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THERMAL EFFECTS ACCOMPANYING NYLON-6 DEHYDRATION

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The thermophysical behaviour of Nylon-6 with various moisture contents was studied. It was shown that the thermal effects occurring below the Nylon-6 melting temperature are due to the dehydration process. The temperature of the heat flow maximum is a function of the state of the water molecules in the polymer. It was found that the thermophysical study of Nylon-6 in the temperature region below the polymer melting temperature allows a more precise value of its melting heat to be obtained.

Keywords: dehydration, Nylon-6, polymers

Introduction

There is an extensive literature on the thermophysical properties of films and fibres based on Nylon-6. The aim of most of the published works has been to characterize the influence of various regimes of polymer moulding and structural modification on temperature transition [1–3]. Nylon-6 is known to be a hydrophilic polymer able to sorb appreciable amounts of water (up to 10–14%). The presence of water molecules in this polymer exerts a considerable influence on the thermophysical properties of this polymer. It has been shown that marked changes in these properties should most likely be observed in the region between the water melting and evaporation temperatures.

The thermophysical properties of water in protein and in a few polymeric systems have been traditionally studied only at low temperatures. This means that only low-temperature transitions and the water melting process have been taken into account [4, 5]. As concerns the thermal dehydration effects, studies on this subject have been reported only for inorganic compounds [6, 7]. It has been shown that a DSC study of endothermic signals associated with dehydration allows an explanation of the nature of the interactions between compounds and water molecules.

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The water melting heat is equal to 333.1 J/g. The water evaporation heat is higher, at 2 255.1 J/g. Therefore, studies of the polymer/water system should evidently be more precise if the latter parameter is used. The work described in this paper is concerned with the thermal effects accompanying Nylon-6 heating over a temperature range corresponding to the water evaporation process.

Samples of commercially available unoriented Nylon-6 films (thickness 130 μm) and biaxially stretched Nylon-6 film (thickness 25 μm) were studied. All Nylon-6 samples were conditioned at various humidities, and the water content was then measured gravimetrically. DSC studies were performed with a DuPont-1090 thermoanalyzer. The heating rates were 20, 10 and 5 deg/min. The sample weight was 5–10 mg.

DSC curves of Nylon-6 films with different water contents are presented in Fig. 1. A well-defined endothermic signal can be observed in a wide temperature region below the Nylon-6 melting temperature. This effect can be attributed to water removal from the polymeric matrix. This statement seems to be true since this endothermic peak disappears if the Nylon-6 sample has been conditioned at zero humidity or if the sample has already been dehydrated as a result of the first DSC measurement (Fig. 1, curve 1). The intensity of this signal increases on increase of the water content in the polymer (Fig. 1, curves 2 and 3).

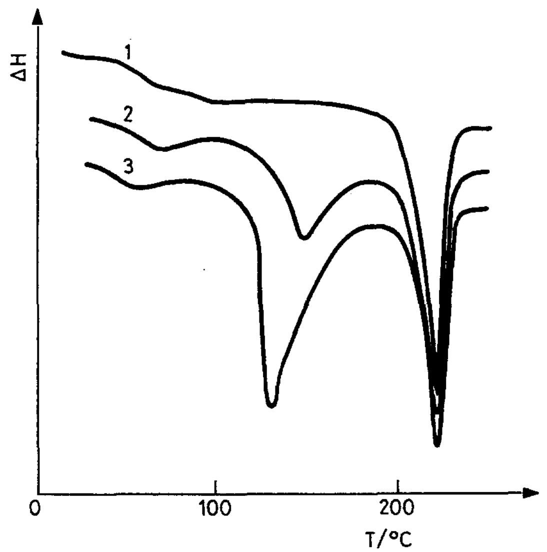

Fig. 1 DSC curves of Nylon-6 with different water content: 1–0%; 2–2.9%; 3–6.4%

From the above DSC curves, the values of the evaporation heats were estimated for Nylon-6 samples conditioned at various humidities. The water contents in the samples studied were determined in sorption experiments. These results and the theoretical straight line demonstrating how the evaporation heat depends on the moisture content in the polymer are shown in Fig. 2. The latter dependence was calculated by assuming that the evaporation heat is equal to zero and to 2255.1 J/g at 0% and 100% water contents, respectively. The experimental data on the evaporation heat are found to be in good agreement with theoretical estimates. This provides convincing evidence that the evaporation heat values determined with the DSC method could be effectively applied to determine the water contents in Nylon-6 samples.

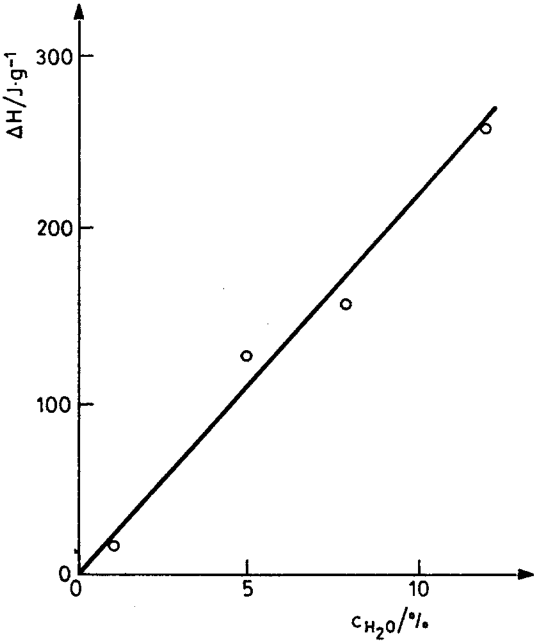

Fig. 2 Water evaporation heat versus its concentration in Nylon-6 samples

Is was found that water removal from Nylon-6 upon heating proceeds up to the polymer melting temperature. This phenomenon is most probably due to the different states of the water molecules sorbed in the polymer. It has been convincingly proved [8–10] that the water molecules in Nylon-6 can be present in three different states: 'strongly bound' water (in this case the water molecules interact with amide groups free of hydrogen-bonds); 'weakly bound' water (the water molecules break down hydrogen-bonds between amide groups to form new hydrogen-bonds between the carbonyl group of one amide group and another NH group); and free water. It has been shown that the free water is the first to leave Nylon-6 upon heating, followed by the 'weakly bound' water, and finally the 'strongly bound' water.

When the heating rate is high enough, the two endothermic signals associated with dehydration and polymer melting are found to be superimposed. To distinguish between these signals, one should decrease the heating rate. It is worth mentioning that in all the cases studied the heat flow maximum is observed at temperatures above the water boiling temperature.

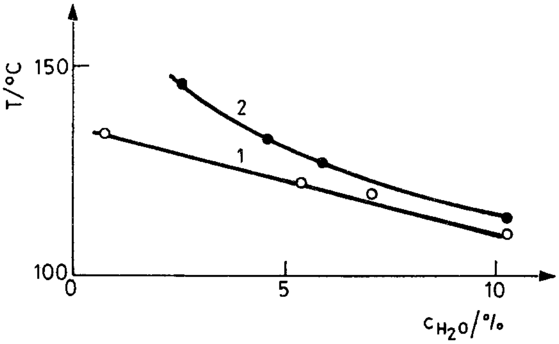

Fig. 3 Temperature of heat flow maximum *vs.* water content in Nylon-6. 1 – heating rate e 5 deg/min, 2 – heating rate 20 deg/min

In Fig. 3 the temperature of the heat flow maximum is plotted against the moisture content in Nylon-6 for two different heating rates. It can be seen that the temperature of the heat flow maximum increases on increase of the heating rate. In a general case, water removal from Nylon-6 is closely associated with the energy required to break down the intermolecular bonds in the Nylon-6/water system and to overcome the energy barriers of diffusion of water molecules from the polymer in the process of thermal dehydration. It has been demonstrated that, under the same conditions of water diffusion from the polymer (i.e. a constant heating rate and similar film thicknesses), the lower the moisture content in Nylon-6, the higher is the temperature of the heat flow maximum. This means that, at low moisture content in the polymer, the water is present in the form of 'strongly bound' water.

Table 1 Dependence of Nylon-6 melting heat (ΔH_m) on moisture content

Moisture content in Nylon-6/%	ΔH_m / J / g with the account for for moisture content	ΔH_m / J / g without account for moisture content
0	53.5	53.5
1	57.2	57.7
4.6	64.0	67.1
7.7	66.3	71.8

Analysis of the DSC curves with consideration of the water content allows more precise values of the Nylon-6 melting heats to be obtained. The values of the Nylon-6 melting heats are usually calculated from the weights of samples whose moisture contents are high enough. After calculation of the moisture content in the polymer from the value of the evaporation heat, the values of the melting heat and crystallinity can be determined immediately from the true weight of the sample. The values of the Nylon-6 melting heats with and without consideration of the moisture content are listed in Table 1. It follows from this Table that, at high moisture contents in Nylon-6 samples, the differences between the values of the melting heats calculated with and without consideration of the moisture content are significant.

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Zusammenfassung — Es wurde das thermophysikalische Verhalten von Nylon-6-Proben mit verschiedenem Feuchtegehalt untersucht. Man fand, daß die thermischen Effekte unterhalb der Schmelztemperatur von Nylon-6 in Verbindung mit dem Dehydratationsprozeß stehen. Die Temperatur für den maximalen Wärmefluß ist eine Funktion des Status der Wassermoleküle im Polymer. Es wurde gezeigt, daß die thermophysikalischen Untersuchungen an Nylon-6 im Temperaturbereich unterhalb der Schmelztemperatur des Polymers die Bestimmung präziserer Werte für die Schmelzwärme erlauben.