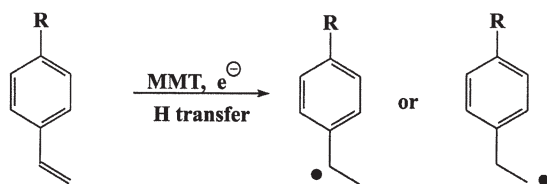


fied MMTs, however their intensity for samples containing B salt is very low. For the modified



IR spectroscopy

Fig.4. Possible mechanism of hydrogen abstraction.

MMT, the band at 2850 cm^{-1} is growing, probably due to interaction of the salts with MMT. Additionally, characteristic bands in the range of $1100\text{-}1400\text{ cm}^{-1}$ (probably C-C and aromatic C=C stretch-

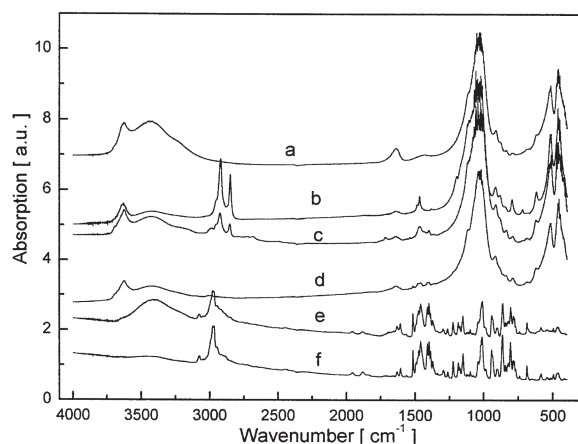


Fig.5. IR spectra of: a – unmodified MMT, b – commercially modified MMT, c – MMT modified with salt A, d – MMT modified with salt B, e – salt B, f – salt A. All samples in the form of KBr pellets.

ing) also appear. In these ranges pure MMT does not absorb, thus identification of the signals is unambiguous. The correlation between IR and diffraction measurements is apparent – low intensity of salt B absorption in the modified MMT results from insignificant intercalation reflected by a small shift in basal spacing measured by the WAXS method.

Thermogravimetric analysis

Although salt A is stable up to 200°C , decomposition of MMT modified with this compound starts at about 170°C (Fig.6). Similar process was confirmed for MMT modified with salt B. On the

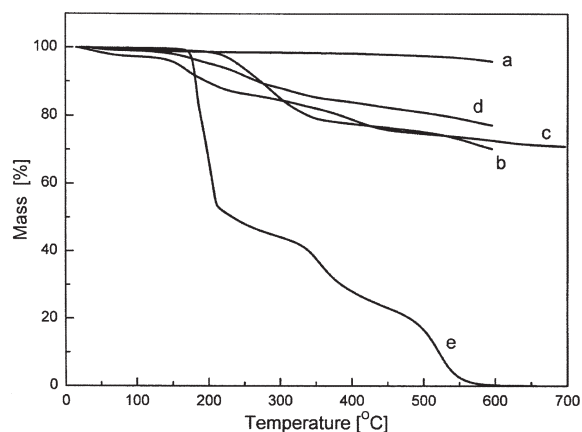


Fig.6. TGA measurements: a – MMT, b – MMT modified with salt A, c – MMT modified with salt B, d – commercially modified MMT, e – salt A.

other hand, commercially modified MMT remains stable up to 230°C . No effect of sample irradiation on the thermal decomposition processes is observed. TGA results also confirm the intercalation of the salts.

Conclusions

We synthesized quaternary ammonium salts containing unsaturated bonds designed for the modification of MMT and forming relatively stable radicals that in mixing process initiate chemical bonds between the filler and polymer matrix.

The prepared ammonium salts probably intercalate into MMT layers, as was found by the WAXS IR methods and TGA.

Mechanism of the radiation-induced processes in the modified MMT, consisting in the transfer of hydrogen atoms from MMT to unsaturated bond and formation of alkyl-type, radical was proposed.

The obtained products can be used as fillers in *in situ* polymerization, polycondensation or hardening of some monomers or resins, but the method of mixing must be improved.

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THE INFLUENCE OF IONIZING RADIATION ON THE THERMAL PROPERTIES OF SEGMENTED POLYURETHANES FOR BIOMEDICAL PURPOSES

Marta Walo, Grażyna Przybytniak

Segmented polyurethanes (PUs) have found application in medicine as biomaterials due to good biocompatibility, hydrolytic and oxidative biostability, excellent mechanical properties and good processibility [1]. Polyurethanes represent a class of synthetic elastomers whose physicochemical properties may be modified by changing the ratio

between soft and hard segments. Therefore, they are commonly used for production of scaffolds in tissue engineering and for manufacturing medical devices, such as vascular grafts, artificial hearts, catheters, mammary implants [2].

The aim of this study was to characterize the influence of ionizing radiation on the thermal

properties of segmented polyurethane, which can be potentially used as a biomaterial for medical applications.

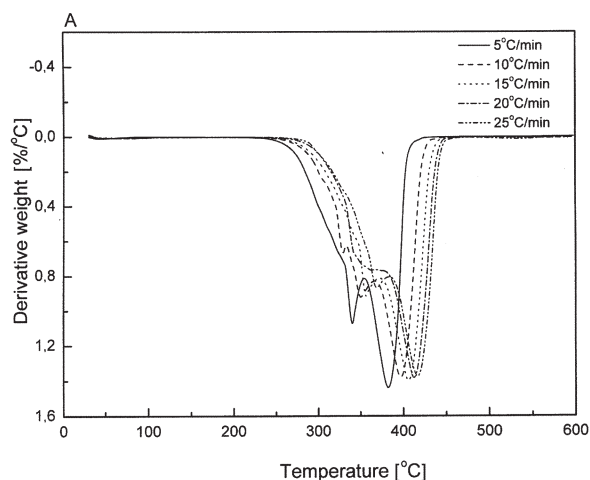
The thermal degradation behavior of neat and electron beam irradiated PU were investigated using two methods, which do not demand a precise knowledge of the reaction mechanism. The activation energy E can be determined by using Kissinger's method (1) and Flynn-Wall-Ozawa's (2) method according to the following equations [3,4]:

$$\ln\left(\frac{q}{T_{\max}^2}\right) = -\frac{E}{RT_{\max}} + \text{const} \quad (1)$$

$$\ln(q) = \ln(f(\alpha)) - \frac{1.05E}{RT_i} \quad (2)$$

where: T_{\max} – the temperature of the maximal rate of decomposition, q – heating rate, T_i – the temperature at which the degree of conversion α is attained.

Segmented polyurethane based on poly(1,4-butylene adipate)diol end-capped by –OH group



ture rises with increasing heating rate. Obtained polyurethane remains thermally stable up to 270°C, and above this temperature the first stage of decomposition is observed. The character of thermograms points out to a multi-stage mechanism of the decomposition. The temperature of maximum mass loss was observed in the range of 383–417°C and 381–415°C, for neat and irradiated polyurethane, respectively. The thermogravimetric analysis showed that the polymer is slightly more stable before than after irradiation with a dose of 112 kGy. It is necessary to stress that an applied dose of 112 kGy is substantially higher than a standard dose used usually for sterilization of medical devices. Therefore, upon exposition to a sterilization dose of about 25 kGy polyurethane undoubtedly preserves thermal stability.

The activation energies obtained using Flynn-Wall-Ozawa's method are shown in Table (Fig.2 (I)). From these data it seems that in the case of irradiated polymer, E decreases with growing degree of conversion, α . The E values decrease from 153 to 117 kJ/mol for 5 and 20% degree of conver-

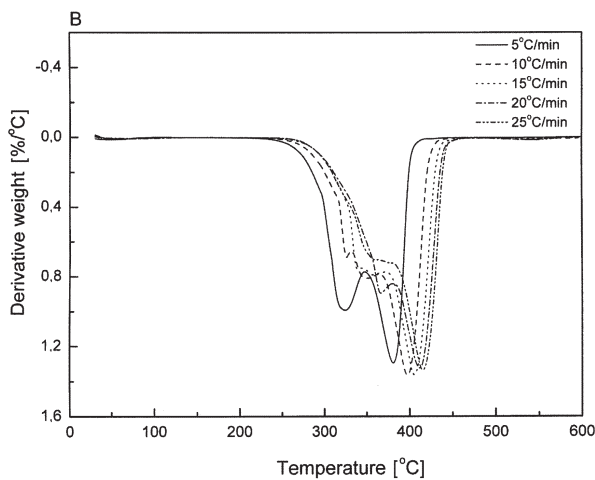


Fig.1. DTG thermograms of PU: (A) before irradiation and (B) after irradiation with a dose of 112 kGy.

(PBA) of molecular weight $MW = 1000$, isophorone diisocyanate (IPDI) and 1,4-butanediol (BDO) were synthesized in bulk by a two-step reaction. The molar ratio of PBA:IPDI:BDO was 1:1.66:0.66. The polycondensation process was carried out without catalyst. The samples used for measurements were irradiated in air with an electron beam in an accelerator Elektronika 10/10 to a dose of 112 kGy. Thermogravimetric analysis (TGA) was performed on TA Instruments (Q500) thermal analyzer under nitrogen atmosphere from 30 to 600°C at various heating rates: 5, 10, 15, 20, 25°C/min. DSC (differential scanning calorimetry) experiments were carried out on a TA Instruments differential scanning calorimeter (MDSC 2920) under nitrogen atmosphere. The samples were scanned at a heating rate of 10°C/min for a temperature range from -100 to 250°C.

Thermal degradation derivatives obtained at various heating rates: 5, 10, 15, 20 and 25°C/min are shown in Fig.1. DTG (derivative thermogravimetry) curves for non-irradiated and irradiated polyurethanes show that the degradation tempera-

tion. For non-irradiated polyurethane, the changes are noticeable smaller and vary in the range of 141–132 kJ/mol. The activation energy was also determined using Kissinger's method, according to equation (1) – Fig.2 (II). The activation energies of 162 and 155 kJ/mol were found for neat and irradiated sample, respectively.

The DSC thermogram of PU for the second cycle of heating is shown in Fig.3. Glass transition

Table. Activation energies of PU obtained from Flynn-Wall-Ozawa's method.

Degree of conversion [%]	Activation energy [kJ/mol]	
	dose	
	0 kGy	112 kGy
5	141	153
10	132	132
15	141	124
20	137	117

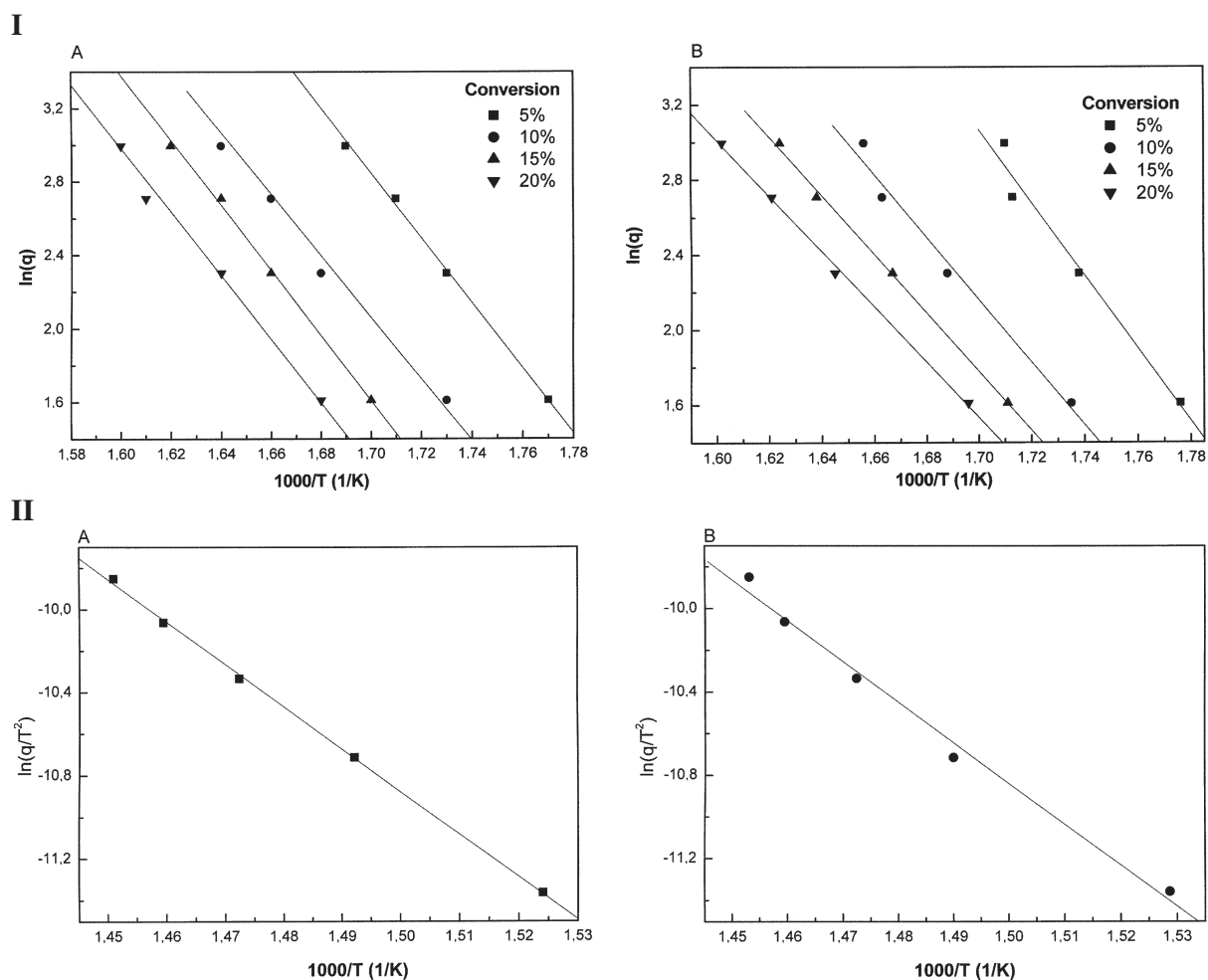


Fig.2. Flynn-Wall-Ozawa's (I) and Kissinger's (II) analysis of the thermal degradation of PU: (A) before irradiation and (B) after irradiation with a dose of 112 kGy.

of the soft segment chains were observed at -31.3 and -32.4°C for neat and irradiated polyurethane, respectively. The endothermic peaks that correspond to the melting phase transition of the hard segment domain were observed at 100.1°C for non-irradiated PU. For PU irradiated with a dose of 112 kGy this temperature is shifted to 111°C . The significant enhancement of the temperature results from crosslinking of polyurethane initiated by ionizing radiation.

Investigation of thermal properties enables to estimate the changes in irradiated polymeric ma-

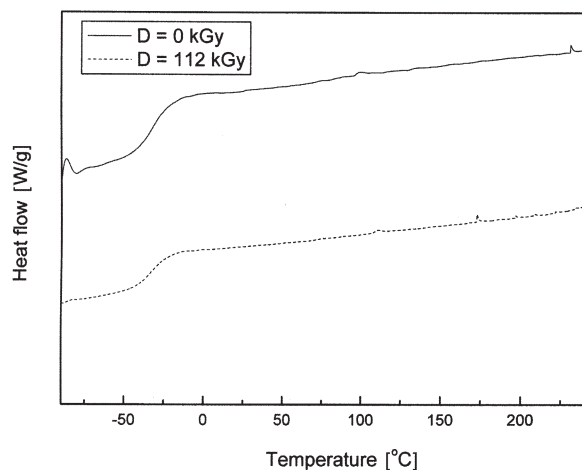


Fig.3. DSC thermogram of PU.

terials. Reduction of activation energy in PU upon exposure to ionizing radiation with degree of conversion might result from oxidative degradation since carbon centered radicals generated by irradiation are usually converted to peroxy radical that is a precursor of many oxygen containing groups. Decay of easily decomposed carbonyl, carboxyl or hydroperoxy groups gives rise to the decrease in onset temperature as well as activation energy. Rate of emission of the volatile substances is in such a case faster, especially during the first stage of decomposition. On the other hand, simultaneously crosslinking of hard segments proceeds as seen from the increase of melting transition temperature for irradiated polyurethane. Thus, two parallel, competitive processes were confirmed, however, their efficiency for a dose of 112 kGy is limited.

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