THERMAL DECOMPOSITION PROCESSES IN ANNEALED NYLON 66

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Abstract

Thermal decomposition processes in unannealed and annealed nylon 66 samples were investigated by thermogravimetry, elemental analysis and mass spectrometry. The annealed nylon 66 was decomposed in two steps in the thermogravimetry (TG) curve at 370°C and 420°C, whereas the unannealed nylon 66 was decomposed almost completely in one step in the TG curve at 430°C. The carbonization of the unannealed sample at 530°C was more complete than that of the annealed sample and the activation energy of thermal decomposition of the former sample was slightly larger than that of the latter. The breakdown products were fragments smaller than the structural unit of nylon 66. Fourteen peaks were observed at m/z of 28 to 226 (structural unit) by increasing steps of 14 (corresponds to CH2), 15 (NH) and 28 (CO).

1. Introduction

In the previous papers,1,2) the properties of nylon 66 annealed in glycerol were investigated at a wide range of temperature (−150 to 350°C) by comparing with those of the unannealed or cross-linked sample. Since the sample annealed severely showed the properties similar to those of the crosslinked sample, we concluded that the severely annealed sample easily sets to gel accompanying thermal degradation during annealing in glycerol.

In this paper, thermal decomposition processes (at the temperatures above 350°C) in these samples were investigated by TG/DTA (thermogravimetry/differential thermal analysis). The H, C, N and O contents of residual ash of the samples heated up to 370°C and 500°C were determined by elemental analysis. The samples were heated up to 370°C and 500°C and volatilized completely, and the condensed volatiles were analyzed by gas chromatography/mass spectrometry (GC/MS), and the thermal decomposition process in nylon 66 was discussed.

2. Experimental

The unannealed sample was prepared from a 3% solution of nylon in 60% aqueous formic acid dissolved at 95°C. Purified nylon was precipitated on cooling to room temperature (RT) and then isolated, washed and dried. Typical annealed sample was prepared by annealing the unannealed sample in glycerol at 204°C for 72 hr, as described in the previous paper.1)

The simultaneous TG/DTA (thermogravimetry and differential thermal analysis) measurements were carried out with a Shimadzu DTG-30 thermal analyzer at various heating rates up to 600°C under nitrogen or air atmosphere (the flow rate was adjusted to 60 ml/min). The granulated nylon 66 sample of 10 mg was packed in an open-type sample pan.

The GC/MS measurement was carried out with a Shimadzu GC/MS-QP1000 mass spectrometer. The sample was volatilized at 370°C or 500°C and electron impact (EI) mass spectra for the condensed volatiles were obtained at 70 eV and at a column temperature of 255°C.

3. Results and discussion

3.1 TG and elemental analysis of the unannealed and annealed samples

Figure 1 shows TG and DTA curves of the unannealed and annealed samples in nitrogen atmosphere. The annealed nylon 66 was decomposed in two steps in the TG curve at 370 and 420°C, whereas the unannealed nylon 66 was
decomposed almost completely in one step in the TG curve at 430°C. In contrast, the annealed sample was somewhat stabler against thermal decomposition above 450°C, i.e., the residual ash of annealed sample heated up to 600°C weighed ca. 10% to the initial sample weight, while that of the unannealed sample was less than 5% (at the heating rate of 5°C/min). Endothermic peaks in the DTA curves are observed at the temperatures corresponding to melting points of both samples (252 and 260°C for the unannealed sample, and 274 and 290°C for the annealed sample). Broad and large endothermic peaks are also observed at the temperatures corresponding to the respective abrupt weight loss in the TG curves. The TG and DTA curves of the unannealed sample in air atmosphere are also shown in Figure 1, where the TG curve shifts to lower temperature by ca. 10°C because of oxidation of the sample. Little ash remained as a result of the more complete combustion in air atmosphere. From the data obtained at different heating rates,3) activation energies were estimated to be 34 kcal/mol for the unannealed sample and 30 kcal/mol for the annealed sample, which are close to the value reported for nylon 6 (30 kcal/mol).4) In general, deterioration of the sample is caused by annealing, which results in the wider temperature range of decomposition and the smaller activation energy.

Elemental analysis of the residual ash of both samples is shown in Table 1. The H, C, N and O contents of residual ash of the unannealed sample heated up to 370°C was almost the same to those of the unheated sample (RT), while those of residual ash of the unannealed sample heated up to 530°C largely increased in the C content and decreased in the H, N and O contents compared to the unheated sample (and the one heated up to 370°C). The residual ash of the annealed samples heated up to 370°C and 530°C showed the increase in the C content and decrease in the H, N and O contents, whereas the residual ash of the annealed sample heated up to 530°C showed somewhat larger N and O contents than those of the unannealed sample heated up to 530°C. The difference in elemental analysis is caused by structural change in the samples such as gelation which has been reported elsewhere.1,2) Once gelation has occurred in the sample during annealing, the sample becomes somewhat stabler against
the thermal decomposition, which results in slight increases in the weight of residual ash and in the N and O contents of the annealed samples heated up to 600°C and 530°C compared to those of the unannealed samples as shown in Figure 1 and Table 1, respectively.

3.2 Mass spectrometry of nylon 66 samples

GC/MS spectra of the unannealed and the annealed samples are shown in Figure 2. Some studies have been reported on pyrolysis of nylon 6 and nylon 66,5) where the major breakdown products (heated at 400°C) in the volatilization at room temperature are CO₂ (m/z=44) and H₂O (18) in the same amounts of about 45%. Somewhat outstanding is the yield of cyclopentanone (m/z=84) as compared to the other hydrocarbons. In this study, the sample was heated up to 370°C or 500°C and the condensed volatiles were analyzed by the EI mass spectrometer at the column temperature of 255°C. The fragments smaller than the structural unit of nylon 66 were observed as breakdown products in the samples heated at 370°C and 500°C, and we could hardly find the fragments larger than the structural unit. This implies that all of the amide bonds (CO-NH) act as breaking points in molecular chains at high temperatures. In mass spectra are observed 14 peaks at m/z of 28 (CO or CH₂=CH₂) to 226 (structural unit) by an increasing step of 14 (corresponds to CH₂), 15 (NH) and 28 (CO). Especially, a series of peaks from m/z=43 to 197 in Figure 2 (a) are exactly increased by m/z=14, but this is apparently observed because intermediate fragments by an increasing step of 15 or 28 must be included. The volatilized fragments at 500°C show widely dispersed peaks. A fragment found at m/z=198 is smaller by 28 (CO) than that of 226 (corresponds to structural unit), and the more smaller fragments shown in Figure 2 (b) were obtained by reducing by 14(±1). Small difference in m/z value is observed between samples volatilized at 370°C and 500°C, which is caused by the difference in completeness of decomposition in samples at different temperatures (it is decomposed more completely at higher temperature). The main peaks are m/z=28 (conceivable fragments; CO or CH₂=CH₂) or 30 (HCHO, CH₃-CH₂) or 27 (H-C≡N), 41 (H₂C=CH-CH₂, CH₃-C≡N) or 43 (N≡C-OH, NH₂-CH=CH₂, CO-CH₃), and 55 (CH₃-CH₂-C≡N) or 56 (CH₂=CHCHO) or 57 (NH₂-CH=CH-CH₃, CO-CH₂-CH₃) and others.

The release of NH₃, CO₂ and H₂O has been reported, but here we could find various forms of amines and aldehydes instead of them. Actually, the volatile gas at 370°C and 500°C was checked by a Nessler's reagent, a Schiff's reagent or a Fehling solution and lime water in order to detect NH₃, aldehyde and carbon dioxide, by which were found NH₃, aldehydes and carbon dioxide gas. We could also detect H₂O. In the GC/MS measurement, it is difficult to distinguish

![Fig. 2 GC/MS spectra of the unannealed sample (a) volatilized at 370°C and the annealed sample (b) volatilized at 500°C. The column temperature was 255°C. (----) means magnification region of 20 times.](image-url)
mass fragments lower than 28 because it is inevitable to be mixed with a small quantity of air. Therefore, other El mass spectrum was obtained using a JEOL JMS-07 mass spectrometer (at 20 eV and at 420°C), whose major peaks appeared at m/z=17 (NH3), 18 (H2O), 28 (CO), 30 (HCHO), and 44 (CO2, CH3CHO). There was no essential difference in mass spectra between the unannealed and annealed samples.

In the elemental analysis, the decrease in the N, H and O contents was observed as a result of carbonization of the sample when it was decomposed at above 500°C. Small difference in the TG curves of the unannealed and annealed samples is attributed to the different amount of volatilization, 90% for the annealed sample and 95% for the unannealed sample, reflecting the difference of carbonization. The severely annealed sample easily sets to gel (namely, N-N bonding) accompanying thermal degradation or oxidation during the annealing, which becomes somewhat stabler against thermal decomposition and carbonization.

Therefore, the annealed sample heated up to 530°C showed the N and O contents of residual ash slightly larger than those of the unannealed sample.

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**References**