Polymer Bulletin 5, 209-215 (1981)

Polymer Bulletin

Induced Electrical Conductivity in Irradiated PVC, PS, and PMMA

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ABSTRACT

A comparative study has been carried out on the electrical conductivity of PS, PMMA, and PVC before and after irradiation with γ-rays up to a dose of 100 MR. The obtained results are explained on the basis of electron trapping theory by making use of a formula suitable for calculating the characteristic parameter Δ. The conclusion that the average value of Δ is near to the theoretical value $\Delta = 0.5$ indicates that these polymers possess long decay times and have a large number of exponentially distributed traps.

INTRODUCTION

Many polymers are insulators, but their conductivity is greatly increased by high energy radiation even at very low intensities insufficient to cause appreciable chemical changes. Despite the great amount of work dealt with polymeric materials, there is no unaminous point of view concerning the mechanism of conductivity in this type of solids (1). One form of conduction is the electronic conduction which usually occurs in polymers having a conjugated backbone structure. The actually measured conductivity in such a system will be controlled by the ability of the electrons to hop from one chain to another (2) Another form of conduction is the ionic one where ionic impurities are a major source of conductivity (3-6). In practice it is difficult to distinguish between electronic and ionic conduction in many polymers. Even for one synthetic polymer published reports propose different mechanisms. For example, FLEMMING and RANICAR (7), interpreting their results for PVC in terms of the energy band theory, are in favour of electronic conduction, while KOSAKI et al (8) of hopping ionic conduction. OSTER (9) suggested a conduction mechanism based on electronic hopping favoured by the micro Brownian- motion responsible for dielectrics. In case of crystalline, semicrystalline and oriented polymers, the problem is more

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0170-0839/81/0005/0209/$01.40

complicated. Sophisticated theories have been developed for conduction in polyethylene (10).

In this work we attempt to carry out a comparative study on the induced conductivity in γ-irradiated samples of PVC, PMMA and PS. These materials are all of the vinyl type polymers which have carbon-carbon main chains, but differing in their side chain substituents. They represent three classes of polymers having different structures, polarities and stabilities towards damage and aging. In addition these materials are widely used in radiation environment.

EXPERIMENTAL

Films of commercial PS, PMMA and plasticised PVC have been irradiated in a 60_{Co} cell at a dose rate of 4.8x 10^5 rad/hr , at room temperature in air. The conductivity measurements were carried out using a conventional circuit incorporating a multimeter level , type TM9A. The method of guard rings was followed in order to avoid the effects due to surface conductivity (11).

RESULTS AND DISCUSSION

(A) Electrical properties before irradiation:

An investigation of the temperature dependence of conductivity in PVC is given in Fig. 1. This figure shows that the static conductivity σ increases with temperature in a way satisfying the general equation of Arrhenius.A slight break however , is observed in the region of about 80°C. It is also observed that at low temperature this conductivity is dependent on the period of time of the application of the electric field, but at high temperature this dependence does not exist. An activation energy of the order of 0.505 eV can be calculated from the slope of these lines. This slope usually depends on temperature as well as plasticiser content (12).

It has been established by LUPU et al (12) that in case of PVC there are three regimes of conduction depending upon temperature. The transition temperature between regime I and regime II , $T_{(I\leftrightarrow II)}$ is assumed to be the glass transition temperature of the polymer , while $T_{(II\leftrightarrow III)}$, is associated with a secondary transition , caused by intermolecular structural changes and the dissolution of structural aggregates and clusters.

In our PVC samples regime I does not exist , probably due to the plasticiser , and the break observed is associated with the second transition of LUPU.

According to PARRINI (13) conductivity in PVC follows two mechanisms, the polarisation mechanism , which usually predominates at low temperature, and the ionic mechanism, which predominates at a temperature higher than T_g. In our work calculated value of the activation energy supports mainly the ionic mechanism(14).

The transitions observed in the plots of Fig.1. look like such transitions which are usually observed in case of oriented and crystalline polymers (15), and have been related to α-relaxation. This has to be taken as if there should not be a connection between such transition and the change in the conduction mechanism.

The fact that PVC has some degree of orderliness (16), supports such point of view. Calculated degree of crystallinity from x-ray analysis, is in the order of about 15%.

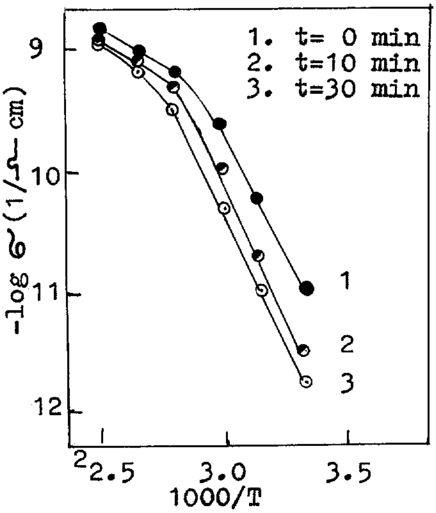


Fig. 1. Effect of temperature on conductivity for non-irradiated PVC.

For PS and PMMA the behaviour is quite different. Fig.2. shows that the conductivity values are lower than those of PVC. In addition , conductivity does not show any change with temperature below T_g but starts to increase linearly at higher values. No time dependence of current has been observed , suggesting the absence of high field polarisation in these polymers at the conditions of the experiment.

The variation of conductivity with temperature , as given in Figs. 1 and 2, will be adopted to represent the " normal state " of non-irradiated samples

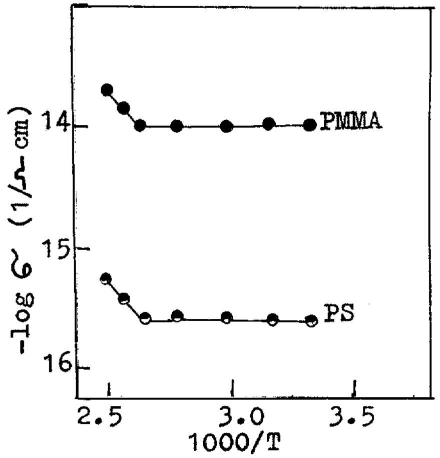
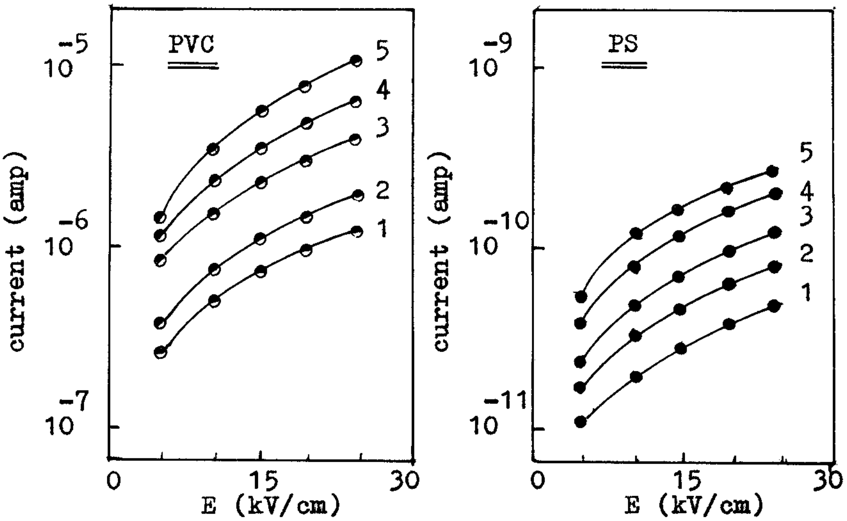
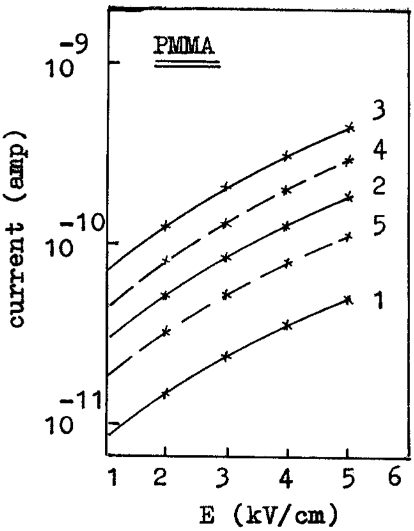


Fig. 2. Effect of temperature on the conductivity of non-irradiated PMMA and PS.

(B) Electrical Properties of Irradiated Polymers:

Figs. 3 and 4 indicate that conduction current increases continiously with the absorbed dose for PVC and PS respectively. This is also observed for PMMA only up to a dose of 50 MR. followed by a decrease in current by increasing dose , Fig. 5. At this dose the material becomes foamy and full of cracks.





Figs. 3 , 4 and 5 .

Effect of γ-ray dose on the field strength - current relations.

1. nonirradiated.
2. 25 MR.
3. 50 MR.
4. 75 MR.
5. 100 MR.

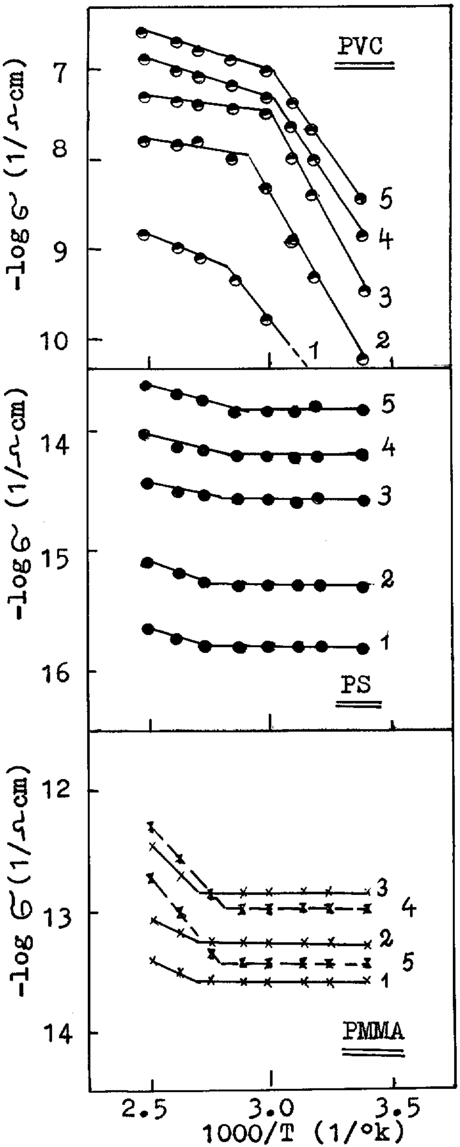
Relations of log σ vs 1/T for irradiated PVC, PS, and PMMA are given in figs.6,7 and 8 respectively.
The obtained results can be discussed in terms of the model suggested by FOWLER (17) to explain the induced conductivity in insulating materials due to ionizing radiation.
According to this model the measured conductivity σ after irradiation will be the sum of an induced and static conductivities.
Consequently the calculated activation energy E will be the sum of an induced activation energy E_x and the depth E_o below the conduction level.
The model predicts that the induced conductivity σ_x during irradiation should vary with radiation intensity or radiation rate R according to the relation:

$$\sigma_x = a R \Delta$$

where a is a proportionality constant and Δ has the theoretical value between 0.5 and 1, depending on the given substance and the distribution of electron traps.

Figs. 9 and 10 illustrate the variation of σ and E at 100 °C with radiation dose for the samples under investigation.

It can be seen that the conduction free carriers which are mainly electrons, due to ionizing radiation,



Figs. 6, 7 and 8.

Conductivity - temperature relations at different doses.
1. nonirradiated 2. 25MR.
3. 50 MR. 4, 75 MR.
5. 100 MR.

may become trapped in localised trapping centres which are assumed to be of unspecified nature. This in addition to the scattering effect of impurities and additives on the mobility of charge carriers may be included in the factor affecting the conduction process. Therefore , the calculated E_x for the irradiated samples will thus be proportional to the number of released electrons.

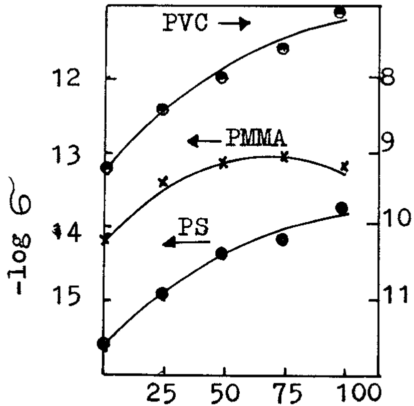


Fig. 9 . Radiation dose and conductivity for irradiated polymers at 100°C.

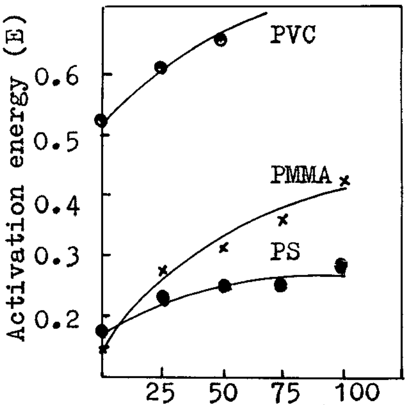


Fig. 10. Radiation dose and activation energy.

In order to obtain some information about the distribution of trapping centres in the polymers , we shall make use of the equation :

$$\sigma_x = \sigma_o R \Delta e^{-E_x/kT}$$

This equation was used by one of the authers to explain the post-irradiation effects in mica on the basis of the electron trapping theory (18). Later on (19) it was also used to calculate the characteristic parameter Δ for some ferroelectric crystals. In the present work it can find further evidence of its applicability to polymers.

The calculated values of Δ for PVC, PMMA and PS are given in table I.

A significant increase of Δ with radiation dose can be observed. The fact that the average value of Δ is close to theoretical value Δ = 0.5 suggests

TABLE I

The variation of Δ with dose

Dose (MR)	Δ		
	PVC	PMMA	PS
25	0.46	0.47	0.26
50	0.57	0.48	0.33
75	0.82	0.57	0.37
100	0.78	0.70	0.48

that the distribution of electron traps in these polymers is exponential in nature. Thus they belong to the class of materials which possess long decay times and have a large number of traps.

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Received May 7, 1981
Revised July 11, 1981
Accepted July 16, 1981