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STUDIES OF STRUCTURAL REORGANIZATION IN NYLON 1010 DURING HEATING SCANNING

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The process of structural reorganization and thermal history recurrence in Nylon 1010 were studied by using DSC through different heat treatments. The characteristics of both endothermic and exothermic peaks on DSC curve is explained reasonably. The viewpoint is advanced that crystallites assembly is characterized by premelting crystallisation peak. The temperature range sensitive to the crystal perfection is determined. The results provide theoretical basis for the processing and application of Nylon 1010.

As the structure and property of semicrystalline polymers are connected directly with their thermal history, researchers shown great interest in studies of thermal history. Over the past decade, the relations between thermal behaviour and structure, morphology, property of various polymers, such as Nylon 66 [1] polyethylene [2], polypropylene [3] PET [4] and Nylon 610 [5] have been investigated through different heat treatments. It was stated that the multiple melting peaks of these polymers on DSC curves are strongly depend on thermal history memory and the ability of structural reorganization. Nylon 1010 is the sole engineering plastic in our country, but few investigation on thermal history has been made [6, 7]. This paper is to make further investigation of thermal history memory and structural reorganization in Nylon 1010 by means of DSC.

Experimental

The sample is Nylon 1010 resin particle produced by Jilin United Chemical Engineering Factory. Its molecular weight is approximately 20,000. The heat treatment and scanning were carried out in Perkin-Elmer DSC-2C with

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3600 Data-Station in pure nitrogen. Indium was used to calibrated temperature and enthalpy of the sample. The sample was weighted approximately 10 mg in AD-2Z autobalance. The heating rate is 2.5 deg/min, the cooling rate is 80 deg/min unless otherwise indicated.

Results and discussion

The samples were cooled to low temperature from the melt at the same cooling rate (10 deg/min), and scanned at two heating rates, as shown in Fig. 1. Two endothermic peaks were observed on DSC curve at the higher heating rate, while three endothermic peaks and one exothermic peak were observed at the lower one, which indicates low scanning rate can manifest the melting and recrystallization behaviour. With a view to probe into the complicated thermal behaviour, especially the cause and varying law of exothermic peak, the following studies were carried out.

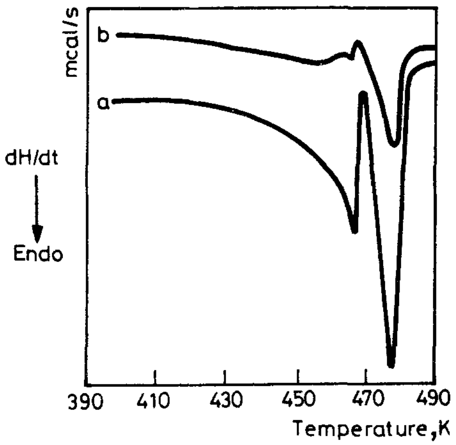

Fig. 1 DSC curves of the sample at two heating rates a) 10; b) 2.5 deg/min

Effects of cooling to different temperature on melting and crystallization behaviour

The samples were heated beyond melting point 30K, kept at this temperature for 10 min, so the previous thermal history were erased, then cooled respectively to 223, 403, 433, 443, 453, 465K at the same cooling rate (80 deg/min), and scanned at the same heating rate (2.5 deg/min), as shown in Fig. 2. The sample was cooled to different temperature from the melt, i.e.

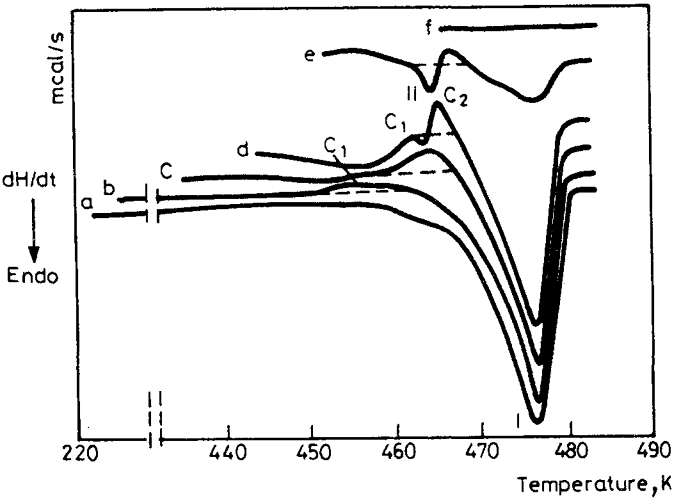

Fig. 2 Effects of cooling to different temperatures on melting and crystallization behaviour
a) 223; b) 403; c) d) 443; e) 453; f) 465 K

virtually the time taken for cooling and heating scanning is different. The sample cooled to low temperature at the high cooling rate, the crystallites formed during cooling process are far imperfect. In the course of heating scanning, both melting and recrystallization were going on simultaneously and the process lasted longer, the traces were hidden in the base line of DSC [3], therefore, only melting peak I was observed (curve a), which characterized the melting of crystals formed through structural reorganization during heating scanning. When the sample cooled to higher temperature, the crystallites formed were turning less imperfect, during heating scanning, the aggregate crystallites formed an assembly, which is manifested as a flat exothermic peak C_1 (curve b) named premelting crystallization peak. This peak was getting more obvious and sharp, while the peak temperature and area increased as cooling to higher temperature (curve c). Also, the part in the assembly of crystallites melted during scanning process, which was showed as an endothermic peak below the dotted line of curve d, then it was recrystallized, together with the unmelted assembly of crystallites, which was characterized by the exothermic peak C_2 above the dotted line, consequently, this peak area is larger than that of the endothermic one. When the sample cooled close to melting range, the degree of perfection of crystals became quite high, the melting of crystals was symbolized by peak II. The area of peak II is approximately equal to that of peak C_2 (curve e), therefore, peak C_2 characterized the recrystallization of the crystals formed during cooling process. As cooling to the melting range, few crystals were formed. No melting and recrystallization behaviours were observed on DSC curve (curve f). The experimental results reveal directly the continuous process of structural reorganization of the sample.

Effects of cooling rate on melting and crystallization behaviour

When the samples were heated until melted completely, so the previous thermal history were erased, then cooled to 373K at a cooling rate of 80, 40, 20, 10, 5 deg/min respectively and scanned at the same heating rate (2.5 deg/min) as shown in Fig. 3.

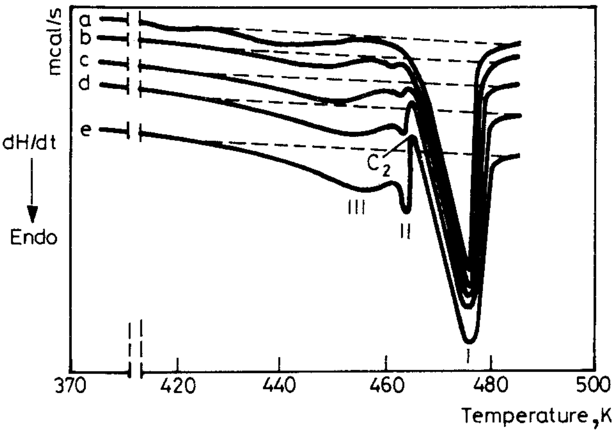

Fig. 3 Effects of cooling rate on melting and crystallization behaviour a) 80; b) 40; c) 20; d) 10; e) 5 deg/min

Changing the cooling rate is actually changing the cooling crystallization process. As the cooling rate decreased, the supercooled degree of the melt decreased, the degree of perfection of crystals formed from the melt increased. At high cooling rate, two endothermic peaks appeared on curve a. While at lower cooling rate, three endothermic peaks and one exothermic peak appeared on curves c, d, e, in which the characteristics of peak I, II, and C_2 is the same as that of the corresponding peaks at the previous experiment. A flat endothermic peak III appeared at the lower temperature. Its peak shape showed that the degree of perfection of crystallites characterized by peak III is lower than that of crystal by peak II. From Fig. 3 a, peak III is easily judged to be the melting of crystallites formed through cooling from the melt. If peak III is assumed the melting of crystallites among the large crystallizing boundary of Nylon 1010, the time for perfection of crystallites is enough under the circumstance of lower cooling rate, the degree of perfection of crystallites among large crystallizing boundary should be larger than that of the crystallites under one of higher cooling rate, which manifested the temperature of peak III shifted gradually to high temperature and its enthalpy increased with the cooling rate decreased. The crystals of large size did not melt until the crystallites among the boundary melted, which characterized by peak II. For the same reason, both the temperature and enthalpy of peak II increased with the cooling rate decreased, but the change was not as notable as that of peak III, as shown in Fig. 4. Peak C_2 emerged at higher temperature accompanying peak II, whose temperature and enthalpy increased with the cooling rate decreased. Therefore, the thermal history of the sample was reproduced.

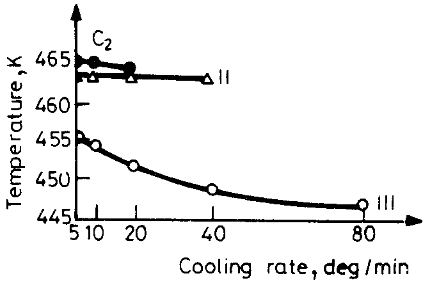

Fig. 4a Effects of cooling rate on peak temperature of peaks II III and C_2

Effects of crystallization temperature on crystal growth

The sample was melted completely, erased previous thermal history, cooled to different crystallization temperatures, T_c, kept for 30 min, and continually cooled to 433K, then scanned at the same heating rate (2.5 deg/min), as shown in Fig. 5. All peaks except peak A were discussed before. Peak A overlapped with peak III, which characterized the melting of the stabilized crystallites at this temperature [6]. Figure 6 showed effects of T_c on peaks II and C_2. Peaks II and C_2 shifted to high temperature with T_c increased which demonstrate that the higher T_c is, the more perfect crystals formed becomes in isothermal crystallization. As crystallization is made up

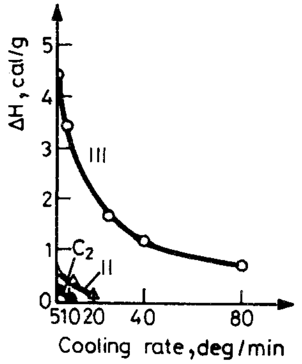

Fig. 4b Effects of cooling rate on enthalpy of peaks II, III and C2

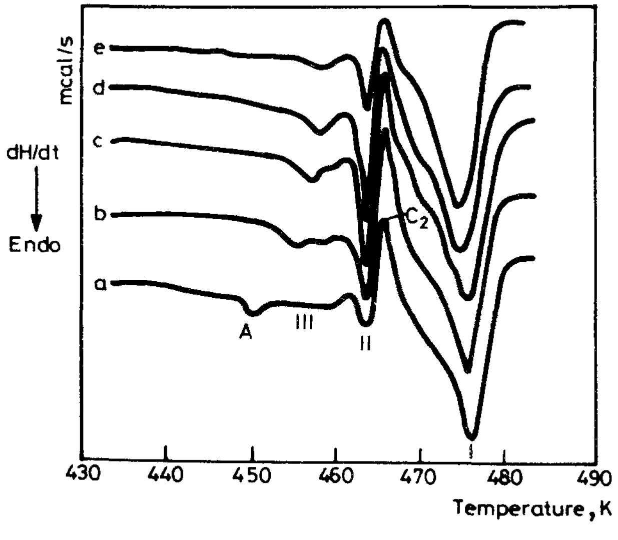

Fig. 5 Effects of crystallization temperature on crystal growth a) 448; b) 453; c) 455; d) 457; e) 458 K

of nucleation and growth, an optimum crystallization temperature range should exist, which accelerated the growth of crystals. According to the above the crystalline theory, the enthalpies of peaks II and C2 should exist a maximum value. As shown in Fig. 6, only when the *Tc* range is 452-458K, does the perfect crystallization occur easily and crystals grow rapidly.

As shown in Fig. 7, if the ratio (*n*) of the enthalpy of peak C2 to that of peak II is taken as an expression for the driving force of recrystallization, it increased with T_c decreased.This is understandable because the lower T_c is, the less perfect the crystals formed becomes in isothermal crystallization and the more obvious the recrystallization turns.

In accordance with the above experiment, the more suitable temperature range of heat treatment is 452-458K. The data should be of value to controlling the processing condition of Nylon 1010.

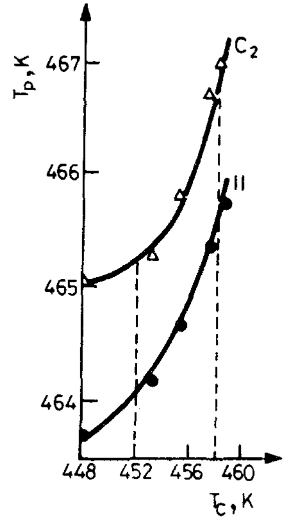

Fig. 6a Effects of crystallization temperature of peaks II and C2

Conclusion

DSC curve of Nylon 1010 reveals not only melting and crystallization of the sample, but also the continuous process of structural reorganization during scanning. Low scanning rate can easily manifest the behaviour of the melting and recrystallization. Peaks II and III chiefly characterized the degree of perfection of crystals, while peaks C1, C2 and I recur directly the process of structural reorganization. The temperature range sensitive to the perfect crystallization is 452-458K.

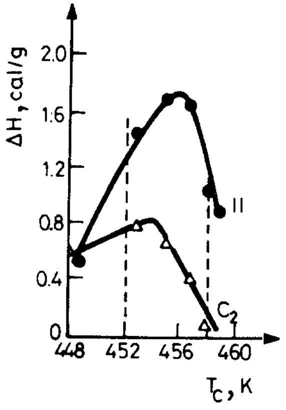

Fig. 6b Effects of crystallization temperature on enthalpy of peaks II and C_2

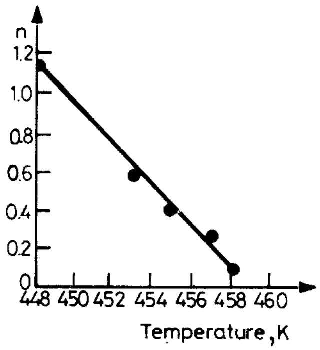

Fig. 7 Relation between crystallization temperature and driving force of recrystallization

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Zusammenfassung — Mittels DSC bei verschiedenen Wärmebehandlungen wurde der Vorgang der strukturellen Rückordnung und das thermische Vorleben von Nylon 1010 untersucht. Sowohl exotherme als auch endotherme Peaks an der DSC-Kurve konnten plausibel erklärt werden. Das Kristallitgefüge wird durch einen Premelting Kristallisationspeak bestimmt. Der für die Kristallvollkommenheit ausschlaggebende Temperaturbereich wurde bestimmt. Die Ergebnisse liefern eine theoretische Grundlage für den Umgang und die Anwendungen von Nylon 1010.