EFFECT OF IRRADIATION ON DIELECTRIC BEHAVIOR OF POLYETHERKETONE WITH CARDO GROUP*

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ABSTRACT

It is found in this paper that the dielectric behavior of polyetherketone with cardo group (PEK- C) irradiated at a dose of 2.02 MGy has an obvious change. For the irradiated PEK- C, both the temperature spectrum of dielectric loss factor (ε'') within a range of 20— 200 °C and the frequency spectrum of dielectric coefficient (ε') in a range of 30 Hz—1 MHz show that ε'' and ε' increase from 5.4×10^{-3} to 4.6×10^{-1} and from 3 to 5, respectively.

Keywords: Polyetherketone (PEK- C) Irradiation Dielectric behavior Temperature spectrum Frequency spectrum

1 INTRODUCTION

Soluble polyetherketone with cardo group (PEK- C) is a novel engineering plastic with good resistance to high temperature, hydrolysis and chemical corrosion and has the property of self- lubrication. Therefore, it may be used in the fields of aviation, spaceflight, mechanical industry and so on. In this paper the effects of γ - irradiation on the dielectric behavior of PEK- C are discussed. Obviously, the dielectric behavior of γ - irradiated PEK- C is entirely different from those of polyalkene[1] because the main chain of PEK- C contains many phenyl rings and larger side groups.

The measurement of dielectric temperature spectrum and frequency spectrum of polymer are an excellent method for evaluating the effects of γ - irradiation on polymer[2,3]. It was found from the research on the dielectric behavior of γ - irradiated PEK- C that the macrotransition and the relaxation arisen from the molecular motion of polymer is in close relationship with the structure of polymer.

2 EXPERIMENTAL

2.1 The preparation of samples

The powder of PEK- C ($M_n = 12000$) was pressed at 330 °C under 152 MPa to three kinds of sheets, with thicknesses of 0.595, 0.795 and 0.904 mm naming after 1#, 2#

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and 3# respectively.

2.2 Irradiation

The sample sheets prepared as mentioned above was introduced into a Pyrex ampoule for irradiation. Irradiation was carried out under vacuum (0.133 Pa) at room temperature in ^{60}Co source- room.

2.3 Measurement of the dielectric properties

The dielectric spectrum of irradiated samples were measured with TRS - 10C type of dielectric loss device made in Japan. The three electrode system with available diameter of 38 mm was used in measurement. In order to make the electrode system contact well with the surface of the sample sheet, the sub- electrode was made by sticking a copper foil of 0.02 mm thickness to the surface of measured sample sheet. On the other hand, a comparison between the properties of samples sticked copper foil (sub- electrode) and those of samples without copper foil was made through the small three electrodes system in which the diameter of electrode is 9.5 mm.

3 RESULTS AND DISCUSSION

3.1 Dielectric frequency spectrum of PEK- C

Fig.1 shows that the relationship between dielectric coefficient (ε') and the frequency for the sample 1# in the cases of irradiation or unirradiation. It was found from curve 1 in Fig.1 that the dielectric coefficient of unirradiated PEK- C is very small, which is about 3.1, and it essentially does not vary with the frequency.

After PEK- C was irradiated 2.02 MGy the ε' value becomes larger and is approximate to 6 at 30 Hz, which is two times as large as that of unirradiated PEK- C. Moreover, the values of ε' decrease with increasing of the frequency (curve 2). It was found from the curve 3 that values of ε' for PEK- C irradiated 2.02 MGy obviously reduce after annealing for 1 h, the top value is 4.2 only at 30 Hz, it may be caused by elapse of the radicals produced from irradiation (curve 3). When irradiation dose increases to 3.06 MGy, ε' values increase, and to 9.5 at 30 Hz (curve 4).

Fig.2 shows that the effects of γ - irradiation on dielectric loss factor (ε'') for sample 1#. From Fig.2, it can be seen that $\varepsilon''$of unirradiated sample is relatively large at 30 Hz and decreases with increasing of the frequency. When the frequency reaches to 1 kHz, a valley appears on the curve, and then ε'' increases with increasing of the frequency untill ε'' exhibits a maximum at 1 MHz. After irradiating 2.02 MGy, ε'' decreases with increasing of frequency.

In fact, the change of ε'' values reflects the variation behavior of motional unit of polymer with the added electric field. The obvious increase of ε'' for irradiated PEK- C shows that there are the trapped radicals with high polarizability produced by irradiation in the structure of PEK- C, which have a certain stability. The result that ε″ of sample 1# annealed at 200 °C for 1 h still is in the range of 10^{-1} (curve 3) proves this stability.

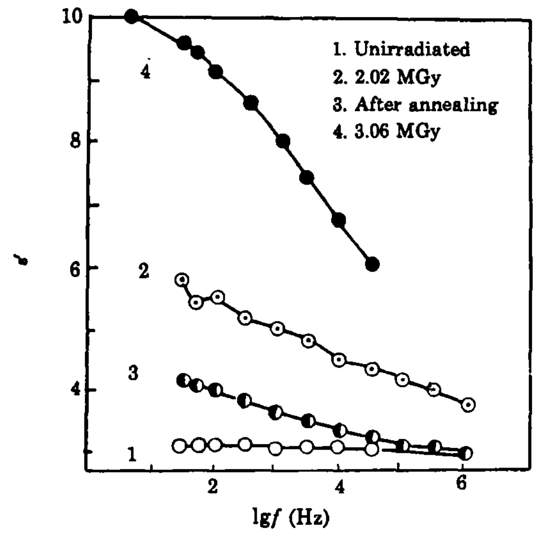

Fig.1 The relationship between ε′ and lg *f* for PEK-C

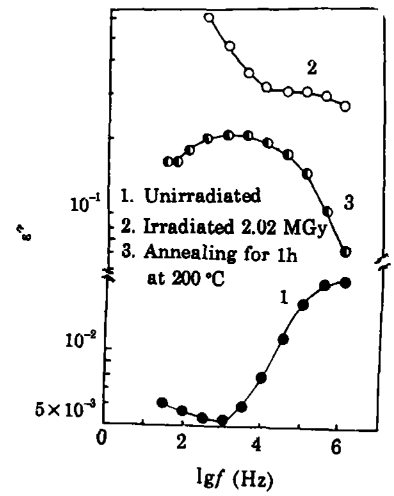

Fig.2 The frequency spectrum of ε″ for PEK-C at 20 °C

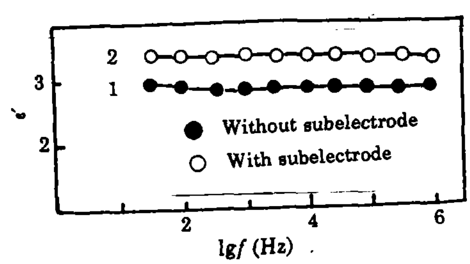

Fig.3 The relationship between ε′ and lg *f* at 20 °C

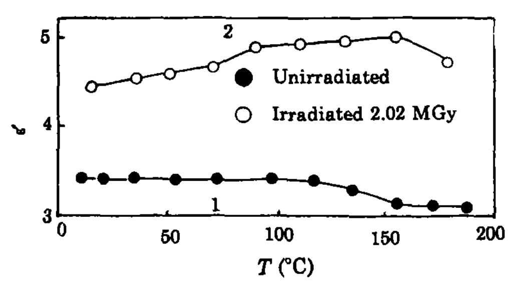

Fig.4 The temperature spectrum of ε′ for sample 1# of PEK-C

On the other hand, we studied the effects on ε′ without subelectrode. The results (Fig.3) show that for unirradiated sample 2# in the case of non-subelectrode ε′ is 0.5 lower than that of the subelectrode stuck. This shows to stick a subelectrode is reasonable. The reason maybe is that there is an air crack between the sample of non-subelectrode and measuring electrode, which gives an extra deviation in measurement. The result obtained from measuring irradiated sample 3# is similar to that from sample 1# for the relationship between ε′, ε″ and frequency.

3.2 Dielectric temperature spectrum of PEK-C

Fig.4 shows the relationship between ε′ and temperature. It was found that the ε′ of unirradiated PEK-C does not vary with the temperature below 120 °C, but have a slight decreases after 120 °C since heat expansion brought about the increase of thickness of sample. ε′ of irradiated PEK-C slightly increases with increasing of temperature because polarization of the sample containing radicals increases with the temperature. When the temperature is near to 180 °C, ε′ decreases. This may be ascribed to increasing of thickness of sample with temperature and to vanishing of radicals. From Fig.4, it can also be seen that the ε′ of irradiated PEK-C is higher than that of the unirradiated PEK-C.

It is of interest to note the variation behavior of ε″ of PEK-C with temperature and the effects of γ-irradiation on the temperature spectrum of ε″ (Fig.5). It is shown in Fig.5 that ε″ is relatively larger at 15 °C and there is a valley on ε″-*T* curve. The valley temperature is relative to the measurement frequency, which increases with increasing of measurement frequency. The valley temperature, for example, is about 80 °C at 3 kHz, 100 °C at 10 kHz and 130 °C at 30 kHz.

It is also found from Fig.5 that below the valley temperature ε″ for PEK-C increases with the measuring frequency, while above the valley temperature ε″ decreases with increasing of measurement frequency. This phenomenon fully indicates the properties of relaxation for the motion of the groups and chain segments of polymer. The increasing of ε″ above the valley with temperature may be ascribed to that increasing of temperature brings about increase of the loss produced by

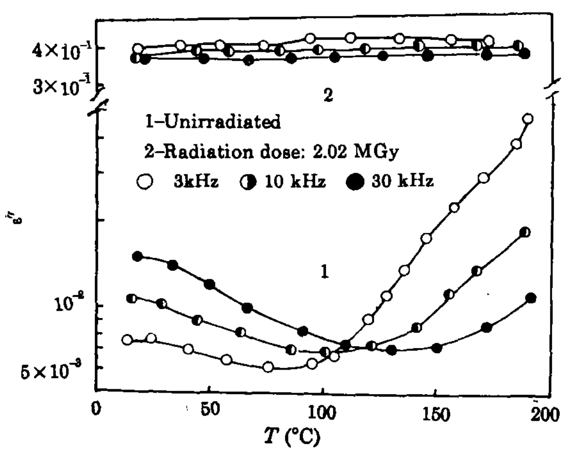

Fig.5 The temperature spectrum of ε″ for PEK-C

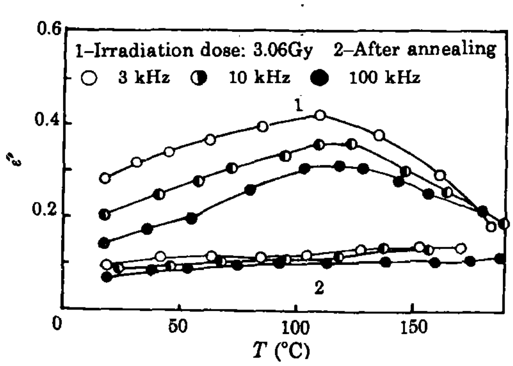

Fig.6 The relationship between ε″ and temperature for sample 1# after again irradiating and annealing

leakage of electricity and that the closer the temperature to the glass transition (227 °C), the larger motion of relatively large chain segment. In nature, the variation of ε″ with temperature for PEK-C irradiated 2.02 MGy is different from that of unirradiated, as shows curve 2 in Fig.5. ε″ of irradiated PEK-C is 1—1.5 order higher than that of unirradiated and the form of the curve is different from the one of unirradiated. In fact, the temperature spectrum for ε″ of unirradiated PEK-C reflects the relaxation properties of motion unit, while ε″ of irradiated PEK-C does not change with the temperature, and only slightly decreases with increase of the frequency. This result is characteristic of the polymers which have the properties of resistance to high temperature, such as PEK-C. It reflects a change in the microstructure of γ-irradiated PEK-C.

On the basis of ε' and ε'' values, PEK-C may be considered as a polymer with small polarity. There are a number of stable three-benzene-radicals after irradiation. The loss produced by leakage of electricity of molecular chain with these radicals becomes large, so that the motion of the unit molecules is covered. Therefore, ε'' of irradiated PEK-C is higher than that of unirradiated. On the other hand, since the stable three-benzene-radicals do not elapse under experimental conditions, ε'' does not vary with measurement temperature.

In order to investigate the stability of the trapped three-benzene-radicals produced by irradiation, the irradiated sample 1# was irradiated again, the dose was 3.06 MGy. Curve 1 in Fig.6 shows the relationship between ε'' and temperature for the reirradiated sample. It was found that ε'' values of PEK-C irradiated by two doses (3.06 and 2.02 MGy) are of same order, but there is a smooth peak on ε''-T curve for secondly irradiated PEK-C at about 110°C. The smooth peak appears slightly shifts to high temperature with increasing of frequency. This means that the motion unit forming the loss peak has characteristic of relaxation. The motion unit may be the shorter chain segments to which the remained radicals produced by first irradiating and the new radicals produced by second irradiating adhered. Curve 2 in Fig.6 shows the relationship between ε'' and temperature for the PEK-C sample which is sticked on subelectrode after it was annealled through heating it to 200°C and remaining this temperature for 1 h, then cooling it to room temperature. From curve 2, it can be seen that there are not the smooth peaks and that ε'' values decrease, but still are in the range of 10^{-1} order which is 0.5—1 order higher than that of unirradiated. This shows that parts of the three-benzene-radical have disappeared after annealing and that these three-benzene-radicals are very stable.

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