Polymer 42 (2001) 4759–4761

polymer

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Polymer Communication

The dependence of non-volatile residue formation in nylon 6 and nylon 6,6 during thermal degradation on hydrogen bonding in the melt

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Received 24 October 2000; received in revised form 24 November 2000; accepted 28 November 2000

Abstract

This paper is concerned with the temperature dependence of cross-linked residue formation during the thermal degradation of nylon 6,6. The relationship between non-volatile residue formation and initial hydrogen bonding in nylon 6 and nylon 6,6 was established using thermogravimetry and hotstage-Fourier Transform infrared spectroscopy. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Thermogravimetry; FTIR spectroscopy; Nylon 6

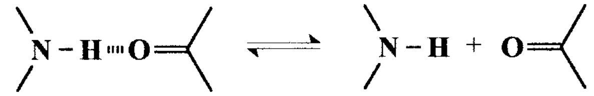
1. Introduction

In a recent publication [1], it was shown that the amount of non-volatile residue produced on the thermal degradation of nylon 6,6 decreased with increasing degradation temperature; at 410°C, 9 wt% was produced, whilst at 290°C, 75 wt% was formed. While the thermal degradation of nylon 6 over the temperature range 370–410°C led to amounts of non-volatile residue which varied little with temperature (typically 6 wt%) [2]. The purpose of this paper is to demonstrate that there is a correlation between the amount of char formation and the extent of hydrogen bonding in the nylons, using the infrared spectroscopic method developed by Garcia and Starkweather [3].

When nylon is heated, the N–H$_{(str)}$ band of the infrared spectrum broadens progressively with temperature, and simultaneously develops a shoulder above 3400 cm^{-1}, associated with non-bonded N–H$_{(str)}$. The method developed by Garcia and Starkweather [3] uses literature extinction coefficients to calculate the hydrogen bonded fraction from the area of the N–H$_{(str)}$ band, using the equation:

$$X_b = \frac{A/A_0 - \epsilon_f/\epsilon_b}{1 - \epsilon_f/\epsilon_b} \qquad (1)$$

where X_b is the hydrogen bonded fraction; A the area of the N–H$_{(str)}$ band at a given temperature; A_0 the area at room temperature; ϵ_f is the extinction coefficient for free N–H bonds; and ϵ_b the extinction coefficient for hydrogen bonded N–H bonds. Assuming,



the equilibrium constant, K, can be calculated from

$$K = C_0(1 - X_b)^2/X_b \qquad (2)$$

where C_0 is the concentration of amide bonds. Eq. (2) can be expressed in van't Hoff form,

$$\ln K = \ln C_0 + \ln\left(\frac{(1 - X_b)^2}{X_b}\right) = -\frac{\Delta H}{\mathrm{R}}\frac{1}{T} + \frac{\Delta S}{\mathrm{R}} \qquad (3)$$

where ΔH is the enthalpy of hydrogen bonding; ΔS the entropy; R the universal gas constant; and T the temperature.

2. Materials

Nylon 6 was supplied by BASF, and had a viscosity average molecular weight of 28,700 g mol^{-1}. Nylon 6,6 was supplied by Solutia, and had a viscosity average molecular weight of 25,000 g mol^{-1}.

3. Experimental

Thin films of nylon 6 and nylon 6,6 were deposited onto KBr disks from solutions of formic acid. The KBr discs were placed in a Linkam 600 hotstage unit, purged with argon gas, in the beam of a Nicolet Magna-IR 760 infrared spectrometer. Sets of 256 infrared scans were

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PII: S0032-3861(00)00868-5

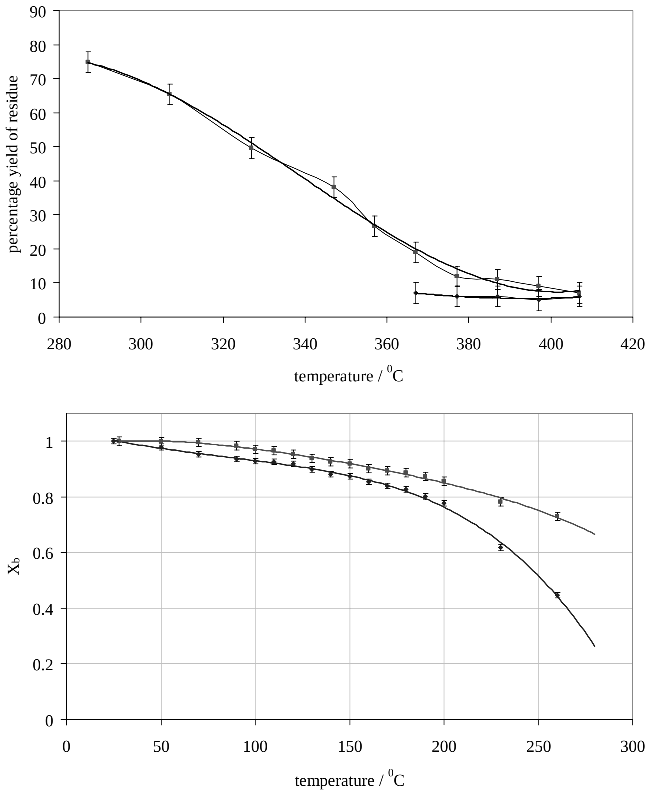


Fig. 1. (a) Effect of degradation temperature on non-volatile residue formation in nylon 6 —◆— and nylon 6,6 —■—; (b) change in hydrogen bonded fraction of nylon 6 —◆— and nylon 6,6 —■— with temperature.

taken at 10°C intervals up to 260°C at a resolution of 4 cm^{-1}.

4. Results

The dependence of non-volatile residue yield on degradation temperature for nylon 6 and nylon 6,6 is shown in Fig. 1(a) [1]. Nylon 6,6 led to greater yields of non-volatile residue than nylon 6. It was also found that the yield of non-volatile residue from nylon 6,6 increased markedly with decreasing degradation temperature.

The change in hydrogen bonded fraction of nylon 6 and nylon 6,6 with temperature is shown in Fig. 1(b). It was found that the hydrogen-bonded fraction of nylon 6 reduced more quickly than that of nylon 6,6. When the data was extrapolated to 280°C, it was found that nylon 6,6 had retained 65% of its hydrogen bonding, whereas that of nylon 6 had reduced to 25%. The data also indicated that hydrogen bonding in nylon 6 diminished before 300°C, whereas in nylon 6,6 hydrogen bonding was still present above 300°C.

The calculated hydrogen bonded fractions were used to produce a van't Hoff plot (Fig. 2(a)). For nylon 6, a kink in van't Hoff plot was observed at 180°C. This was considered

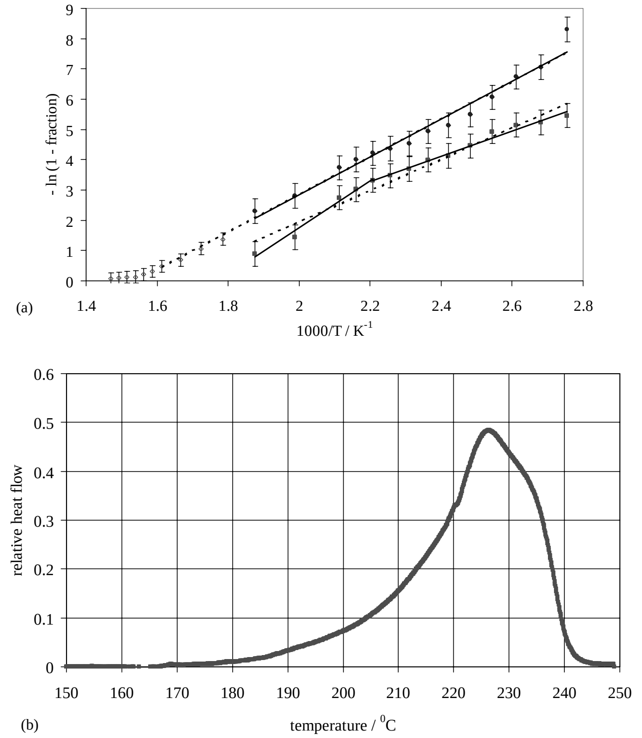


Fig. 2. (a) Van't Hoff plot showing correlation of char formation with hydrogen bonding in nylon 6 —■—, nylon 6,6 —●—, non-volatile residue —◇—; (b) DSC thermogram of nylon 6 at 10°C min^{-1}.

to be due to the onset of melting of the crystalline regions of the polymer [4], which was confirmed by differential scanning calorimetry (Fig. 2(b)).

The bond enthalpy for hydrogen bonding was calculated from van't Hoff plot shown in Fig. 2(a). For nylon 6, the overall value of the hydrogen-bond enthalpy (90–260°C) was 45 ± 5 kJ mol^{-1}. However, the overall hydrogen bond enthalpy was split into two regions, i.e. between 90 and 180°C it was 35 ± 3 kJ mol^{-1}, and between 180 and 260°C it was 65 ± 5 kJ mol^{-1}, corresponding to the onset of melting.

The hydrogen-bond enthalpy for nylon 6,6 was 52 ± 3 kJ mol^{-1}. No kink in van't Hoff plot was observed, and it was considered that this value represented the hydrogen bond enthalpy before melting. This value was higher than calculated for nylon 6, 45 ± 3 kJ mol^{-1} (35 ± 3 kJ mol^{-1} between 90 and 180°C), and indicated that hydrogen bonding was stronger in nylon 6,6, which is consistent with nylon 6,6 having the higher crystalline melting point. Starkweather and Garcia calculated the hydrogen bond enthalpy as 62 ± 3 kJ mol^{-1} by the same spectroscopic method. The difference between these values may be attributed to the differences in temperature measurements or sample specification. Elsewhere in the literature [4] the hydrogen bonding enthalpy for nylons has been quoted in the region of 46–50 kJ mol^{-1}, which is consistent with those found in this study.

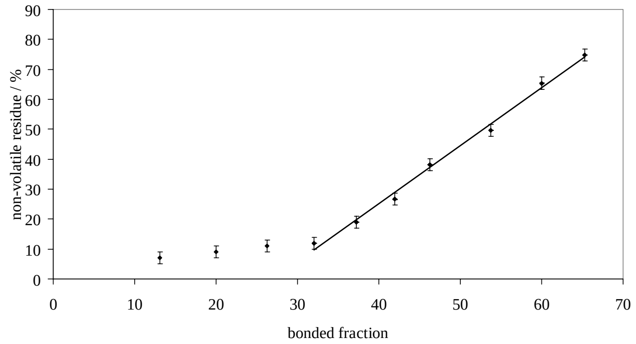
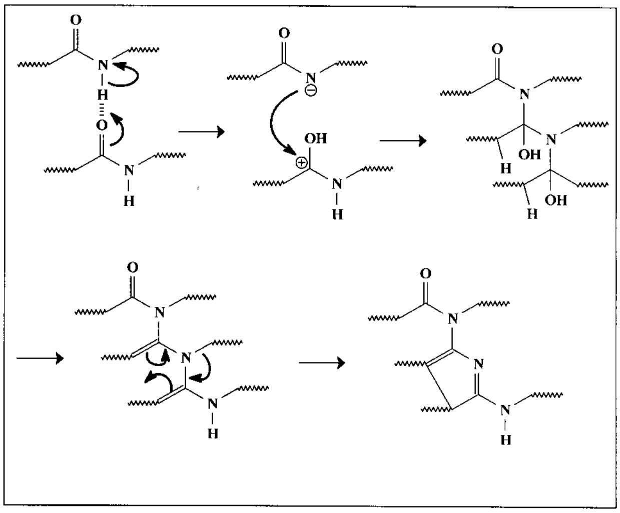


Fig. 3. Effect of hydrogen bonded percentage on the formation of non-volatile residue in nylon 6,6.



Scheme 1.

In the case of nylon 6,6, it was found that by extrapolating the char yield, from literature data [1], in van't Hoff form to higher temperatures, the dependence of fractional non-volatile residue yield on degradation temperature reflected the hydrogen bonding content accurately (see Fig. 2(a)). Furthermore, a plot of percentage non-volatile residue yield versus hydrogen bonded percentage (Fig. 3) demonstrated a linear dependence of non-volatile residue on hydrogen bonded percentage from 65 to 32%. Below 32% percent hydrogen bonded, production of non-volatile residue became less strongly dependent on initial hydrogen bonding.

It was considered from the above evidence that nylon 6,6 produced greater quantities of non-volatile residue than nylon 6 because nylon 6,6 retained hydrogen bonding to higher temperatures. It was assumed that hydrogen bonding promoted cross-linking by holding polymer chains closer together during degradation in the melt than they would be in their absence. Hydrogen bonding may lead to abstraction of the hydrogen from the nitrogen position, leading to cross-linking and formation of a pyrrole-like conjugated material, as shown in Scheme 1 (proposed mechanism for the production of non-volatile residue from nylon). Pyrrole structures have previously been identified as being present in the char of nylon 6,6 [5,6].

5. Conclusions

The amount of non-volatile residue formed during the thermal degradation of nylon 6,6 was found to depend upon the extent of hydrogen bonding in the polymer. The higher retention of hydrogen bonding in nylon 6,6 than in nylon 6 at elevated temperature explained why less non-volatile residue was produced by nylon 6 at the degradation temperatures used.

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