

Effect of electron beam irradiation on thermal and mechanical properties of epoxy polymer

A T Nguyen¹, P M Visakh¹, O B Nazarenko¹, C S Chandran² and T V Melnikova¹

¹Tomsk Polytechnic University, Lenin av. 30, 634050 Tomsk, Russia

²School of Chemical Science, Mahathma Gandhi University, Kottayam, Kerala, India

E-mail: obnaz@mail.ru

Abstract. This study investigates the thermal and mechanical properties of epoxy polymer after exposure to different doses of electron beam irradiation. The epoxy polymer was prepared using epoxy-diane resin ED-20 cured by polyethylenepolyamine. The irradiation of the samples was carried out with doses of 30, 100 and 300 kGy. The effects of doses on thermal and mechanical properties of the epoxy polymer were investigated by the methods of thermal gravimetric analysis, tensile test, and dynamic mechanical analysis. The thermal properties of the epoxy polymer slightly increased after irradiation at the heating in air. The tensile strength and Young's modulus of the epoxy polymer increased by the action of electron beam up to dose of 100 kGy and then decreased. The elongation at break decreased with increasing the irradiation dose.

1. Introduction

The operation of nuclear power plants, mining and refining of uranium ore, industrial and medical use of isotopes generate radioactive waste. The nature of this kind of waste needs proper management and treatment methods in order to protect people and environment at present time and in the future [1]. The methods of nuclear waste management include the handling, pretreatment, treatment, conditioning, transport, storage and disposal of radioactive waste [2–4].

For immobilization of radioactive waste the following methods can be applied depending on the matrix materials: cementation, bituminization, vitrification, polymerization. Immobilization of radioactive waste using cement has such advantages as low cost and the use of relatively simple process plant. Cement is usually used for conditioning of large amount of low level radioactive waste. However, cementation is poorly incorporated with organic waste. Bitumenization is a process of mixing the waste with liquid bitumen in which free water evaporates and waste volume reduced [3, 4]. Bitumen could be used to immobilize organic waste. As a high molecular hydrocarbon, bitumen is expected to withstand well against environmental conditions. However, bitumen is flammable and requires special precautions to prevent its accidental ignition. Vitrification is a method for immobilization of radioactive waste for a long time in compact solid, insoluble form by combining solid waste with glass-forming material like borosilicates, and then heating the mixture under high temperature to form glass-like solid form [5, 6]. However, this method is expensive and can be applied for small scale facilities. For immobilization of radioactive waste, which cannot be treated by previously mentioned methods, polymers can be used. Polymers are chemically inert and have considerable resistance against corrosive elements and leaching the radionuclides [7, 8].



Epoxy resins are thermosetting polymers, which have cross-link polymer chain to form the solid form when adding curing elements. During the process of curing, the epoxy resins can take waste molecules into their molecular network and have tightly fixed them there, thus effectively immobilize radionuclides when treating radioactive wastes. However, the epoxy matrix can accumulate considerable radiation doses due to self-irradiation of the waste, which can deteriorate the properties of polymer. That is why it is necessary to study the possible effect of radiation on the changes in the properties of candidate polymeric materials for immobilization of radioactive waste. In this work, the effect of electron beam irradiation on the thermal and mechanical properties of epoxy polymer was studied.

2. Experimental

The epoxy polymer samples were prepared using epoxy-diane resin ED-20 cured by polyethylenepolyamine. The irradiation of the samples was carried out with doses of 30, 100 and 300 kGy using electron beam generated by the linear electron accelerator ELU-4 (Tomsk Polytechnic University). The sample coding and dose of radiation are given in table 1.

Table 1. The sample coding.

Samples	Radiation dose (kGy)	Code
Epoxy	0	E0-0
Epoxy	30	E0-1
Epoxy	100	E0-2
Epoxy	300	E0-3

The non-irradiated and irradiated epoxy samples were examined using the method of thermal gravimetric analysis (TG). TG was performed with a SDT Q600 thermal analyzer (TA instrument). The thermal decomposition in argon and air atmosphere was investigated at a heating rate of 10 °C/min from room temperature to 1000 °C, with a gas flow rate of 100 mL min⁻¹. The sample weight was about 10 mg.

The tensile properties of the epoxy polymer such as stress-strain behavior, tensile modulus and elongation at break were measured using a H50KT (Tinius Olsen) Universal Testing Machine (UTM) with a load cell of 1000 N. A crosshead speed was 50 mm min⁻¹. The sample size had a length 10 cm, a thickness 2 mm and a width 1 cm.

Dynamic mechanical analysis (DMA) of epoxy samples was carried out with a dynamic mechanical analyzer, DMA D800 (TA instrument), in the tensile mode. The rectangular strips with dimensions around 40×5×1 mm³ from all nanocomposite films. The tests were performed at a heating rate of 2 °C under isochronal conditions at 1 Hz. The strain amplitude was limited to 0.05 % to be in the linear-viscoelastic range of the material. The storage tensile modulus (E') and loss angle tangent ($\tan \delta$) of the materials were evaluated as a function of temperature.

3. Results and discussion

During electron irradiation the color change of the epoxy polymer occurs from light brown to dark brown color, as it is shown in figure 1.

Figure 2(a) and (b) shows the TG results of the epoxy polymer before and after exposure to different doses of radiation, in the presence of argon and air, respectively. We can see from the TG results that there is no significant increment for the thermal stability after radiation treatment. The parameters of the thermal behavior of the studied samples are presented in table 2 (at the heating in argon) and in table 3 (at the heating in air).

The initial temperature of degradation ($T_{5\%}$) is considered as the temperature at which the mass loss is 5 wt. %. At the heating of the epoxy sample in argon the temperature $T_{5\%}$ decreased by 4 °C after

exposure to dose of 100 kGy and then increased by 8 °C compared to that of non-irradiated sample. The mid-point temperature $T_{50\%}$ which is corresponded to a 50 % mass loss did not undergo any change and it was 377 °C for all samples. The thermal degradation of the epoxy polymer finished at ~600 °C. The residue at 600 °C was maximal for non-irradiated sample and decreased with increasing the irradiation dose.

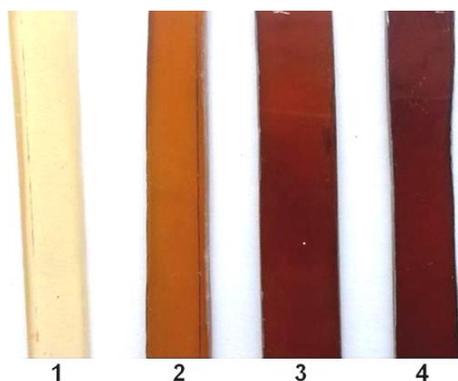


Figure 1. Epoxy polymer samples before (1) and after exposure to dose 30 kGy (2), 100 kGy (3) and 400 kGy (4)

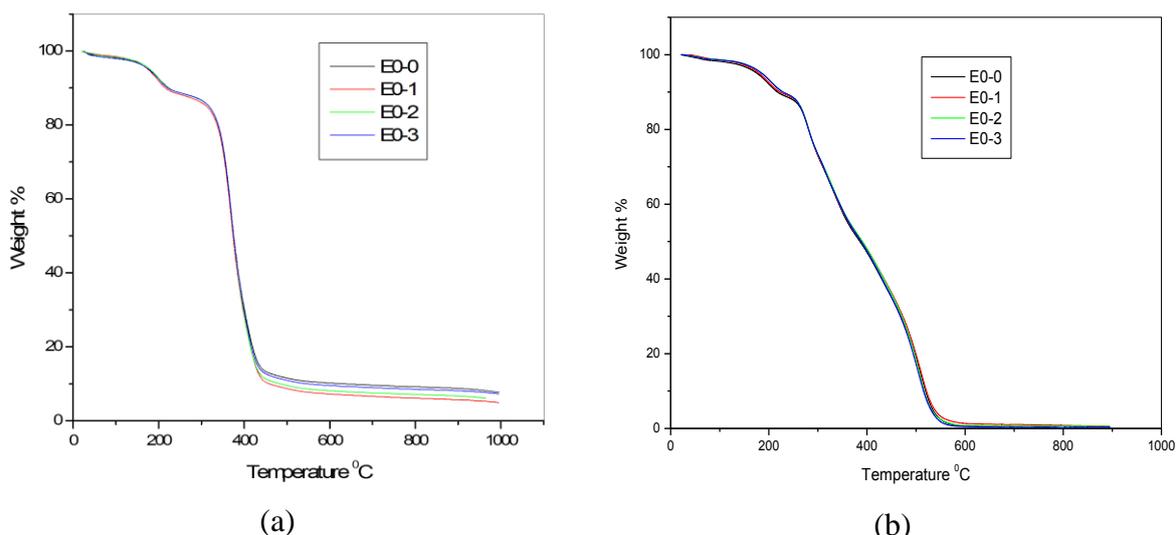


Figure 2. TG curves of the epoxy polymer after irradiation at the heating: (a) in argon; (b) in air.

Table 2. Thermal properties of the epoxy polymer after electron beam irradiation at the heating in argon.

Samples	Dose (kGy)	Degradation temperature (°C)		Residue at 600 °C (%)
		$T_{5\%}$	$T_{50\%}$	
E0-0	0	174	377	9.3
E0-1	30	174	377	7.5
E0-2	100	170	377	6.6
E0-3	300	178	377	6.9

The thermal stability of the epoxy polymer at the heating in air slightly increased after radiation treatment. The temperature $T_{5\%}$ increased by 4 °C after exposure to dose of 30 kGy and by 10 °C after

increasing the dose up to 100 and 300 kGy compared to that of non-irradiated sample. The temperature $T_{50\%}$ increased by 4 °C at the dose of 30 kGy in comparison with the sample before irradiation, then it increased by 1 °C after increasing the dose up to 100 kGy. After further increasing the dose the temperature $T_{50\%}$ of the epoxy polymer decreased by 3 °C. The similar changes are typical for the residue at 600 °C.

Table 3. Thermal properties of the epoxy polymer after electron beam irradiation at the heating in air.

Samples	Dose (kGy)	Degradation temperature (°C)		Residue at 600 °C (%)
		$T_{5\%}$	$T_{50\%}$	
E0-0	0	176	386	0.4
E0-1	30	180	390	0.6
E0-2	100	186	391	0.6
E0-3	300	186	388	0.4

The typical processes that occur during irradiation of the epoxy polymer are cross-linking and chain scission reactions [9]. The cross-linking processes prevail in the dose range up to 100 kGy and leads to formation of chemical bonds between two adjacent polymer molecules. In the dose range higher than 100 kGy chain scission reactions dominate and the thermal stability decreases because of polymer chain break.

Typical stress vs strain curves for the epoxy polymer after exposure to different doses of radiation are shown in figure 3. The tensile properties, including tensile strength, elongation at break, and Young’s modulus of the epoxy samples after irradiation are summarized in table 4.

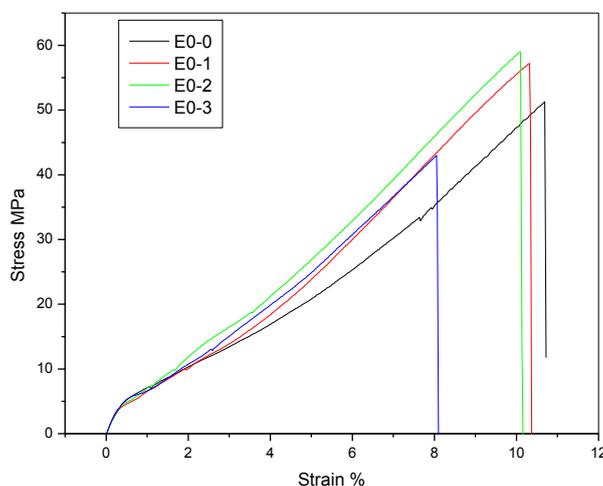


Figure 3. Mechanical properties of neat epoxy film and epoxy film with different dose of radiation treatment

Table 4. Tensile properties of epoxy polymer.

Dose (kGy)	Tensile strength (MPa)	Elongation at break (%)	Young’s modulus (MPa)
0	51.1±3	10.55± 0.8	4.84
30	56.8±4	10.24±0.6	5.55
100	58.8±5	10.04±0.8	5.86
300	42.6±6	7.98±0.3	5.34

As followed from table 4, the tensile strength for non-irradiated sample is 51.1 MPa and increased after irradiation with doses 30 and 100 kGy to 56.8 and 58.8 MPa, correspondingly. However, after further increasing the dose to 300 kGy the tensile strength decreased to 42.6 MPa. A similar dependence was obtained for the Young's modulus of the epoxy polymer. The elongation at break decreased for the epoxy polymer after exposure to electron beam irradiation.

The improvement of the tensile properties after exposure to the doses of 30 and 100 kGy can be explained by the action of cross-linking reactions. At the higher doses up to 300 kGy, it was found that the irradiation of epoxy resins decreases the mechanical properties as a result of chain scissions reactions.

The representative curves of the storage modulus (E') of the epoxy samples before and after exposure to different doses of radiation are shown in figure 4(a) and the $\tan\delta$ is shown in figure 4(b). The values of the glass transition temperature and the position and intensity of the $\tan\delta$ peaks for the studied epoxy samples are shown in table 5.

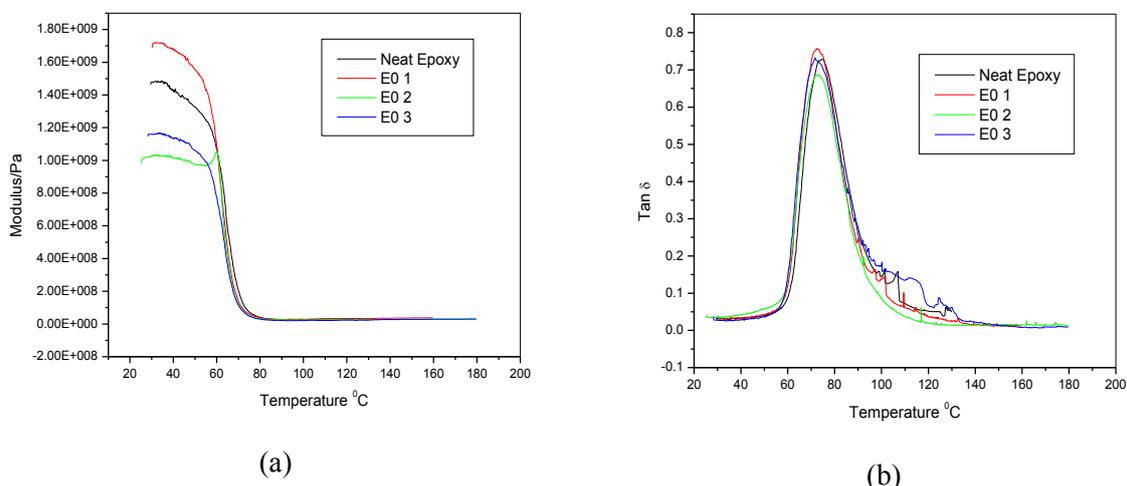


Figure 4. Tensile modulus E' vs temperature (a) and $\tan\delta$ vs temperature (b) of epoxy polymer before and after radiation treatment

Table 5. The values for the temperature and height of the $\tan\delta$ peaks for neat epoxy and epoxy composites with different dose of radiation treatment.

Samples	Temperature $\tan\delta$ peak (°C) (T _g)	Height $\tan\delta$ peak
E0-0 (Neat epoxy)	74.6	0.72
E0-1	72.4	0.75
E0-2	72.9	0.68
E0-3	71.7	0.73

The samples of both non-irradiated epoxy polymer and irradiated epoxy samples are in the glass state at temperatures below 60 °C and in the rubber state at temperatures above 80 °C; thus, the glass transition region for these samples is from about 60 to 80 °C. In the glass transition region of all samples, the storage modulus drops sharply from its original value in the glass state to the lower value in the rubber state. At low temperatures (below 40 °C), modules are very different from one another (figure 4(a)). The value of modulus is higher for the sample irradiated with dose of 30 kGy than that of other samples. This is due to the fact that in the glassy state, molecular motions are largely restricted to

vibration and short-range rotational motions. As the temperature increases, the studied samples show only a decrease in the storage modulus. The decrease in storage modulus can be assigned to the relaxation of the polymer chains at glass transition region. All samples showed a single transition in the temperature range of 60 to 80 °C.

4. Conclusions

The epoxy polymers were prepared using epoxy resin ED-20 cured by polyethylenepolyamine. These epoxy samples were exposed to electron beam irradiation with doses of 30, 100 and 300 kGy. The effect of electron beam irradiation on thermal and mechanical properties of the epoxy polymers was investigated. The results of thermal analysis showed that the thermal stability of the studied samples at the heating in air slightly increased. The tensile strength and Young's modulus increase up to dose of 100 kGy. All samples showed a single transition in the temperature range of 60 to 80 °C.

Thus, the obtained results showed that the mechanical characteristics of the epoxy resin are improved after the action of electron beam with dose up to 100 kGy. Epoxy resin ED-20 is considered as a polymer with high resistance to radiation and can be recommended to immobilize radioactive wastes after further additional investigation.

Acknowledgments

The authors are thankful to the Scientific and Analyzing Centre of Tomsk Polytechnic University for the providing the TG measurements.

References

- [1] Rao K R 2001 *Curr. Sci.* **81** 1534
- [2] Baisden P A and Atkins-Duffin C E 2011 *Radioactive Waste Management Handbook of Nuclear Chemistry* Eds A Vertes, S Nagy, Z Klencsar, R G Lovas and F Rösch (New York: Springer US) 2797–2835
- [3] Tang Y S and Saling J H 1990 *Radioactive Waste Management* (Washington: Hemisphere Publishing Corporation)
- [4] Nagasaki S and Nakayama S 2015 *Radioactive Waste Engineering and Management* (Tokyo: Springer Japan)
- [5] Donald I W, Metcalfe B L and Taylor R N J 1997 *J. Mater. Sci.* **32** 5851
- [6] Ojovan M I and Lee W E 2005 *An Introduction to Nuclear Waste Immobilisation* (Amsterdam: Elsevier)
- [7] Dawson J, Smith V, Clifford J and Williams S J 2012 *Mineral. Mag.* **76** 2985.
- [8] Efremkov V M 1989 *IAEA Bull.* **4** 37
- [9] Kircher J F and Bowman R E 1964 *Effects of Radiation on Materials and Components* (New York: Reinhold Publishing Corporation)