Durability of Radiation-Sterilized Polymers. VI. Irradiation Effect of Thermal Quenching Polymer

INTRODUCTION

Polypropylene (PP) has been widely used as material for medical supplies because of its high transparency and mechanical properties. However, radiation sterilization of medical supplies made of PP is limited due to the radiation degradation of PP. Several articles reported the prevention of the degradation of PP by irradiation, the addition of radical scavenger[1] and heat treatment of irradiated sample.[2] However, studies in the radiation resistance of PP have not been sufficient.

The radiation degradation of medical supplies made of polypropylene (PP) has been studied.[3-6] The durability of the irradiated PP depends on the degree of oxidation during and after irradiations. The degree of oxidation can be estimated by the chemiluminescence method. It was also found that the degree of durability of electron beam irradiated polymer is smaller compared to γ-irradiated one. In addition, the decrease in mechanical properties of polypropylene containing 6% ethylene (Co-PP) by irradiation was smaller compared to PP, although its main chain scission occurs as the same level of PP. The effect of ethylene in Co-PP on the radiation resistance does not retard the molecular scission, but it changes the morphology of polymer, which is known to be closely related to radiation resistance.[6] In this article, the effect of thermal quenching is reported in order to make clear the effect of the morphology on the radiation stability of the polymers.

EXPERIMENTAL

Materials

A commercial grade polypropylene containing antioxidant was used. The preparation of sheet of PP was carried out as follows; PP chips were molded under a pressure of 150 kg/cm^2 for 5 min at 200°C using spacer of 0.5 mm after preheating for 10 min at the same temperature. Then, it was immediately quenched at -60°C in a dry ice–methanol bath and in a tap water bath at room temperature for samples A and B, respectively. Sample C was cooled between the plates of cold press themselves with tap water at 20°C.

Test pieces (dumbbell-shaped specimens) of 0.5 mm thickness for the tensile test were cut from the sheet.

IRRADIATION AND POST-IRRADIATION MEASUREMENT

The samples were irradiated at a dose rate of 10 kGy/h by γ-rays from a Co-60 source. The tension speed was 100 mm/min in the tension test. The results given in the following section are an average of eight readings. The tension test of PP was done within 24 h after irradiation. The thermal analysis was carried out an Perkin-Elmer Model DSC-1B. The measurements were performed at a heating rate of 16°C/min under nitrogen, after 5 mg of sample was set in the sample cell of the DSC using an aluminum pan.

RESULTS AND DISCUSSION

Figure 1 shows the relationship between absorbed dose and elongation at break. The elongation at break (E_b) of the unirradiated sample C, which was prepared by cold press cooling with tap water, is smaller than those of the quenched samples (A and B). It shows that E_b of sample C decreases remarkably by irradiation with a sterilization dose of 25 kGy and it decreases to the E_b value of 10% only. On the contrary, in the quenched polymer (samples A and B), E_b of the unirradiated sample reaches 750%, and these two samples are stable up to 25 kGy of irradiation dose, as shown by Figure 1. The polymer which has the larger E_b shows a smaller effect of degradation by irradiation. Therefore, it was concluded that the quenched polymer is more stable

Journal of Applied Polymer Science, Vol. 32, 5669–5671 (1986)

CCC 0021-8995/86/065669-03$04.00

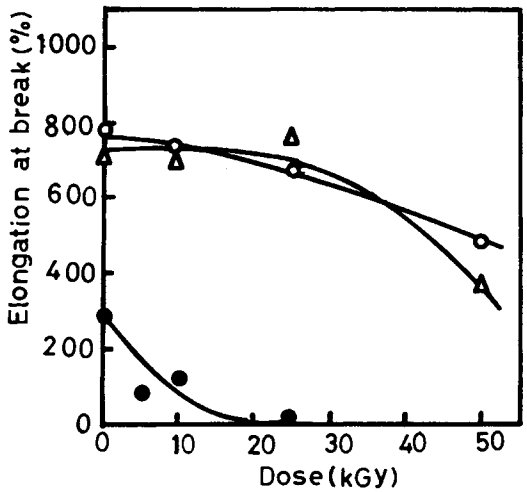

Fig. 1. Elongation at break of quenched polypropylene: (○) in dry ice–methanol at −60°C; (△) in water at room temperature; (●) in cold press cooling with water.

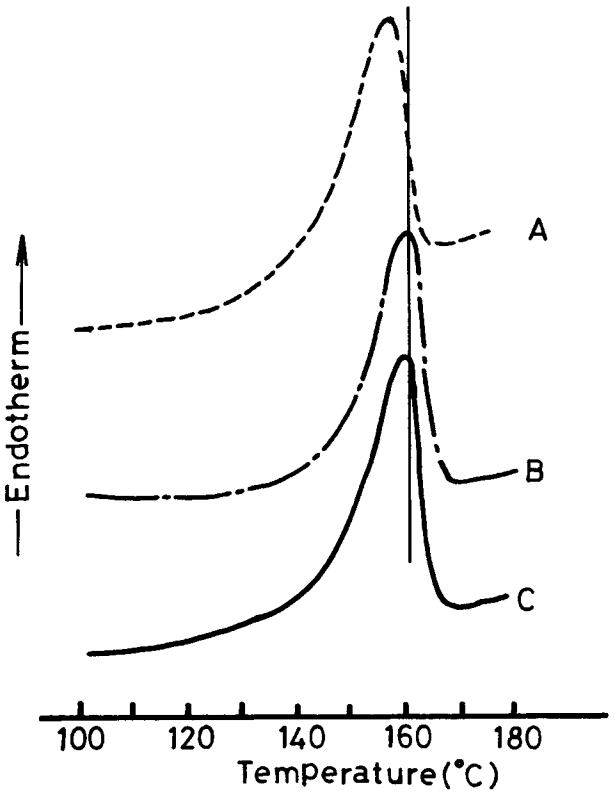

Fig. 2. DSC diagrams of quenched polypropylene: (A) in dry ice–methanol at −60°C; (B) in water at room temperature; (C) between the plates of cold press cooling with water.

against irradiation. The yield strength value in the stress–strain curves is hardly affected by irradiation. Tensile strength shows the same tendency with Figure 1.

Melt behavior of the polymer quenched by various treatments is shown in Figure 2. Then melting point (T_m) of the original PP is 160°C. The initial temperature of melting and the peak temperature (melting point) of sample B are almost the same as those of sample C. On the contrary, sample A begins to melt at a lower temperature than do the other samples. Crystallinity of the polymer estimated by the peak area shows no significant difference among the three samples. This fact means that the changes in the degree of crystallinity hardly occurs by the quenching. Therefore, the crystal structure of the quenched polymer (samples A and B), which is more stable against irradiation, might differ from polymer crystallized in the cold press (sample C). From these results, it was concluded that formation of melt component at a lower temperature is favorable to enhance radiation resistance.

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Received November 12, 1985
Accepted February 14, 1986