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Studies on radiation-induced current in polymeric insulating materials and their fine structure

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Radiation-induced current (conductivity) (RIC) has been investigated in polymeric materials degraded under combined conditions of heat and radiation. Crystalline materials such as polyethylene, and non-crystalline materials such as ethylene–propylene rubber used for the insulation of wire and cable have been studied. Fine structure changes have been investigated by studying X-ray crystallinity, melting behaviour, the glass transition temperature, and tensile properties. RIC and its decay are affected more by the degree of crystallinity than its perfection. In crystalline samples irradiation after heating causes less degradation than heating after irradiation. Numbers of short-lived carriers increase with a decrease in the degree of crystallinity, indicating the trapping of short-lived carriers in the non-crystalline region and long-lived carriers in the crystalline region.

1. Introduction

It is well known that radiation-induced currents are generally observed in polymeric organic materials. Theoretical considerations of these currents have been reported in the temperature regions above [1] and below [2] room temperature. The number of carriers induced by irradiation and their characteristics depend on the chemical composition and on the fine structure of the materials [3].

We have investigated the radiation-induced currents in polymeric materials used for insulating electrical cables. In previous papers the temperature dependence of radiation-induced conductivity (RIC) above room temperature and the effect of dose rate were studied both in the original materials [4] and in materials degraded under specified conditions. These conditions were "normal" and those of a postulated accident in a nuclear power generating station [5].

In this paper, the relationship between RIC and the morphology of the sample is investigated in detail. Here, the morphology changes of samples are achieved by treatment under heat and radiation, both separately and combined.

2. Experimental procedure

2.1. Samples

High density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), ethylene–propylene rubber (EPR), polystyrene (PS), and polyimide (PIm) were used. Sheets of 1 mm thickness of each sample were prepared from the fundamental compoundings except PIm. A PIm sheet of 50 μm thickness was prepared by a solvent casting process. The evaporated gold electrode was formed on the sample sheet (100 mm × 100 mm) prior to treatment and measurement.

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2.2. Treatments

The treatment conditions used to change the morphology of the samples are listed in Table I. The original sample (O) is degraded by heat or radiation or both. Heating (H) is equivalent to the ageing during the installed life of the reactor (40 years), and the irradiation (γ) with ^{60}Co γ-rays to the exposure dose during accidents.

In the case of a combined condition of (γ) and (H) treatments, two different treatments are applied which depending on the order of the conditions, that is, (γ + H) means γ-ray irradiation (γ) followed by heating (H), and (H + γ) means the opposite.

2.3. Measurements

The applied voltage during conductivity measurement under the irradiation (1000 Gy/h) was 500 V d.c. for the 1 mm-sheets and 200 V d.c. for the 50 μm sheets. σ_0 was defined as the conductivity before irradiation, σ_{eq} as that at an equilibrium state during irradiation, and $\sigma_d(t)$ as that after irradiation. Here, $\sigma_d(t)$ means a decay curve of the conductivity after irradiation. Details of the apparatus and circuit for the measurement have been described elsewhere [4, 5].

The X-ray crystallinities of the samples used were calculated from the wide-angle X-ray scattering (WAXS) curves by a conventional method [6]. The X-ray apparatus was operated at 35 kV, 12 mA, using CuKα radiation with Ni-filter and 2 mm-width collimation. Melting behaviour was investigated using a differential scanning calorimeter (DSC) under a nitrogen atmosphere (sample weight of 4 to 12 mg and heating rate of 10° C min^{-1}. Here, indium was used as a standard material for temperature and enthalpy measurements. The glass transition temperatures of the samples were obtained by studying their changes in rigidity as the temperature was raised step-wise by units of 5° C and kept at each temperature for at least 5 min. The tensile properties were measured using an elongation rate of 500 mm min^{-1} according to JIS C 3004.

TABLE I Treatment conditions of polymeric materials

Items		Treatment conditions
Original	O	no-treatment
Heating	H	121° C, 7 days
γ-ray irradiation	γ γ'	150 Mrad } 1 × 10^6 R/h 186 Mrad } in air
Combined	γ + H H + γ	(H) after (γ) (γ) after (H)

3. Results and discussion

In the preceding paper [4], it was reported that the increase of RIC at a higher temperature was attributable to the increase of short-lived carriers in crystalline samples such as PE and PP, while long-lived carriers increases in non-crystalline samples such as EPR, and PIm. At room temperature, long-lived carriers were predominant in the RIC of crystalline samples.

In order to understand the relationship between the existence of long-lived carriers and the crystallinity of samples, the samples were annealed at temperatures near their melting points, and the RIC of the annealed samples was investigated. It was reported [7] that annealing at a temperature near the melting point of the samples caused an increase in their crystallinity together with an increase of uniformity and of melting temperature. This fact suggests that the perfection of crystallinity is increased through the rearrangement of polymer chains during annealing.

Figure 1 shows the DSC heating curves of LDPE annealed step-wise at a temperature below the melting point (the starting temperature of melting). By increasing the temperature in steps the endothermic profile became sharp, indicating

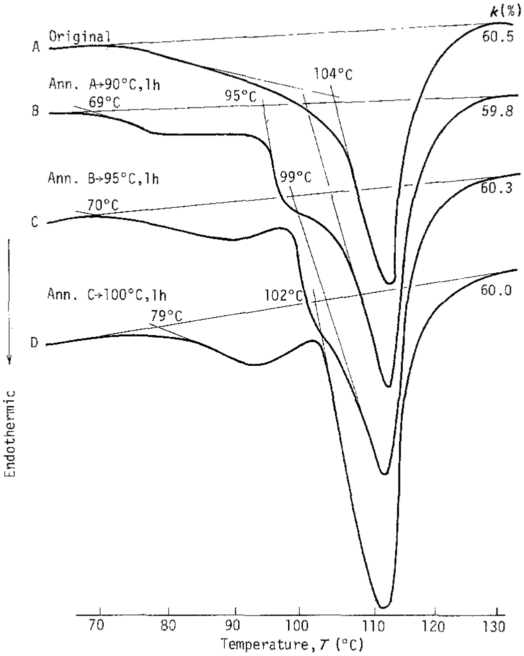

Figure 1 DSC heating curves of annealed LDPE and their X-ray crystallinity (k).

an increase of the perfection of crystallinity. In all samples except the original, a shoulder, or a small peak, was noticed in the heating curves at temperatures below the annealing temperature. This broad endothermic peak corresponds to the melting of the crystals formed during the cooling process from the annealing temperature.

The enthalpy of melting (ΔH_m) is calculated from the area enclosed by the base line and the endothermic peak. The ΔH_m of each sample is similar, indicating the similarity in the degree of crystallinity. This fact is supported by the constant values of X-ray crystallinity of each annealed sample as shown in Fig. 1.

Figure 2 shows the RIC of those annealed samples measured at 20° C and 80° C. At 80° C, the equilibrium conductivity (σ_{eq}) is about one order of magnitude higher than σ_{eq} at 20° C, but at each temperature, no difference of σ_{eq} is observed in various samples.

Decay curves of RIC after irradiation ($\sigma_d(t)$) are also quite similar to each other irrespective of the annealing conditions. Decrease of $\sigma_d(t)$ at 80° C is quite rapid compared with that at 20° C, indicating the formation of large numbers of short-lived carriers [4]. On taking the case of DSC heating curves as shown in Fig. 1, it is suspected that not many trapping sites for long-lived carriers can be found in the samples at 80° C, at which temperature the partial melting of the sample takes place. This means that the trapping sites of long-lived carriers are related to the crystallites, moreover, the perfection of crystallites does not affect RIC when the degree of crystallinity is kept constant.

In order to investigate the relationship between the degree of crystallinity and the RIC, crystalline samples were treated under the conditions specified in Table I before RIC measurements.

Table II shows X-ray crystallinity, thermal properties and tensile properties of the treated samples. The degree of crytallinity of the samples treated under the combined conditions of heat after irradiation decreased considerably. In the cases of LDPE and HDPE, no endothermic peak is observed. On the other hand, in the case of PP, an endothermic peak was obtained in the heating curve of the sample treated by (γ+ H). The reason for this difference will be discussed later.

In the samples treated with irradiation after heating (H + γ), no decrease of crystallinity and an endothermic peak in the heating curves of HDPE and PP were observed. In the case of LDPE, the sample sheets could not keep their shape after (H) treatment, since the heating temperature of 121° C was a little higher than their melting point. Accordingly, the next treatment, i.e. irradiation, was not possible. In the case of (γ+ H) treatment of LDPE, cross-linking takes place during irradition so that it can withstand 121° C, or (H) treatment.

HDPE treated by (H + γ), and all treated PP, became quite brittle, giving no elongation, i.e. $E_b = 0$. On the other hand, the samples of HDPE and LDPE after (γ+ H) treatment became quite soft, just like rubber, giving small values of

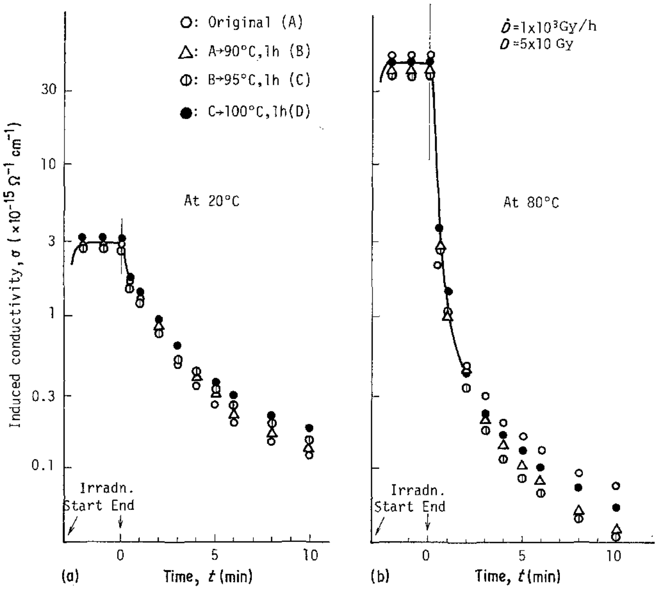

Figure 2 Radiation-induced conductivity and its subsequent decay in LDPE annealed under various conditions.

TABLE II X-ray crystallinity (k), melting behaviour (T_s, ΔH_m), glass transition temperature (T_g) and retention fraction of tensile elongation at break (E_b) and tensile strength at break (T_b) of the treated samples

Sample	Treatment	K (%)	T_s (°C)	ΔH_m (g)	T_g (°C)	E_b (%)	T_b (%)
HDPE	O	73	124	96	−18	100	100
	(H + γ)	79	122	88	−15	0	20
	(γ + H)	49	no endotherm		−37	10	46
LDPE	O	60	103	54	−45	100	100
	(γ + H)	48	no endotherm		−32	8	40
PP	O	52	147	71	−20	100	100
	(H + γ)	57	131	113	−8	0	36
	(γ′)	50	114	113	*	0	10
	(γ′ + H)	36	130	71	*	0	*

*Unable to measure due to brittleness.

elongation (E_b) and strength (T_b). The large decrease of X-ray crystallinity combined with a lack of endothermic peak in the DSC heating curve of these samples indicates the destruction of crystallites.

It is well known that cross-linking by irradiation is usual in PE. The higher the dose and the lower the dose rate, the greater the formation of peroxide cross-links which decompose when PE is heated above 150° C [8]. In our case, heating (H) after irradiation (γ) was at 121° C as shown in Table I, but the decomposition of peroxide cross-links in the sample might to some extent reduce the crystallinity.

In our case of PP, no softening was observed and only a reduction of the crystallinity was noticed as seen in Table II. A similar discussion as for the case of PE mentioned above is not applicable. The relationship between the degree of crystallinity and crystalline form in PP samples was investigated, since two types of crystalline form, the α-form in normal sample and the β-form in samples quenched from the melt, have been reported [9].

Figure 3 shows the wide-angle X-ray scattering (WAXS) curves of the treated PP. Original PP (O) shows typical characteristics of α-form with a quite small amount of β-form indicated by the shoulder at 16° (2θ). This shoulder, the β-form, disappeared after (H) treatment to give only the α-form, and the subsequent irradiation (in the (H + γ) treated sample) produced the large amount of β-form crystal as shown in Fig. 3.

In the irradiated sample, β-form crystals are produced to give the similar WAXS patterns to that of the (H + γ) treated sample. Heating of the irradiated sample caused the change of β-form into α-form in the (γ′ + H) treated sample as shown in Fig. 3.

It was clarified that the PP sample had decreased crystallinity after (γ + H) treatment, but exhibited an endothermic peak corresponding to the melting of the sample in the heating curve, unlike the cases of LDPE and HDPE.

Irradiation in air might cause chain-scission in PP, but the polymer molecules may crystallize even after chain-scission to produce β-form crystallites just as in the quenched sample.

Figure 4 shows the RIC of various samples

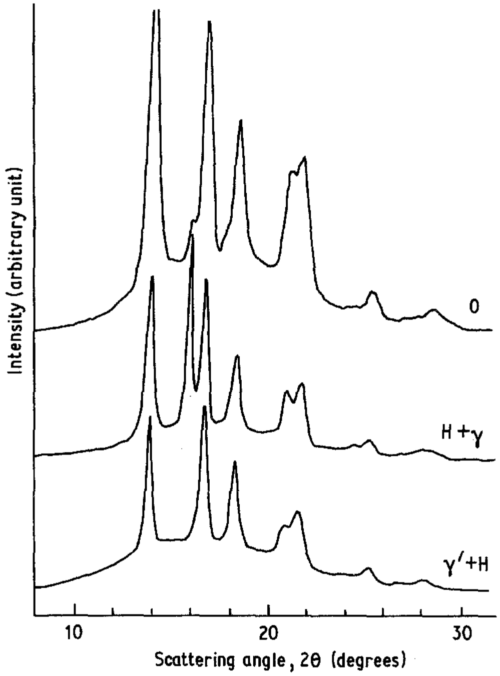

Figure 3 Wide-angle X-ray scattering curves of the original PP sample, and samples treated by a combination of heating and γ-ray irradiation.

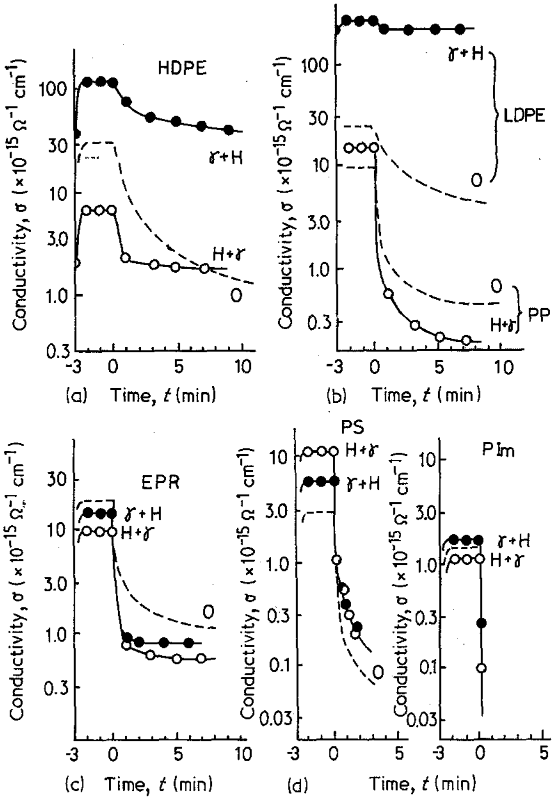

Figure 4 Radiation-induced conductivity and its subsequent decay in various polymers treated by a combination of heating and γ-ray irradiation.

treated by (γ + H) or (H + γ) conditions. The RIC curves of LDPE treated by (H + γ) and of PP treated by (γ' + H) were not recorded, since the LDPE sample sheet was melted down during (H) treatment and the PP sample sheet was broken before being set into the RIC measuring apparatus because of its brittleness.

It is clearly noticeable that HDPE and LDPE treated by (γ + H) show quite high values of σ_0, σ_{eq} and $\sigma_d(t)$, while other samples, i.e. HDPE and PP treated by (H + γ) and non-crystalline samples treated by (H + γ) or (γ + H), do not show remarkable changes in RIC from those of the original samples.

In the HDPE and LDPE treated by (γ + H), the following two remarks are valuable; the large σ_0 suggests the implantation of carriers during the application of 500 V d.c. and the small increase of σ_{eq} from σ_0 and also the rapid recovery, of $\sigma_d(t)$ to σ_0 suggest the production of a small number short-lived carriers during irradiation.

In other words, in samples with a low degree of crystallinity in which crystallites cannot be detected by thermal analysis, only short-lived carriers are produced, suggesting that there are no trapping sites for long-lived carriers.

4. Conclusions

In crystalline samples such as PE and PP, the RIC is affected by the degree of crystallinity, but not by the crystalline perfection. By treatments with combined conditions of heating and irradiation, both in air, crystalline samples change their fine structure such as degree of crystallinity and crystalline form. Heating after irradiation causes large changes in polyethylene samples, for example, no endothermic peak, high dark current (σ_0) and a small increase of RIC are observed. The increase of RIC is mainly attributed to the presence short-lived carriers. Increase in the number of the short-lived carriers in the samples with lower degrees of crystallinity suggests that the trapping sites of long-lived carriers are in crystalline regions and those of short-lived ones in non-crystalline regions.

In non-crystalline samples such as EPR, PS and PIm, treatment with combined conditions of heating and irradiation caused no special effect on RIC because of the lack of crystalline regions which could cause fine structure change.

It is suggested that the non-crystalline material can be used satisfactorily as electrical insulation for cables in the containment of atomic power generating stations because the RIC does not change very much even after deterioration.

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