

## THERMAL PROPERTIES OF POLYACRYLIC ACID AND THE EFFECT OF NEUTRON IRRADIATION

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**ABSTRACT** - This paper includes study of thermal properties of polyacrylic acid specimens. Thermal conductivity measurements have been made before and after irradiation of specimens by neutrons, for different periods of time, in the temperature range (300-400) K. The specimens shape was a disc of 1.9 cm in diameter and 0.19 cm in thickness with density of 1.382 g/cm<sup>3</sup>. The thermal conductivity measurement was taken when a temperature gradient at steady state took place. The behaviour of temperature dependence on thermal conductivity and also the dependence on period of irradiation was studied: The results reveal that this polymer has a low conductivity which is in good agreement with values of amorphous polymers. And the conductivity at glass transition temperature ( $T_g$ ) increases with increasing the period of irradiation. It is also noticed that a shift in  $T_g$  values took place. This can be attributed to the irradiation.

### INTRODUCTION

Polyacrylic acid (-CH<sub>2</sub>-CHCOOH-) is one of the electrolytes that contains an ionized group on the polymeric chain. It can be prepared chemically directly from ethylenecyanohydrines or by the addition polymerization of acrylic acid monomer by using benzoyl-peroxide as thermal initiator to increase the rate of polymerization [1]. This procedure has been used to prepare the specimens employed in this investigation.

Polyacrylic acid is a thermal polymer which solidified, carbonized and then brittle with heating. It can be used as thickening for the adhesive material because of its high viscosity. It is found that the molecular weight of the polyacrylic acid reaches high value with glass transition temperature,  $T_g$ , of about 379 K, when the polymerization process is completed. Ionizing radiations leads to crosslinking of the polymer which stiffen and become insoluble [2].

Theoretically, the thermal conductivity of amorphous polymers below their glass transition temperature,  $T_g$ , should increase as the temperature increase and above  $T_g$ , should decrease as the temperature increases [3]. This can be explained in terms of the Debye treatment of heat conduction,  $\lambda_{cv}vl$  [4], by considering the variation of the density of a polymer with temperature, which leads to the relation  $\lambda_{cv}vpl$ , and also in terms of  $\lambda_{cv}vpl$  [5] in which  $l$  represents the distance between the molecules in adjacent isothermal layers. According to these two relations the behaviour of thermal conductivity is the

multiplication of the temperature behaviour of the components  $c_p$ ,  $\rho$ ,  $v$  in the equation, the mean free path,  $l$ , is considered constant for amorphous polymers.

For crystalline polymers the thermal conductivity should decrease or remain the same as the temperature increases. This also can be explained according to the Debye relation above by considering  $c_v$ ,  $\rho$  and  $v$  as being independent of temperature and  $l$  as the only factor which depends on the temperature. The mean free path  $l$  decreases with increasing temperature in crystalline substances at temperatures above the thermal conductivity maximum ( $T > 0/20$ ), which leads to a decrease in the thermal conductivity with increasing temperature. In crystalline polymers the molecules are generally folded, the crystalline order is important, and crystallization is seldom complete. The presence of very highly organized local order of the repeat units in the molecules is not manifest in the macroscopic thermal conductivity, because  $l$  is limited by various larger scale imperfections which cause scattering of the phonons. These imperfections, which decrease the symmetry or the order, lower the thermal conductivity of the specimen.

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 [6].

The terms ionizing radiation or high-energy radiation usually cover a large number of different types of radiations some of which are beams of charged particles which directly ionize the molecules of the irradiated medium; but the same terms are also used to designate other types of radiations such as photons or fast moving uncharged particles which do not produce ionizations directly but are capable of transferring their energy to charged particles which are themselves ejected from the absorbing molecules and create secondary ionizing tracks. This second group of radiations comprises electromagnetic waves of high energy (X- and  $\gamma$ -rays) and neutrons [7].

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 [8]. The principle interactions of neutrons with matter include elastic scattering, inelastic scattering, nuclear reaction, and capture.

The irradiated polymers may either cross-link or degrade depending on their chemical nature. The process that appears predominant in irradiated polyacrylic acid is the cross-linking [9,10]. The net result of cross-linking is that the molecular weight of the polymer increases with increasing doses until a three-dimensional network is formed where each polymer chain is linked to an other chain on the average [8].

## EXPERIMENTAL MEASUREMENTS

This work includes the measurements of thermal conductivity for polyacrylic acid specimens before and after irradiation by neutrons for different periods of time. The specimens thickness is 0.19 cm and 1.9 cm in diameter. The measurements carried out in temperature range 300-400 K.

The aim is to study the temperature behaviour of the thermal conductivity and also the effect of neutrons. The specimens were exposed to neutron flux for different periods of time, the longest period of exposure was 10080 min. All measurements were carried out inside an oven of controlled temperature.

The irradiation of the specimens was carried out by using neutron source type ( $\alpha, n$ ) 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 [11]. 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 centre of the bath with depth of 40 cm. Water moderates the fast neutrons to be thermal neutrons.

The preparation of the polyacrylic acid specimens was by using thermaql initiator (Benzoyl peroxide) with concentration of  $10^{-2}$  M for 1 M of monomer. The specimens mass obtained was 0.744 g.

The irradiation by neutrons was for different periods of time, and these periods are tabulated in Table (1).

Specimen	D <sub>0</sub>	D <sub>1</sub>	D <sub>2</sub>	D <sub>3</sub>	D <sub>4</sub>	D <sub>5</sub>	D <sub>6</sub>	D <sub>7</sub>
Period of exposure (min)	0.0	120	300	1440	2880	5760	7200	10080
T <sub>g</sub> (K)	378	380	378	383	378	383	388	383
$\lambda_{Tg} \times 10^{-3}$ W / cm. K	5.426	5.474	5.494	5.493	5.878	6.127	6.442	6.711

In this work hot plate method is used to measure the thermal conductivity which is one of the steady state methods [12]. It is convenient for the measurements of the bad conductor materials. This method is characterized by its simplicity and that the ratio of the specimen length to its diameter is small, to let as large as possible of heat to conduct through the specimen.

Thermal conductivity was calculated from the relation,  $\lambda = \dot{Q}L / A\Delta T$ , where  $\lambda$  is the thermal conductivity coefficient,  $\dot{Q}$  is the thermal flux rate or the 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.

Two similar specimens were employed to be located at the faces of the heater of a disc shape. The heat quantity  $\dot{Q}$  is calculated from the power supplied to the heater by a wire of constantan of 38 SWG. This power is the total quantity generated by the heater which is divided into two equal quantities of  $\dot{Q}/2$  flowing from the heater through the specimens. Thus,  $\dot{Q}/2$  only is used in the calculation of the thermal conductivity, i.e.,  $\lambda = \dot{Q}L / 2A\Delta T$ . A Cu-constantan thermocouples have been used to measure the temperature which are of gauge 38 SWG.

The possible error that may be expected for the calculated thermal conductivity was calculated to be about  $\pm 0.36\%$ .

## RESULTS AND DISCUSSION

The discussion includes two parts, first is concentrated on the thermal conductivity behaviour as a function of temperature before and after irradiation by neutrons for different periods of time. The second part describes the thermal conductivity behaviour as a function of irradiation periods at glass transition temperature,  $T_g$ , of the specimen.

It can be noticed clearly that the thermal conductivity is increasing as the temperature increases reaching a broad maximum at a certain temperature, after that the thermal conductivity start to decrease as temperature increases, as shown in Figure (1). From Figures (1 & 2) and Table (1), it can be noticed clearly that in the range of temperatures 378 K to 388 K the thermal conductivity start to decrease. The glass transition temperature of polyacrylic acid reported is 379 K [4], so the temperature behaviour of thermal conductivity reported here agrees with that predicted theoretically as we have seen earlier.

Figure (2-left) shows a linear relationship between ( $T_g$ ) and  $I$ , where  $I$  is the irradiation period. Also from Fig. (2-right) a fluctuated increase in  $T$  is shown as the period of irradiation increases. This means that a shift in  $T_g$  value is taken place.

The increase in thermal conductivity with irradiation can be attributed to the occurrence of cross-linking and side branching of the polymer chains. With continuous increase of irradiation periods the branching of polymer chains increases and then cross-linking occurs. As a sequence the rigidity of the polymer increases and the solubility decreases, i.e., the increase of  $T_g$ . Also, the collision of neutrons with atoms of the polymer will displace the nuclei from their position with a large kinetic energy; and a formation of active free radicals occurs. This may contribute to increase the thermal conductivity, but this contribution is very small because the nuclei may return to loss their energy and become as an impurity. In Fig. (2), an obvious increase in thermal conductivity with increase of irradiation can be noticed. The increase of the



period of irradiation leads to an increase in cross-linking and then increase in density, which in turn leads to an increase in thermal conductivity. The highest value of thermal conductivity is  $6.711 \times 10^{-3}$  W/cm. K at temperature 383 K of sample D<sub>7</sub>.

From the discussion above one can conclude that the behaviour of thermal conductivity with irradiation at glass transition temperature (linear increase) 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 new method for the detection of the new solid state nuclear detectors.

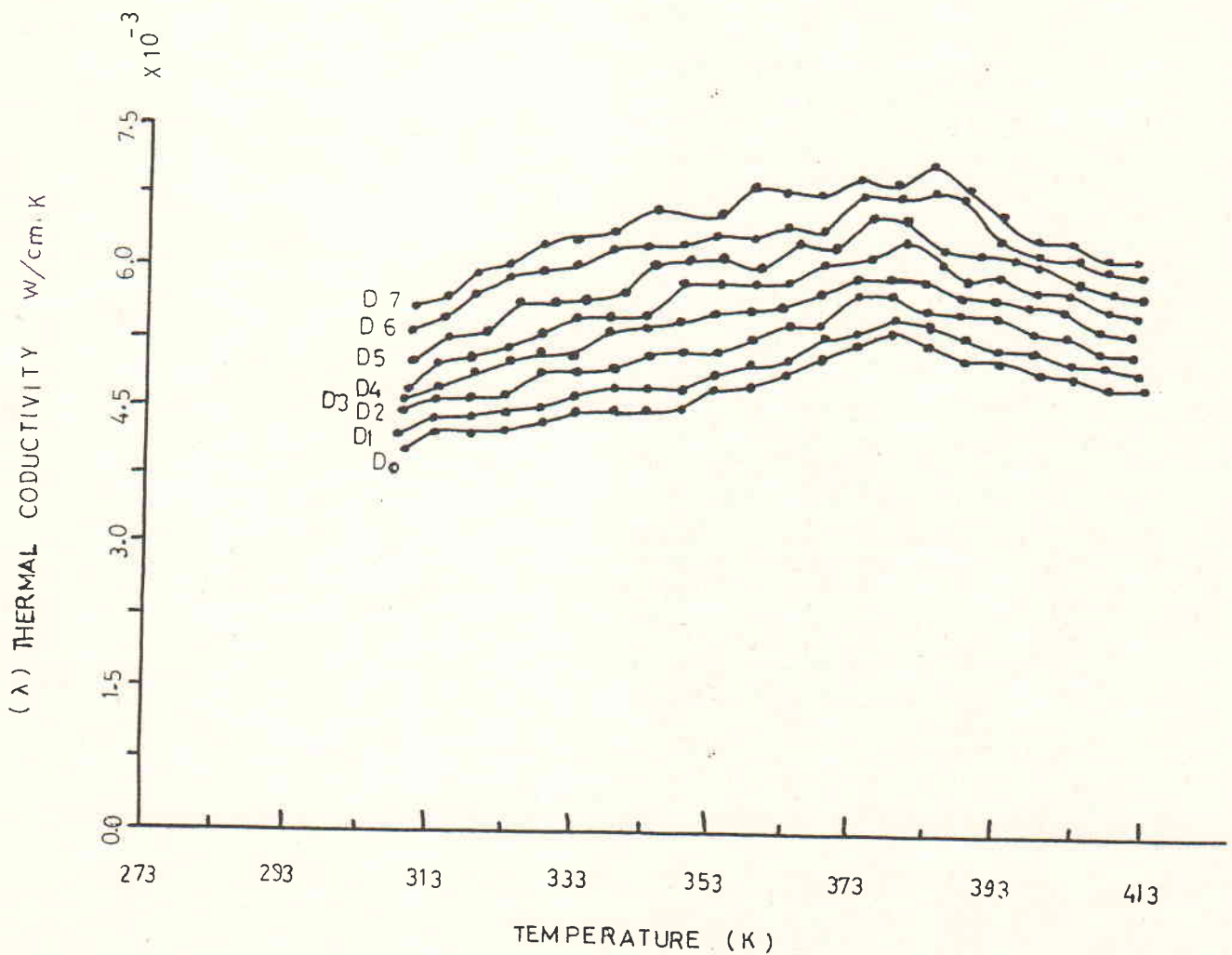


Fig. (1) : Thermal conductivity variation with temperature for the specimens D<sub>0</sub>, D<sub>1</sub>, D<sub>2</sub>, D<sub>3</sub>, D<sub>4</sub>, D<sub>5</sub>, D<sub>6</sub> and D<sub>7</sub>.

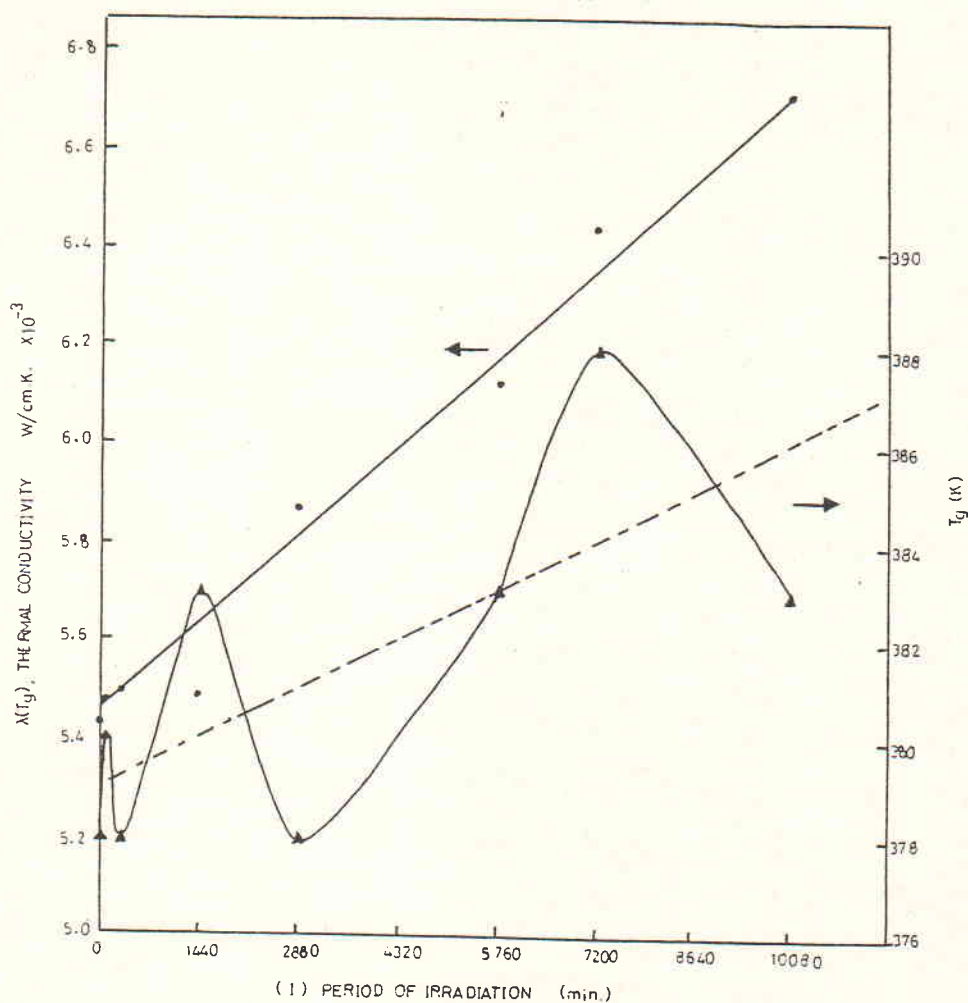


Fig. (2) : The variation of thermal conductivity at  $T_g$  with the period of irradiation by neutrons (•) (left-side) and the variation of  $T_g$  with the period of irradiation by neutrons ( $\Delta$ ).

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### المستخلص

تناول البحث دراسة الخواص الحرارية لعينات من بولي حامض الاكريليك فقد تم قياس التوصيل الحراري للعينات قبل وبعد تعريضها للنيوترونات وضمن مدى درجات الحرارة يتراوح بين (300 K - 400 K) وكانت العينات المستخدمة ذات مواصفات متطابقة وعلى شكل اقراص دائرية قطر الواحدة (1.9 cm) وسمكها (0.19) وكثافتها (1.382 gm/cm<sup>3</sup>). عند توليد انحدار حراري على طرفي العينة يقاس التوصيل الحراري بصورة مباشرة بعد الوصول الى حالة الاستقرار من قياس معدل التدفق الحراري عبر العينة (Q) وفرق درجات الحرارة على طرفي العينة (T) .

لقد تبين لنا من النتائج التي حصلنا عليها ان هذا البوليمر ذو توصيل حراري واطىء حيث تتفق النتائج مع قيم التوصيلية الحرارية للبوليمرات غير المتبلورة . وان زيادة فترة التعرض للنيوترونات التي يتعرض لها البوليمر تؤدي الى زيادة التوصيل الحراري زيادة خطية واضحة . كما لاحظنا ان درجة الانتقال الزجاجي حصل لها ازاحة طفيفة من 378 K الى 388 K بتأثير تعرض العينة للنيوترونات .