Electron Beam Curing of Methacrylated Gelatin. I. Dependence of the Degree of Crosslinking on the Irradiation Dose

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ABSTRACT: Gelatin was chemically modified with different amounts of glycidyl methacrylate. The methacrylated gelatins were crosslinked by electron irradiation. The resulting solid polymer-like coatings were analytically characterized with respect to the content of residual double bonds and the amount of extractables. The dose dependence of these features was studied using FT-Raman spectroscopy and HPLC. The degree of cure was found to be strongly dependent on the water content in the coating during the curing process. EPR investigations confirmed a significantly lower radical concentration in wet cured films. Additionally, the amount of gaseous and volatile products generated during electron beam irradiation of the samples was analyzed by GC, ion chromatography, and GC/MS. The results indicate that radiolytic decomposition of the gelatin derivatives during electron beam curing is of minor importance. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1303–1312, 1997

Key words: methacrylated gelatin; electron beam curing; dose dependence of the crosslinking behavior; electron-induced side reactions; analytical characterization

INTRODUCTION

In recent years there has been an increasing interest in the development of biodegradable polymers for specialized applications such as drug-delivery systems or surgical implant materials.[1–3] Another important application of degradable plastics will be their use in packaging materials which can be disposed of after use in an economically and ecologically acceptable way. The chemical modification of natural polymers such as polysaccharides and proteins is a promising way for the development of such materials using the inherent biodegradability of the base products.

Gelatin is one of the most versatile natural products known. It consists of a mixture of water-soluble polypeptides of very high average molecular weight. Gelatin is derived from collagenous materials such as pig skin, cattle hide, and cattle bone by controlled acid or alkaline hydrolysis.

Gelatin possesses an interesting property profile. Due to the combination of gelling properties and high surface activity, it is capable of stabilizing suspensions of immiscible mixtures of liquids and solids or different liquids. In dilute aqueous solutions, it forms elastic gels. If the solutions are even more diluted, gelatin acts as a polyelectrolyte and can flocculate suspended particles. Upon casting the solution on a suitable substrate, gelatin shows excellent film forming properties.

Gelatin both in its native or modified form is used in a wide variety of different applications. A large proportion of gelatin is used as an ingredient in the food industry. Other important applications are in pharmaceutical and photographic industries and as a protective colloid used to stabilize suspensions.

Due to the unique properties and the wide-

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spread potential of practical applications of gelatin, the modification of gelatin has been attracting interest with the objective of improving or modifying its properties and to develop new materials combining the desirable properties of both natural and synthetic polymers. Gelatin chains carry various functional groups such as hydroxy, carboxylic, and amino groups along the chain. The number and the variety of these reactive sites open up a large field of potential reagents. Several authors reported on the graft copolymerization of gelatin with acrylates and methacrylates.[4–8] Kaur et al.[9] studied the grafting of acrylonitrile and methacrylonitrile onto gelatin using γ-radiation as the source of initiation.

An alternative way for the modification of gelatin was described by Koepff, Bräumer, and Babel.[10] Glycidyl methacrylate was used for the functionalization of the reactive side groups of the peptide backbone chain with C=C double bonds. In this way, the gelatin becomes crosslinkable, offering the possibility for the development of novel materials with quite unconventional properties. In the present paper, crosslinking of methacrylated gelatin derivatives was performed by electron beam curing, which has been proven to be a very efficient technique for the crosslinking of acrylates and methacrylates.[11–14] Alternatively, the coatings can also be cured by UV irradiation if a suitable photoinitiator soluble in water is used. However, UV curing will not be considered in this paper.

EXPERIMENTAL

Materials

Gelatins extracted from acid-processed pig skin (type A) or from alkali-treated cattle hide (type B) were modified with glycidyl methacrylate (GMA). Gelatin samples with a Bloom value of approximately 280 and a number-average molecular weight of 1.2×10^5 g/mol (GPC) prior to modification were used. Gels at a concentration of 20% were prepared with derivatization degrees ranging from 7 to 45 mmol GMA per 100 g of gel. After the modification procedure, an average molecular weight of about 1.1×10^5 g/mol was determined. The derivatization process is described in detail in ref. 10. The gelatin derivatives were kindly supplied by Dr. W. Babel (Deutsche Gelatine-Fabriken Stoess AG, Eberbach, Germany).

Sample Preparation

Film samples were prepared by melting the gels at 50°C. The solutions were coated on a polyethylene carrier film using a SIMEX AF 1 coating machine equipped with drawing bars. The thickness of the wet films was 200 μm. The samples were crosslinked either immediately following the coating procedure or after drying for 24 h at room temperature. After irradiation, the gelatin films were peeled off the substrate.

Electron Beam Curing

Electron beam curing was performed at the irradiation facilities at the Institute of Surface Modification. These experimental units are equipped with low energy electron accelerators of the LEA type. The LEA accelerators as well as the complete pilot systems were described elsewhere.[15,16] The accelerators were operated at a high voltage of 180 kV and with an electron current of 15 mA. The oxygen concentration in the irradiation zone was reduced by nitrogen inertization to a residual concentration of less than 200 ppm.

The irradiation dose can be varied by the speed of the conveyor carrying the samples across the exit window of the accelerator. The exact dose absorbed by the samples was determined by radiochromic film dosimeters (Risø National Laboratory, Denmark) irradiated simultaneously.

Analytical Characterization

FTIR Spectroscopy

FTIR-ATR spectra were recorded on a Perkin Elmer 1760 X Fourier transform infrared spectrometer equipped with a Spectra Tech ATR device (45°, ZnSe).

FT-Raman Spectroscopy

The conversion of the methacrylate functionalities in the crosslinked gelatin networks was determined by FT-Raman spectroscopy. The Raman spectra were obtained using a Bruker RFS 100 Fourier transform Raman spectrometer equipped with a 350 mW Nd : YAG laser operating at 1.064 μm. Spectra with 1024 scans were recorded at 2 cm^{-1} resolution. The content of residual double bonds was determined from the intensity of the υ C=C stretching mode at 1640 cm^{-1}. The intensity of this band in the spectra of the unirradiated

film samples was set as 100% value. The peak at 1450 cm^{-1} was used as reference band.

EPR Spectroscopy

EPR spectra were recorded with a Bruker ESP-300 E spectrometer using the standard resonator ER 4102 ST. The field was modulated at 100 kHz, and the microwave power was 1 mW. Measurements were performed at room temperature.

HPLC

Samples were extracted in water at 40°C using an ultrasonic bath. The extracts were directly injected into a Perkin Elmer LC 480 HPLC system equipped with a diode array detector and using a RP 18 column. The calibration was based on the chromatograms of the unirradiated gel. Its water content was taken into consideration.

Gas Chromatography and Ion Chromatography

Gelatin film samples for gas and ion chromatography were cured in a special irradiation cell with a 15 μm titanium foil as the electron beam window. The cell with a volume of 21.5 mL is vacuum tight and was carefully flushed with nitrogen before curing.

Gas chromatography was carried out with a Chrompack Micro GC model CP-2002 P equipped with two thermal conductivity detectors. The separation of H_2, CO, CO_2, and C_1 to C_4 hydrocarbons was performed at 100°C using a 0.25 m Molsieve 5 A and a 0.25 m Haye Sep A column with argon as carrier gas at a flow rate of 2 ml/min.

Ion chromatographic analysis was used to study the formation of ammonia. After bubbling the gas through aqueous sulfuric acid, it was injected into a Metrohm IC 690 ion chromatograph equipped with a conductivity detector and a Super Sep IC Kationen column.

GC/MS

GC/MS measurements were performed on a Fisons Trio 1000 quadrupole MS system fitted to a 8000 series gas chromatograph. Gelatin was analyzed with the GC head space technique. The samples were heated to 100°C for 1 h. Head space analysis was performed using an ANALYT microwave sampler MW-1 equipped with a charcoal type adsorbent trap which is adapted to the inlet system of the GC.

RESULTS AND DISCUSSION

The irradiation of acrylates and methacrylates with electrons having energies between 120 and 300 kV leads to nearly instantaneous curing of the coating by the formation of radicals starting both polymerization and crosslinking. However, apart from these two main reactions, electron-induced side reactions such as chain scission can occur simultaneously leading to radiolytic degradation processes in the polymer network formed.[14] Crosslinking and degradation are competing processes. It depends on the kinetic rate constants of both reactions which process becomes dominant. The rate constants are influenced in a complex manner by factors such as the chemical structure of the polymer, the presence of sensitizing or desensitizing additives, and dose rate effects.[11] Moreover, the ratio of both rate constants depends on the applied irradiation dose. In order to find out the optimum irradiation conditions for both achieving maximum conversion of the methacrylate functionalities and avoiding extensive radiolytic degradation, the dose dependence of the crosslinking process was studied. Additionally, gaseous and volatile products generated during electron beam curing were analyzed.

Dose Dependence of the Degree of Crosslinking

The gelatin derivatives were crosslinked in two different ways: half of the samples were cured in the wet state within 1 min after the coating procedure. The other films were first dried at room temperature for 24 h. Gelatin is hygroscopic, and, therefore, a residual amount of water (approximately 10–12% wt/wt depending on temperature and humidity) remains in the sample. The drying kinetics of methacrylated gelatin coatings at room temperature is shown in Figure 1. After 2 h, the amount of water remaining in the films has reached a constant level, and when the samples are irradiated 24 h after coating, the moisture content is at equilibrium.

After electron beam curing, the gelatin films were peeled off the polyethylene substrate. Before the analytical characterization, they were stored for at least 1 day in order to allow the postradiative processes to occur.

Usually, FTIR spectroscopy in combination with the ATR technique is the most efficient way to determine the conversion of double bonds in coatings based on acrylates or methacrylates.[17,18] Accordingly, FTIR/ATR spectra of irradiated gel-

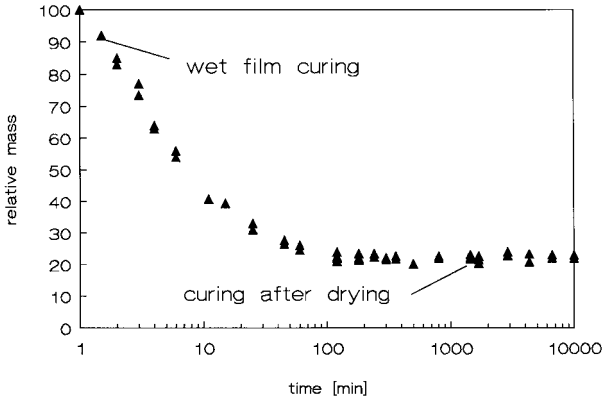


Figure 1 Drying behavior of methacrylated gelatin at room temperature.

atin films were recorded in order to study the dose dependence of the degree of cure. The spectra of cured and uncured methacrylated gelatin are plotted in Figure 2. Surprisingly, the spectra of both films are almost identical (moreover, they show the same spectrum as pure gelatin), and no differences can be observed around 1640 cm^{-1}, where the characteristic peak for double bonds is expected. The considerable intensity of the amide bands in the 1580–1730 cm^{-1} region completely covers the weak band of the methacrylic functionalities. Another very weak peak of the C=C bonds at about 810 cm^{-1} is masked by the decreasing transparency of the ATR crystal in this region of the spectrum. Consequently, IR spectroscopy is not a suitable method for the characterization of the curing process in the gelatin derivatives.

Raman spectroscopy is much more sensitive to

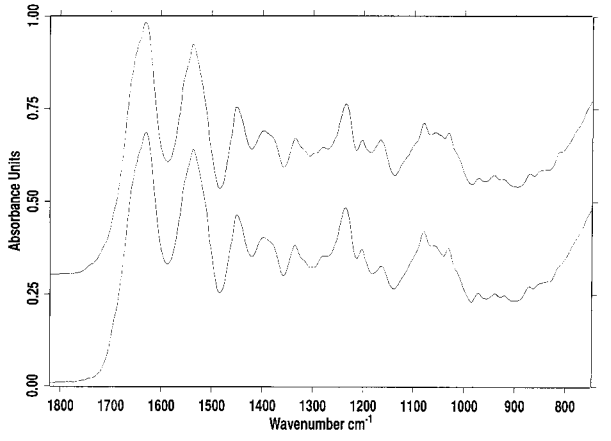


Figure 2 FTIR/ATR spectra of methacrylated gelatin (gelatin type A; degree of derivatization 45 mmol GMA per 100 g gel; top: uncured sample, bottom: cured with 40 kGy).

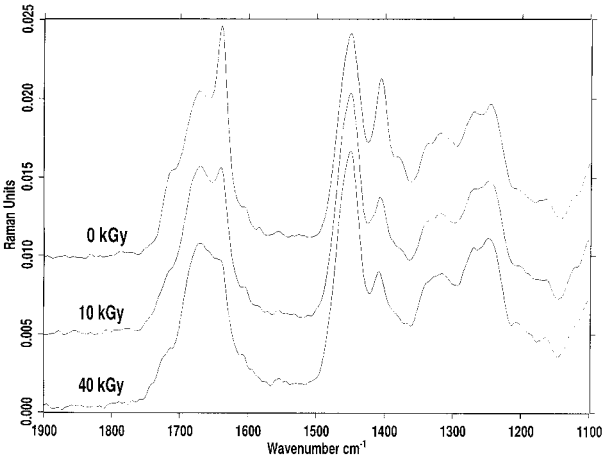


Figure 3 FT-Raman spectra of methacrylated gelatin (gelatin type A, modified with 45 mmol GMA per 100 g gel; uncured or irradiated with 10 or 40 kGy, respectively).

C=C double bonds. Accordingly, FT-Raman spectra of the gelatin derivatives were recorded. However, gelatin is a very poor Raman scatterer. Therefore, the film samples were folded several times, and 1024 scans had to be collected in order to achieve a sufficient signal-to-noise ratio. In Figure 3, the FT-Raman spectra of gelatin methacrylate irradiated with 10 or 40 kGy, respectively, are plotted together with the spectrum of an uncrosslinked sample. Two peaks being assigned to double bonds can be clearly identified in the spectra (at 1420 and 1640 cm^{-1}). The conversion of the methacrylate functionalities in the crosslinked gelatin networks was determined from the intensity of the ν C=C stretching mode at 1640 cm^{-1}. Before integration of the peak area, the spectrum of unmodified gelatin (either type A or B, depending on the derivative) was subtracted. The content of residual double bonds as a function of the absorbed irradiation dose is shown in Figures 4 and 5.

The dose dependence of the degree of cure of the methacrylated gelatins resembles that of many other acrylates or methacrylates.[18–20] The methacrylate conversion in the dry coatings reaches its maximum value already at doses of about 30 kGy. At larger irradiation doses, almost no additional cure occurs. Different derivatization degrees of the gelatin also do not influence the curing behavior.

Gelatin derivatives with the same degree of modification, but based on different gelatin raw materials, i.e., pig skin or cattle hide, show a similar dependence on the irradiation dose (see Fig.

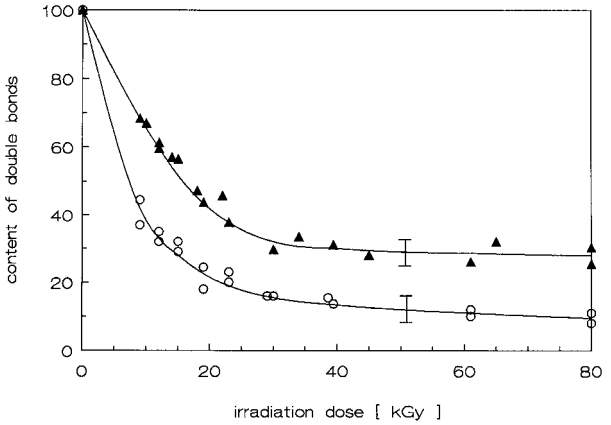


Figure 4 Dose dependence of the methacrylate conversion as determined by FT-Raman spectroscopy (degree of derivatization 45 mmol GMA per 100 g gel; ○, gelatin type A; ▲, gelatin type B; irradiation of the dried films).

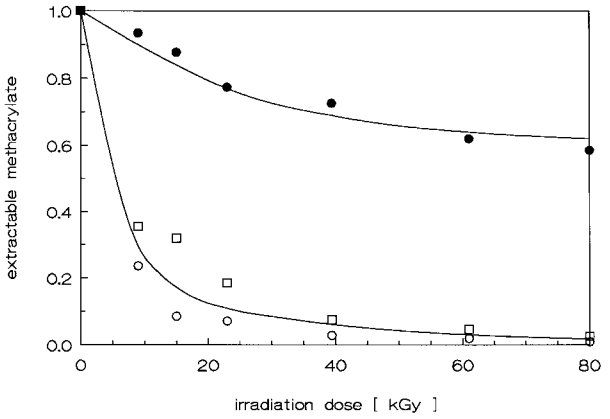


Figure 6 Dose dependence of the quantity of extractable methacrylate as determined by HPLC (□, 20 mmol, irradiation of the dried film; ○/●, 45 mmol, irradiation of the dried or the wet film, respectively).

4). However, the absolute conversions in both types of modified gelatin differ considerably. This rather unexpected result was verified using several gelatin batches of both types, each with the same degree of derivatization. The difference between the two curves was clearly confirmed. The electron-induced radical formation rate in both types of gelatin was found to be identical as determined by EPR spectroscopy. This reflects the equal degree of substitution with glycidyl methacrylate.

Gelatins derived from pig skin and cattle hide slightly differ with respect to the relative amounts of amino acids. Moreover, they show some differences in the molecular weight distribution and the primary protein structure. Gelatin is an ampholytic material containing hydroxyl, carboxyl, and amine groups. Their relative amounts substantially influence its behavior. Gelatin of type B is produced by alkali treatment of collagen. This results in the partial hydrolysis of the amide groups of glutamine and asparagine and the formation of additional acid groups.[21,22] The mildly acidic pretreatment of pig skin collagen removes only very few amide groups instead of almost complete conversion during alkali processing of cattle hide. These differences in the chemical composition obviously influence the molecular charge conditions. It might be assumed that these changes could influence the curing behavior of the type B gelatin, e.g., by inhibition of the free-radical polymerization and crosslinking processes. However, further investigation of this topic is necessary.

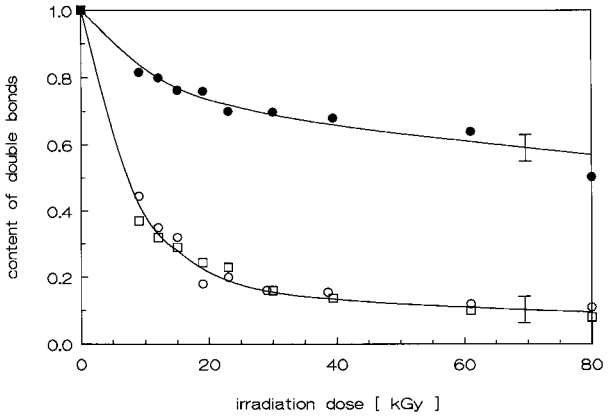


Figure 5 Content of residual methacrylate double bonds as determined by FT-Raman spectroscopy as a function of the irradiation dose (gelatin type A: □, 20 mmol, irradiation of the dried film; ○/●, 45 mmol, irradiation of the dried or the wet film, respectively).

Another significant influence on the degree of cure can be seen in Figure 5. The conversion of methacrylic double bonds strongly depends on the water content in the gelatin coatings during electron irradiation. In the wet cured samples, the degree of cure is considerably lower than in the dried films. Methacrylate conversion does not exceed approximately 40–50% even at doses up to 80 kGy.

Due to the low conversion, it is obvious that large amounts of nonreacted methacrylate remain in the films. For quantification, the amount of extractables from the cured films was determined by HPLC. In Figure 6, the fraction of methacrylate functionalities extractable from the electron beam

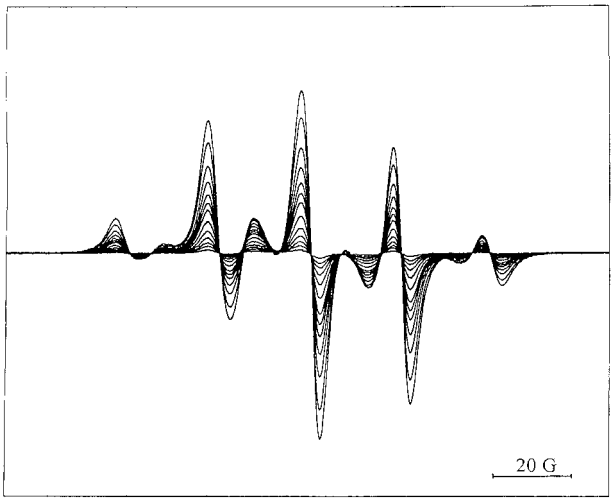
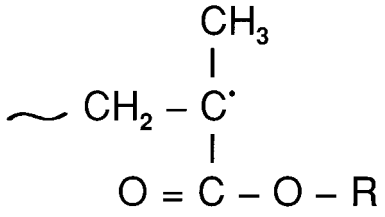


Figure 7 EPR spectrum of methacrylated gelatin recorded as a function of the time after irradiation with 50 kGy (gelatin type A; degree of derivatization 28 mmol GMA per 100 g gel; irradiation of the dried film).

cured networks is plotted as a function of the absorbed irradiation dose. It can be seen that the HPLC measurements clearly reflect the results found by FT-Raman spectroscopy. Both methods lead to similar dose dependence curves. The conversion derived from extraction appears to be a little bit higher. This is caused by the fact that the spectroscopic method also includes the pendant double bonds, whereas this is not the case for the extraction method. However, the different behavior of wet and dry cured gelatin is clearly confirmed by HPLC. Nearly 60% nonreacted methacrylate is extractable from the samples which were irradiated immediately after coating.

In order to study the different crosslinking behavior of wet and dry cured methacrylated gelatin, EPR spectra of both films were recorded. After irradiation with 50 kGy, samples were rapidly transferred into the EPR sample tube and measured at room temperature. In Figure 7, a series of EPR spectra recorded consecutively as a function of the time elapsed is plotted. The observed nine-line spectrum of the radicals formed during electron beam curing is identical with those found in other methacrylates after UV, β-, or γ-irradiation. It can be attributed to the propagating chain radical shown in Scheme 1.[23] The EPR pattern can be simulated by a superposition of the spectra due to two stable conformations.[24,25]

In Figure 8, the decay of the spin concentration in the methacrylated gelatins calculated from the spectra shown in Figure 7 is plotted versus time



Scheme 1

after irradiation. The radical concentrations in both samples which were irradiated after the two drying procedures differ considerably. The spin concentration in the samples which were irradiated immediately after coating is nearly one order of magnitude lower than that in the dried films. This observation can be explained by the radiation-induced formation of water radiolysis products such as hydroxyl radicals, which terminate the crosslinking process in the wet gelatin films.

Despite the different absolute concentration of spins, the decay of the radical content in both gelatin films was completed after similar periods of time. This indicates that the crosslinking mechanism remains unchanged.

Moreover, EPR spectroscopy gives some information regarding the postcuring behavior of the crosslinked gelatin derivatives at room temperature. The curves shown in Figure 8 demonstrate

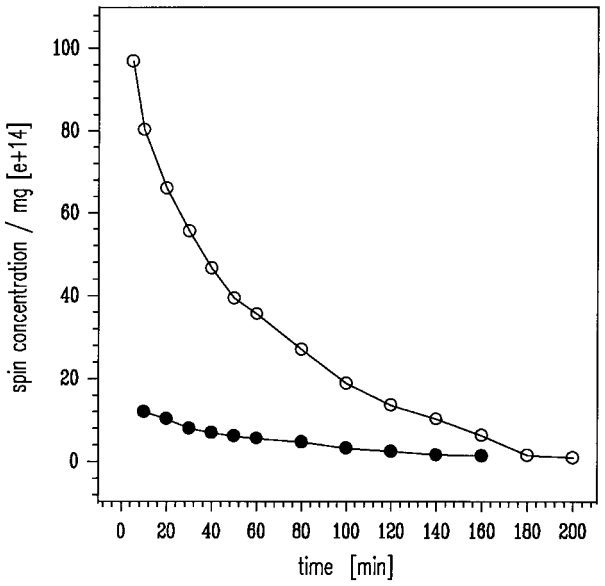


Figure 8 Decay of the radical concentration in methacrylated gelatin after irradiation of a wet (●) and a dried (○) film with 50 kGy, studied by EPR spectroscopy (degree of derivatization 28 mmol GMA per 100 g gel).

Table I Amount of Released Gaseous Degradation Products and G Values for Their Formation

	Hydrogen		Carbon Dioxide		Ammonia	
Dose	Yield	G	Yield	G	Yield	G
(kGy)	(mg/kg)	(10^{-7} mol J^{-1})	(mg/kg)	(10^{-7} mol J^{-1})	(mg/kg)	(10^{-7} mol J^{-1})
10	3.3	1.64	15.3	0.35	0.21	0.012
40	12.7	1.59	61.5	0.34	0.83	0.012
100	29.6	1.48	158.3	0.34	2.1	0.012
400	117.5	1.47	597.1	0.33	7.4	0.010

that the postradiative curing processes in the methacrylated gelatins have been finished approximately 3 h after irradiation of the samples.

Radiation-Induced Degradation

Electron beam curing of acrylates and methacrylates can be accompanied by destructive side reactions.[19] Therefore, in addition to the investigation of the dose dependence of the degree of cure, gaseous and volatile products generated during electron irradiation of the gelatin derivatives were studied in order to characterize the extent of radiolytic degradation effects.

Gaseous radiolysis products were identified and quantitatively analyzed by gas and ion chromatography. Methacrylated gelatin of type A with a degree of derivatization of 45 mmol GMA/100 g gel was irradiated with doses in the range from 10 to 400 kGy. The main degradation products released from the gelatin films are hydrogen, carbon dioxide, and ammonia. Moreover, traces of carbon monoxide, methane, and ethane are detectable. Results from the quantitative analysis of the main products are summarized in Table I. Besides the absolute quantities of released gases, the *G* values for their formation are given. The *G* value characterizes the yield of radiation-induced chemical reactions. It is defined as the amount of formed or changed species per 1 Joule of absorbed radiation energy.[11]

The yield of gaseous products increases with increasing irradiation dose. The *G* values for the formation of H_2 and CO_2 are a little bit higher than the corresponding values for electron beam cured acrylates and methacrylates.[19] However, the total amount of gaseous degradation products is small in comparison to the yield of chain starting radicals and crosslink formation.

The *G* value for H_2 release slightly diminishes with increasing dose. H abstraction is the main path for hydrogen formation. However, H radicals can also add to double bonds acting as an internal scavenger or react with various radicals generated during electron irradiation. At higher doses, the concentration of radical sites along the chain should increase due to some scission of side groups. H radicals may add to such radical sites or react with the lower molecular fragments formed. For example, ammonia is formed by the cleavage of amino groups from amino acids. The lower *G* value for hydrogen formation at higher doses is assumed to be due to such side reactions. However, the slight extent of the decrease indicates that these processes are insignificant.

Besides the gaseous degradation products, organic volatiles were identified. GC/MS and GC head space technique were used for the characterization of these substances trapped in the cured gelatin films. They were released from the samples by heating to 100°C. The samples were irradiated with the same doses as during the analysis of the gaseous products. Results are shown in Figures 9 and 10. The spectra are plotted together with the chromatogram of an uncured film. The largest peak in each scan is set at 100%. The relative amount of volatile products is correlated with the total ion current (TIC) of the most intense peak, which is given in the upper right corner of every chromatogram.

In Figure 9, the observed total ion current is plotted. Figure 10 shows the signal at $m/e = 69$, which is the characteristic ratio of the most frequently occurring methacrylate fragment. The most prominent peaks appearing in Figures 9 and 10 and their identification are listed in Table II. Some of these substances were already observed in the nonirradiated sample and were identified as traces of additives and stabilizers. Acetic acid was added to the modified gelatin for pH adjustment. Alcohol was used as solvent for the phenolic

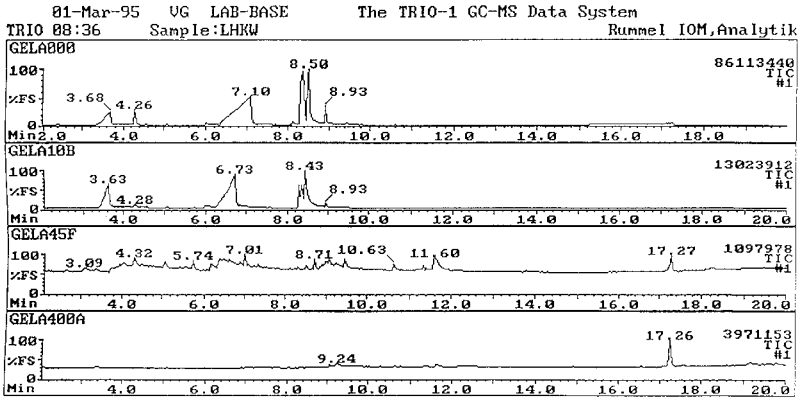


Figure 9 GC/MS analysis (total ion current) of volatile products released from methacrylated gelatin at 100°C after irradiation with 0, 10, 40, and 400 kGy (from top to bottom).

polymerization inhibitor improving storage stability.

With increasing dose, a rapid decrease of the total amount of released products as well as of specific components such as methacrylic acid methyl ester, methacrylic acid, and glycidyl methacrylate was found. These substances were also identified in the uncured film, i.e., they were not formed by radiolysis of the gelatin derivatives but during the derivatization process. During curing, methacrylic acid and glycidyl methacrylate are incorporated into the polymer network. The lower content of acetic acid and alcohol in films irradiated at higher doses should be caused by the partial evaporation during irradiation due to the slight heating of the samples in the electron beam.

The occurrence of higher molecular weight species of methacrylic acid and its derivatives indicates the propagation of the crosslinking process with increasing dose. However, higher oligomers are no longer volatile and cannot be detected with the GC head space technique.

Volatile degradation products formed by radiolysis of the methacrylated gelatin can be observed only at 400 kGy (see Fig. 10). However, the signals of the methacrylate fragments at $\sim$ 12–14 min are very weak despite the extremely high dose absorbed. Note that the total amount of all released products with $m/e = 69$ is only about 1% of that in the unirradiated sample.

The results of chromatographic analyses indicate that radiolytic decomposition of the gelatin derivatives during electron beam curing is of minor importance, at least at the usual doses below 100 kGy. In a preceding paper on radiation-induced degradation processes in electron beam cured acrylates and methacrylates, the formation of various extractables as well as of gaseous and

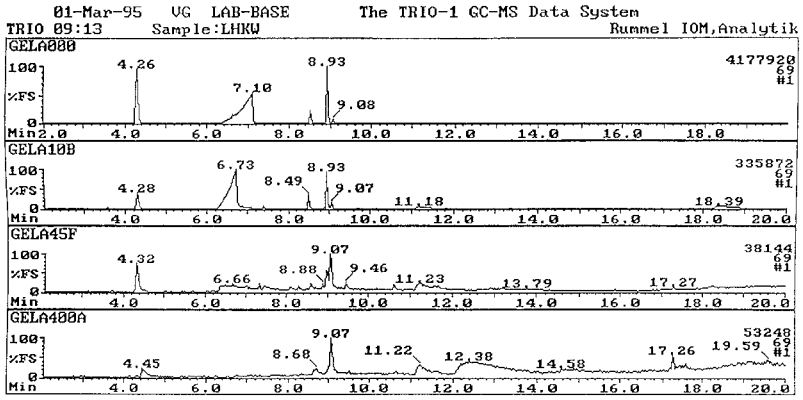


Figure 10 GC/MS signal at $m/e = 69$ of volatiles released from methacrylated gelatin at 100°C (gelatin type A modified with 45 mmol GMA/100 g gel; irradiation dose from top to bottom: 0, 10, 40, and 400 kGy, respectively).

Table II Identification of GC/MS Peaks in Figures 9 and 10

Retention Time (min)	Identification
3.6	Acetic acid
4.3	Methacrylic acid methyl ester
6.7–7.1	Methacrylic acid
8.5	Alcohol
8.9	Glycidyl methacrylate
11.2	Methacrylate fragments
12.4	Methacrylate fragments
17.3	Phenolic polymerization inhibitor
18.4	Methacrylate fragments

volatile radiolysis products was reported.[19] Radiolytic decomposition of the ester group was found to be the main degradation process. However, the total yield of radiolytic degradation products was found to be small. The protein skeleton of the methacrylated gelatins might be somewhat more prone to radiation-induced degradation. Accordingly, further products such as amino acids or peptide fragments could be expected to be formed. These nonvolatile substances are not detectable by the head space method used in the present study. Therefore, the search for such extractable products will be the subject of further investigation.

CONCLUSION

Methacrylated gelatins were crosslinked by electron irradiation, thereby forming solid polymer-like coatings. The dose dependence of the crosslinking behavior was studied with respect to the content of residual double bonds and the amount of extractables using FT-Raman spectroscopy and HPLC. Both analytical methods result in analogous findings. The degree of cure in the gelatin derivatives was found to show a similar dose dependence as synthetic acrylates or methacrylates. It strongly depends on the water content in the coating during electron irradiation. In dry samples, the methacrylate conversion reaches its maximum already at about 30 kGy, and no additional cure is observed at larger irradiation doses. In the wet cured films, the degree of cure is considerably lower. Methacrylate conversion does not exceed ~40–50% even at doses up to 80 kGy. Using EPR spectroscopy, a significantly lower radical concentration was observed in wet films. This is attributed to the occurrence of hydroxyl radicals due to the radiolysis of the water affecting the crosslinking process.

Additionally, gaseous and volatile products generated during electron beam irradiation of the samples were analyzed in order to estimate the extent of radiation-induced side reaction in the curing process. The results indicate that radiolytic degradation of the gelatin derivatives is of minor importance in the dose range relevant for sufficient crosslinking.

The polymer-like gelatin coatings were found to have some remarkable properties.[26] They are resistant against boiling water and show a very low oxygen permeability. In spite of the modification with methacrylate, the electron beam cured gelatin derivatives are completely biodegradable. Results on the characterization of the coatings will be reported in a forthcoming paper.

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