D-36[b]	1:1	1.2:0.8	3
D-37[b]	1:1	1:1	0.5
D-38[b]	1:1	1:1	2
D-381[b]	1:1	1:1	6
	PE:BMA-*co*-MMA	BMA:EMA	
D-29[b]	1:1	1.2:0.8	4
D-30	1:1	1.0:1.0	4
D-31[b]	1:1	0.8:1.2	4
D-32	1:1	1.2:0.8	2
D-33	1:1	1.2:0.8	6
	PE:EHMA-*co*-MMA	EHMA:MMA	
D-50[b]	1:1	1:1	4

[a] For DMA-*co*-MMA-based IPNs see [3]

[b] The corresponding pure methacrylate copolymers were also synthesized

Table 3 Compositions and gel contents of semi-IPNs and pure copolymers without methacrylate cross-linking agent

Sample	Molar ratio PE:methacrylate	Molar ratio	PE content (wt%)	Gel content (wt%)
		DMA:MMA (for comparison)		
D-24 A	1:1	1:6	21.6	81.7
D-40	0:1	1:6	0	80.9
		BMA:EMA		
D-30 A	1:1	1:1	17.9	50.3
D-39	0:1	1:1	0	26.8
		BMA:MMA		
D-35 A	1:1	1:1	18.8	53.3
D-42	0:1	1:1	0	18.3

initiator were added. This mixture was poured between two plates sealed with silicone tubing. Methacrylate copolymerization was carried out at 115°C for 6 h (first stage). Then the temperature was raised to 160°C for 1 h. This caused complete decay of the peroxide, resulting in PE crosslinking and grafting reactions (second stage)[9]. In all syntheses the concentration of Luperox 101 was 3 wt%. Only the model substances for investigating the grafting and degradation reactions during IPN synthesis were synthesized with different peroxide concentrations.

The IPN samples were prepared from PE with three pairs of methacrylate monomers in various ratios (*Table 2*). At a specified monomer ratio the BDDM content was varied to detect the influence of the degree of crosslinking of the methacrylate phase on the morphology and mechanical properties of the IPNs. Furthermore, semi-IPNs and pure methacrylates without methacrylate crosslinking agent were synthesized to investigate grafting as well as crosslinking reactions within the methacrylate phase (*Table 3*).

Methods

Solvent extraction. The gel content of the polymer networks was determined by Soxhlet-like extraction (system Soxtec HT6, Tecator) in boiling xylene for 25 h. To demonstrate the existence of grafts the xylene-soluble PE fraction was precipitated by adding acetone.

To investigate the degradation reactions caused by peroxide during the synthesis of PEPBMA IPNs, methanol was used as a solvent for extracting unreacted monomers and low-MW decomposition products. Methyl ethyl ketone was used as a solvent for the further extraction of these samples to separate non-crosslinked and non-grafted PBMA from the semi-IPNs. The extractions were carried out at the boiling point of the solvents for 6 h (methanol) or 20 h (methyl ethyl ketone).

Pyrolysis gas chromatography (p.g.c.–m.s.). The equipment for pyrolysis gas chromatography comprised a Pyroprobe 2000 (CDS Instruments) and a HP 5890 series II with mass-selective detection (Hewlett Packard). The pyrolysis reaction was performed in a helium stream at 700°C for 10 s. The interface was arranged in front of the g.c. injector.

Electron microscopy. Transmission electron microscopy (TEM) was performed using a TEM Tesla BS 540, operating at 80 keV. Prior to the examination, cryo ultrathin sections (prepared at 200 K) were stained in OsO_4 vapour for 24 h.

Differential scanning calorimetry (d.s.c.). A Perkin-Elmer DSC-7 calorimeter was used. Samples were subjected to a cycle of first heating, cooling and second heating with a scan rate of 10 K min^{-1} over the temperature range from -10°C to $+150$°C.

Since the processing conditions can influence the thermal behaviour in the first heating, only the second heating was evaluated. The glass transition temperature T_g was estimated using the half-step method. The melting temperature T_m is the temperature at the maximum of the melting peak. The PE crystallinity α_{PE} was estimated by integrating the heat flow between T_1 and T_2 and using the value for the heat of fusion of 100% crystalline PE, $\Delta H_0 = 293$ J g^{-1} [10].

Dynamic mechanical analysis (d.m.a.). Samples of dimensions 50 × 10 × 2 mm were analysed using an Explexor 150N instrument (GABO Qualimeter) in the

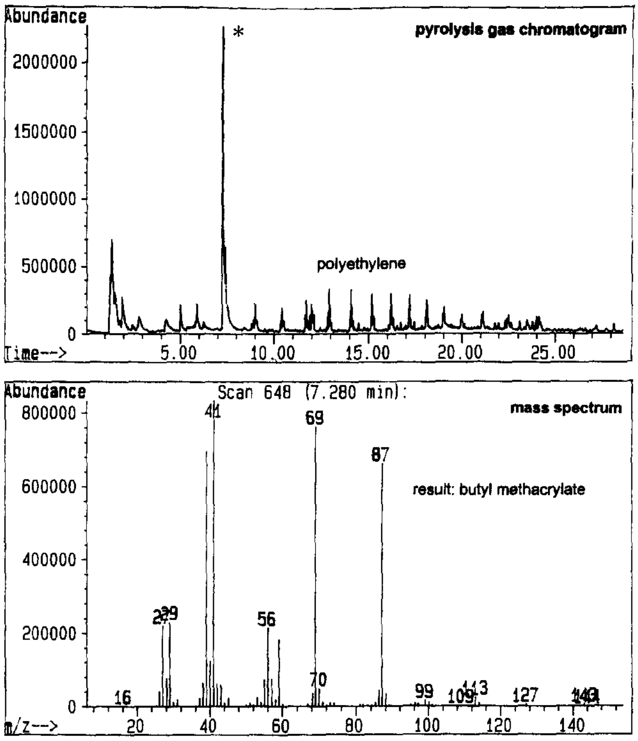

Figure 1 Pyrolysis gas chromatogram of the PE fraction of sample PEPBMA 1:1 and mass spectrum of the fraction with the highest intensity (*) in the chromatogram

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

Sample	Melting temperature of PE crystallites, $T_m(m_{PE} \rightarrow 0)$ (°C)	Degree of PE crosslinking (gel content) estimated from T_m (wt%)
	PEBMA-*co*-EMA	
D-29	98.6	91.3
D-30	98.6	91.3
D-31	100.5	85.2
D-32	98.5	91.7
D-33	98.2	92.2
	PEBMA-*co*-MMA	
D-35	97.4	94.0
D-36	97.4	94.0
D-37	99.4	89.1
D-38	98.8	90.9

temperature range between − 90 and + 90°C. The heating rate was 2 K min^{-1} and the frequency 1 Hz.

Determination of mechanical properties. Samples of dimensions 80 × 10 × 2 mm were tested using a Zwick 1456 universal testing machine. Tensile strength and elongation at break were determined with a deformation rate of 20 mm min^{-1} and a clamping distance of 45 mm.

RESULTS AND DISCUSSION

Grafting between PE and methacrylate copolymer

To demonstrate the existence of grafts a combination of solvent extraction with p.g.c.–m.s. was carried out on model compounds. For this purpose PEPBMA, PEPEHMA and PEPDMA semi-IPNs with a molar ratio of 1:1 and without methacrylate crosslinker were synthesized. The polymers were extracted with xylene for 25 h. The xylene-soluble fraction contained non-crosslinked PE and polymethacrylate. The PE content was separated by selective precipitation with acetone; ungrafted polymethacrylate remained in solution. The results of p.g.c.–m.s. indicated that the PE fractions of the three semi-IPNs investigated contained methacrylate. *Figure 1* shows the pyrolysis gas chromatogram of the soluble PE fraction of the PEPBMA sample. The mass spectrum of the fraction with the highest intensity of the chromatogram at a retention time $t = 7.28$ min shows clearly the presence of butyl methacrylate. From this result it is concluded that grafting between PE and methacrylate occurs.

The grafting of PE with alkyl methacrylates starts during the first stage of IPN synthesis (i.e. methacrylate polymerization and crosslinking at 110°C) by radical transfer reaction to the branched PE. In the later stage of the synthesis, crosslinking of the PE is expected.

Grafting and degradation reactions during the synthesis

To investigate the grafting and degradation reactions during different steps of IPN synthesis, model compounds (semi-IPNs) based on PEPBMA (molar ratio 1: 1) were used[9]. The semi-IPNs were synthesized analogously to the IPNs with initiator concentrations between 0.05 and 3 wt%. The synthesis was stopped either after the first stage, the BMA polymerization, or after the second stage, the crosslinking of PE. The conversion of the polymerization was determined by extracting the unpolymerized monomers with methanol. A rise in the methanol-extractable content with increasing initiator concentration was observed. Moreover, the content of extractable monomers increased after complete synthesis (stages 1 and 2) compared with those samples in which the reaction was stopped after the first stage. This clearly indicates degradation of the PBMA phase during the second stage of the polymerization, caused by free radicals arising from initiator residues.

After the extraction with methanol, the samples were extracted with methyl ethyl ketone. An increase in grafting of BMA onto the PE phase with increasing peroxide concentration could be demonstrated. The grafting efficiency of BMA as a function of the peroxide concentration is described by Lazár *et al.*[9] by:

$$[\mathrm{BMA}_{\mathrm{grafted}}] = k[\mathrm{peroxide}]^{0.38}$$

The small value of the exponent indicates termination of radical chains by the reaction of macro radicals with primary radicals or a transfer reaction of the macro radicals to the initiator. Grafting of BMA on to PE occurs by reaction of the growing PBMA radicals with PE.

Estimation of degree of crosslinking in IPNs

The degree of crosslinking of one component in a blend based on polymer networks cannot be determined by methods commonly used for pure networks, such as measurement of compression modulus.

Analogously to the IPN system PEDMA-*co*-MMA studied earlier[3], the degree of crosslinking of PE within the IPNs was estimated by means of the maximum temperature of the PE crystallite melting peak T_m (*Table 4*), which depends on the gel content of PE. The gel contents (used as a measure of the degree of PE crosslinking) are in the range 85–94 wt%. The results should not be confused with M_c values often used in network characterization. Also, the fact has to be considered that in this way the total crosslinks in PE are described and a separation of PE chains crosslinked by methacrylate from those crosslinked by peroxide is not possible.

The content of crosslinks within the methacrylate phase of the IPNs can be estimated from the content of methacrylate crosslinker. However, there is a additional crosslinking of the methacrylates caused by peroxidic-initiated radical reactions at the aliphatic side chains. To investigate this type of crosslinking (which we call 'self-crosslinking'), model compounds of IPNs and methacrylate copolymers were used which had been synthesized without the methacrylate crosslinker BDDM (*Table 3*). The determination of the gel contents in these semi-IPNs (only PE is crosslinked) and in the copolymers permits the estimation of the self-crosslinking reaction within the methacrylate phase. Copolymers based on BMA have significantly lower gel contents due to self-crosslinking than DMA-based copolymers. This is caused by the shorter aliphatic substituent in the ester group of BMA.

In this context it is necessary to note that adding small amounts of BDDM raises the gel content tremendously, e.g. the addition of only 0.5 mol% BDDM results in an increase of the gel content from 18 to 90 wt% in the BMA-*co*-MMA copolymer. It is also interesting that the presence of PE raises the gel content in the case of BMA-*co*-MMA copolymer and the corresponding semi-IPNs from 18 to 53 wt% (*Table 3*). This is of course the contribution of the PE network formed in the presence of peroxide in the reaction mixture, but the proved grafting reactions between PE and methacrylates resulting in heterogeneous cross-linked structures must also be taken into account.

The first evidence for self-crosslinking reactions within methacrylates was found when studying poly(dodecyl methacrylate) (PDMA) (U. Schulze, unpublished work). It was observed that it is not possible to extract more than 20 wt% PDMA from PEPDMA semi-IPNs and to dissolve pure PDMA to > 15 wt% when both materials had been synthesized without divinyl crosslinker. Analogously, the gel contents of DMA-*co*-MMA-based semi-IPNs and of the pure copolymer (*Table 3*) are very high and similar to each other (82 or 81 wt%). This is due to the accessibility of the long aliphatic ester groups in PDMA and in the copolymer for peroxidic-initiated self-crosslinking.

Further investigations of IPNs with different BDDM contents showed that the gel content does not correlate with the BDDM content. This was observed for all IPNs (PEDMA-*co*-MMA, PEBMA-*co*-MMA and PEBMA-*co*-EMA). With 1–4 wt% of BDDM all the IPNs studied had a gel content of > 90 wt%.

Morphology of PEmethacrylate copolymer IPNs

The morphology of IPNs was investigated by TEM as a function of the monomer composition and the BDDM content. At a high content of crosslinking agent (3 mol%), coarse-disperse light methacrylate spheres were observed in the IPN-like systems PEBMA-*co*-MMA and PEBMA-*co*-EMA. In these IPN systems sharp phase boundaries were visible.

In PEBMA-*co*-MMA IPNs a finer and more homogeneous dispersion of the methacrylate phase was achieved by lowering the BDDM content from 3 to 2 mol% or lower (*Figure 2*), but still very sharp phase boundaries appeared. To explain this result it is assumed that the relative rate between phase separation and network formation is reduced in these systems.

PEBMA-*co*-EMA IPNs with high BMA content have a homogeneous dispersion, but the phase size of the methacrylate component is rather coarse and of the order of that of the PEDMA-*co*-MMA IPN with high MMA content[3]. With increasing EMA content the dispersion becomes very inhomogeneous. The phase size is independent of the concentration of methacrylate crosslinker.

Figure 2 TEM micrographs of IPN-like material PEBMA-*co*-MMA, BMA:MMA = 1:1. BDDM content (mol%): (a) 0.5; (b) 2; (c) 3

Glass transition behaviour

The glass transition behaviour was investigated by dynamic mechanical analysis.

Table 5 Glass transition temperatures based on tan δ_{max}

Sample	Molar ratio	BDDM content (mol%)	T_g (pure copolymer) (°C)	T_g (methacrylate phase in IPNs) (°C)
	BMA:MMA			
D-37	1:1	0.5	50	61
D-38	1:1	2	50	62
D-35	1:1	3	58	67
D-381	1:1	6	69	69
D-36	1.2:0.8	3	53	61
D-35	1:1	3	58	67
D-341	0.6:1.4	3	68	72
	BMA:EMA			
D-29	1.2:0.8	4	45	51
D-30	1:1	4	n.d.[a]	56
D-31	0.8:1.2	4	46	61
D-32	1.2:0.8	2	n.d.	48
D-29	1.2:0.8	4	45	51
D-33	1.2:0.8	6	n.d.	58
	DMA:MMA			
D-17	1:1	4	10	− 6
	EHMA:MMA			
D-58	1:1	4	32	37
	BMA:MMA			
D-35	1:1	3	58	67

[a] Not determined

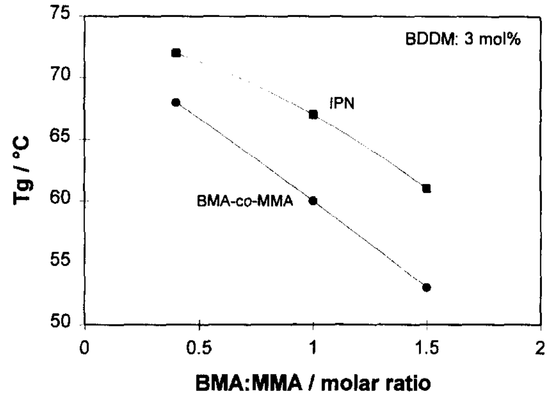

Figure 3 Glass transition temperature of the methacrylate phase in PEBMA-*co*-MMA IPNs and of the corresponding pure copolymers *versus* composition, determined by d.m.a.

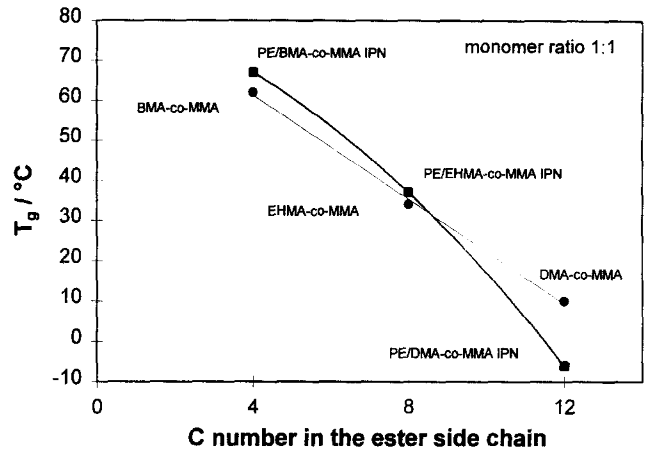

Figure 4 Glass transition temperature of the methacrylate phase in PEcomonomer-*co*-MMA IPNs and of the corresponding methacrylate copolymers *versus* C number of the ester side chain of the comonomer (BDDM content 3 or 4 mol%), determined by d.m.a.

The glass transition temperature (T_g) of the PE phase and its changes caused by differences in the methacrylate components could not be determined, since the relaxation of the methacrylate component overlaps the α- and β-relaxation of PE. Therefore discussion of the glass transition behaviour is restricted to the methacrylate phase.

Analogously to the copolymer DMA-*co*-MMA [1], T_g of the copolymer BMA-*co*-MMA, characterized by the tan δ maximum of the α-relaxation, shifts to higher temperatures with increasing MMA content. This can be understood as a consequence of the increasing content of stiff MMA units. The same tendency is observed in the corresponding IPNs with PE (*Table 5*, *Figure 3*). However, the glass transition behaviour of the IPNs investigated shows characteristic differences. In the PEDMA-*co*-MMA system[3], T_g of the methacrylate phase in the IPNs is lower than that of the corresponding pure copolymer. The difference between the two values increases with decreasing MMA content (i.e. with increasing DMA content). The copolymer with the lowest MMA content has the best compatibility with PE or the best interpenetration of both networks, because the PE chains are chemically more similar to DMA than to MMA. This corresponds to the observed dissolution characteristics during the syntheses and to the results of electron microscopy[3].

In contrast, the glass transition of the methacrylate phase in the IPN-like systems PEBMA-*co*-MMA and PEBMA-*co*-EMA is higher than that of the corresponding pure copolymer (*Figure 3*, *Table 5*), owing to the restriction of flexibility of the methacrylate segments due to grafting to PE. This points to a high degree of grafting in IPNs based on short-side-chain methacrylates compared with IPNs based on DMA. However, it is not possible to deduce correlations

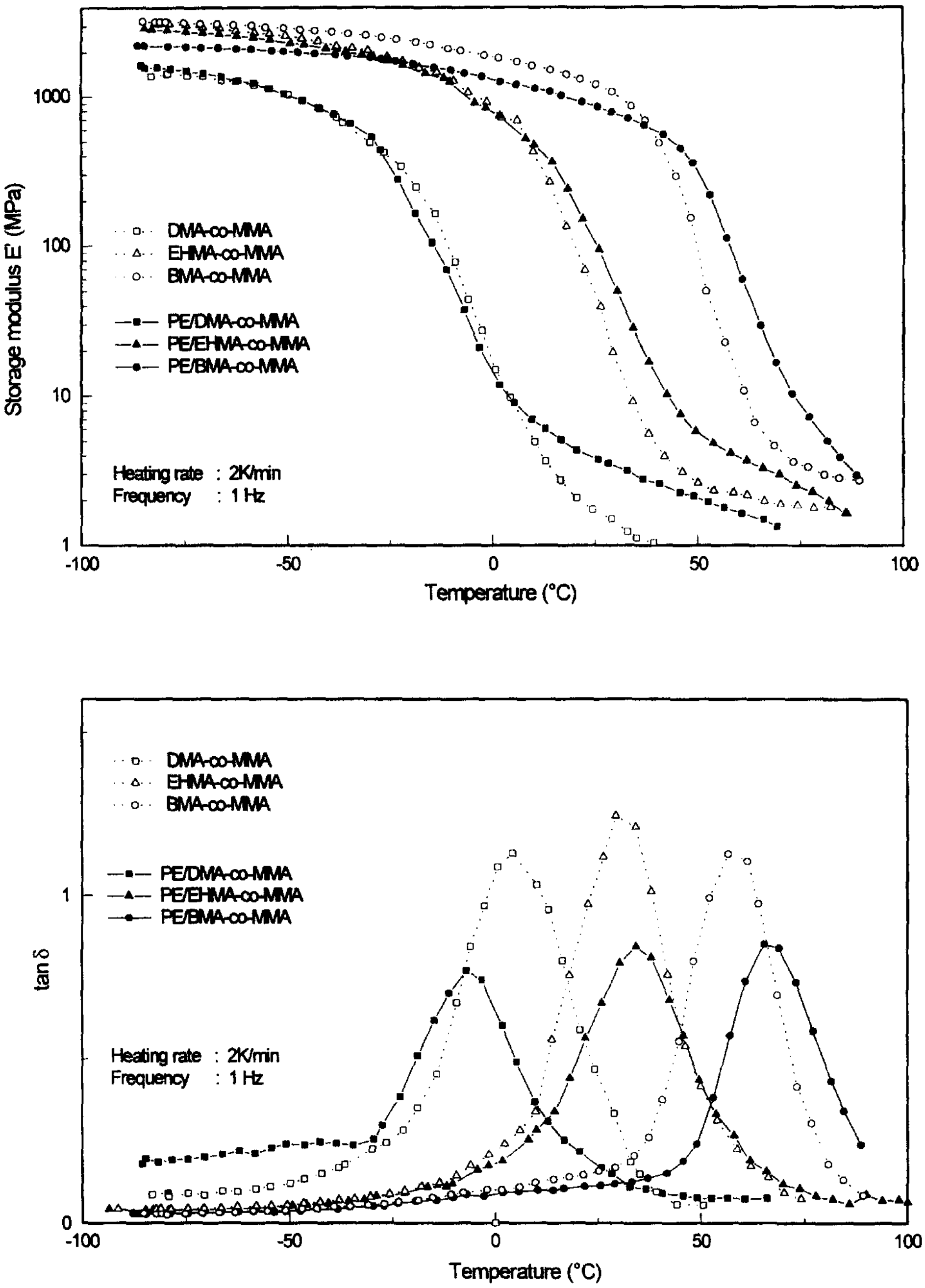

Figure 5 Storage modulus and damping term tan δ of PEcomonomer-*co*-MMA IPNs and corresponding copolymers (comonomer: MMA = 1:1; BDDM content 3 or 4 mol%)

between glass transition and degree of grafting, because the glass transition temperature is also influenced by changes in compatibility and in morphology due to grafting. Grafting causes a finer dispersion of PE and the methacrylate component in one another, which results in a glass transition shift contrary to the grafting effect.

A comparison of the relaxation behaviour of the IPNs PEDMA-*co*-MMA, PEEHMA-*co*-MMA and PEBMA-*co*-MMA with that of the corresponding copolymers (*Figure 4*) clearly indicates that with shorter length of the pendant side chains in the comonomers the glass transition temperatures of the methacrylate phase in the IPNs are shifted to higher temperatures (*Figure 5*). In IPNs with shorter aliphatic side groups the compatibilizing effect of these groups is reduced, and the hindered mobility of the methacrylate phase due to grafting becomes dominant.

The influence of the crosslinking agent (BDDM) on T_g of PEBMA-*co*-EMA IPNs is shown in *Figure 6*. T_g of the methacrylate phase increases with increasing amount of BDDM. Simultaneously the intensity of tan δ decreases due to the reduced flexibility of the copolymer chains caused by crosslinking. In the PEBMA-*co*-MMA IPN system, T_g also rises with increasing crosslinking of the methacrylate phase both in the copolymers and in the IPNs. The difference between the corresponding T_g values becomes smaller with increasing network density of the methacrylate copolymer (*Figure 7*). It is assumed that the mobility of the methacrylic phase is strongly hindered at high degrees of crosslinking and that the grafting of the methacrylate onto PE does not result in an additional increase in T_g.

Melting and crystallization behaviour

The influences of the copolymer composition and of the content of crosslinking agent on the crystallinity of the PE phase in the IPNs could be estimated only qualitatively. In

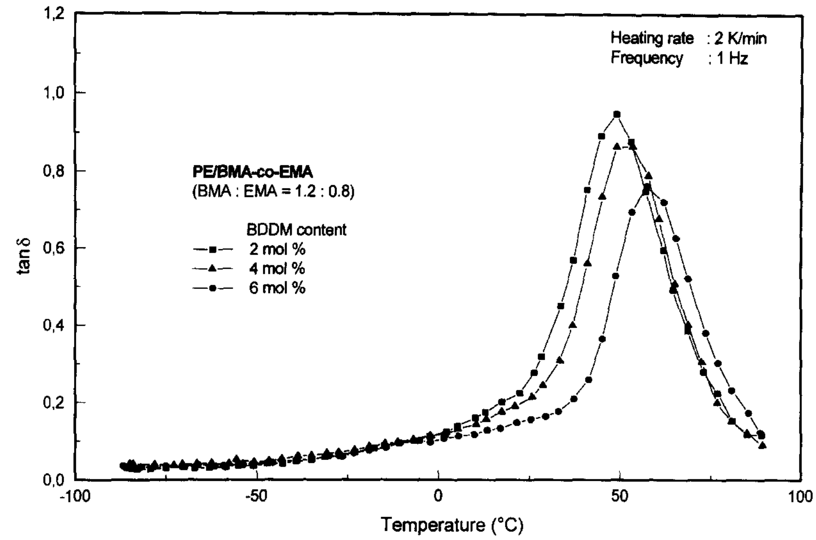

Figure 6 Damping term tan δ of IPN-like material PEBMA-*co*-EMA with different contents of methacrylic crosslinking agent

Table 6 Changes in characteristic d.s.c. values with comonomer composition in different IPN systems

Sample	IPN system	Molar ratio	$T_{g,d.s.c.}$ [a,b] (°C)	$T^{c}_{c,o}$ (°C)	α^{a}_{PE} (%)
		DMA:MMA			
D-17	PEDMA-*co*-MMA	1:1	− 5	84	27
D-22		1:6	47	82	17
		BMA:MMA			
D-36	PEBMA-*co*-MMA	1.2:0.8	37	84	32
D-341		0.6:1.4	71	84	27
		BMA:EMA			
D-29	PEBMA-*co*-EMA	1.2:0.8	32	84	29
D-31		0.8:1.2	42	86	35

[a] Estimated from the second heat
[b] $T_{g,d.s.c.}$ of pure copolymers
[c] Extrapolated onset temperature of PE crystallization during the cooling scan at 10 K min^{-1}

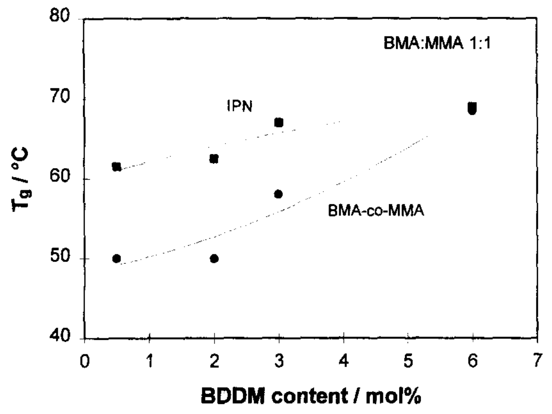

Figure 7 Glass transition temperature of the methacrylate phase in PEBMA-*co*-MMA IPNs and of the corresponding pure copolymers versus BDDM content, determined by d.m.a.

the IPNs a correct separation of the heat of fusion of the PE from the glass transition of the methacrylate phase is complicated, since the melting of PE and the glass transition of copolymers partly overlap (*Figure 8*). In spite of this, some trends can be demonstrated.

For all IPNs, including the system PEDMA-*co*-MMA in Part 1[3], the BDDM content has no marked influence on the PE crystallinity within the accuracy limit (±3%). However, the crystallinity of the PE in the IPNs is influenced by the type and composition of the copolymer (*Table 6*). The non-isothermal PE crystallization can be characterized by the extrapolated onset temperature $T_{c,o}$. It was observed that the change in α_{PE} correlates with the change in $T_{c,o}$. In the IPN-like systems PEBMA-*co*-MMA and PEDMA-*co*-MMA, both with MMA as a comonomer, $T_{c,o}$ decreases or is unchanged with increasing MMA content. This is associated with decreasing α_{PE}. The IPNs PEDMA-*co*-MMA have the smallest PE crystallinity (IPN D22: $\alpha_{PE} = 17\%$), which corresponds to a high degree of crosslinking in PE (96.3 wt%[3]).

In the IPNs based on BMA-*co*-MMA and on BMA-*co*-EMA, the PE crystallinity is improved relative to DMA-*co*-MMA-based IPNs. In the case of PEBMA-*co*-EMA, $T_{c,o}$ increases slightly with increasing EMA content, while the PE crystallinity increases to 35%, the highest value observed for all IPNs investigated (*Table 6*). Overall, a good correlation between $T_{c,o}$, α_{PE} and the degree of PE cross-linking was found.

Tensile strength and elongation

Tests of mechanical properties at room temperature were focused on the measurement of tensile strength and elongation at break.

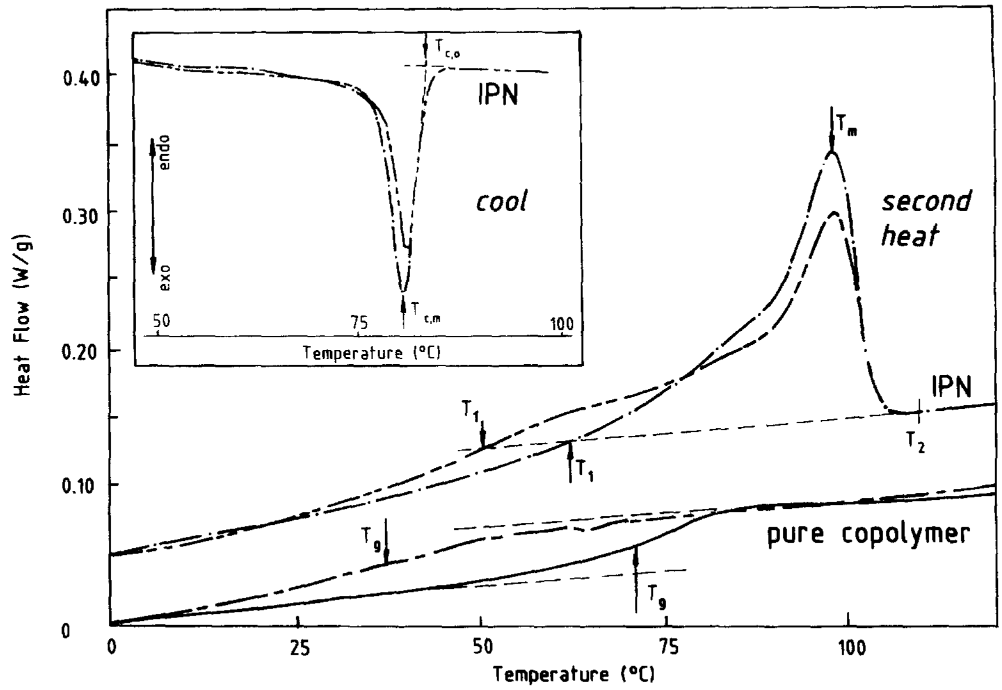

Figure 8 D.s.c. thermograms of IPN-like material PEBMA-*co*-MMA and of the corresponding copolymers at different molar ratios of methacrylate monomers (BDDM content 3 mol%)

BMA:MMA	IPN	pure copolymer
1.2:0.8	——— - - ———	————— — —————
0.6:1.4	————·————	—————

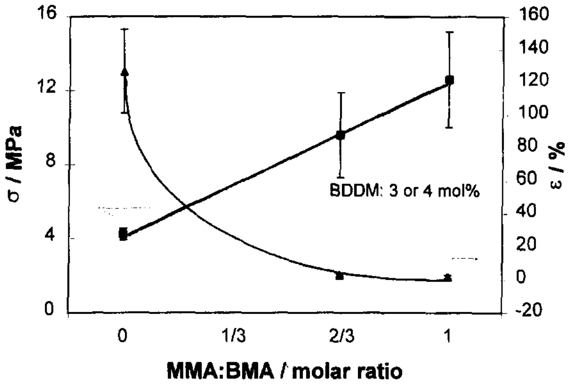

Figure 9 Tensile strength σ (■) and elongation at break ε (▲) of PEBMA-*co*-MMA *versus* molar ratio of methacrylate monomers

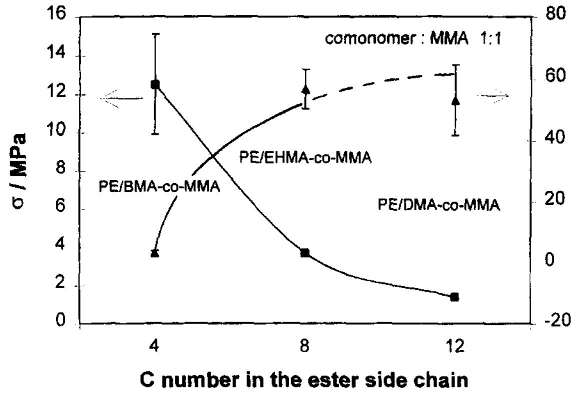

Figure 10 Tensile strength σ (■) and elongation at break ε (▲) of PEcomonomer-*co*-MMA *versus* C number of the ester side chain (BDDM content 3 or 4 mol%)

The relation between tensile strength or elongation and the monomer ratio is shown for PEBMA-*co*-MMA IPNs in *Figure 9*. With increasing MMA content in the IPNs a significant increase in tensile strength is observed. No significant influence of the content of crosslinking agent on the tensile strength could be observed. A reduction in the chain length of the ester substituent in methacrylate comonomers is favourable for the tensile strength of the IPNs (*Figure 10*). IPNs based on BMA-*co*-MMA combine good processability with good mechanical properties. On the one hand, butyl methacrylate comonomers have a sufficient solvating power for PE and thus permit the synthesis of the IPNs. On the other hand, they result in the best mechanical strengths among the IPNs synthesized at high amounts of MMA. Evidence for the high rigidity of the PEBMA-*co*-MMA samples was provided by d.m.a. measurements of the storage modulus (*Figure 6*).

CONCLUSIONS

The IPN-like systems PEBMA-*co*-MMA, PEBMA-*co*-EMA and PEEHMA-*co*-MMA were studied and compared with results for PEDMA-*co*-MMA IPNs obtained earlier. The molar ratio of the methacrylate monomers has a strong influence on crosslinking and grafting during the synthesis, and consequently on the morphology and properties of the resulting IPNs. However, these effects differ for different methacrylate combinations in the IPNs.

The IPN-like systems PEBMA-*co*-MMA have a heterogeneous size distribution with a coarse dispersed methacrylate phase at high content of crosslinking agent. Sharp phase boundaries are observed. Decreasing content of crosslinking agent results in a fine and homogeneous dispersion while the sharp phase boundaries continue to exist. In contrast, the dispersity of the system PEBMA-*co*-EMA is mainly determined by the composition of the methacrylate copolymer.

In contrast to previous observations on PEDMA-*co*-MMA IPNs, T_g of the BMA and EHMA copolymers in the IPNs are in general higher than that of the pure copolymers. This can be attributed to the increased tendency for grafting of the methacrylate comonomers with short substituents at the ester group onto the PE chains and therefore to a restriction in mobility of the methacrylate segments. Generally, reduced compatibility between PE and the copolymer phases with shorter length of the ester side groups was determined.

The gel content of PE as a measure of the degree of PE crosslinking in the IPNs was estimated from the melting temperature T_m. The gel content was determined to be $\simeq$85–95 wt%, relatively independent of the copolymer composition and of the content of the methacrylic crosslinking agent.

The mechanical properties depend mainly on the ratio of the methacrylate monomers in the IPN systems. The tensile strength rises with increasing MMA content and the elongation at break falls. A decrease in the chain length of the pendant ester group of the methacrylate comonomer, in the order DMA > EHMA > BMA, is advantageous for tensile strength and modulus of the IPNs. Butyl methacrylate as a comonomer provides both simple handling of the IPN synthesis and good mechanical strength.

ACKNOWLEDGEMENTS

The authors thank Mrs Viktoria Albrecht for the experimental part of the pyrolysis gas chromatography investigations. They wish to acknowledge financial support by the German Federal Ministry of Research and Technology.

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