Journal of Radiation Research and Applied Sciences 10 (2017) 53–56

Contents lists available at ScienceDirect

Journal of Radiation Research and Applied Sciences

journal homepage: http://www.elsevier.com/locate/jrras

# The effect of neutron irradiation on glass-transition temperature and rigidity of PMMA

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ARTICLE INFO

*Article history:*
Received 28 September 2016
Received in revised form
23 November 2016
Accepted 23 November 2016
Available online 6 December 2016

*Keywords:*
Polymers
Thermal properties
Neutron irradiation
Thermal conductivity
Glass-transition temperature
Rigidity

ABSTRACT

Present work includes a study of the effect of neutron irradiation on glass-transition temperature, $T_g$ and rigidity, G of PMMA [Poly (methyl methacrylate)] by using the variation of thermal conductivity with Temperature T. The thermal conductivity measured before and after irradiation of specimens by neutrons, for different periods of time, in variation with temperature. The specimens shape was a disc of 24 mm in diameter and 6 mm in thickness. The behavior of thermal conductivity with temperature and also with period of irradiation was studied. The dependence of rigidity on irradiation was also studied by calculating the rigidity of the specimens in variation with temperature.

The results revealed that the conductivity depends greatly on irradiation which has maximum value at 18 days of irradiation. The variation of rigidity with irradiation follows the same behavior of $T_g$ with irradiation.



## 1. Introduction

The operation of radiations on polymer composites is of great importance which leads to the modification of polymer properties under ionizing radiation (Davenas et al., 2002). It is a subject of great interest due to the increasing uses of polymers in various fields like hard radiation environments encountered in nuclear power plants, space-crafts industry, sterilization irradiators, high energy particle accelerators *etc.* (Mallick et al., 2009). It is also worthwhile to study the modifications in the structure and thermal properties of polymer due to irradiation. Among the synthetic polymers, Poly (methyl methacrylate) (PMMA), is significant because of its mechanical strength, inertness to chemical action and resistance to thermal environment.

However, the effectiveness of these changes produced depends on the structural conformation of the polymer as well as the experimental conditions of irradiation (Dole, 1972; Singh, Kumar, & Prasad, 2013). Neutron irradiation significantly changes the properties of polymeric materials by the displacement of lattice atoms and the generation of helium and hydrogen by nuclear transmutation (Srivastava & Virk, 2000; Abou Taleb, Madi, Kassem, & El-Khatib, 1996; Mallick, Behera, & Patel, 2005). When neutron undergoes an interaction, it does so with a nucleus of the absorbing-material; as a result, materials gain enough energy; hence modification in the material properties takes place (Mallick et al., 2009).

Since neutrons are uncharged, they interact almost entirely with atomic nuclei and produce essentially no ionization directly. The products of such interactions often cause ionization, and hence result in typical radiation-chemical reactions. The principle ions produced are protons and heavier positive ions, and the chemical reactions caused are similar to those resulting from irradiation with heavy positive particles. Because of their great penetration, the results of neutron irradiation are not limited to the surface layer of the substrate irradiated (Wilson, 1974). The principle interactions of neutrons with matter include elastic scattering, inelastic scattering, nuclear reaction, and capture.

Thermal conductivity of polymers is greatly affected by the modification in the structure due to the irradiation by neutrons. Theoretically, the thermal conductivity of amorphous polymers below their glass-transition temperature $T_g$, should increase as the temperature increases and above $T_g$, should decrease as the temperature increases (Krevelen, 1976). This can be explained in term of the Debye temperature of heat conduction, $\lambda \propto c_v v l$ (Kittel, 1986). By

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Peer review under responsibility of The Egyptian Society of Radiation Sciences and Applications.

http://dx.doi.org/10.1016/j.jrras.2016.11.004

considering the variation of the density of a polymer with temperature, leads to the relation, $\lambda \propto c_v \nu \rho l$, and also in terms of, $\lambda \propto c_p \nu \rho l$ (Sakiadis and Coates, 1955 and 1956) in which $l$ represents the distance between the molecules in adjacent isothermal layers. According to these two relations the behavior of thermal conductivity is the multiplication of the temperature behavior of the components $c_p$, $\rho$, $\nu$ in the equation while $l$ is considered constant for amorphous polymers. Since amorphous polymers have more disordered structure than partially crystalline ones, amorphous polymers would be expected to have lower conductivities. The thermal conductivity decreases as disorder increases (Knappe, 1971).

## 2. Experimental procedure

Measurements of thermal conductivity for PMMA specimens have been made before and after irradiation by neutrons for different periods of time. The specimens are of 6 mm in thickness and 24 mm in diameter. The measurements were carried out in temperature range (100–450) K. The specimens were exposed to neutron flux of different periods of time as shown in Table 1. All measurements were carried out in a system elsewhere (Fadhel, 1995). The irradiation of the specimens was carried out by using neutron source type (α, n) manufactured by 'The Radio chemical Center, Amersham'. The source is alloy of (Am-Be) of 3 cm in diameter and 6 cm in length. The rate of neutron emission is $1.1 \times 10^7$ n/s, measured in March 1982 by the manufacturing company. The activity is of about 5 Ci and the average energy is about 4.5 MeV. The container of the neutron source in Basrah University (BUV facility) considered as neutrons calibration tools, which is a water bath of 64.6 cm in diameter and the neutron source is inside. The neutron source is located in the center of the bath with depth of 40 cm. Water moderates the fast neutrons to be thermal neutrons.

Thermal conductivity is calculated by using the relation

$$\lambda = \frac{Q^{\bullet} L}{A\, \Delta T}$$

where λ is the thermal conductivity coefficient, $Q^{*}$ is the thermal flux rate or heat quantity that flows through the specimen, $L$ is the specimen thickness, $A$ is the cross-section of the specimen, and $\Delta T$ is the temperature difference between specimen faces.

The possible error that may be expected for the calculated thermal conductivity was calculated to be about ±0.4%.

The rigidity was calculated utilizing the empirical relations (Krevelen, 1976)

$$G(298) = \frac{3 \times 10^9}{1 + \frac{600}{T_g}} \mathrm{N/m^2} \quad \text{for} \quad T_g > 298\mathrm{K}$$

$$G(T) = \left[\frac{\frac{T_g}{T_R} + 2}{\frac{T_g}{T_R} + \frac{2T}{T_R}}\right] G(T_R) \quad \text{for} \quad T < T_g$$

$T_g$ is a refernce temperature (Room Temperature = 298K)

The percentage variation of thermal conductivity at $T_g$ with the irradiation time, with respect to the thermal conductivity of the unirradiated specimen of PMMA was calculated using the formula.

$$\lambda\% = \frac{\lambda_i - \lambda_0}{\lambda_0} \text{ x } 100\%$$

**Table 1**
Exposure of specimens to neutron flux for different periods of time.

| Specimen No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Irradiation time (day) | 0 | 2 | 18 | 29 | 35 | 47 | 58 | 62 |

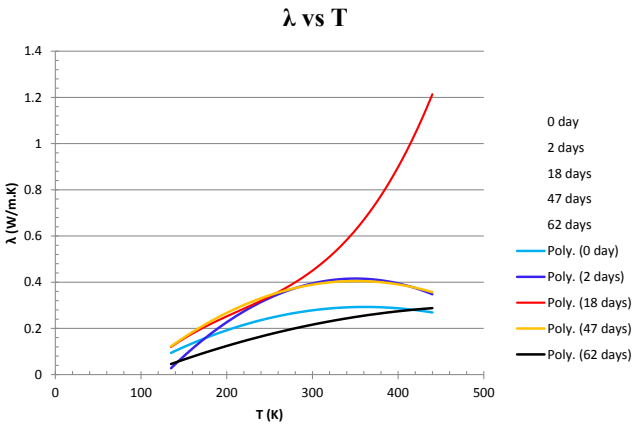


**Fig. 1.** Thermal conductivity versus temperature for different periods of irradiation of PMMA.

## 3. Results and discussion

Our concern is to study the effect of irradiation on glass-transition temperature ($T_g$), so Fig. 1 gives the variation of thermal conductivity (λ) in the temperature range (300–450) K, because $T_g$ values are in this range of temperature.

For the variation of thermal conductivity with temperature, the behavior follows the general shape of $\lambda$-$T$ curve of amorphous polymers described earlier in the introduction.

Because PMMA is an amorphous polymer, in which thermal conductivity increases with increasing temperature reaching a flat maximum at the $T_g$ range, after that start decreasing.

From Fig. 1 it can be noticed that for the irradiated specimens of different periods of irradiation the behavior of thermal conductivity with temperature still have the same trend, in general, but the thermal conductivity values start to increase with the time of exposure reaching the maximum value $\lambda(T_g) = 1.116$ W/m.K at the 18 days of irradiation with $T_g = 420$ K then return back to decrease again with increasing the exposure time reaching the same values of unirradiated specimen. The large change of thermal conductivity values are seen clearly as the temperature are closing to the $T_g$ range, i.e. in the range (350–450) K as it is shown in Fig. 2-left. It is

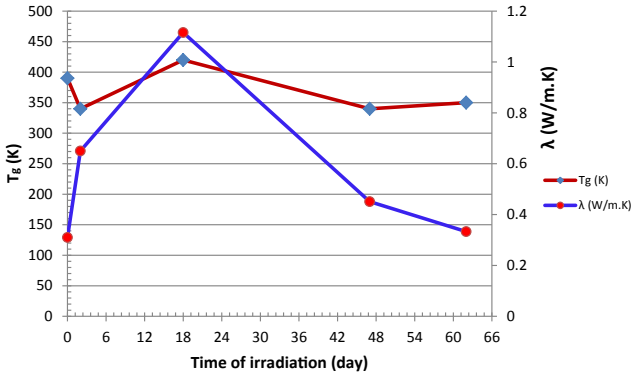


**Fig. 2.** Thermal conductivity λ ($T_g$) and $T_g$ versus the period of irradiation of PMMA.

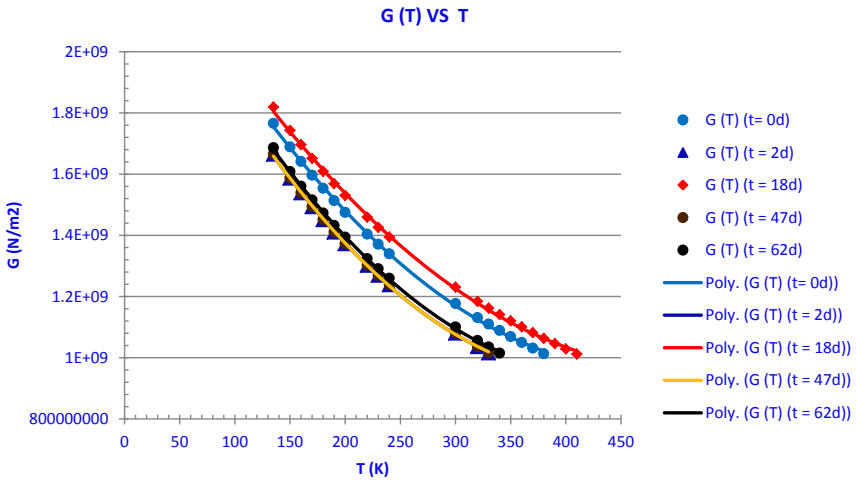


**Fig. 3.** Rigidity versus temperature for different periods of irradiation of PMMA.

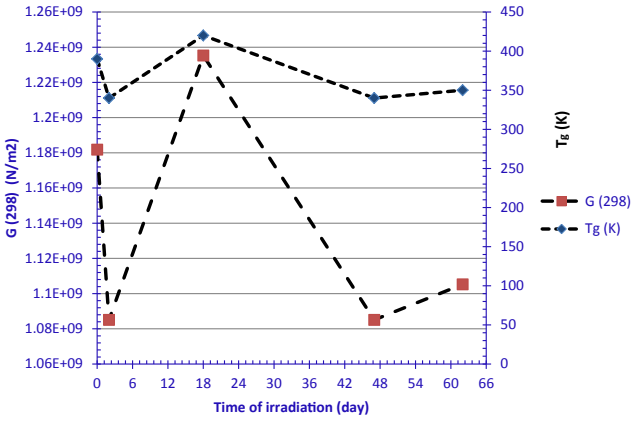


**Fig. 4.** Rigidity G (298) and $T_g$ versus the period of irradiation of PMMA.

also shown in Fig. 2-right the variation of $T_g$ with time of irradiation, in which $T_g$ has its maximum value at 18 days of irradiation and fluctuated at other values of irradiation which leads as a sequence that the rigidity of the polymer follows the variation of $T_g$ with irradiation as it is shown in Fig. 3 and obviously are seen in Fig. 4, which have the highest values of rigidity for 18 days of irradiation in variation with temperature.

The percentage variation of thermal conductivity at $T_g$ with the irradiation time, with respect to the thermal conductivity of the unirradiated specimen of PMMA is shown in Fig. 5 and Fig. 6. The thermal conductivity at the 18 days of irradiation is 260% of that of the unirradiated specimen, while it is less on both sides.

The large change of λ values at temperature closing to the $T_g$ range can be interpreted according to the correlation between the behavior of thermal conductivity with temperature and irradiation (Majdi & Fadhel, 1997). This may be attributed to the change that may takes place in the structure of the polymer due to the irradiation in which the reaction products formed in the early stages are branched macromolecules with increasing in molecular weight. This occurs at 2 days and 18 days of irradiation. This means that the branching or the bridges that occur due to the irradiation will increase the density and become as easy passage to the phonons to pass, which will increase the phonon velocity. But at the temperature below $T_g$ the product $\rho\ c_p\ v$ has small values because of the small values of $c_p$ at low temperature (Wunderlich, 1996). So the influence of irradiation is great at $T_g$ because $c_p$ has large values at this temperature.

In the later stage of irradiation, i.e., at 47 and 62 days, the influence of irradiation will cause a scission in the main chain which will decrease the average molecular weight, i.e., a decrease in density and phonon velocity, which then affects the product $\rho\ c_p\ v$ in the whole range of temperatures, i.e., decrease in thermal conductivity.

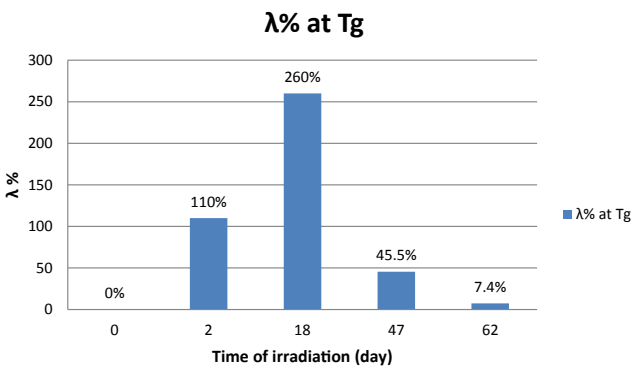


**Fig. 5.** The percentage variation of thermal conductivity at $T_g$ with the irradiation time, with respect to the thermal conductivity of the unirradiated specimen of PMMA.

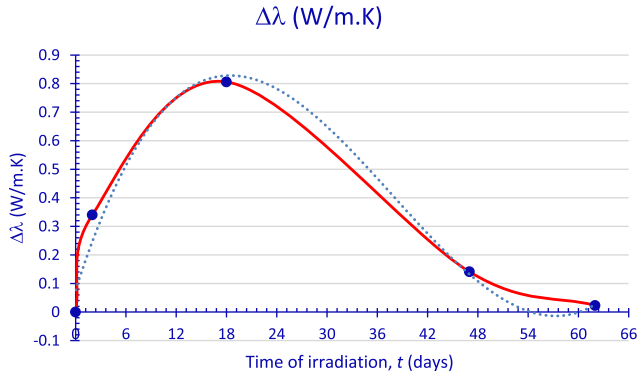


**Fig. 6.** The variation of thermal conductivity difference at $T_g$ with the irradiation time, with respect to the thermal conductivity of the unirradiated specimen of PMMA.

## 4. Conclusion

The glass transition, $T_g$, is a highly cooperative process. This cooperativeness of the process is due to the specific morphology of polymeric chains, which effected greatly by the irradiation and temperature. From the discussion above one can conclude that the behavior of thermal conductivity with irradiation at glass transition temperature can give an indication that this polymer can be used as a dosimetry for the different flux of neutrons. Also, this method may be considered as a method for the detection of the radiations.

## Acknowledgement

The authors would like to thank Physics department- College of Science at University of Basrah for providing the facilities to do the experimental work and also the Soran University.

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