

ADVANCED THERMAL ANALYSIS OF DRAWN CRYSTALLINE POLYMERS

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ABSTRACT

The basis of the three techniques which are in common use in our laboratory for obtaining the DSC melting curves of drawn, crystalline polymers has been reviewed briefly and then their application to industrial fields exemplified.

INTRODUCTION

The study of melting behavior of polymers is important in the field of polymer technology for manufacturing fibers, textiles and films, as well as in the practical use of these products at high temperatures which is governed by their melting characteristics. At present, melting curves of polymers can be easily measured with a small sample size using commercially available DSC. Therefore, the study of melting behavior of polymers should be refined further so that it might serve to characterize the fine structure of polymer products produced commercially. In this presentation, three techniques which are in common use in the author's laboratory for measuring the DSC melting curves of drawn polymers will be reviewed briefly and then their application to industrial fields will be exemplified for nylon 6, nylon 66, PET (polyethylene terephthalate) and PP (polypropylene).

THREE TYPES OF METHODS FOR MEASURING MELTING CURVES

The basis of three techniques termed here as Technique A, B and C will be reviewed, illustrating the case of variously drawn nylon 6 yarns. Fig.1 shows the results for 5.0 X drawn yarn and Fig.2 summarizes the three kinds of melting points as a function of draw ratio, changing draw temperature of the yarns.¹

Technique A is for measuring the melting curve without reorganization of imperfect crystals during the DSC scan. Therefore, this provides the information about a crystal size distribution in the sample according to the Thomson-Gibbs equation, $T_m = T_m^0 (1 - 2\sigma_e/l\Delta H_u)$ where T_m^0 , ΔH_u and T_m are the equilibrium melting point, heat of fusion and melting point of a crystal with a lamellar thickness l and end surface energy σ_e , respectively.² Our device to realize the idea of Technique A is to irradiate the sample with γ -rays in acetylene gas before the DSC analysis so as to introduce specified amount of crosslinks into the amorphous part.³ Curve A in Fig.1 is a thus obtained melting curve. Note

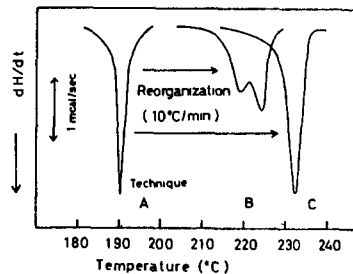
that there exist no endothermic peaks around 220 °C which is conventionally recognized as the melting point of nylon 6. As Fig.2 shows, melting points with Technique A vary reasonably with the drawing conditions of the yarns.

Technique B is the conventional one which was found to yield a scan-induced reorganization.⁴ As curve B in Fig.1 shows, well-known double endothermic peaks exist around 220 °C. The history of the sample scarcely affects the melting point as Fig.2 confirms, meaning that we can't get correct information about thermal history of the sample with Technique B. In spite of this disadvantage, however, the conventional technique has been found still useful for analytical purpose in industrial fields as will be demonstrated later.

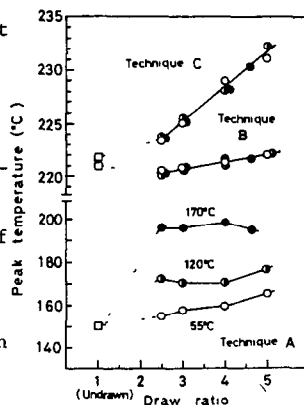
Technique C is for measuring the melting curve of the sample prevented from shrinking during the analysis.¹ The prevention of shrinking was found to affect the way of reorganization,¹ yielding curve C with a single peak at a higher temperature instead of the double peaks. The elevation of melting point was successfully explained by one of the entropy effects predicted by Zachmann.^{1,5} In Fig.2 the melting point with Technique C increases lineally with increasing draw ratio with a slope of 3.2 °C per 100 % draw ratio, independently of the original melting point (Technique A). This result indicates the possibility that Technique C provides an alternative measure for molecular orientation of drawn samples. Actually, we can discriminate between samples differing in draw ratio by as small as 0.1 times since the precision in Technique C is within ± 0.2 °C. This sensitivity is equal or superior to that in X-ray diffraction or birefringence measurements for the determination of molecular orientation. Another notable advantage of Technique C is that it can detect inhomogeneity in crystal orientation in a sample as will be illustrated later.

The reorganization behavior during heating with Techniques B and C has been studied quantitatively elsewhere.^{1,4}

We will demonstrate below that the results described for nylon 6 so far are generally valid for other drawn crystalline polymers such as nylon 66, PET and PP.



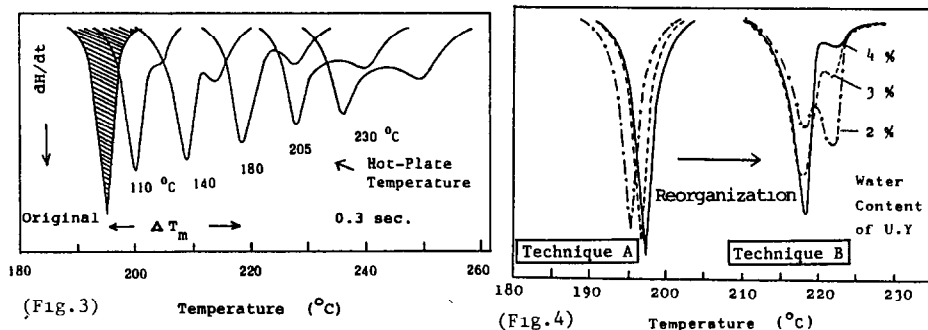
(Fig.1)



(Fig.2)

APPLICATION OF THREE TECHNIQUES TO THERMAL CHARACTERIZATION
OF INDUSTRIAL POLYMER PRODUCTS

Technique A. Technique A provides the direct information about thermal history of commercial products impressed during their manufacturing and practical use. Fig.3 shows DSC curves of original nylon 66 yarn and the falsely twisted bulky yarns. With increasing hot plate temperature, the melting point of the sample tends to increase toward the conventional melting point of nylon 66. The shape of the curve varies from unimodal in the original yarn to bimodal, indicating the formation of two types of crystals differing in their size or perfection. It should be noted that the original yarn has only the melting point less than 200 °C. The crimp tenacity of the twisted yarns has been found to be correlated linearly to the melting point difference between the original yarn and twisted ones, meaning that the difference can be an excellent measure of the structural change in the yarn on the twisting process.



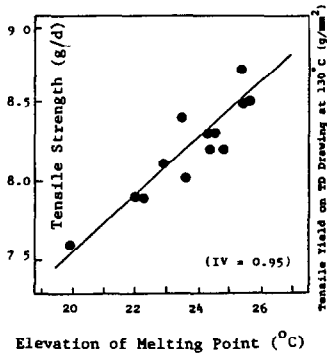
(Fig.3)

(Fig.4)

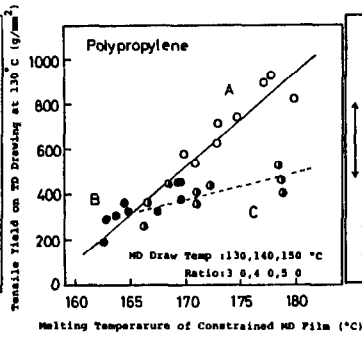
Technique B. Three kinds of nylon 6 undrawn yarns differing in the water content (2,3 and 4 %) were drawn to 5.0 times via cold-pin/hot-plate process. The hot-plate temperature was varied in such a way that all the drawn samples have a similar crystal size, as can be confirmed in Fig.4. The yarns were also analyzed with Technique B. Each curve B in Fig.4 exhibits two endothermic peaks whose ratio depends strongly on the amount of water on drawing. Remembering that all the samples possessed almost the same crystal size, we notice that the difference in the shape of the double melting peaks was caused by the change in way of the reorganization of the original crystal. Clearly this way had been destined by the drawing condition, the water content of the undrawn yarn in this case. This implies that we can get an idea about drawing conditions of an unknown sample by inspecting the shape of the Technique B-melting curve as a so-called "Finger Print" of the sample, or can at least discriminate a sample whose identity is unknown from others.

Technique C. Various PET tire yarns produced commercially were analyzed

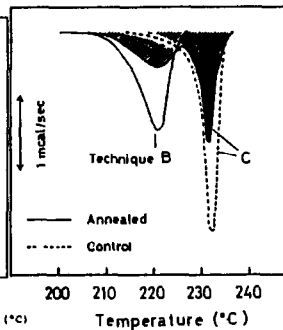
with Technique C, and their tensile tenacities are plotted against their melting points in Fig.5. A small difference in the tenacity can be elucidated by the difference in molecular orientation estimated by the DSC analysis. Uniaxially drawn PP films were also analyzed with the fixed ends. The tensile yield stress on their subsequent transverse drawing which is believed to play an important role in the biaxial film manufacturing is plotted against the melting point in Fig.6. Again a distinct relationship between the two parameters is observed for each of the three raw materials A(O), B(●) and C(●). Finally, Fig.7 is a typical indication that Technique C is effective for detecting inhomogeneous orientation of coexisting crystals.¹ The nylon 6 yarn strongly annealed at constant length shows a single peak when analyzed with Technique B. This splits into two peaks with Technique C: a small part still remains as it was and the remainder shifts up. Clearly the former corresponds to disoriented crystal and the latter to the crystal retaining the original orientation prior to the annealing.



(Fig.5)



(Fig.6)



(Fig.7)

CONCLUSION

We can now know much about manufacturing conditions and thermal history of an unknown drawn polymers by combining three melting techniques even only small size of the sample is available.

REFERENCES

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