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APPLICATION OF THERMOLUMINESCENCE (TL) TO CHARACTERIZATION OF PET FIBERS

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Introduction

This note is prepared to show the usefulness of the thermoluminescence (TL) technique for the characterization of PET fibers. TL is the glow which a solid organic material irradiated at low temperature makes as it is heated. The secondary electrons extracted from the molecules by the irradiation (x-ray in this case), after having spent their kinetic energies, are trapped without recombining with their parents or any other positive ions in their vicinity. As the sample is heated, the trapped electrons are released to glow the luminescence at particular temperatures depending on the stability of the trapping sites. It is well known that TL is very sensitive to the relaxation behaviour of polymers. For example, Zlatkevich and Crabb¹⁾ recently studied the TL of Polyethylene (PE) specimens prepared by different ways to show that the TL glow curves were sensitive enough to distinguish each one from others. According to them, the TL was highly correlated with the NMR data obtained by Kitamaru and his coworkers²⁾. The TL glow of PET has been studied by some researchers mainly with their interests concentrated into the identification of the glow peaks. For example, Ito and Nakakita³⁾ measured simultaneously TL, TSC (Thermally stimulated Current) and dielectric loss, and attributed the low temperature TL peaks to three different relaxation mechanisms. It was natural that PET film specimens have been used in their TL measurements instead of fiber specimens, because of the easy treatment and the expected high accuracy in the experiments.

In this note our interest is concentrated into a

possibility of TL application to the characterization of PET fibers. We often meet a difficulty in distinguishing fibers with different properties by usual polymer characterization techniques such as x-ray, birefringence, IR spectrum, density, etc. This means that some properties depend on the structure finer than that detected by these techniques. The high sensitivity of TL may make a useful method to characterize such a delicate structure.

Experimentals

Sample: Five kinds of PET fibers, provided by courtesy of Teijin Co. Ltd, were used after washing with acetone to remove the lubricant. As seen in Table 1, they were prepared under very different conditions; Sample 1, 2 and 3 are as-spun fibers made at different spinning speeds, Sample 4 is a drawn fiber prepared by drawing Sample 1 under a usual conditions for commercial yarn making, and Sample 5 is a drawn fiber prepared under conditions particular to tire-yarn making and the molecular weight is larger than that of other four samples. X-ray diffraction photographs in Fig. 1 shows that the degree of crystalline orientation is high in all crystalline samples.

TL measurement: Each yarn was densely wound parallel on a sample holder of Cu plate, and set in a vacuum cryostat kept at a pressure of 10^{-3} Torr. Being cooled to -180°C using liquid nitrogen, it was irradiated for 30 minutes by x-ray from a Cu tube on a Rigakudenki D3F apparatus under a condition of 30 KV and 50 mA. Thirty minutes after the irradiation, the sample was heated up to 250°C at a rate of $10^{\circ}\text{C}/\text{min.}$ The glow was measured as a function of temperature with a

Table 1 Sample characterization.

No.	$[\eta]$ at 25°C in OCP	spinning speed m/min.	drawing	[de/fil]	density g/cm ³	birefringence $\times 10^3$
1. UD	0.60	1100	undrawn	195/24	1.33	0.008
2. POY	0.60	3400	undrawn	75/24	1.34	0.05
3. USY	0.60	6000	undrawn	75/24	1.38	0.09
4. FOY	0.60	1100	drawn	75/24	1.37 _s	0.15
5. TY	0.89	—	drawn	1000/250	1.39 _s	0.19

Naming: UD (Undrawn), POY (Partially Oriented Yarn), USY (Ultra-Speed Yarn),
FOY (Fully Oriented Yarn), TY (Tire Cord Yarn)

$[\eta]$ is the value measured for fiber sample. These data were given by Teijin Co.
together with samples. [de/fil] means the total denier and number of filaments
in each yarn.

Fig. 1 X-ray diffraction photographs of PET fibers used in this study. The naming of each sample should be referred to Table 1.

photomultiplier (Hamamatsu TV R292). It should be remarked that the temperature control of fiber specimen was necessarily less accurate than that of film specimen. The dose of irradiation and the wave length distribution of x-ray were not measured in this study.

Figure 2 shows the low temperature TL curves of PET fibers. The glow in the Figure is approximately from ca. 50mg of sample. Each glow curve has a similar broad peak around -150°C which

trails at higher temperature, as already reported by Ito et al.³⁾ for PET film. This results indicate that TL technique is applicable for the fibers as well as for the films. The asymmetric shape of the low temperature peak is attributed to three relaxation mechanisms, β_1 , β_2 and β_3 ³⁾. A distinct shoulder is observed on the low temperature peak of USY fiber, which may be a specialty of the fibers prepared by high speed spinning. It is remarked that the low temperature glow of TY

Fig. 2 Low temperature glow curves of PET fibers.

fiber is much smaller than these of others. With these exceptions of the shoulder of USY and weak glow of TY fibers, it is difficult to distinguish a fiber from others by the low temperature TL curves. The situation, however, becomes quite different at high temperature where the difference of the glow curves is remarkable. Figure 3 shows the high temperature glow curves. The TL is characterized as follows; (1) UD fiber: it has a peak with a maximum at 90°C, a shoulder at 120°C and a very weak maximum at 160°C. It was possible to detect the 160°C maximum on the original chart, although it is difficult to recognize it in Fig. 3. The glow increases with increasing temperature above ca. 180°C. The 90°C maximum may be attributed to the glass transition. (2) POY fiber: The TL curve is very similar to that of UD fiber, although the 170°C peak is more distinct than that of UD fiber. It is well known that the annealing effect on the fine structure of PET changes discontinuously at about 160°C⁴). This is related to the stepwise increase in the chain mobility within the crystal and also in the crystal boundaries at the temperature. The 160°–170°C peak must be related to this characteristic temperature. (3) USY fiber: The TL curve has a maximum at 120°C without any other structure

Fig. 3 High temperature glow curves of PET fibers.

such as seen on the curves of UD and POY fibers. As a whole, the glow curve shifts to higher temperatures than those of UD and POY fibers. The glow increases with increasing temperature above 200°C. Shimizu and his coworkers⁵) showed that the degree of amorphous orientation of PET fibers made by high speed spinning procedure is much lower than that of usual drawn fibers. This makes us suppose that the amorphous chains are highly relaxed, and as the results, that the high temperature TL curve of USY fiber may be similar rather to these of UD and POY than to these of FOY and TY fibers. The results shown in Fig. 3, however, indicate that the supposition is not probable. This may be due to the fact that the relaxation behavior of PET amorphous chains is much affected by coexisting crystalline phase⁶). (4) FOY fiber: The TL curve has a widely distributed peak with three weak maximums at 110°C, 140°C and 180°C. The glow increases monotonously above 200°C. Although the identification of these maxima is difficult, the flat shape of the TL curve indicates that the usual drawing causes a widely distributed state of aggregation of the amorphous chains. (5) TY fiber: The high temperature TL glow is very strong, whereas the low temperature glow was

very weak as seen in Fig. 2. It is rather similar to that of USY, but is quite different from that of FOY prepared by after drawing as in the case of TY fiber. The anti-fatigue property seems to be correlated to the strong and comparatively sharp high temperature TL peak. This indicates a usefulness of TL technique in the characterization of the fatigue property of TY fibers. The similarity of TL peak of TY fiber to that of USY seems to support a widely believed idea that a soft structure is necessary for the anti-fatigue property of tire yarns.

Conclusion

The TL technique was applied to the PET fibers to show that the TL glow, particularly at high temperatures above 100°C, could distinguish the PET fibers prepared under different conditions. The technique will be one of the most useful methods for the PET fiber characterization, when further systematic studies are made to clarify the

correlation between the fine structure and the TL glow.

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TLのPET繊維の特徴づけへの応用

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製造条件の異なる5種のPET繊維のTLを測定した結果、低温の β 分散に関するTLには余り大きな差異はみられなかったが、約100°C以上の高温TLには大きな差が現われることがわかった。紡速1000m/min程度の未延伸糸、3000m/min程度のPOYの未延伸糸は基本的には三つの極大をもつ同形の高温TLカーブを示す。しかし170°Cのピークは後者が明瞭になる。6000m/minの高速紡糸系では、TLは全体として高温に移ると

ともに1100m、3400m/minにみられたピークの構造が失われ単一のピークになる。後延伸による延伸糸のTLは非常に平坦であったが、幾分構造が残され幾つかの極大がみられる。タイヤコード糸は高温のTLの強度が強く、また形は6000m/minの高速紡糸糸のそれに類似である。以上の結果、TLは(特に高温のTLは)PET繊維の特性化に有用であることが示された。