

# Study on the radiation degradation of polyether-polyurethane induced by electron beam

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Polyether-urethane samples were irradiated at the dose range from 10 to 2000 kGy by 2 MeV electron beams. Volatile species from the polymer degradation were analyzed quantitatively and qualitatively with GC/MS. Thermal properties and micro-phase separation of the samples were examined by TG and the morphology was studied by TEM and SEM. The results show that the irradiated polyether-polyurethane evolves CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>, etc. The thermal stabilities between the hard and soft segments in the irradiated samples are different. At high doses, the phase separation in the sample is predominant and the hard segment of sample is more stable. The dose rate affects the soft segment of the irradiated sample much more.

## Introduction

Urethane as an important polymer in plastic engineering finds wide uses in industries.<sup>1,2</sup> In coating application, on account of its CO content, photo oxidation degradation has been the main concern. According to the report of IRUSTAL et al.,<sup>3</sup> aromatic polyurethane exposed in sun light discolors easily. Non-segmented MDI based polyurethanes show a higher susceptibility to photolysis than their corresponding segmented polyether urethanes. Reference 4 reports the degradation mechanism of polyurethane elastomer irradiated by UV light. The molecular weight of the material has a trend of decline. Moreover, carboxylic acid and p-benzophenone are generated. Mutual stabilization effect between urethane and ether group was fine in segmented polyether urethane. The effect was thought to be related with the physical state of the polyurethane as a material with excellent physical properties and chemical properties<sup>5</sup> such as resistance to oil and chemical corrosion, ability to bear abrasion, avulsion and vibration, excellent elasticity, adhesive property and excellent mechanical property, which makes it a most preferred polymer material used in space technology. However, like long time exposure to space radiation limits its usages. MURPHYA<sup>6</sup> did a study of volatile evoluent induced by energetic He<sup>2+</sup> ions. To simulate  $\alpha$ -radiation in space, polyether based polyurethane was irradiated with He<sup>2+</sup> ions from a particle accelerator. In our former work,<sup>7</sup> the radiation effect of polyether-urethane foam in the gamma-radiation field has been discussed. The most abundant volatile species identified is CO<sub>2</sub>. And the general mechanical properties of polyether-urethane foam irradiated by  $\gamma$ -rays at the dose of 8.0·10<sup>5</sup> Gy is excellent. To investigate the characteristic of polyether-urethane foam irradiated by electron beam, this paper

covers the radiation degradation of polyether-urethane foam under the action of electron beam.

## Experimental

### Materials and sample preparation

Materials are diphenylmethane diisocyanate (MDI), polyether polyol (brand 303) and triethanolmine which are distilled in vacuum. The segmented polyether-urethane foam was synthesized through casting and curing at room temperature at Material Institute of Chemistry and Engineering in China Academy of Engineering Physics. There are no vesicant and other additives in the product. The samples were cut into 2 mm thick disks. After preparation, the samples were dried at 50 °C under vacuum for 24 hours, then stored in the desiccator.

### Irradiation and analysis

Van de Graff accelerator was provided by the Nuclear Institute of Science and Technology in Sichuan University. Its energy is 2 MeV, and the electric current is 0.25 mA. The dose rate is changed through adjusting the electron energy and current, and the voltage alternates. Intermittent radiation is adopted to scatter heat. The dose rate is determined by a thermoluminescence dosimeter, which is calibrated by the standard dosimeter in Shanghai Applied Radiation Institute at Shanghai University.

Volatile products from irradiated samples were collected by the negative pressure device, and analyzed by gas chromatography (HP6890) and mass spectroscopy (Finnigan MAT98 B-E) (GC/MS). The weight-loss ratio of sample was analyzed in nitrogen by thermal gravity analysis instrument (TGA7, Setaram).

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The heating rate is 10 °C/min over a temperature range from room temperature to 750 °C in a nitrogen atmosphere. The sectional porous structure of samples was analyzed by a scanning electron microscope (SEM) (Model S-250MK3). The morphology of polyurethane was observed by a transmission electron microscope (TEM) (Model JEOL.JEM-1200EXII). The sample embedded in epoxy resin is cured at room temperature, then chipped into slices by ultrathin microtome. The slice is dyed by OsO<sub>4</sub> before being observed by TEM.

## Results and discussion

### *The composition and yields of gases from irradiated samples*

The main radiolysis gaseous products evolved in polyurethane are determined by gas chromatography. Comparing with the standard gases, they are H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and so on.

The relationship of gas yields and the absorbed dose are listed in Table 1. It can be seen from Table 1 that the quantity of CO<sub>2</sub> increases with the dose during irradiations up to 1.5·10<sup>6</sup> Gy. The H<sub>2</sub> yield has a trend of raising, while the CH<sub>4</sub> yield rose to a maximum before it decreases to a stable level.

The yields of H<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> from the irradiation of polyurethane with the dose rate are listed in Table 2. It indicates that the CO<sub>2</sub> yield is similar to the H<sub>2</sub> yield. The effect of dose rate on the CH<sub>4</sub> yield is less, and its maximum yield appears at the dose rate of 1.2·10<sup>5</sup> Gy·min<sup>-1</sup>.

### *The thermal analysis of samples after and before irradiation*

Because the soft and hard segments on ETPU chains are thermally compatible, phase separation takes place in its inner part. Irradiated samples were heated up according to the procedure and DTG graphs. There are two maximum peaks on the DTG combination graph (Fig. 1), which shows that the samples go to phase separations at a thermal decomposition peak of 325–335 °C which stands for the phase separation of the hard segment, and at 470–485 °C for the soft segment. The lower temperature peak was stronger than the high temperature peak, and this indicated different thermal stabilities of the soft and hard segments.

The relationship of the peak temperature corresponding to the maximum weight-loss ratio ( $T_{max}$ ) of irradiated samples with the dose and the dose rate are listed in Tables 3 and 4. The result in Table 3 shows that the dose has little effect on the maximum thermal decomposition. The left peak indicates that the hard segment of sample is rather stable after and before irradiation, but the obvious change of the right thermal

decomposition peak proves that the soft segment of sample has lower stability.

From Table 4 it can be seen that the effect of dose rate is not prominent in the thermal decomposition peak temperature of the hard segment when it is irradiated at higher dose rate (>7.5·10<sup>4</sup> Gy/min), but it has some effect at low dose rate: the dose rate affects the soft segment of the irradiated sample much more.

### *The morphology structure change of segmented polyether-urethane foam after and before radiation*

Figure 2 are scanning electron micrographs (SEM) of samples irradiated at different doses. It illustrates that the spherical pores of polyurethane collapse to form cracks at low doses, and they are damaged seriously at high doses.

SEM images of the irradiated samples under the action of constant stress are shown in Fig. 3. It indicates that the elasticity of the sample is seriously destroyed due to the deformed pores of the sample after compression.

Table 1. Effect of dose on the gas yield from irradiated sample

Gas	Absorbed dose, ×10 <sup>5</sup> Gy	Gas yield, ml·g <sup>-1</sup>
H <sub>2</sub>	2.0	0.0163
	8.0	0.1050
	15.0	0.1490
	25.0	0.1840
CH <sub>4</sub>	2.0	0.0007
	8.0	0.0063
	15.0	0.0047
	25.0	0.0047
CO <sub>2</sub>	2.0	0.2600
	8.0	0.6600
	15.0	0.9410
	25.0	0.9340

Dose rate = 1.2·10<sup>5</sup> Gy·min<sup>-1</sup>.

Table 2. Effect of dose rate on the gas yield from irradiated sample

Gas	Dose rate, ×10 <sup>4</sup> Gy·min <sup>-1</sup>	Gas yield, ml·g <sup>-1</sup>
H <sub>2</sub>	3.0	0.0287
	7.5	0.0248
	12.0	0.1050
	16.5	0.0257
CH <sub>4</sub>	3.0	0.0005
	7.5	0.0005
	12.0	0.0063
	16.5	0.0060
CO <sub>2</sub>	3.0	0.2680
	7.5	0.2260
	12.0	0.6600
	16.5	0.2450

Absorbed dose = 2·10<sup>5</sup> Gy.

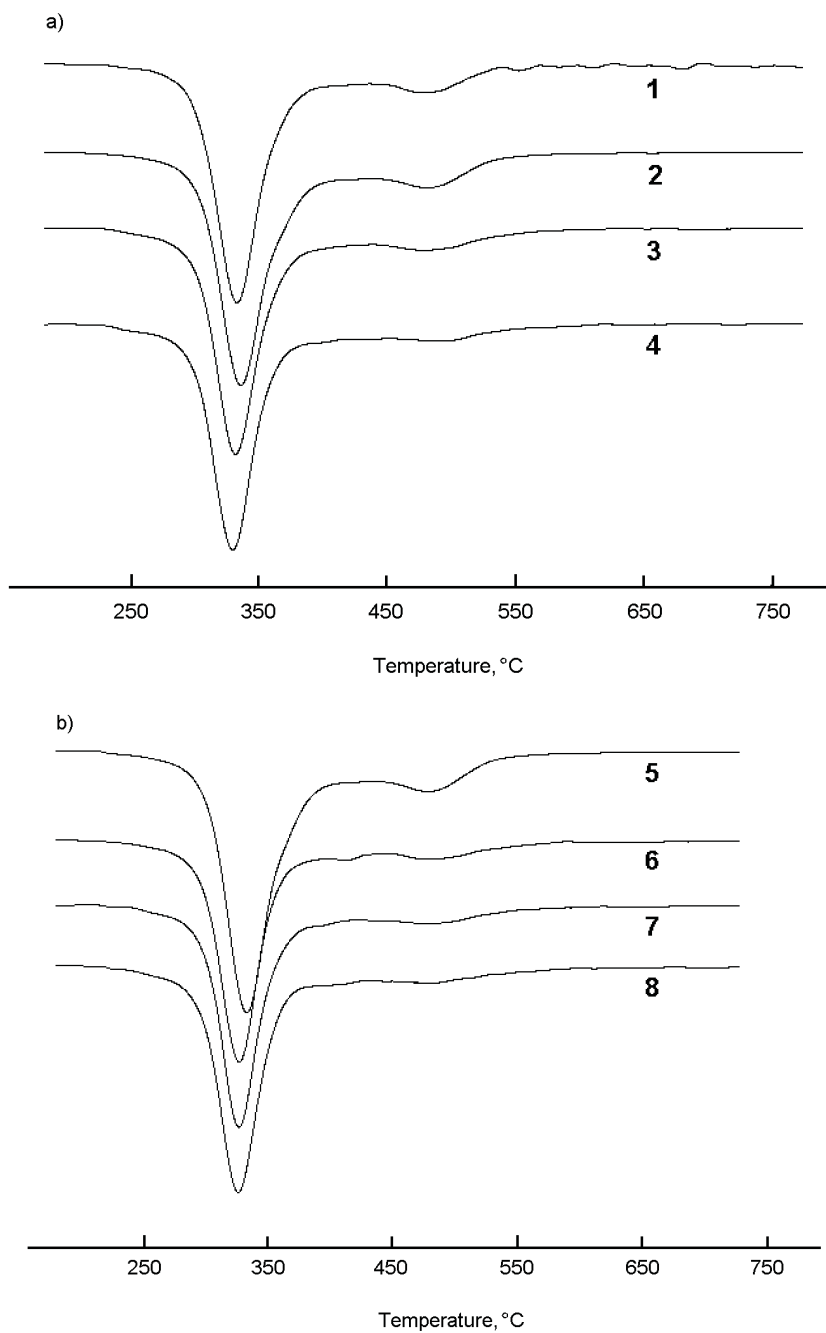


Fig. 1. DTG curves of irradiated samples. Change with the dose (a) (dose rate =  $1.2 \cdot 10^5 \text{ Gy} \cdot \text{min}^{-1}$ ) 1 –  $2 \cdot 10^5 \text{ Gy}$ ; 2 –  $8 \cdot 10^5 \text{ Gy}$ ; 3 –  $1.5 \cdot 10^6 \text{ Gy}$ ; 4 –  $2.5 \cdot 10^6 \text{ Gy}$ . Change with the dose rate (b) (absorbed dose =  $2 \cdot 10^5 \text{ Gy}$ ); 5 –  $3 \cdot 10^4 \text{ Gy} \cdot \text{min}^{-1}$ ; 6 –  $7.5 \cdot 10^4 \text{ Gy} \cdot \text{min}^{-1}$ ; 7 –  $1.2 \cdot 10^5 \text{ Gy} \cdot \text{min}^{-1}$ ; 8 –  $1.65 \cdot 10^5 \text{ Gy} \cdot \text{min}^{-1}$

Table 3. Relationship of the TG peak temperature of irradiated samples with the dose

Peak position	Absorbed dose, $\times 10^5 \text{ Gy}$				
	0	2	8	15	25
Lower peak temperature, °C	331.3	332.4	334.4	330.3	328.3
High peak temperature, °C	483.0	471.0	479.0	480.0	–

Dose rate =  $1.2 \cdot 10^5 \text{ Gy} \cdot \text{min}^{-1}$ .

Table 4. Relationship between the TG peak temperature of irradiated samples with the dose rate

Peak position	Dose rate, $\times 10^4 \text{ Gy min}^{-1}$			
	3.0	7.5	12.0	16.5
Lower peak temperature, $^{\circ}\text{C}$	334.4	328.3	328.3	327.3
High peak temperature, $^{\circ}\text{C}$	479.0	474.0	483.0	—

Absorbed dose =  $2 \cdot 10^5 \text{ Gy}$ .

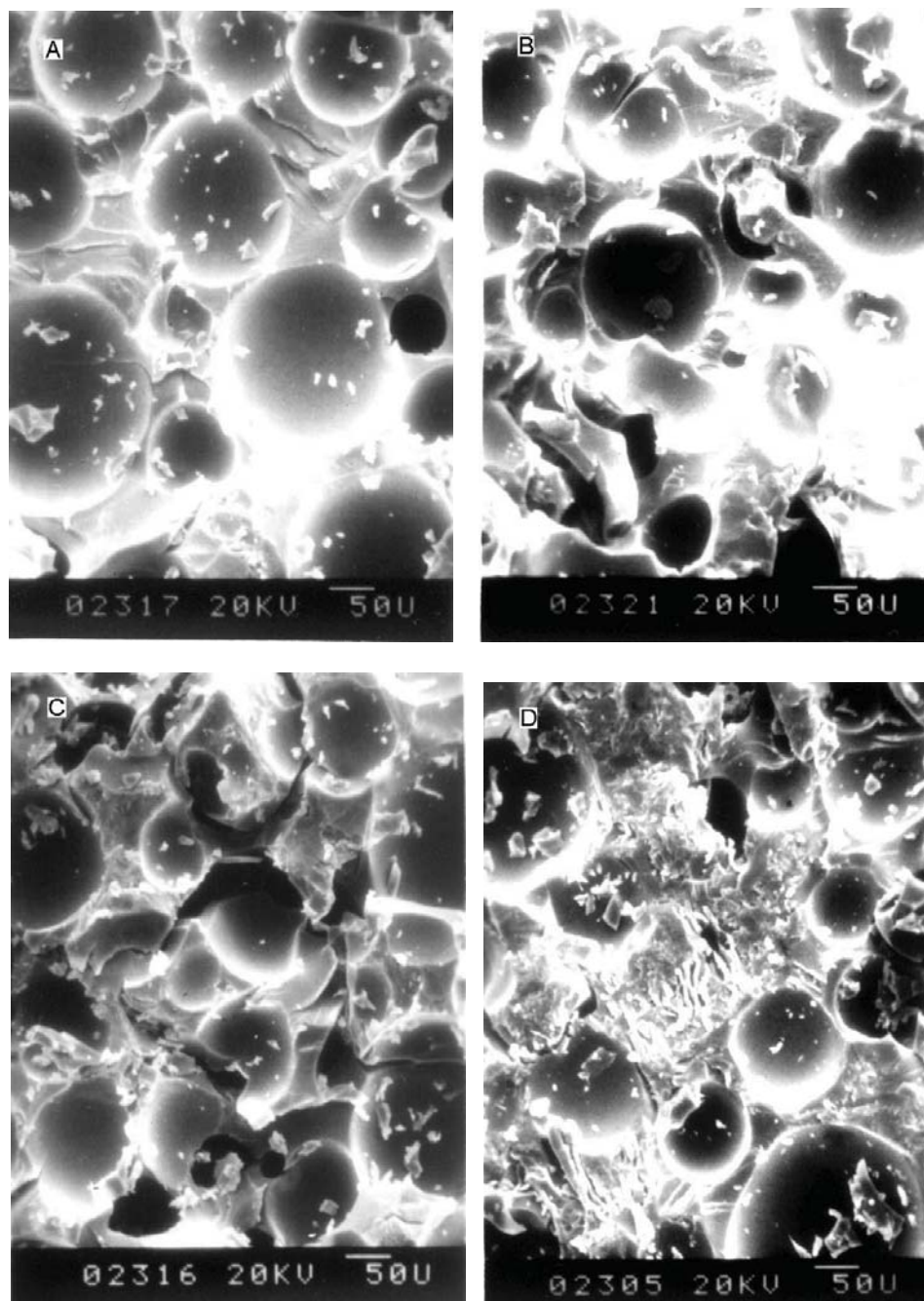


Fig. 2. SEM images of irradiated samples (dose rate= $1.2 \cdot 10^5 \text{ Gy min}^{-1}$ ); A:  $5 \cdot 10^4 \text{ Gy}$ ; B:  $5 \cdot 10^5 \text{ Gy}$ ; C:  $8 \cdot 10^5 \text{ Gy}$ ; D:  $1.5 \cdot 10^6 \text{ Gy}$

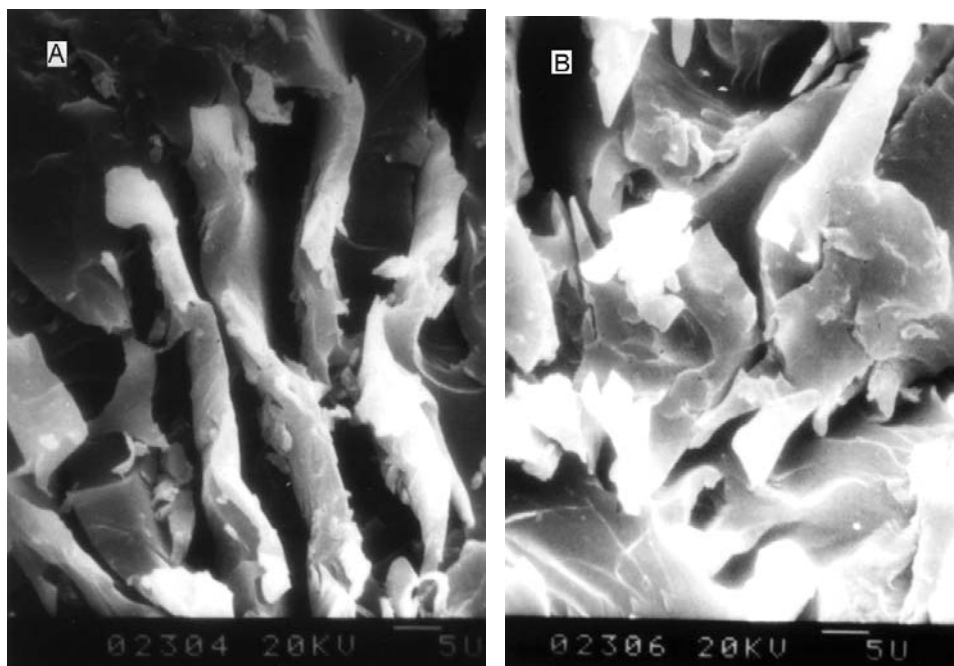


Fig. 3. SEM images of irradiated samples under the action of constant force

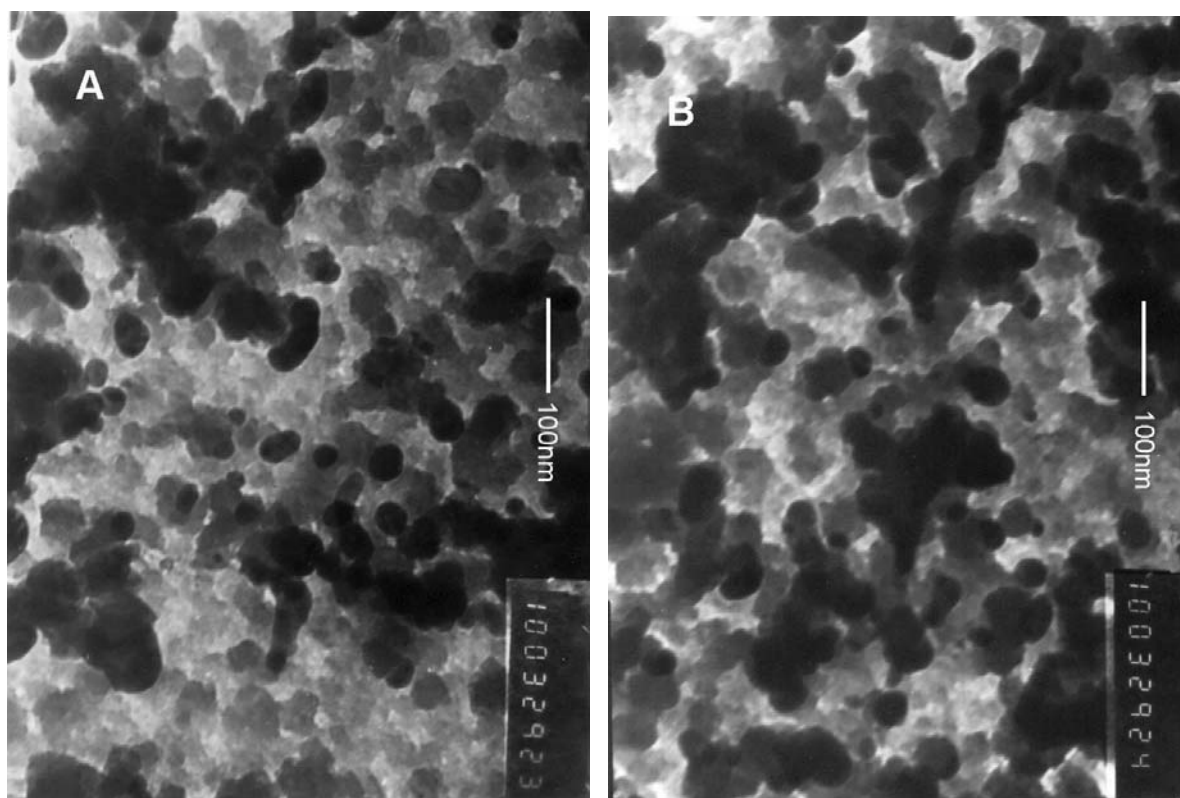


Fig. 4. TEM images of irradiated samples A:  $8 \cdot 10^5$  Gy; B:  $1.5 \cdot 10^6$  Gy

TEM is used to intuitively observe the micro-structure of samples. Figure 4 shows the TEM images (black part stands for the sample's hard segment dyed by  $\text{OsO}_4$ , and white part stands for the undyed soft segments). TEM images of unirradiated samples and those irradiated at low dose are not listed out, for they are almost white and it is hard to identify. It indicates the excellent compatibility of the hard and soft segments in the samples irradiated to low dose. But it can be clearly seen from the TEM images that there are two phases in the sample irradiated to over 800 kGy. The electrons break the hydrogen bond of  $>\text{NH}$  and  $>\text{C}=\text{O}$  on the hard segment and  $-\text{O}-$  on the soft part. Due to the disappearance of hydrogen band, compatibility degree of the soft and hard segments reduces, phase range of soft segment increases, which results in the obvious phase separation.

### Conclusions

The irradiated polyether-polyurethane evolves mainly  $\text{CO}_2$  along with  $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ , etc. After irradiated by electron beams, the hard segment of samples is more stable than the soft segment. The phase separation in the sample irradiated up to the dose of  $8 \cdot 10^5$  Gy becomes obvious due to the disappearance of hydrogen band.

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