ELSEVIER

Polymer 41 (2000) 7915–7923

polymer

www.elsevier.nl/locate/polymer

Characterisation of radiation behaviour of polyethylene/polymethacrylates interpenetrating polymer networks

J. Pionteck[a,*], J. Hu[a], G. Pompe[a], V. Albrecht[a], U. Schulze[a], E. Borsig[b]

[a]*Institute of Polymer Research Dresden, Hohe Str. 6, D-01069 Dresden, Germany*
[b]*Polymer Institute, Slovak Academy of Sciences, Dúbravska cesta 9, 842 36 Bratislava, Slovak Republic*

Received 9 January 2000; accepted 24 January 2000

Abstract

Although polymethacrylates generally degrade under ionising irradiation, differences in degradation behaviour exist amongst various polymethacrylates. The radiation behaviour of different methacrylate polymers was investigated on interpenetrating polymer networks (IPN) based on polyethylene and methacrylate copolymers, synthesised via an in situ method. Changes in chemical structure such as hydroxyl groups, unsaturated C=C bonds, crosslinking, main chain scission and in composition caused by irradiation have been characterised by FTIR. Linking between the two IPN components caused by irradiation has been observed by TGA and pyrolysis-GC-MS. Mechanical properties in dependence on radiation doses have been characterised by tensile test and dynamic-mechanical analysis. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyethylene; Polymethacrylates; Interpenetrating networks

1. Introduction

Depending on their structures, polymeric materials can be degraded or crosslinked by ionising irradiation [1,2]. The interpenetrating polymer network (IPN) system based on polyethylene (PE) and polymethacrylates (PMAs) contains degrading and crosslinking species in one material. We have reported in our previous work about the radiation behaviour of the IPN systems, such as the degradation of the individual PMAs and the possibility to create porous structure [3], the impact of radiation on the thermal stability [4], and the dependence of the gel content on the synthesis conditions [5].

According to the principles of radiation chemistry, firstly macromolecules of polymer materials will be excited under ionising radiation. Then active species, such as cations, anions or radicals, can be generated from the excited macromolecules [6]. They can either react with one another or are able to initiate further reactions among the polymeric chains and give rise to changes in the material properties. For example, the combination of two radicals leads to crosslinking of the polymer while the chain transfer and the subsequent splitting lowers the molecular weight. In this way, the properties of the irradiated materials can be changed.

The purpose of our project is the development of materials with a porous structure that may be suitable as membranes [3–5]. Since in a membrane process the membrane material and the substances to be separated interact with each other, the characterisation of structural changes caused by irradiation in the materials is of significance.

Various methods have been used to characterise irradiated materials. Methods like viscometry and gel permeation chromatography (GPC) are often chosen to obtain correlations between the radiation dose and changes in the molecular weight, while spectroscopic methods like transmission FTIR, ATR-FTIR and NMR are used for the detection of structural changes caused by the irradiation. In comparison to these methods, the use of thermal methods for the characterisation of irradiated polymers has been reported very rarely. However, we found that thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are very useful in elucidating the effect of electron radiation on IPN systems. In addition, tensile test and dynamic-mechanical analysis (DMA) were used to reveal the influences of irradiation on their mechanical behaviour.

2. Experimental

2.1. Materials

Methyl (MMA), ethyl (EMA), and butyl (BMA) methacrylates (Aldrich) were freed from inhibitor by distillation

---

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

E-mail address: pionteck@ipfdd.de (J. Pionteck).

0032-3861/00/$ - see front matter
PII: S0032-3861(00)00155-5

Table 1
Composition of the IPN systems

IPN	Methacrylates	Molar ratio of the methacrylates	BDDM (wt%[a])	Trigonox-101 (wt%[b])
PE/PBMA	BMA		0.5	1
PE/BMA-*co*-MMA	BMA/MMA	1:1	1	1
PE/BMA-*co*-MMA	BMA/MMA	3:2	1	3
BE/DMA-*co*-EMA	DMA/EMA	1:4	1	1

[a] Related to the weight of the PMA phase.
[b] Related to the weight of the PMA and PE phase.

under reduced pressure shortly before use. Dodecyl methacrylate (DMA) was washed with aqueous sodium hydroxide and dried at first with anhydrous calcium chloride and then over 4A molecular sieves. 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 received.

2.2. Sample preparation

IPN films of about 200 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 mixture was kept at 115°C for 6 h followed by 1 h at 160°C. The detailed description of the sample preparation is given elsewhere [3].

For the synthesis of the IPN thin films the molar ratio of the monomer units ethylene: methacrylate was kept constant at 1:1 in all investigated samples, while the methacrylate compositions of the PMA phase, the BDDM-content and the content of the peroxide Trigonox-101 were varied (Table 1).

The 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.

2.3. Thermogravimetric analysis

The TGA was realised on a Perkin–Elmer TGA-7 in nitrogen atmosphere with a heating rate of 10 K/min. Before the TGA measurements all samples were extracted with boiling methanol and dried under vacuum at 50°C for 10 h in order to remove unreacted monomers and decomposed products of low molecular weight.

2.4. Pyrolysis-gas chromatography-mass spectroscopy (Py-GC-MS)

The samples were investigated by a pyrolysis-gas chromatography-mass spectrometer. The pyrolysis was done in a Pyroprobe 2000 (CDS-Instruments) at different temperatures. The gas chromatograph HP 5890 II (Hewlett Packard) containing a 25-m capillary quartz column HP-FFAP (inside diameter = 0.2 mm) was coupled with a quadrupole mass spectrometer HP 5971 (Hewlett Packard, ionisation energy 70 eV, detector: dynode electron multiplier). The pyrolysis temperatures were 230, 310, 440 (pyrolysis time 20 s), and 600°C (pyrolysis time 10 s). The pyrolysis was done stepwise with raising temperature. The carrier gas was helium 5.0 with a flow rate of 1 ml/min.

2.5. FTIR-measurements

Measurements of structural changes were performed on a FTIR spectrometer (FTS 155, Bio-Rad Win-IR). IPN films of 170 μm thickness were cut in small discs to the size of the sample holder. The discs were marked on the edge prior to the FTIR studies to insure that the repeating measurements were made at the identical position. The specimens were studied before and after irradiation. The differential spectra were acquired by subtracting the absorbencies of the unirradiated sample from that of the corresponding irradiated sample.

For the characterisation of the irradiated surface ATR-spectra of the films were obtained on the FTIR-Spectrometer IFS66v/s (Bruker). Specimens of 1 *cm* × 5 *cm* were prepared and studied before and after irradiation.

2.6. Dynamic-mechanical analysis

The dynamic-mechanical properties were investigated on the dynamic-mechanical analyser Eplexor 150 (Gabo). The specimens with a dimension of 10 mm × 50 mm × 0.23 mm were prepared and measured from −100 to +100°C at 10 Hz with a heating rate of 2 K/min.

2.7. Tensile test

Tensile tests were conducted on a tensile machine Z010/1446 (Zwick). Dumbbell-shaped specimens of 75 mm in length and 12.5 mm in width were prepared with a gauge length section of 30 mm × 4 mm. The thickness of the specimens was in the range of 0.2–0.3 mm depending on the synthesis conditions. Ten specimens of each sample were measured and the average values were used for the evaluation of the tensile strength. The tensile velocities were 5 mm/min for the PE/BMA-*co*-MMA and 20 mm/min for the PE/DMA-*co*-EMA IPN.

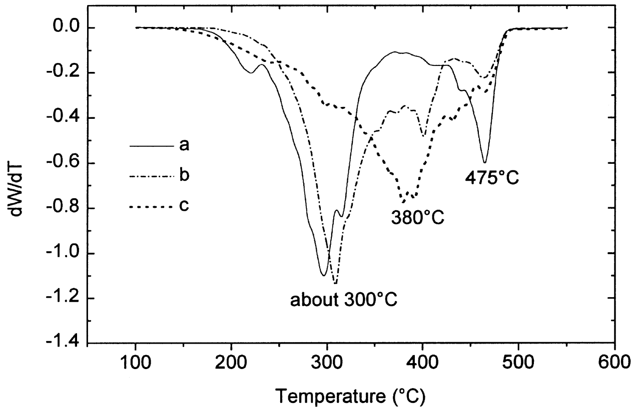


Fig. 1. First derivative curve of the weight loss of PE/PBMA IPN determined by TGA: (a) untreated IPN; (b) IPN, extracted with xylene; and (c) IPN extracted and irradiated at 800 kGy).

3. Results and discussion

3.1. Effect of the irradiation on the thermal stability

The process of thermal decomposition of a polymer is influenced by its chain structure. Though the thermal decomposition of PMMA yields almost 100% monomer, the decomposition mechanism may differ depending on the synthesis pathway [7,8]. PMMA prepared by radical polymerisation partially contains unsaturated double bonds at the chain ends due to the termination by disproportionation. Its thermal degradation proceeds in two steps. The first step at about 280°C corresponds to the depolymerisation which is initiated from the unsaturated bonds whereas the second one at about 370°C is caused by the statistical chain scission. PMMA synthesised by anionic polymerisation contains no double bonds at the chain ends and so just the statistical chain scission at about 370°C can be observed [7]. Similar behaviour has been found also for PBMA. The depolymerisation temperature is 260°C and the statistical chain scissoring occurs at about 330 and 360°C. The depolymerisation may be hampered if structural defects along the main chain are present [7].

In our experiments the two-step decomposition was observed by TGA as well for PMMA and PBMA as for their copolymers synthesised radically [4]. The depolymerisation initiated by the double bonds at chain ends at about 270–300°C prevails clearly over the statistical chain scission in the unirradiated samples. The proportion between depolymerisation and chain scission in the thermographs was strikingly changed after the samples were subjected to electron beam irradiation. The chain scission that takes place at higher temperature became dominant, implying that the thermal stability has been raised.

This is consistent with the work of Grassie et al. who raised the thermal stability of PBMA by UV irradiation [7]. Irradiation results in a partial destruction of the unsaturated end groups. Parallel to that other types of defect sites will be created along the polymer chains that hamper the depolymerisation. They include grafting or crosslinking points and other structural changes formed by the active species such as free radicals, cations and anions arising from the irradiation.

In contrast to the behaviour of the PMAs, the irradiation seems to have almost no influence on the thermal stability of pure PE. At medium irradiation doses is only a small shift in the onset temperature of the weight loss and the weight loss maximum (about 475°C) visible (about 400 kGy) while higher irradiation doses (800 kGy) show a slight stabilising effect due to crosslinking. In our previous work we found that the thermal stability of PE/BMA-*co*-MMA IPN has been improved by irradiation [4]. From the results above this improvement in thermal stability can be attributed mainly to the contribution of the methacrylate component of the IPN.

The influence of irradiation on the thermal behaviour of the individual components of the PE/PBMA IPN is shown in Fig. 1. Three degradation steps can be seen in the first derivative curves of the weight loss determined by TGA. The peak at about 475°C corresponds to the decomposition of PE, whereas the other two peaks at lower temperatures are caused by the PBMA degradation (depolymerisation at 300°C and chain scission at 380°C). Despite the careful drying before the TGA the small weight loss at about 220°C (Fig. 1a) seems to be caused by the evaporation of monomers and oligomers remaining from the synthesis. These volatile components are completely extractable with xylene (Fig. 1b). In addition, after extraction with xylene the peak of PE decomposition is strongly reduced while those of PBMA remained almost unchanged. This means the extraction removed mainly PE that had not been crosslinked during the IPN synthesis. The remaining decomposition peak can be attributed to PE crosslinking and grafting between PE and PBMA during the synthesis.

The chain scission of PBMA in the range of 380–400°C is clearly pronounced after the IPN was irradiated at 800 kGy (Fig. 1c), comparing to the unirradiated sample (Fig. 1b). The suppression of the depolymerisation of PBMA is assumed to be caused by the defect formation along the PBMA chains due to crosslinking or grafting, like in the case of the homopolymer.

3.2. Irradiation initiated interactions detected by Py-GC-MS

Grafting and crosslinking caused by irradiation will result in defects along the polymethacrylate chains. Thus, the content of linear repeating units of the PMA will be reduced after irradiation. This assumption has been proven by Py-GC-MS. For these studies, the same PE/PBMA IPN as in the TGA has been used.

At the pyrolysis temperature (T_p) of 230°C and 310°C just butyl methacrylate has been detected by GC-MS. At 440°C BMA and decomposition products of PBMA like

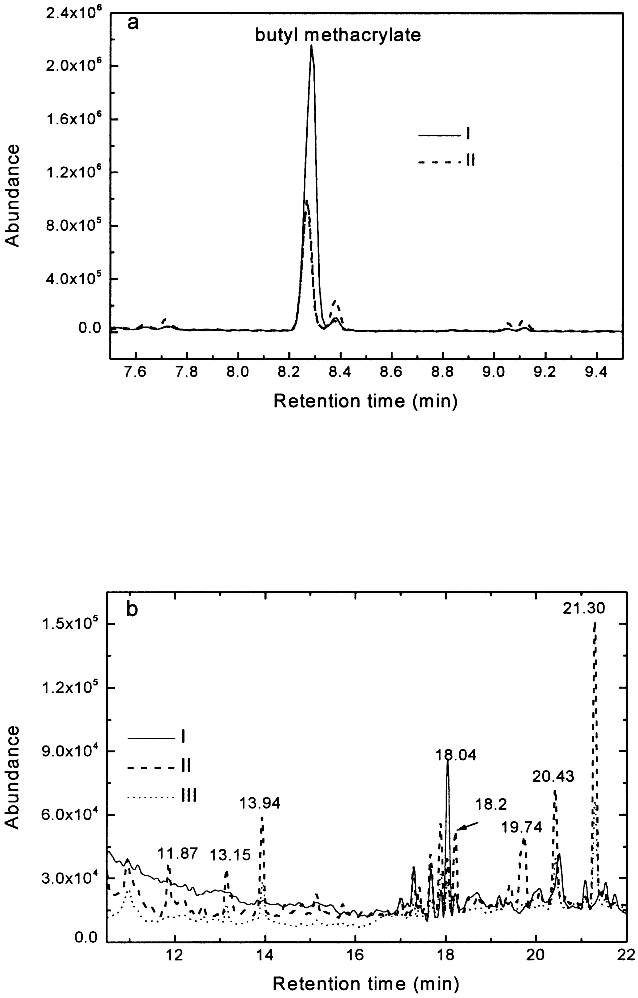


Fig. 2. Pyrolysis-GC-MS of the PE/PBMA IPN ($T_P = 600°C$ (a) or 440°C (b); I: IPN, extracted with xylene; II: IPN extracted and irradiated at 800 kGy; III: IPN extracted, irradiated at 800 kGy, and extracted again with xylene).

methacrylic acid, methyl propane acid and their esters were visible. Additionally, at the pyrolysis temperature of 600°C alkenes of various lengths which are characteristic for the pyrolysis of PE appeared. The BMA visible at 230°C are mainly residual monomers from the synthesis which is in agreement with the small weight loss at this temperature during the TGA. Since the Py-GC-MS was carried out with one sample raising the temperature stepwise from 230 to 600°C the BMA evolution at 600°C must result exclusively from the PBMA decomposition. The content of butyl methacrylate on the chromatograms at $T_P = 600°C$ was clearly lowered after the sample was subjected to irradiation with 800 kGy (Fig. 2a). This means that the content of linear PBMA chains in the IPN had been reduced by irradiation, implying structural changes of the repeating units.

The intensities of some fragments marked with their retention time in Fig. 2b ($T_p = 440°C$) have been raised or even are caused due to irradiation at the expense of butyl methacrylate, indicating the formation of new structural units. Some of them are not visible when the IPN was extracted again with xylene after irradiation while some other are not extractable. Obviously some interactions between chains of PE and PBMA have been taken place during irradiation.

3.3. Irradiation initiated structural changes detected by FTIR

Electron radiation causes a number of reactions in polymer materials. Besides crosslinking some kinds of break reactions like scissions of backbone chain and break reactions of pendant groups occur which leads to the generation of new structures [2]. To detect such changes the two IPN systems PE/BMA-*co*-MMA and PE/DMA-*co*-EMA have been used which differ in the structure of the side chains and therefore in the irradiation behaviour [5].

Samples of the same thickness were irradiated with 200, 400, 600 and 800 kGy, respectively, and transmission FTIR spectra were made. An increase in the intensity with raising irradiation dose was observed in the differential spectra for both IPN systems at 905, 3076, 3286 and 3535 cm^{-1} (Figs. 3 and 4). The generation of C=C was evident by the deformation vibration of unsaturated C–H at 905 cm^{-1}, which was supported by the stretching vibration at 3076 cm^{-1}. The absorption bands at 3286 and 3535 cm^{-1} (stretching vibration) indicate the generation of two different types of hydroxyl groups, which was observed for irradiated PMMA by Rück et al. just as a wide band in the range of 3000–3600 cm^{-1} [9].

Conversely, a decrease of the intensities in dependence on the radiation dose was obtained for the absorptions at 719 and 730 cm^{-1}.The doublet at 719 and 730 cm^{-1} is caused by the rocking vibration of linear $(CH_2)_n$ segments ($n \geq 5$) [10]. The intensity ratio of 730/719 cm^{-1} is proportional to the ratio of crystalline to amorphous amounts. Though it was difficult to estimate the changes in the absorption ratio, the decreased intensity implies the decrease of the content of $(CH_2)_n$-segments with n larger 5, caused by PE crosslinking and PE-PMA grafting reactions. In addition, reactions in the DMA side chain will reduce the intensity in the DMA containing IPN.

In the sample PE/DMA-*co*-EMA, a loss in the intensity of the absorption band at 749 cm^{-1} with raising irradiation dose could be detected. The absorption band is attributed to backbone vibration of PMAs and influenced by the deformation vibration of C–H on the backbone [11]. This decreasing tendency indicates the scissoring mechanism in the backbone of PMAs.

3.4. Composition change at irradiated surfaces

FTIR-ATR is a method frequently used for surface characterisation. In this work, the irradiated surface of PE/BMA-*co*-MMA IPN was studied with FTIR-ATR.

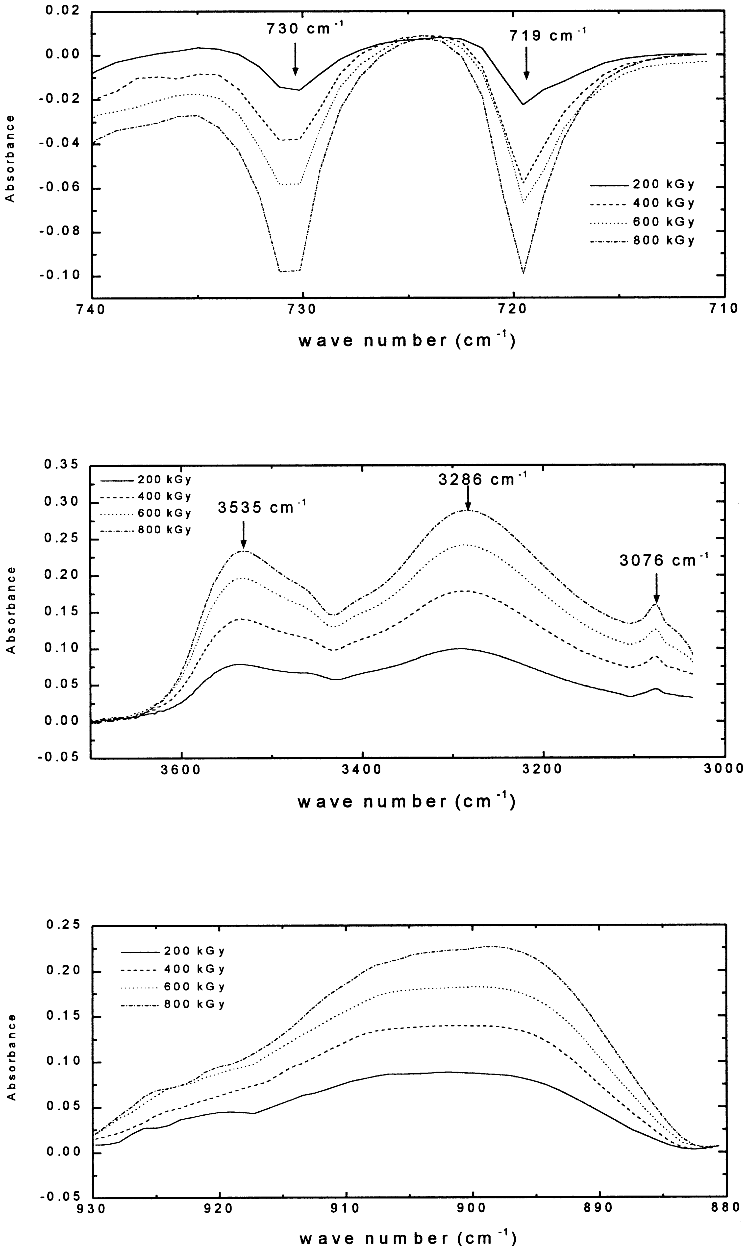


Fig. 3. FTIR differential spectra of the PE/BMA-*co*-MMA (BMA: MMA = 1:1) IPN in dependence on the radiation dose.

New structures at the surface caused by irradiation could not be detected. Differences in the composition are visible only after extraction the irradiated sample with xylene (Fig. 5).

The absorption intensity of PE at 719 cm^{-1} was kept constant as internal standard. The intensities of bands at 1146 and 1725 cm^{-1}, which are characteristic absorptions of carboxyl ester and carbonyl group decreased with raising dose. Obviously, with raising electron irradiation the PMA phase degrades to extractable units while the PE phase crosslinks, changing the composition to higher PE amounts. Due to the changes in the intensity of the absorption at 719 cm^{-1} caused by crosslinking also in pure PE a quantification of the surface composition is not possible. Data of changes in the bulk composition are given in [5].

3.5. Changes in the dynamic-mechanical behaviour by irradiation

PMAs have two characteristic relaxations. One is called the α-relaxation of the glass transition and the other less pronounced relaxation relates to the movement of the pendant ester groups and is known as β-relaxation [12]. The glass transition of PMAs shifts to lower temperature with increased length of their ester groups. The two transitions of PMMA can be easily distinguished while those of PBMA lie closely with each other.

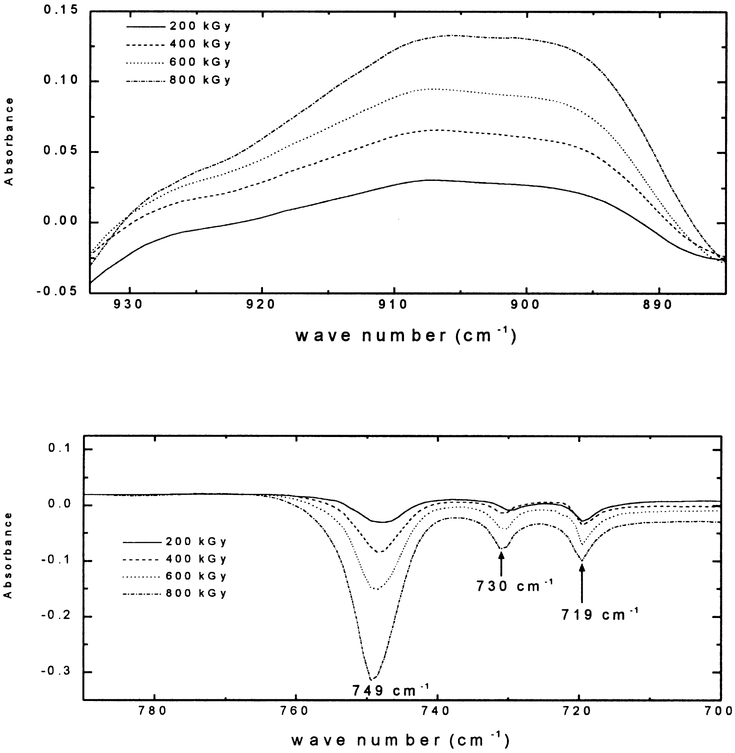


Fig. 4. FTIR differential spectra of the PE/DMA-*co*-EMA IPN in dependence on the radiation dose.

The store and lost moduli of the PE/BMA-*co*-MMA IPN seems to be not influenced by the irradiation (Fig. 6). However, the peak temperature of the α-relaxation (~50°C) was lowered with increased irradiation dose. This can be attributed to the lowering of molecular weight caused by the electron irradiation. In addition, the degraded polymer segments act as plasticiser and also lower the glass temperature. The β-relaxation (~0°C) shifted also to lower temperature, meaning the side groups became more flexible due to irradiation.

The dependency of the dynamic-mechanical behaviour of PE/DMA-*co*-EMA on the irradiation dose is quite different from that of the PE/BMA-*co*-MMA system (Fig. 7). The glass transition temperature (T_g) was raised at doses to 400 kGy. At higher doses the T_g was lowered again and at 800 kGy it reached approximately the value of unirradiated

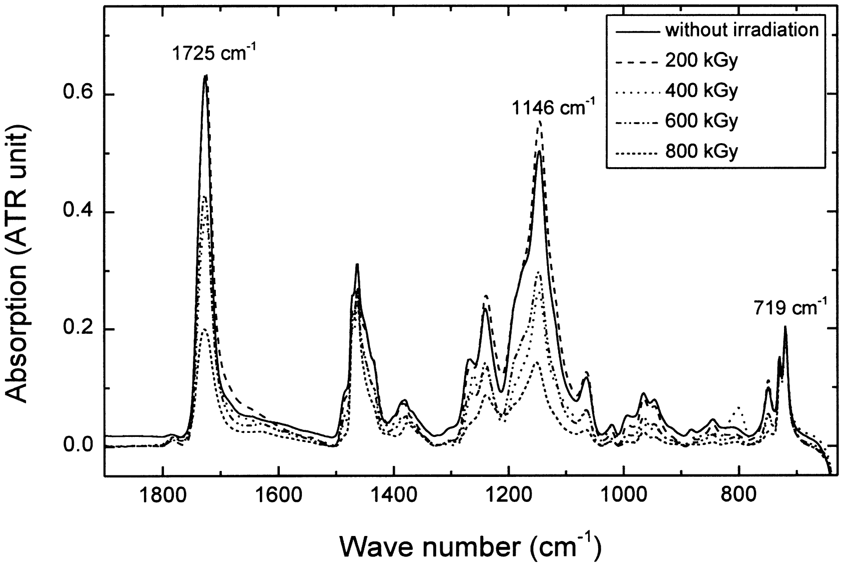
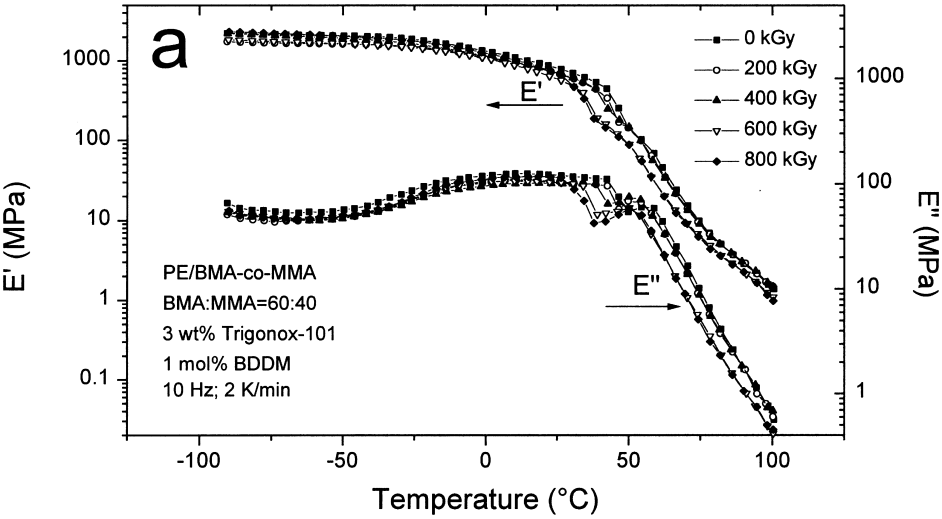


Fig. 5. FTIR-ATR spectra of the PE/BMA-*co*-MMA IPN (BMA: MMA = 1:1) in dependence on the radiation dose.



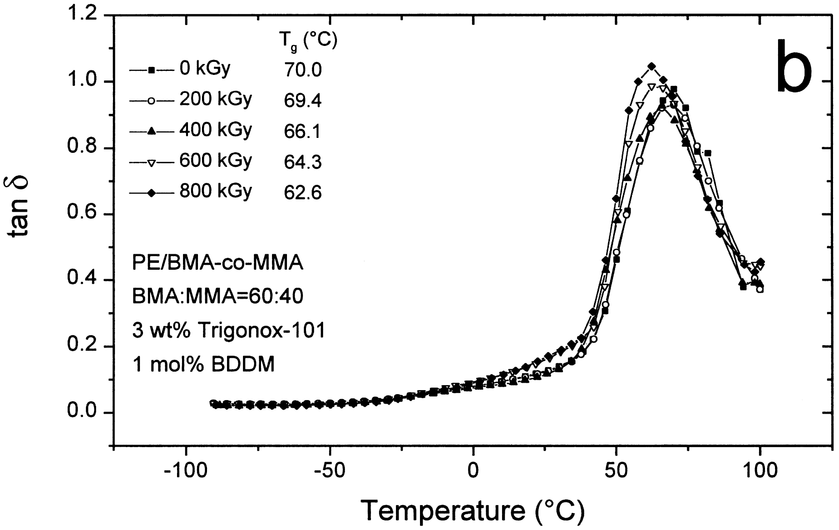


Fig. 6. Dynamic-mechanical properties of PE/BMA-*co*-MMA IPN.

sample. In contrast to the PE/BMA-*co*-MMA the PE/DMA-*co*-EMA contains relatively long ester side groups. It is assumed that at first the irradiation causes crosslinking of these long pendant ester groups raising the T_g. At high irradiation doses, the effect of chain scission in the backbone prevailed and the T_g was lowered again. As will be described below, this is in agreement with the tensile test.

The two relaxations behave similar to each other. The glass transition temperature and the mobility of the side groups correlate with each other. The shifting of the β-relaxation at medium irradiation doses to higher temperature means that the mobility of the pendant ester groups was hampered, which implies crosslinking of the side groups due to the irradiation.

3.6. Influence of the irradiation on the tensile strength

If electron irradiation leads to a decrease in molecular weight of polymers the strength of the material will be lowered. If the radiation causes crosslinking in the material, the strength of the material will be raised. For example, PMMA becomes brittle under the influence of irradiation [13]. Since the tensile strength of PE is mostly dependent on its crystallinity, it will be raised due to the crosslinking of PE by irradiation if PE is irradiated at temperatures below its melting temperature [13].

Fig. 8 shows the different affects of electron irradiation on the different IPN systems. It is well known that the radiation

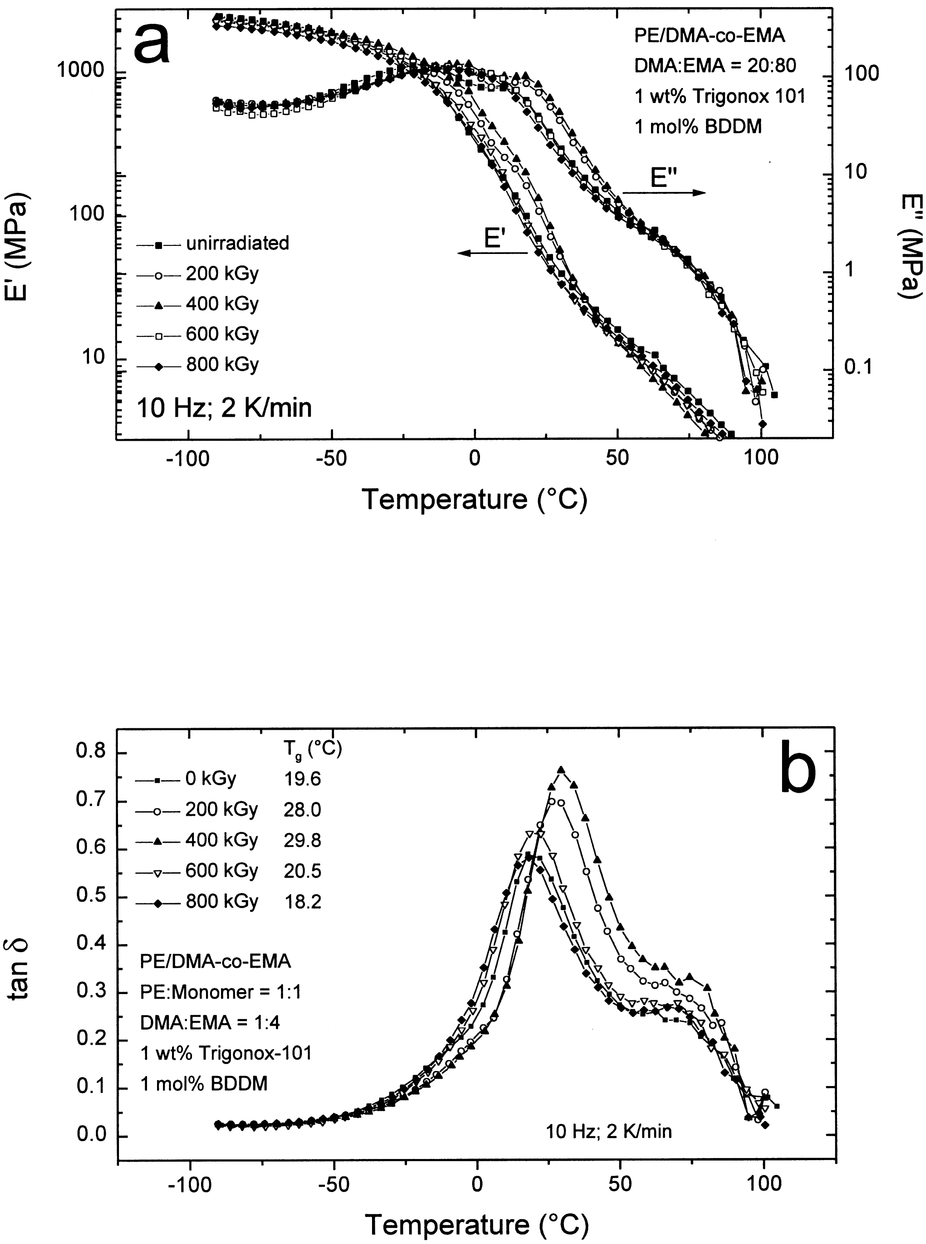


Fig. 7. Dynamic-mechanical properties of PE/DMA-*co*-EMA IPN.

degradation of PMA relates to the length of the alkyl group of the ester side groups [2]. Accordingly, the PMA phase in the PE/BMA-*co*-MMA IPN will degrade and the tensile strength of the IPN decreases with higher irradiation dose (Fig. 8).

In the PE/DMA-*co*-EMA IPN 20 mol% of its PMAs phase is poly(dodecyl methacrylate). Both, chain scission of the main chains and molecular weight increase due to crosslinking in the long aliphatic side groups can take place during irradiation. The combined influences of chain scission and crosslinking led to a maximum in tensile strength at the medium irradiation dose while at higher doses the degradation becomes dominant and the strength reduces.

4. Conclusions

It has been demonstrated that the thermal stability of IPN composed of PE and PMAs can be improved by electron beam irradiation. This is mainly attributed to blocking of the depolymerisation mechanism due to structural changes of the polymethacrylate backbones during the irradiation.

The generation of new chemical structures, crosslinking, grafting and degradation reactions caused by electron beam irradiation have been observed. The degree of the occurrence of these reactions due to irradiation depends on the chemical structure of the IPN. Therefore, also the mechanical properties of the different IPN are influenced differently by electron beam irradiation.

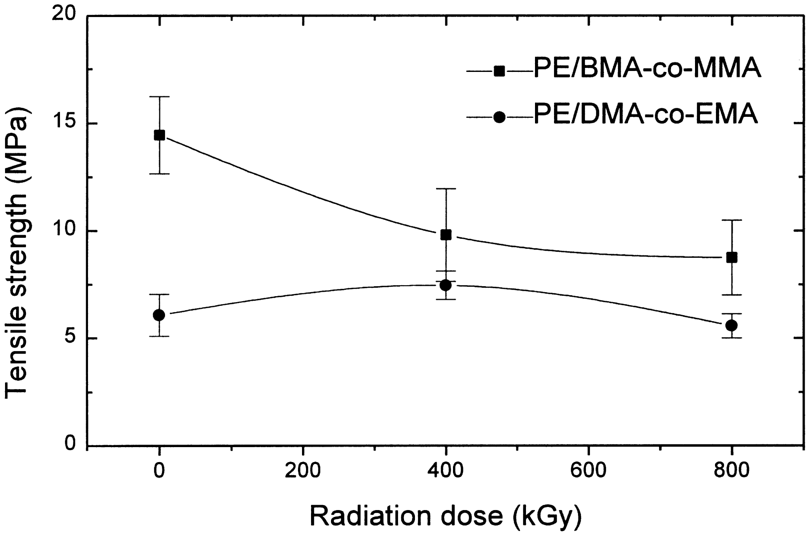


Fig. 8. Tensile strength of PE/DMA-*co*-EMA and PE/BMA-*co*-MMA IPN (BMA: MMA = 1: 1) in dependence on the radiation dose.

Acknowledgements

We are grateful for the financial support by the Sächsisches Ministerium für Wissenschaft und Kunst (project no. 4-7531.50-02-IPF/605) and by the Max-Buchner-Forschungsstiftung (MBFSt-Kennziffer 2031).

References

[1] Dole M. The radiation chemistry of macromolecules, vol. 2. New York: Academic Press, 1973.
[2] Kaindl K, Graul EH. Strahlenchemie. Hüthing: Heidelberg, 1967.
[3] Hu J, Schulze U, Pionteck J, Borsig E. J Macromol Sci, Pure Appl Chem 1998;A35:1285.
[4] Hu J, Pompe G, Schulze U, Pionteck J. Polym Adv Technol 1998;9:746.
[5] Hu J, Schulze U, Pionteck J. Polymer 1999;40:5279.
[6] Mark HF, Bikales NM, Overberger CG. 2nd Ed. Encyclopedia of polymer science and engineering, 4. 1986. p. 418.
[7] Grassie N, Scotney A, Mackinnon L. J Polym Sci: Polym Chem Ed 1977;15:251.
[8] Booth C, Price C. Comprehensive polymer science, vol 2. Oxford: Pergamon Press, 1989. p. 458.
[9] Rück DM, Schulz J, Deusch N. Nucl Instrum Meth Phys Res 1997;B131:149.
[10] Hendus H, Schnell G. Kunststoffe 1961;51:69.
[11] Schneider B, Stokr J, Schmidt P, Mihailov M, Dirlikov S, Peeva N. Polymer 1979;20:705.
[12] Booth C, Price C. Comprehensive polymer science, vol 2. Oxford: Pergamon Press, 1989. p. 556.
[13] Kudoh H, Sasuga T, Seguchi T. Radiat Phys Chem 1996;48:545.