Correlated Color Temperature Detection of Radiation Damage in Thermoplastic Polyurethane

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Synopsis

The correlated color temperature change in a polymer was used as a technique to determine the degree of damage sustained due to radiation exposure. This technique shows fair agreement with the swelling technique. These two methods were used to detect radiation damage in four thermoplastic polyurethane grades of different hardness. Polymers that possess higher amounts of isocyanate groups give better resistance to radiation than to lower isocyanate-content polymers.

INTRODUCTION

When a polymer is exposed to ionizing energy, physical and chemical changes occur.[1] It is considered that radiation-induced changes in polymers may occur through different events: (i) chain scission, (ii) crosslinking, and (iii) recombination of broken chains.[1,2] The degree to which the radiation will affect the polymer depends on the chemical composition, general morphology, free energy state of polymer, and irradiation dose applied.

In this paper, the radiation effect on thermoplastic polyurethane is investigated. The polymer is a block copolymer which consists of polymeric diisocyanate units jointed to hydroxy-group-terminated polyether or polyester polyol, both being joined with low molecular weight glycol chain extender. The hard segments can be considered to act as minute filler particles and produce a polymer that is self-reinforced and physically crosslinked. The morphology of this polymer has been investigated before using differential scanning calorimeter (DSC) and X-ray techniques.[3-6] Several techniques have been used to assess the physical changes in this polymer by radiation doses. These are DSC, X-ray diffraction, swelling, and mechanical property measurements.[7] Recently, Lawandy[8] used color measurements for detection of radiation damage in one polyurethane grade.

In this paper a new technique was used to assess the radiation damage in polymers by measuring the color changes of these polymers due to radiation exposure. The chromaticity points representing the sample's color was used to determine the correlated color temperature using the isotemperature lines of the plankian radiator.[9,10]

EXPERIMENTAL RESULTS AND DISCUSSION

Materials

The thermoplastic polyurethanes were supplied by Elastogram, U.K. The batch number, grade, and hardness are shown in Table I. These polymers are

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TABLE I
Description of Polyurethanes

Code	Batch no.	Grade	Hardness	Optimum injection temp. (°C)
A	1079198	CAP 85AK	85 Shore A	175
B	1079199	CAP 90AK	90 Shore A	180
C	1079200	CAP 55DK	55 Shore D	188
D	1079201	CAP 74DK	74 Shore D	198

basically block copolymer of polycaprolactone/diphenylmethyl-diisocyanate-1,4-butanediol. The different grades were injected-molded at their optimum injection temperatures as determined by DSC[4] using a reciprocating screw type machine, Bipel 70/31 injection molder fitter with $2\frac{1}{4}$-oz shot mold. The molding conditions were (i) screw speed 75 rpm, (ii) injection pressure 15,000 psi, (iii) injection speed, moderate, (iv) mold temperature 40°C, (v) injection time, 13 sec, and (vi) cooling time 20 s.

Irradiation Procedure

A cobalt source providing a gamma radiation flux of 0.09 Mrad/h was used. Samples were exposed to ionizing radiation at room temperature and atmosphere. The exposure doses were 5, 10, and 20 Mrad. These doses are expected to cause radiation damage in this polymer. All samples were examined after 72 h after radiation exposure in order to reach complete stability of the soft and hard chains in the polymer.

Color Measurements and Correlated Color Temperature

A Hilger and Watts J40 colorimeter was used to measure the color changes resulted from the radiation exposure. This colorimeter contains a filter slide which holds three filters and passes through a slot in the optical unit which is illuminated by two standard illuminants. With these filters, the tristimulus values X, Y, and Z are read directly from the potentiometer scale with galvanometer. These values are related to the x–y chromaticity coordinates recommended by the Commission International de l'Echairage (CIE 1931) by the relation

$$x = \frac{X}{X + Y + Z} \quad \text{and} \quad y = \frac{Y}{X + Y + Z}$$

The chromaticity points representing the sample's color before and after radiation exposure were located on an x–y chart, and its correlated color temperature is found by interpolation between two isotemperature lines. This can be shown in Figure 1. The color temperature of a sample is the temperature of a plankian radiator which emits radiation of the same chromaticity as the sample. The isotemperature line is the locus of all chromaticity points

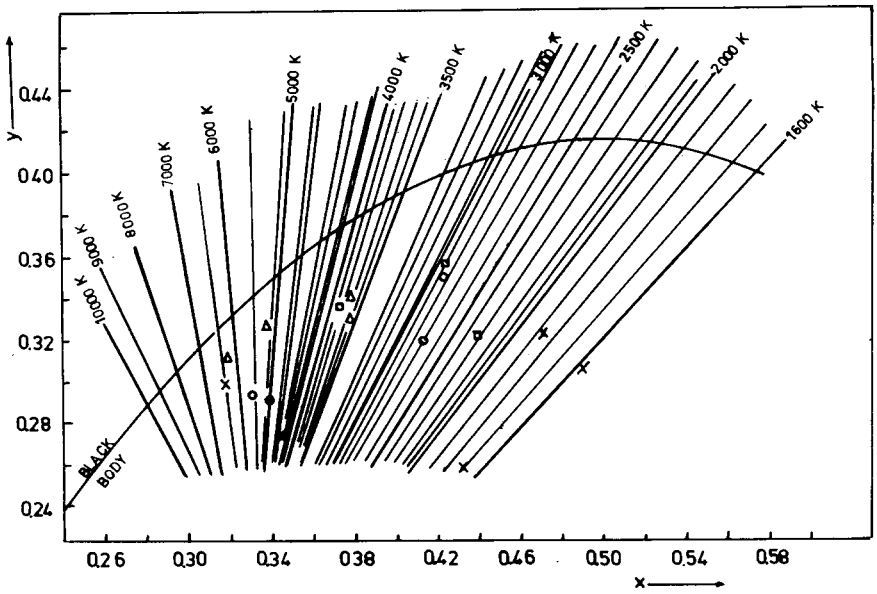

Fig. 1. Isotemperature lines and correlated color temperatures: (○) A; (×) B; (□) C; (△) D.

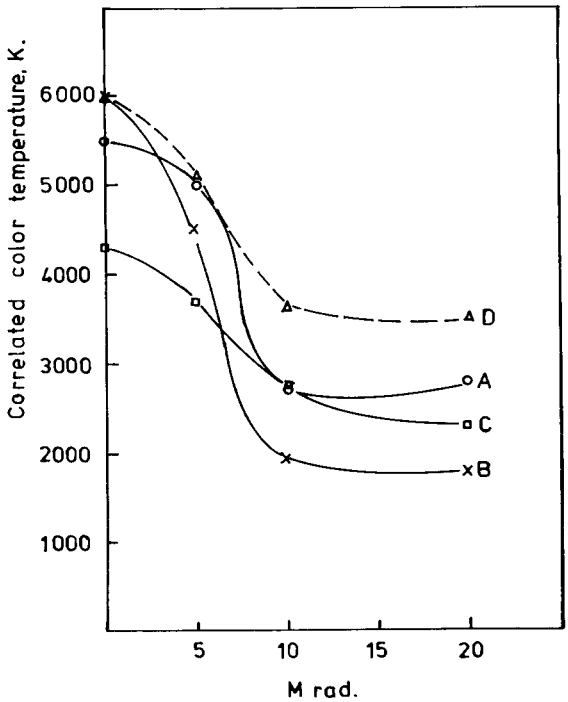

Fig. 2. Radiation doses vs. correlated color temperature.

that have the same temperature as that of the plankian radiator at this temperature. These temperatures are usually given in Kelvin. The method of computing the isotemperature lines was given by Kelly[9] and Robertson.[10]

The color temperature of four thermoplastic polyurethane grades at different exposure doses are shown in Figure 2. From this figure it can be noticed that by exposing these polymer to ionizing radiation doses of 0–10 Mrad the color temperature changes. This change is due to the hot free radicals that are formed by ionization. As the nonradiated samples tend to be either transparent, as in case of polymers A and B, or white, as in case of polymers C and D, their color temperature is relatively high. By radiation exposure, the samples tend to be red in color, signifying that their correlated color temperature became low. This color temperature change is due to the morphological changes which occur in the polymer chains because of damage of the diisocyanate group (which form the crosslink density of the polymer) and the damage to the chain extender which join the different groups of the hard segments. For this reason, samples containing a low degree of diisocyanate groups possess higher chain damage and hence higher correlated color temperature change by the ionizing radiation. However, at higher exposure doses (< 10 Mrad), the ionization to different groups ceased, and the polymer possess a new state of stability. At higher further doses (> 20 Mrad) the polymer may build up new physical crosslinks and recombination of broken chain extender may take place.

Equilibrium Volume Swelling Measurements

The percentage volume swelling for the different polymers at the different exposure doses was measured in toluene. The samples used are the same samples used for measuring the correlated color temperature. The samples were immersed in about 20 mL of toluene. Swelling was allowed to proceed in stoppered glass bottles kept at room temperature for 72 h. At equilibrium swelling, the percentage volume swelling ΔV was calculated as

$$\Delta V = \frac{(W_4 - W_3) - (W_1 - W_2)}{(W_1 - W_2)}$$

where W_1 and W_2 are the weight of the test piece in air and in toluene before swelling; W_3 and W_4 are the weight in air and in toluene after equilibrium swelling. Figure 3 shows a plot of the applied doses vs. the percentage volume swelling. The samples show different degrees in volume swelling depending on the diisocyanate concentration in the polymer. The higher degree of hard segments show a lower degree in volume swelling. Generally, samples show an increase in volume swelling with increase of radiation exposure doses and a state of equilibrium is reached at about 20 Mrad. This volume increase can be explained by the damage that occurs in the hard segments in the polymer by ionizing radiation. However, these curves can be used to assess the degree of resistance to radiation doses and to select the polymer which is suitable for certain engineering application.

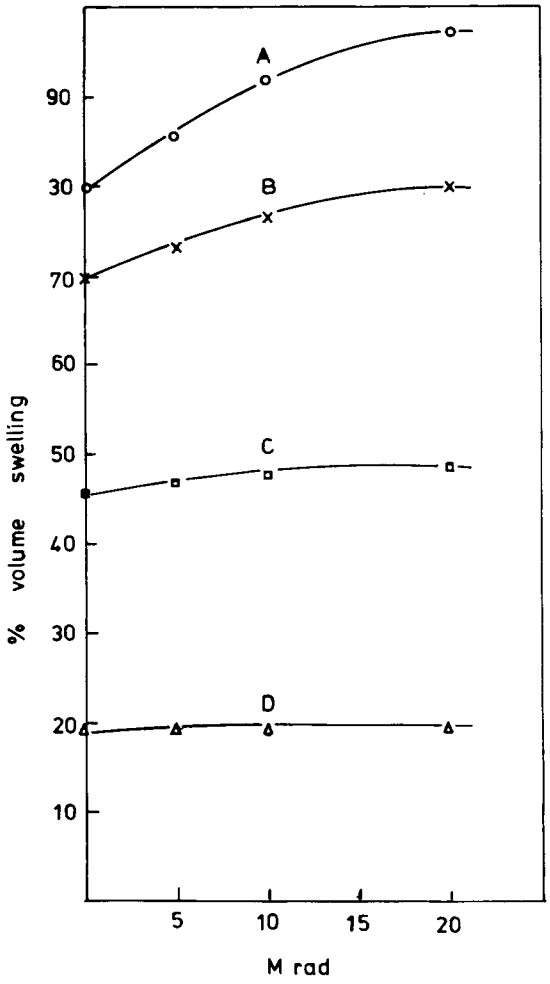

Fig. 3. Radiation doses vs. percentage volume swelling.

In comparing Figures 2 and 3, one can notice that the correlated color temperature measurements are in a fair agreement with the swelling measurements and that the correlated color temperature technique can be used to detect morphological changes in a polymer induced by ionizing radiation.

CONCLUSION

The color temperature is related inversely to the damage of hard segments (the physical crosslinks) by ionizing radiation.

Thermoplastic polyurethane polymers, which have a higher degree of isocyanate groups, possess better resistance to radiation doses than lower diisocyanate content polymers. The damage that occurs to the polymer happens at lower doses (0 to about 15 Mrad), but at higher doses (> 15 Mrad) a state of stability is achieved. Presumably at higher further doses, chemical crosslinks will predominate in the polymer and physical properties may be enhanced.

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