Effect of annealing and drawing on thermoluminescence of poly(ethylene terephthalate)

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(Received 3 April 1987; revised 29 June 1987; accepted 9 July 1987)

As a fundamental study on the structure and properties of poly(ethylene terephthalate) (PET), thermoluminescence (TL) of X-ray irradiated PET films at both low temperatures (starting from liquid-nitrogen temperature) and high temperatures (starting from room temperature) was investigated by means of the glow curve and thermal decay. It is concluded that most of the electron traps in X-ray irradiated PET films are located in the amorphous region in both low- and high-temperature TL. It is especially emphasized that crystal interfaces also contribute to the high-temperature TL of annealed samples and that the relaxed state of amorphous chains is more favourable to TL than the tensioned state.

(Keywords: thermoluminescence; annealing; drawing; glow curve; thermal decay; anti-fatigue property; poly(ethylene terephthalate))

INTRODUCTION

Thermoluminescence (TL) from inorganic materials can be dated back to the early 1940s. Johnson (1939)[1] first studied TL and assumed that glow is due to release of electrons from traps. The TL cumulative intensity is proportional to the probability with which an electron escapes from a trap. Furthermore Randal *et al.*[2,3] studied the thermal stability of trapped electrons and indicated that the probability of release of an electron from a trap of depth E at temperature T is given by $S\exp(-E/kT)$. Where S is a frequency factor, which generally means the jumping frequency of an electron in detrapping from a trap site, k is the Boltzmann constant and E is considered as the thermal activation energy. The change of TL cumulative intensity of a polymer is mainly attributed to the competing effect of S and E. Detailed observations of TL of polymers were initiated by Nikol'skii and Buben[4] and Charlesby and Partridge[5] in the early 1960s. These pioneering studies on polymers indicated a close correlation between TL and molecular motion, and showed the usefulness of TL for studying molecular motion and structural transitions in polymers.

Recently Miyasaka *et al.*[6,7] suggested the possibility of application of TL to the characterization of poly(ethylene terephthalate) (PET) tyre cord. They measured the TL glow curves of PET fibres prepared under different conditions below and above room temperature, and indicated that the fatigue resistance property of the fibre is correlated to the strong and comparatively sharp TL maximum which appears at the glass transition T_g. In order to obtain more detailed information on the molecular motion relating to the fine structure from the TL data, more systematic studies on TL of solid PET must be done. In this report the authors' interest is concentrated on the fundamental aspects of TL of PET to study the relationship between TL and fine structure. It is well known that three aspects are included in the TL study of polymers, i.e. TL species or origin, trap sites and luminescence centres. The third aspect has attracted the interests of many researchers so far[8,9], while the first two have been studied only by a few groups. This paper presents the effects of annealing and drawing of PET film on the TL and discusses the trap sites on the basis of experimental data and their analyses. Because of the easy treatment and expected high accuracy in experiments, PET films instead of fibre specimens were used in this study.

EXPERIMENTAL AND SAMPLE PREPARATION

Samples

An undrawn and unannealed PET film (provided courtesy of Teijin Co. Ltd) was used as the original sample in this study. The intrinsic viscosity of the polymer was 0.65 in *o*-chlorophenol at 35°C. The X-ray diffraction patterns of the film indicated no preferential molecular orientation and very poor crystallinity (almost amorphous). The density of the film was 1.350 g cm^{-3} at 20°C, giving a crystallinity of 10% when 1.515 g cm^{-3} and 1.333 g cm^{-3} were used as the densities of crystalline and amorphous phases[10]. The densities of the samples were determined according to ASTM 1506-60T in an n-heptane/carbon tetrachloride linear gradient at 20°C. Some of the original films were annealed in vacuum at 180°C for various times (1, 10, 100 and 600 min) while others were drawn in water at 80°C. The draw ratio was changed from 2 to 5, the maximum draw ratio under this condition. The variations of crystallinity induced by annealing and drawing are shown in *Figure 1*.

All the samples were purified by repeated extraction with hexane in a Soxhlet apparatus, dried in vacuum at room temperature for 12 h, and finally cut into a rectangle of 20 mm × 18 mm for setting on a sample holder for the TL measurement.

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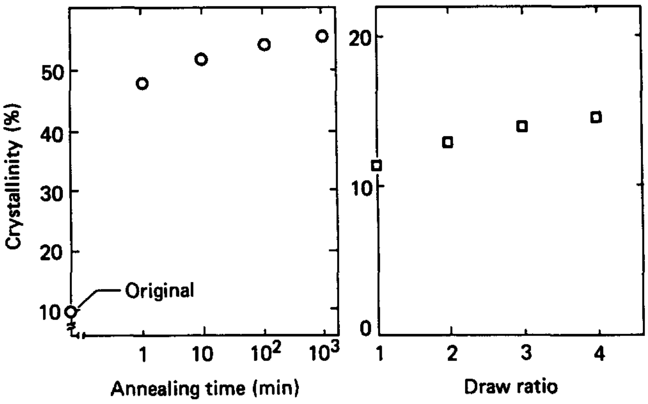

Figure 1 Crystallinity of PET film as a function of annealing time and draw ratio. Annealing was carried out in vacuum at 180°C and drawing was in water at 80°C

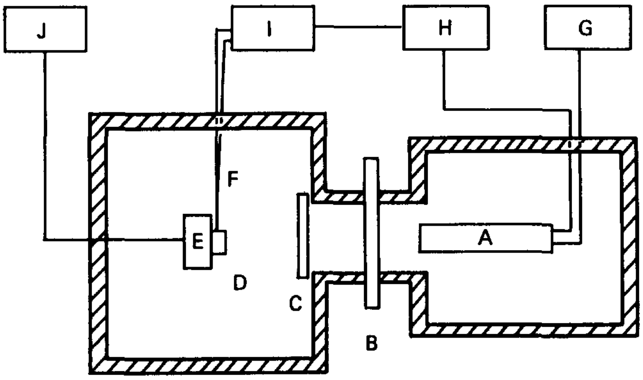

Figure 2 Block diagram of TL intensity-measuring system: A, photomultiplier; B, shutter; C, filter case; D, sample; E, sample holder; F, thermocouple; G, d.c. source; H, current meter; I, recorder; J, temperature controller

Method of thermoluminescence determination

A block diagram showing the measuring procedure of TL is given in *Figure 2* and more detailed descriptions can be found in ref. 11. TL measurement generally involves two operations: irradiation by X-rays and the following measurement of TL glow intensity above the irradiation temperature. In this study the irradiation was carried out by X-rays from Cu targets of Rikadenki RU-3 and DF-3 apparatus operating under 40 kV/50 mA and 35 kV/20 mA for high- and low-temperature TL measurements, respectively. The dose and the wavelength distribution of X-rays used were not measured since they were not essential in this study.

In the high-temperature TL measurement, samples were irradiated in air at room temperature for 2 h and then fixed to a copper sample holder which was set in a vacuum cryostat at a pressure of 10^{-3} torr to prevent oxidation. After free emission for 1 h at room temperature, the sample was warmed up to about 450 K at a rate of 6 K min^{-1} during which the TL glow intensity was continuously measured.

We were afraid of a possible contribution of molecular oxygen to the TL intensity. Particularly, in the case of annealed samples there is a possibility that oxygen works as a luminescence centre when ionized by X-ray irradiation. The effect of oxygen on TL was proven by Charlesby and Partridge in the case of polyethylene, where oxygen removed some peaks and produced an extra peak in the glow curve. It was, however, shown that the effect of oxygen could be avoided by pumping[1,12]. Considering this fact, the TL measurement was carried out under a vacuum of 10^{-3} torr by pumping, and therefore, the influence of oxygen was negligibly small in this study.

In the low-temperature TL measurement the sample set on the sample holder in the cryostat was cooled to about 77 K with liquid nitrogen, and irradiated by X-rays for 1 h at that temperature. The procedures of TL measurement following the irradiation were the same as those for high-temperature TL measurement. The sample was heated up to room temperature.

RESULTS AND DISCUSSIONS

Glow curves of high-temperature thermoluminescence

Figure 3 shows the change in high-temperature TL glow curves with annealing at 180°C. The glow intensity has been standardized by the weight and surface area of each sample. It is seen that the original amorphous sample exhibits a comparatively sharp TL glow peak with a maximum at around 65°C and a long emission tail on the higher-temperature side, making the peak asymmetrical. It is natural to consider that the first glow peak is due to the release of electrons from trap sites in the amorphous region because molecular motion enhanced by T_g is expected to cause a remarkable release of electrons trapped in the region. Although the TL peak maximum at 65°C must be related to the glass transition, the peak is about 15°C lower than the T_g reported[13]. This may be related to the well known fact that the glass transition usually occurs over a comparatively wide range of temperature. *Figure 3* shows that most of the electrons trapped in the amorphous region are released at the

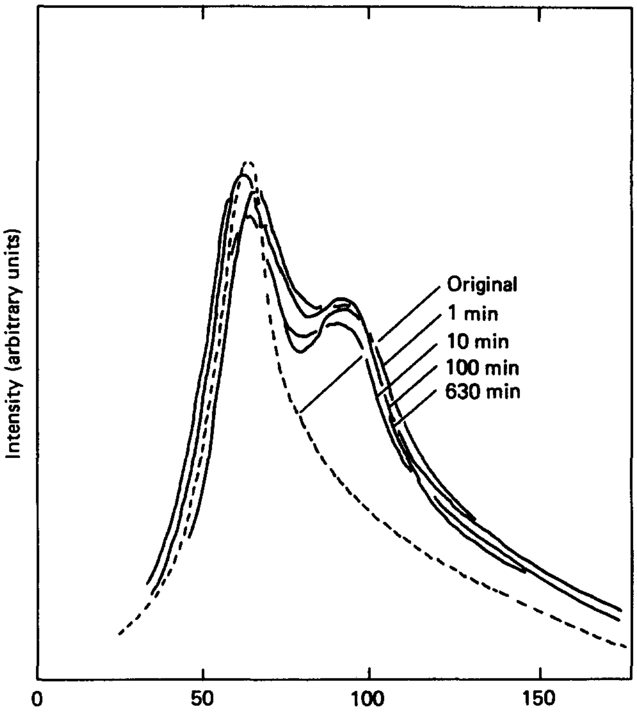

Figure 3 High-temperature TL glow curves of PET films annealed at 180°C for various times

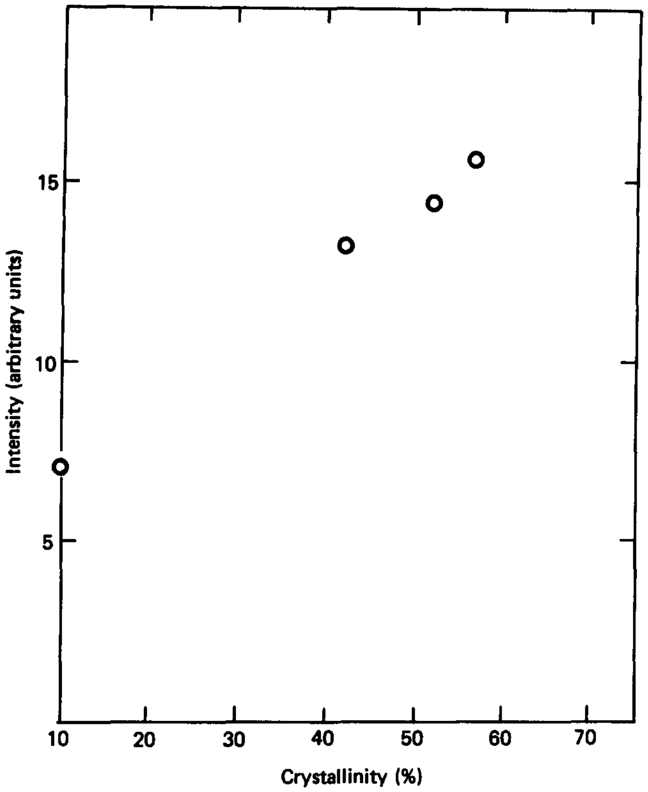

Figure 4 High-temperature TL integrated intensity of PET films annealed at 180°C as a function of crystallinity. The integration was made on the TL glow curves in *Figure 3* between 20 and 180°C

margin of the distributed glass tranisition temperature, in other words, that the detrapping of electrons is caused by Brownian motion of the more localized amorphous segments rather than that of the majority of the segments. This is an important feature of the TL glow of polymers. It should also be remarked that the asymmetrical profile of the high-temperature TL glow curve of the original sample is very similar to the temperature dispersion curves of loss modulus of PET films[14], although the temperature is lower in the former than in the latter. This similarity must be due to the fact that TL glow is affected by as many modes of relaxation as revealed by the mechanical dispersion. *Figure 3* also shows that annealing changed the TL glow of PET from a single peak to a double peak. In addition to the main peak due to T_g a comparatively weak peak appears at around 90°C in the annealed samples. This implies that another trap site population is induced or increased with annealing.

According to *Figure 3*, the TL glow curve changes with annealing in a very short time, which must correspond to the very quick structural changes indicated by the increase in the crystallinity in *Figure 1*. *Figure 4* presents a plot of TL intensity integrated over the glow curves in *Figure 3* between 20 and 180°C as a function of the crystallinity shown in *Figure 1*. It can be seen that the integrated intensity increases with increasing crystallinity, and that the increase in the integrated intensity is mainly attributed to the appearance of the second peak at about 90°C. This implies that the second peak may be related to increased crystallinity, which makes us think that the second peak may be attributed to detrapping on the crystal interfaces or in the less mobile non-crystalline region near the interfaces, as suggested by Havens and coworkers by means of a multiple-pulse ^{1}H n.m.r. study of PET[15]. As mentioned above, the first peak at about 65°C is related to the T_g induced by Brownian motion of the amorphous phase. It should be noted that this amorphous glow remains almost unchanged after annealing in spite of the great decrease in the fraction of the amorphous phase (see *Figure 1*). This indicates that the TL glow ability near T_g of the amorphous phase standardized by unit weight is much increased by annealing. This is completely different from the TL glow ability at low temperature, as will be shown later.

In contrast to annealing, the shape of the glow curve was not much affected by drawing, although the intensity increased to some extent, as seen in *Figure 5*. The result that no remarkable change in the TL profile was induced by drawing may be related to the fact that the crystallinity did not increase remarkably after drawing, as seen in *Figure 1*. It should be remembered that the noticeable change in the profile caused by annealing was accompanied by a remarkable increase in crystallinity. It is well known that drawing induces great structural changes such as molecular orientation[16] and crystallization, although the latter was not so remarkable in this case. These structural changes must cause changes in electron trap sites for TL: some are enhanced by drawing while others are deteriorated. The increase in the TL glow ability near T_g caused by annealing suggests that the relaxed amorphous state formed by annealing increases the TL glow ability. Thus drawing must decrease the TL intensity, for it necessarily causes the tensioned amorphous state. On the other hand, the defects and microvoids that are also necessarily induced by drawing provide more TL trap sites so as to enhance the TL intensity. The competing effects of the two changes may result in the slight increase of TL intensity shown in *Figure 5*.

Thermal decay in high-temperature thermoluminescence

As indicated by the above results, the TL glow curve is effective in distinguishing the trap site populations. The TL glow curve is, however, both time- and temperature-dependent. In the TL glow curve obtained by heating at a constant rate, the temperature effect is emphasized much

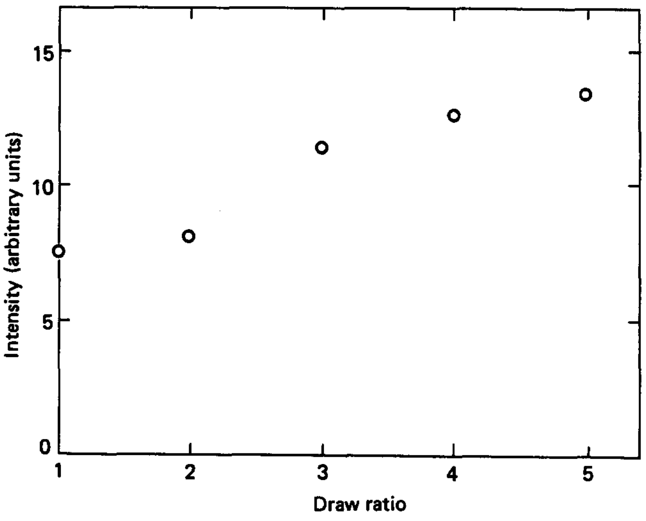

Figure 5 High-temperature TL integrated intensity of PET films drawn in water at 80°C as a function of draw ratio. The integration was made in the same way as that in *Figure 4*

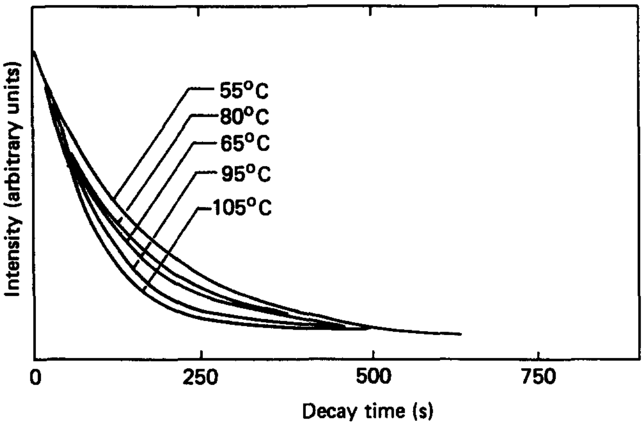

Figure 6 High-temperature TL isothermal decay profiles of PET films annealed at 180°C for 10 min. The temperature on each profile shows that at which the decay was measured isothermally

more than the time effect. This makes the method effective in distinguishing different trap site populations: for example, two trap site populations were distinguished in the annealed films. We next investigated the TL intensity decay with time at a given temperature to study the detailed relaxation properties of the particular trap site populations.

There have been several decay laws[3] suggested for inorganic materials. Of them, exponential decay is the simplest. In general, the decay due to traps is a somewhat complicated phenomenon, especially in the case of polymers. However, we assume that this mode of deday is still essential even in polymers, if retrapping of electrons is negligible.

On the basis of the electron release model referred to in the introduction, we assume that the trap depth E does not have a distribution. If n is the number of trapped electrons and p is the probability for a trapped electron to recombine with the ionized parent luminescence centres, then

$$I \propto pn = -\mathrm{d}n/\mathrm{d}t \qquad (1)$$

and hence

$$I_t = I_0 \exp(-pt) \qquad (2)$$

where I_0 and I_t are intensities of thermoluminescence at time t_0 when the temperature is first reached and at time t afterwards. The decay curve therefore is exponential. On the other hand, according to the proposal of Randal, p is given by

$$p = S \exp(-E/kT) \qquad (3)$$

where E is the thermal activation energy or trap depth and S is the attempt-to-escape frequency factor.

If p is independent of time, the logarithm of the intensity is expected to be linear with time.

Typical TL decay curves above room temperature are presented for annealed PET films in *Figure 6*. The decay experiment was carried out as follows. After a period of glow measurement at a given heating rate, heating was stopped to keep the specimen at a constant temperature, and then the TL intensity was followed as a function of time at that temperature. The TL intensity at $t = 0$ in the decay curve for a given specimen varied depending on the temperature. In *Figure 6* all decay curves are drawn so as to have the same intensity value at $t = 0$, for convenience. One recognizes that the TL decay above room temperature lasts longer than 500 s. *Figure 7*, where the data in *Figure 6* are replotted in a semi-log scale, shows that a linear relationship is found up to 250 s at each temperature. Although the decay curve after 250 s deviates from the linear plot, most of the decay finishes after 250 s. It should also be remarked here that the linear plot is only expected under an assumption that the glow at a given temperature corresponds uniquely to a certain depth of traps. It is clear that the validity of the assumption must become worse with increasing time at a given temperature, and therefore only the data in the linear decay region are discussed here. The slopes of the linear plots of the intensity decay, which are proportional to the rate of detrapping, are shown as a function of temperature for original and annealed specimens in *Figures 8* and *9*, respectively. That the rate of detrapping increases with increasing temperature can be expected from equation (3). *Figures 8* and *9* show the same temperature dependence, but the rate of detrapping of the annealed specimens is less than those in *Figure 8* as a whole. This reveals a complex effect of the activation energy E and frequency factor S, which can be understood from equation (3) too. Thus the result that the rate of detrapping decreased by annealing implies that the fraction having lower mobility was strengthened by annealing. This result is in qualitative agreement with n.m.r. data on the same kind of samples[15]. In other

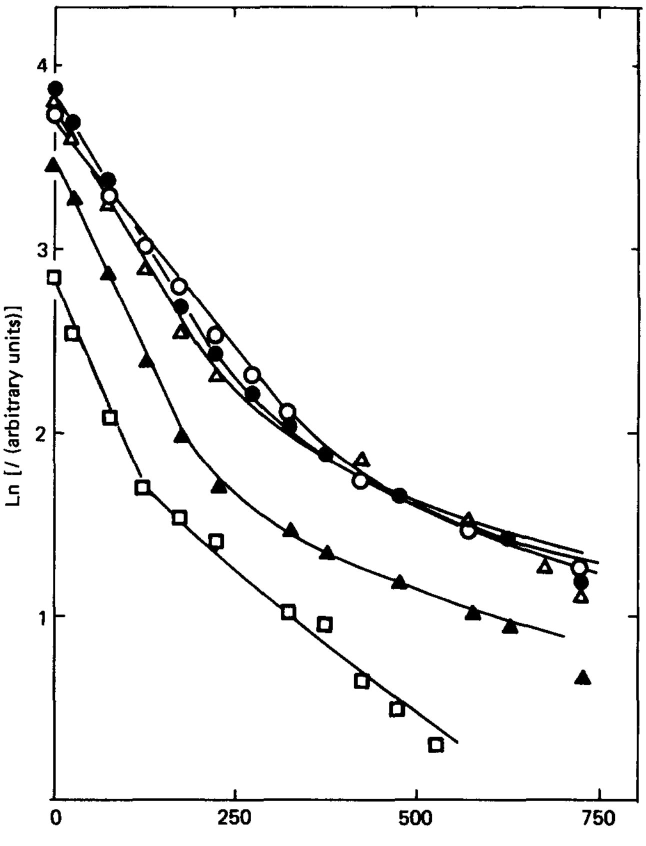

Figure 7 Replot of data in *Figure 6* in semi-log form. Temperature (°C): ○, 55; ●, 65; △, 80; ▲, 95; □, 105

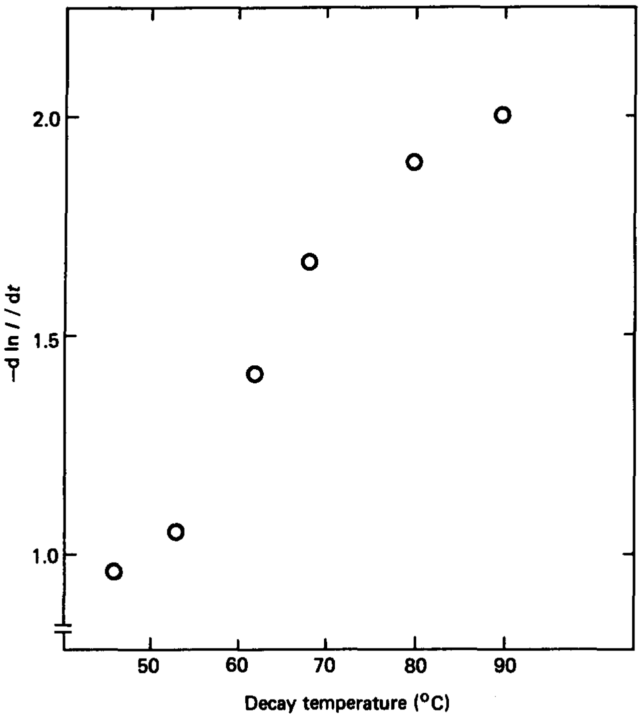

Figure 8 Rate of detrapping of TL of original PET film as a function of the temperature at which the isothermal decay was measured. Rate of detrapping is assumed to be equal to the slope of the plot in *Figure 7*

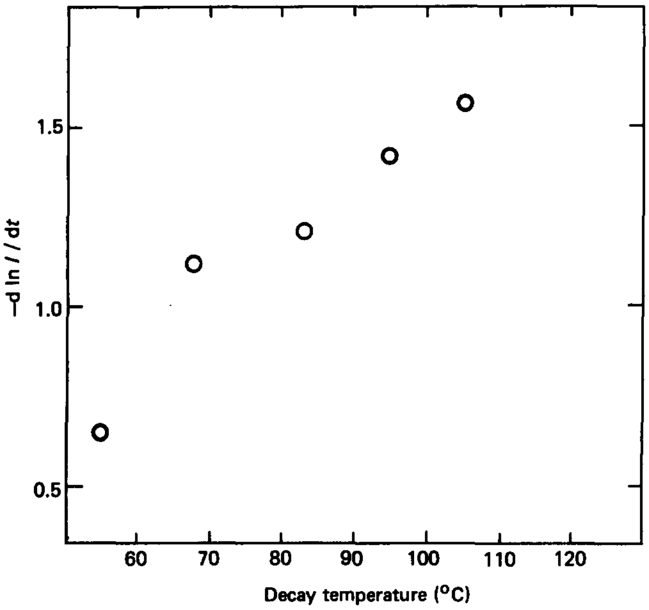

Figure 9 Rate of detrapping of TL at constant temperature as the temperature at which the isothermal decay was measured. The same assumption is made here as in *Figure 8*

words, the fraction of the less mobile non-crystalline regions or crystal interfaces must have been increased by annealing. This also corresponds with the second peak in the glow curves of the annealed samples.

Figure 10a shows semi-log plots of decay curve at 65°C of samples annealed at 180°C for various times and *Figure 10b* shows the rate of detrapping estimated from *Figure 10a*. No notable effect of annealing time is observed on the rate of detrapping in *Figure 10b*. We assumed that the 65°C decay is related to detrapping in the amorphous region. It is interesting that the rate of detrapping in the amorphous phase remains almost unchanged with annealing, while the TL glow ability near T_g standardized by unit weight of the amorphous phase was much higher and increased quickly by annealing, as observed above.

Low-temperature thermoluminescence

Figure 11 shows the effect of annealing on the low-temperature TL glow curves of PET films. As one can see, the glow curves gradually decrease in intensity with increasing annealing time, while the shape of the curves remains almost unchanged. In our previous paper[6], it was shown that the intensity of low-temperature TL or PET tyre cord fibres produced by different companies varied from one another depending on their manufacturing conditions, whereas the profile remained almost unchanged. The profile of low-temperature TL is characterized by a strong peak with a maximum at about –150°C and a tail towards higher temperature, which suggests that there must be several modes of relaxation. According to Ito *et al.*[9], who simultaneously measured the TL, the dielectric dispersion and the thermally stimulated electrical current (TSC) of a PET film, three distinguishable modes of dispersion contribute to the low-temperature TL curve of PET. The TL at low temperature must be related to very localized modes of

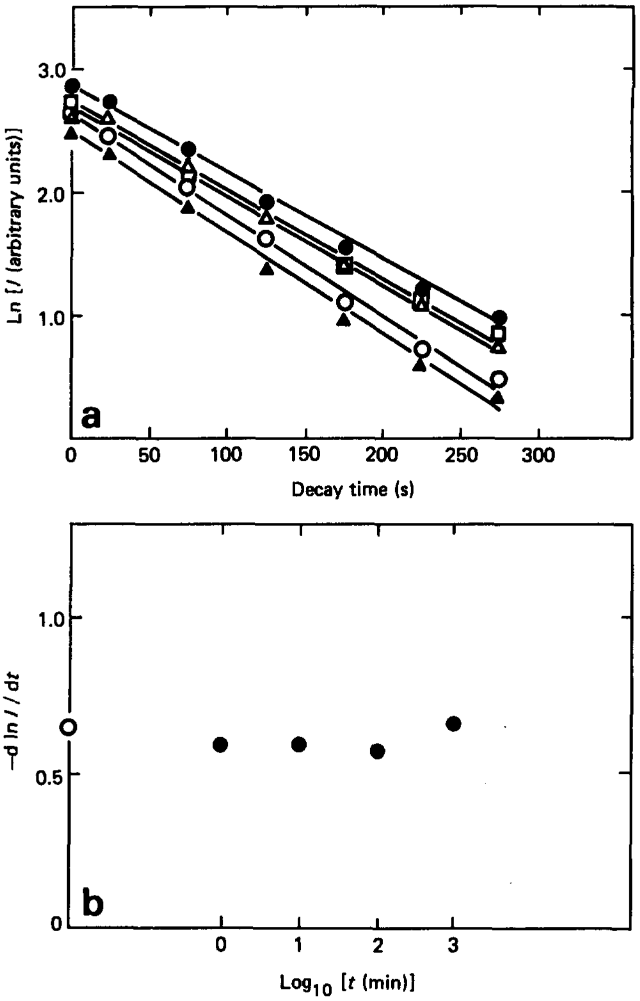

Figure 10 (a) Semi-log plot of high-temperature TL isothermal decay at 65°C for PET films annealed at 180°C for various times (min): ●, 0; □, 1; △, 10; ○, 100; ▲, 630. (b) Rate of detrapping estimated from (a) as a function of annealing time, *t*. The open circle is for the original film

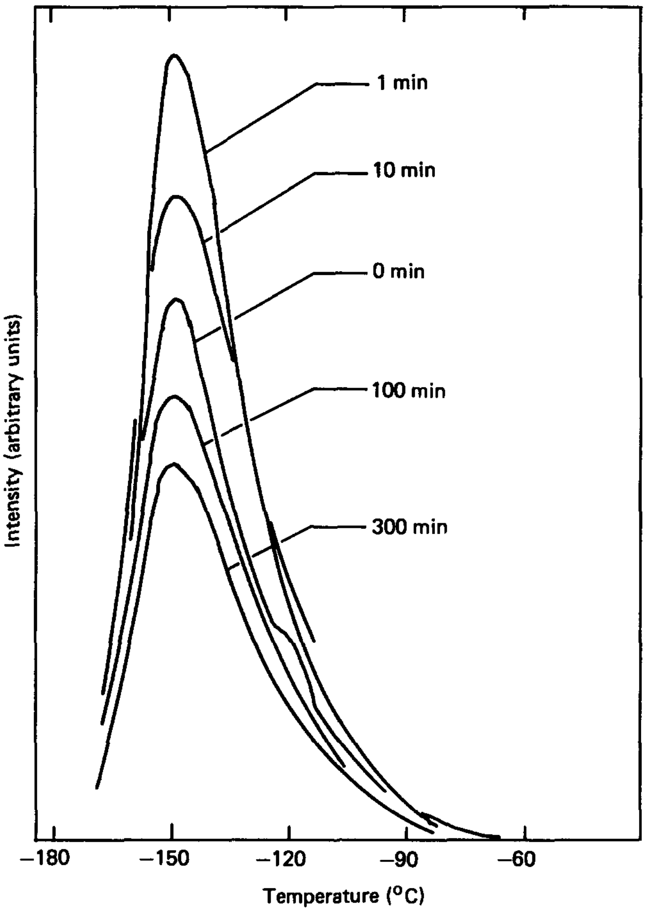

Figure 11 Low-temperature TL glow curves of PET films annealed at 180°C for various times: 0 min: for the original film

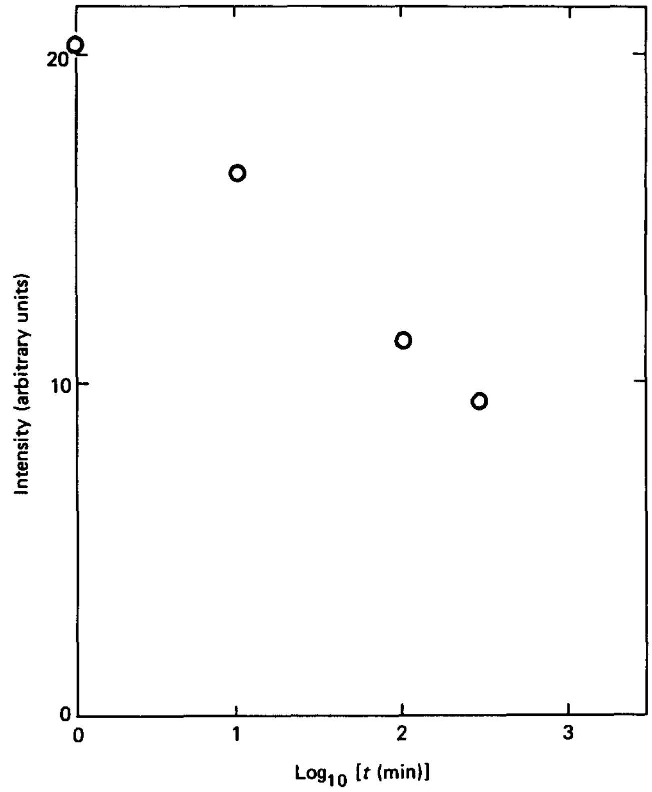

Figure 12 Low-temperature TL integrated intensity of PET films annealed at 180°C as a function of annealing time, *t*. The integration was made on the glow curves in *Figure 11* between −180 and −60°C as a function of annealing time

motion of PET chains, particularly in the amorphous region. Thus the decrease in the intensity shown in *Figure 11* may be directly related to the decrease in the amorphous fraction with annealing. However, the comparison of the change in integrated intensity shown in *Figure 12* with that of crystallinity shown in *Figure 1* indicates that the decrease in the TL intensity cannot be attributed only to decrease in the amorphous fraction, but to some other reasons. This implies that a change in the very fine structure, which may be difficult to characterize by techniques other than TL, is induced by annealing in the amorphous region.

CONCLUSIONS

In this paper we discussed the effects of annealing and drawing of PET films on TL. The high-temperature TL glow curve of PET films exhibits a first peak at about 65°C with a long tail towards higher temperature, and for annealed films, a weaker but noticeable extra peak at about 90°C. The 65°C peak is considered to be related to T_g, and therefore to the detrapping of electrons trapped in the amorphous region. The crystal interfaces or less mobile non-crystalline regions near the interfaces are considered to provide extra trap sites, which make a new peak at 90°C in the high-temperature TL glow curve of annealed films. The rate of detrapping is decreased remarkably by annealing. The intensity of low-temperature TL decreased with annealing time while the profile remained unchanged. The decrease in the low-temperature TL implies that annealing causes some changes in the fine structure in the amorphous region, which is difficult to characterize by techniques other than TL.

ACKNOWLEDGEMENT

This work was supported by a Grant-in-Aid for Scientific Research.

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