ELSEVIER

Polymer 40 (1999) 5279–5284

polymer

Degradation of interpenetrating polymer networks based on PE and polymethacrylates by electron beam irradiation

J. Hu, U. Schulze, J. Pionteck*

Institute of Polymer Research Dresden, Hohe Str. 6, D-01069 Dresden, Germany

Received 10 August 1998; received in revised form 27 October 1998; accepted 27 October 1998

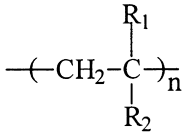
Abstract

This paper describes the synthesis of interpenetrating polymer networks (IPN) materials based on polyethylene (PE) and polymethacrylates and the effect of ionising irradiation on degradation and grafting reactions in these materials. Two IPN systems, polyethylene/poly(butyl methacrylate-co-methyl methacrylate) and polyethylene/poly(dodecyl methacrylate-co-ethyl methacrylate), were synthesized by the in situ method using a peroxidic initiator and a divinyl crosslinker. During the synthesis the PE crosslinks and grafting reactions between PE and polymethacrylates occur. By electron beam irradiation the methacrylate phase partially degrades. After extraction with xylene a porous structure in the material is observed. The effect of the IPN composition, the synthesis conditions, and the electron beam irradiation on the amount of extractable material and the morphology of the IPN has been studied.

Keywords: Interpenetrating polymer network; Electron beam irradiation; Degradation

1. Introduction

Polymers generally undergo structural changes under irradiation [1]. Depending on their chemical structures some polymers crosslink while others degrade. A polymer with the following structure will degrade by irradiation if it has no hydrogen at the α-position ($R_1 \neq H$, $R_2 \neq H$), or crosslink when it contains at least one hydrogen at this position (R_1 or/and $R_2 = H$) [2].



For example, crosslinking will occur in polyethylene, polypropylene, or polystyrene whereas polymethacrylates in which the α-hydrogens in the repeating units are substituted are examples for degrading polymers [2]. The substituents R_1 and R_2 also affect the irradiation behaviour of the polymers. If they contain structures like C=C double bonds or epoxy groups which incline to crosslink, gel formation can be expected. Gel may be produced in polymers with pendant oxirane, allyl, or propargyl groups, although there may be no α-hydrogen in the repeating units. For example, poly(allyl methacrylate) is a negative (crosslinking) electron beam resist [3]. Here the competition reactions of crosslinking in the pendant groups dominate the breaking down of the backbone chains. Poly(dodecyl methacrylate) which has long pendant ester groups was reported to crosslink on irradiation [4] though considerable degradation has been found recently [5]. Practically, some degree of degradation takes place in most polymers. The ratio of main chain fracture to crosslinking determines whether a gel will be produced. If the number of fractures caused by irradiation is 4 times larger than the number of crosslinks no gel will be formed [1].

In this work we prepared interpenetrating polymer networks (IPN) by the in situ method. The two components of the IPN behave differently when exposed to electron beam (EB) irradiation. One component is PE, a typical crosslinking polymer. Polymethacrylates, conventionally used as lithographic positive resists when they contain short aliphatic ester side groups, are chosen as degrading species. For the in situ IPN preparation it is necessary that the PE is dissolved completely in the methacrylate monomers. However, PE is insoluble in methyl methacrylate or ethyl methacrylate. Therefore mixtures of these monomers with methacrylates with longer aliphatic side chains had to be used.

We selected methyl and ethyl methacrylates as monomers with short ester groups and butyl and dodecyl methacrylates as those with longer ester groups, considering the fact

* Corresponding author. Tel.: + 49-351-4658-393; fax: + 49-351-4658-565.

0032-3861/99/$ - see front matter
PII: S0032-3861(98)00757-5

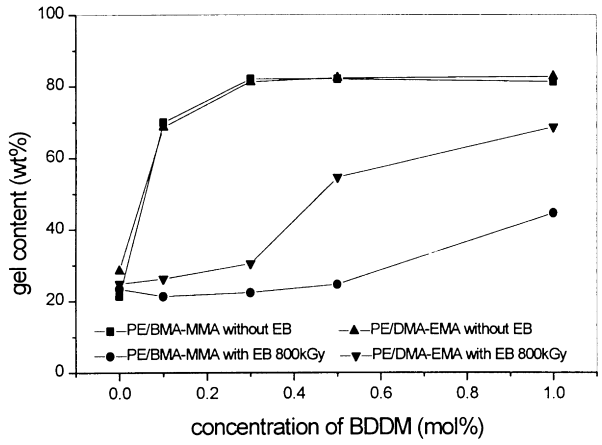


Fig. 1. Gel content of IPN in dependence on BDDM concentration and EB irradiation. (synthesis condition: 1 wt% Trigonox-101; 6 h at 115°C + 1 h at 160°C).

that the radiation decomposition of polymethacrylates is inversely proportional to the length of ester groups of methacrylate monomers [6]. Thus, thin films of two IPN systems polyethylene/poly(butyl methacrylate-co-methyl methacrylate) (PE/BMA-co-MMA) and polyethylene/poly(dodecyl methacrylate-co-ethyl methacrylate) (PE/DMA-co-EMA) were prepared to study the effects of different lengths of aliphatic ester groups on the degradation behaviour.

2. Experimental

2.1. Materials

The methacrylates (Aldrich) were freed from inhibitor. MMA, EMA, and BMA were distilled under reduced pressure in dry nitrogen atmosphere shortly before use. DMA was washed with aqueous sodium hydroxide and dried. Polyethylene (LDPE, Bralen RA 2-19, non-stabilised, Slovnaft), butanediol dimethacrylate (BDDM, Aldrich), and 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane (Trigonox-101, Akzo) were used as obtained.

2.2. Preparation of IPN films

IPN films of about 200 to 300 μm thickness were prepared by the so-called in situ method using a plate reactor. By dissolving powdery PE in a mixture of methacrylate monomers in presence of the divinyl crosslinker a transparent solution was obtained at elevated temperature. The peroxide initiator was then added and mixed and thereafter poured into the plate reactor. The reaction was stopped after the 1st stage, the polymerisation of the methacrylates at 115°C for 6 h (synthesis path A), or after the second stage, additional heating of the reactor to 160°C for 1 h (synthesis path B). The detailed description of the plate reactor is given elsewhere [5].

The molar ratio of the monomers was ethylene : methacrylate = 1 : 1. The methacrylate molar ratio was BMA : MMA = 1 : 1 in the PE/BMA-co-MMA IPN and DMA : EMA = 1 : 4 in the PE/DMA-co-EMA IPN, corresponding to a PE content in the feed composition of 18.8 wt% and 16.5 wt%, respectively. The contents of BDDM and peroxide were varied.

2.3. Solvent extraction

Extractions were carried out in boiling xylene (100 times in weight) for 10 h. Then the samples were dried under vacuum at 50°C for 10 h and kept in vacuum at ambient temperature for additional 10 h. Gel contents were calculated from dry samples before and after extraction.

2.4. Determination of PE content

Quantitative analysis of PE was performed by means of FTIR (FTS 155, Bio-Rad Win-IR). The rocking vibration of long $(CH_2)_n$ segments ($n \geq 5$) at 719 cm^{-1} was used for the quantification. A detailed description is reported in our previous work [7].

2.5. Scanning electron microscopy

The morphology of the cross section of the IPN thin film was observed by means of a low voltage scanning electron microscope (DSM 982 GEMINI, Zeiss). The cross sections were prepared by cryofracturing in liquid nitrogen.

3. Results and discussion

3.1. Influence of crosslinker on gel content

A full IPN consists of at least two polymer networks [8]. In our work the network of polyethylene is formed by the peroxide used as the polymerisation initiator. The second network is made of polymethacrylates as a result of the addition of the divinyl monomer BDDM. During the polymerisation grafting of the methacrylate monomer onto the polyethylene network takes place [9]. So the two polymer networks are bonded together and this type of IPN has been referred to as IPN-like material.

In order to study the influence of the divinyl crosslinker on the gel content a constant amount of 1 wt% peroxide in relation to the total amount of PE and monomers was used. Surprisingly, the effect of BDDM on the gel content was very similar for both IPN systems (Fig. 1). The gel content was increased by about 50% when adding 0.1 mol% BDDM. The addition of 0.3 mol% crosslinker was sufficient to complete the network formation of the polymethacrylates.

Differences appeared only after applying electron beam irradiation. At the same concentration of BDDM the gel content of PE/DMA-co-EMA is higher than that of PE/BMA-co-MMA (Fig. 1). We assume that the self-crosslinking, which was described by Schulze et al. [10], plays a role.

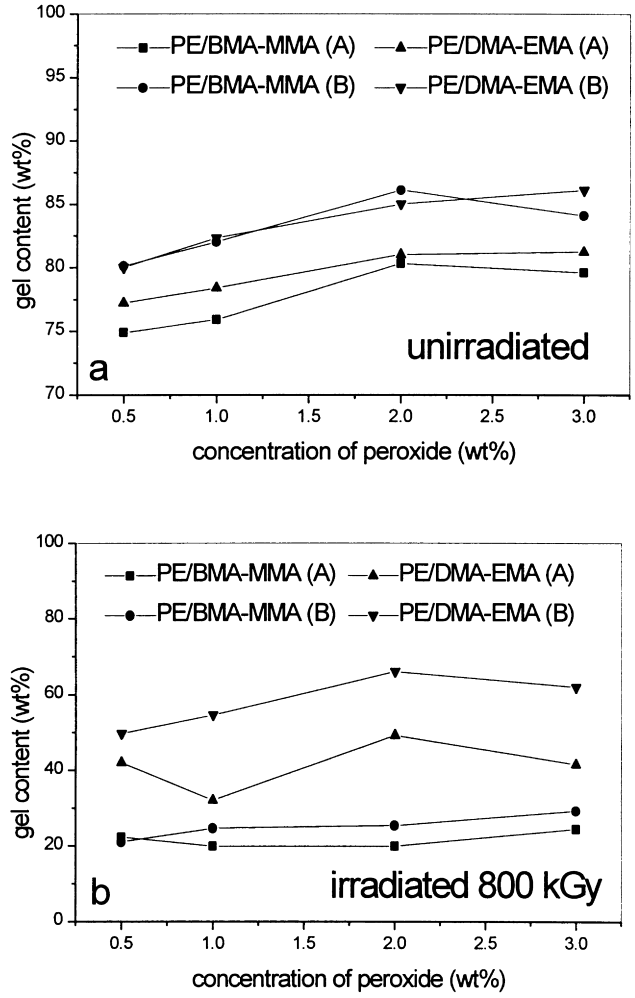


Fig. 2. Influence of peroxide concentration and EB irradiation on gel content. (A: synthesised at 115°C for 6 h; B: synthesised at 115°C for 6 h and 160°C for 1 h).

While in the IPN system PE/BMA-co-MMA EB irradiation results in PE crosslinking only, in the system PE/DMA-co-EMA the dodecyl methacrylate monomer units in the copolymer can participate in the peroxidic initiated crosslinking process because of the long aliphatic side chains. As illustrated in the following section, the backbone chains of the copolymer of butyl and methyl methacrylates were heavily decomposed at the irradiation dose of 800 kGy. The additional crosslinking of the pendant dodecyl groups lowers the possibility of chain breaking down to extractable segments caused by irradiation.

3.2. Influence of temperature and peroxide on gel content

The peroxide Trigonox-101 was used as the radical initiator for the methacrylate polymerisation during the IPN preparation. However, its presence also affects the crosslinking and grafting of polyethylene and the decomposition of the methacrylate polymer during the polymerisation [9]. So, the gel content is related to the concentration of the peroxide as well. While grafting of the polymethacrylate to the PE occurs in both stages, the crosslinking reactions occur only in the second stage of the IPN preparation at 160°C [9]. To investigate the effects of temperature on the gel content the synthesis was performed without (synthesis path A) or with annealing the material at 160°C for 1 h (synthesis path B).

It has been reported [9] that the peroxide has a degrading effect on poly(butyl methacrylate) at 160°C in the system polyethylene/poly(butyl methacrylate) synthesised without addition of divinyl crosslinker. In our experiments, higher gel contents were obtained both for unirradiated and for irradiated samples when the material was treated at 160°C irrespective of the IPN systems investigated (Fig. 2a). This indicates that the crosslinking and grafting effects of peroxide prevailed over its decomposing effects in the presence of a divinyl crosslinker (BDDM).

A maximum in the gel content in dependence on the peroxide concentration appeared in the unirradiated PE/BMA-co-MMA IPN for both synthesis paths, thus indicating the decomposition effect of the peroxide at high concentrations (3%). This is consistent with the statement in Ref. [9] that the polymethacrylate chains split in the presence of the peroxide. However, for the system PE/DMA-co-EMA without irradiation the gel content increased continuously in the whole concentration range studied. This is attributed to the long aliphatic ester groups of dodecyl methacrylate. The decrease in gel content caused by the decomposition of the

Table 1
Composition change of PE/BMA-co-MMA IPN caused by irradiation and extraction

Irradiation dose (kGy)	Gel content (wt%)	PE content in extracted samples (wt%)	PE content after irradiation and extraction (wt%)[a]	Methacrylate content after irradiation and extraction (wt%)[a]
0	not extracted	27.0	100	100
0	83.3	14.1	43.3	98.0
200	75.0	28.4	78.9	73.6
400	64.9	36.3	87.4	41.3
600	54.6	42.7	86.3	31.3
800	44.6	53.9	88.9	20.6

[a] Related to the original value.

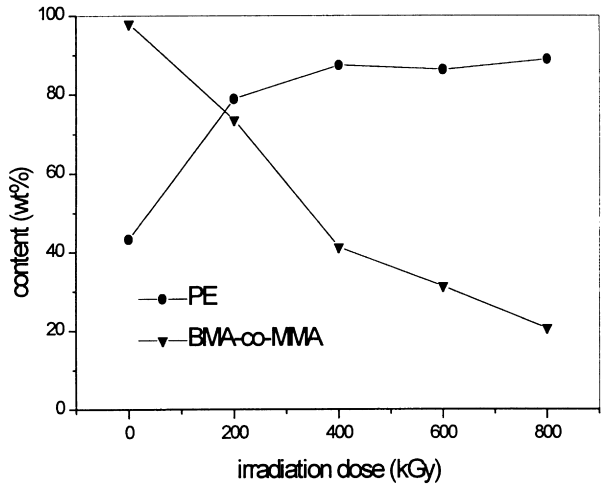


Fig. 3. Gel contents of the PE phase and of the methacrylate phase in dependence on the irradiation dose related to the absolute values in the virgin PE/BMA-co-MMA IPN.

main chains is compensated or even over-compensated by the increase in the gel content caused by the peroxidic crosslinking of the dodecyl groups or the grafting to PE.

After irradiation great differences in the gel content can be seen between the two IPN systems (Fig. 2b). The gel contents of PE/DMA-co-EMA are obviously higher than those of PE/BMA-co-MMA. As can be seen in the next section, the absolute weight of polyethylene remained almost unchanged in the IPN. Therefore, the difference in the gel contents has to be accounted to the different behaviour of the methacrylate components. According to Ref. [4], poly(dodecyl methacrylate) is the only methacrylate used in this work that crosslinks under electron beam irradiation though it undergoes also some degradation [5].

The values of the gel content of the PE/BMA-co-MMA IPN change just slightly with increasing concentration of peroxide. The gel of this IPN consists of almost only PE. So it is difficult to analyse the influence of the peroxide concentration on the degradation and grafting reactions of the methacrylate phase.

The influence of the synthesis conditions remains the same in the irradiated samples compared to the non-radiated samples. For both IPN systems the gel contents are higher after annealing at 160°C for 1 h (Fig. 2b).

3.3. Composition changes during electron beam irradiation

The crosslinking is the dominant reaction in PE during ionising irradiation. Non-irradiated PE is completely soluble in hot xylene. With raising irradiation doses the gel content increases from 63.9 wt% (100 kGy) to about 90 wt% (800 kGy) as well as the network density, proven by a decrease of the melting temperature of the PE crystallites [7]. However, about 10 wt% are still extractable also at very high irradiation doses.

Conversely, most polymethacrylates will degrade under electron beam irradiation. Therefore, the decrease of the gel content in IPN based on PE and methacrylate copolymers caused by EB irradiation should result mainly from the decomposition of polymethacrylates. To prove this, the PE content in the PE/BMA-co-MMA IPN before and after irradiation and extraction with xylene was quantified by FTIR (Table 1, Fig. 3).

The PE/BMA-co-MMA IPN was prepared with the addition of 1 mol% BDDM and 1 wt% Trigonox-101. The IPN contains 27.0 wt% PE and 73.0 wt% polymethacrylates after its preparation. The difference in the PE content between the feed composition (18.8 wt%) and the IPN is caused by evaporation of monomers during the synthesis. After extraction with xylene a gel content of 83.3 wt% was obtained. The composition of the gel was determined to 14.1 wt% PE and 85.9 wt% methacrylate copolymer. Related to the weight of the IPN before extraction these values correspond to 11.7 wt% PE and 71.6 wt% copolymer. In other words, 43.3 wt% of the PE phase and 98 wt% of the methacrylate phase are crosslinked after the

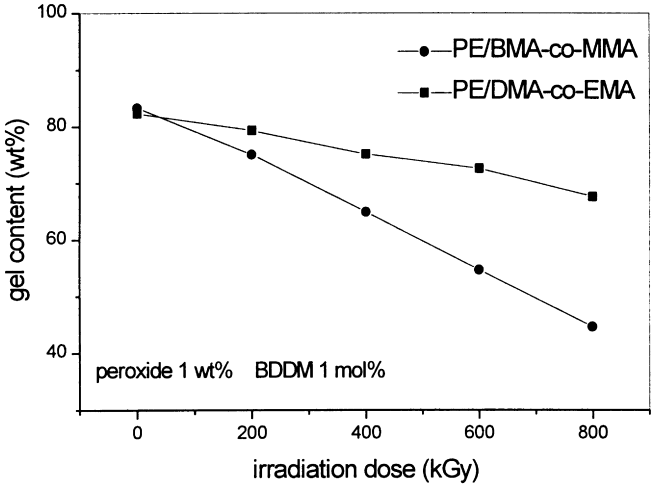


Fig. 4. Gel contents of the IPN in dependence on the irradiation dose.

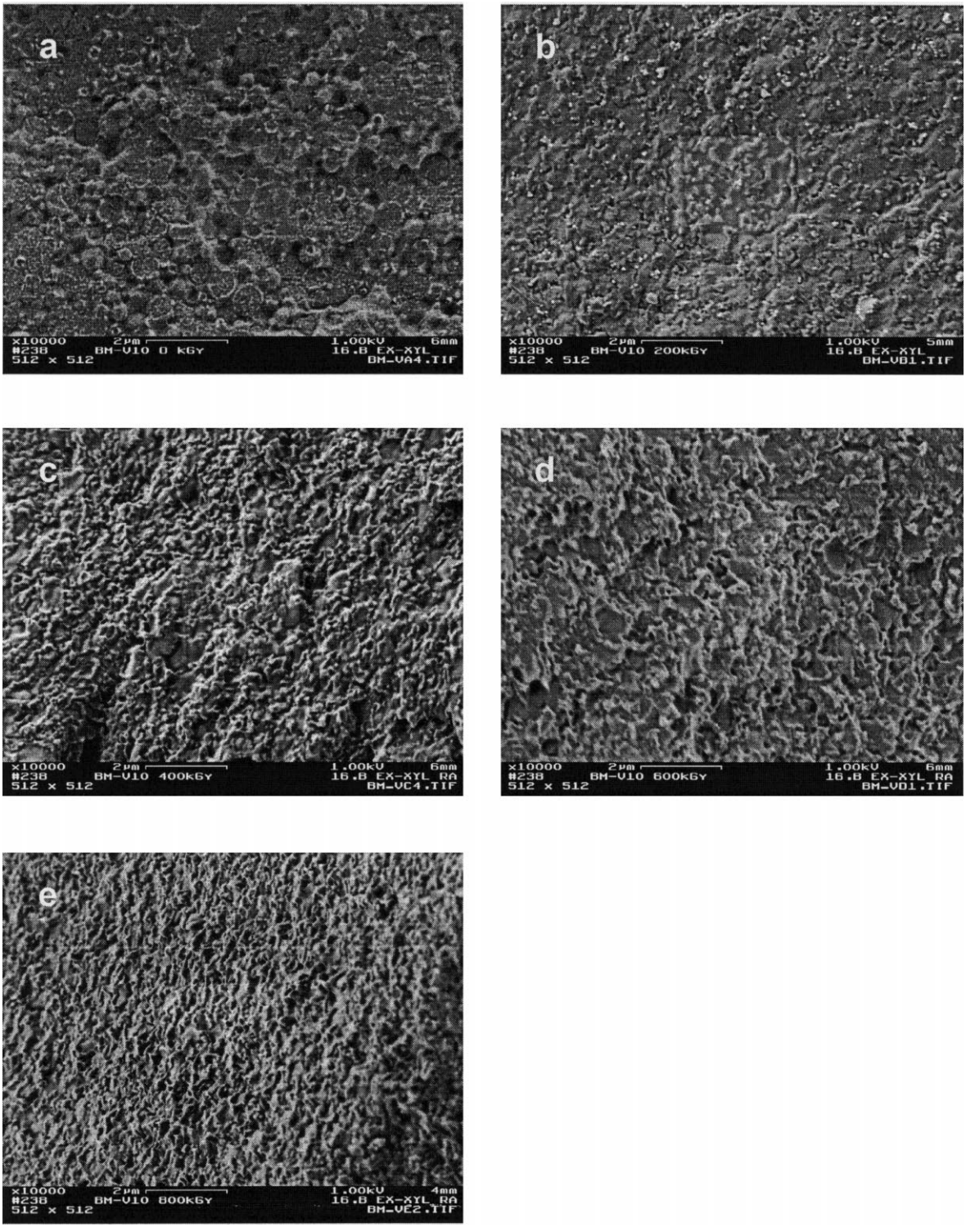


Fig. 5. Morphology of extracted PE/BMA-co-MMA IPN in dependence on the irradiation dose (PE contents see Table 1) (a: non-irradiated; b: 200 kGy; c: 400 kGy; d: 600 kGy; e: 800 kGy).

IPN preparation. With the concentration of 1 mol% BDDM the network of polymethacrylates is almost completely formed and almost only PE is extractable.

By irradiation of the IPN the content of crosslinked PE increases enormously. Even at the rather small irradiation dose of 200 kGy almost 80 wt% of the PE are already crosslinked. At higher doses the degree of PE crosslinking remains constant near to 90 wt%. The weight loss of the irradiated IPN is caused by the decomposition of polymethacrylates which increases steadily with the irradiation

dose (Fig. 3, Table 1). At 800 kGy about 80 wt% of the original methacrylate network is decomposed.

As it is not possible to distinguish between the PE chain and the long aliphatic dodecyl side group by FTIR, the PE content in the PE/ DMA-co-EMA IPN cannot be determined by this method. However, the plot of the overall gel content of the IPN over the irradiation dose clearly shows a steady decrease which is much less pronounced than for the PE/ BMA-co-MMA IPN (Fig. 4). Again it is to conclude that the decomposition of the methacrylate main chain is overlapped by the crosslinking in the dodecyl side chains.

3.4. Morphology of PE/BMA-co-MMA IPN

In all IPN studied PE forms the matrix though the PE content of the virgin IPN is only 27.0 wt% or 16.5 wt% for PE/BMA-co-MMA or PE/DMA-co-EMA, respectively. The methacrylic phase is more or less finely dispersed and forms spheric particles.

The morphology of the irradiated and extracted IPN depends strongly on the irradiation dose. The fracture surface of extracted IPN irradiated with low doses (Fig. 5b) shows spherical particles embedded in a matrix similar to that of the non-irradiated sample (Fig. 5a). With increasing doses the particle structure disappears (Fig. 5c,d) and, finally, at 800 kGy only a sponge-like porous structure is observed (Fig. 5e). Considering the composition of the IPN we conclude that the PE forms the matrix in the IPN and the methacrylates the dispersed particles which decompose under irradiation. After extraction of the decomposed polymethacrylates a porous material is obtained consisting mainly of PE.

4. Summary

Two different IPN systems based on PE and methacrylate copolymers have been prepared and the influence of electron beam irradiation on the crosslinking and decomposition of the IPN components has been studied. During the synthesis the PE partially crosslinks and grafting reactions between the PE and methacrylate copolymers occur. By irradiation the degree of PE crosslinking increases while the methacrylic phases decompose though they are crosslinked by the addition of a divinyl crosslinker. The degree of the decomposition strongly depends on the length of the ester side chains of the methacrylates. The long ester groups of dodecyl methacrylate participate in the irradiation initiated crosslinking process. Therefore, the gel contents of the DMA containing IPN are higher than those of the DMA free samples prepared under similar conditions.

Additional heating at 160°C during the synthesis yielded higher gel contents not only in PE/DMA-co-EMA but in PE/ BMA-co-MMA as well. A degrading effect of the peroxide was observed only in the system PE/BMA-co-MMA whereas the crosslinking effect prevailed in the system PE/DMA-co-EMA.

A quantitative analysis of the gel composition of the PE/ BMA-co-MMA IPN revealed that in non-irradiated samples only PE is extractable while in irradiated samples the extraction of decomposed methacrylates dominates.

Micrographs of the IPN cross sections showed that with increasing irradiation the morphology of the extracted IPN changes from a dense two-phase morphology to a porous, sponge-like structure.

Acknowledgements

We acknowledge the financial support by the Sächsisches Ministerium für Wissenschaft und Kunst (project no. 4-7531.50-02-IPF/605).

References

[1] Dole M. The radiation chemistry of macromolecules, 2. New York: Academic Press, 1973:98.
[2] Wilson JE. Radiation chemistry of monomers, polymers, and plastics. New York: Marcel Dekker, 1974:373.
[3] Allen G, Bevington JC, Eastmond GC, editors. Comprehensive polymer science, 6. Oxford: Pergamon Press, 1989:208.
[4] Shultz AR. J Polym Sci 1959;35:369.
[5] Hu J, Schulze U, Pionteck J, Borsig E. J. M. S.—Pure Appl Chem 1998;A35:1285.
[6] Kaindl K, Graul E H. Strahlenchemie. Heidelberg: Dr. Alfred Hüthig Verlag, 1967:446.
[7] Hu J, Pompe G, Schulze U, Pionteck J. Polym Adv Technol 1998;9:746.
[8] Sperling LH. Interpenetrating polymer networks and related materials. New York: Plenum Press, 1981:3.
[9] Lazar M, Hrckova L, Schulze U, Pionteck J, Borsig E. J. M. S.—Pure Appl Chem 1996;A33:261.
[10] Schulze U, Fiedlerova A, Pompe G, Meyer E, Janke A, Pionteck J, Borsig E. Polymer 1998;39:1289.