Thermochimica Acta, 76 (1984) 97–103
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL AND DIELECTRIC PROPERTIES OF NYLON 6

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(Received 28 November 1983)

ABSTRACT

The thermal decomposition of nylon 6 has been studied between 25 and 550°C. Analysis of the data indicates that nylon 6 decomposes in a first-order reaction with a specific rate constant of 2.55–3.56 min^{-1} and an activation energy of 38.86–52.32 kcal mol^{-1} depending on the degree of crystallinity. The results indicate that the thermal stability of nylon 6 increases with the degree of crystallinity.

The activation energy of relaxation, ΔH_ϵ, calculated from dielectric loss measurements, was found to be 8.9 kcal and attributed to the polarization of the side groups of the polymer.

INTRODUCTION

The thermal decomposition of polyamides has been studied by several investigators [1–8]. Although most of this work was concerned only with the analysis of the decomposition products, a few investigators [1] studied the kinetics of the decomposition reactions. The polyamide molecules break at the C–N bond of the peptide group creating smaller molecules with the same unit of chemical structure. The fragments broken out are evolved as carbon dioxide, carbon monoxide, water and hydrocarbons [8].

Previously, the author studied the effect of temperature, frequency and particle size on the dielectric properties of nylon 6 [9]. The present investigation was undertaken to examine the effect of the degree of crystallinity on the thermal stability of nylon 6 by studying the thermogravimetry (TG), the differential thermogravimetry (TGA) and the differential thermal analysis (DTA) curves and calculating the kinetic parameters. Also, this study has been extended to studying some dielectric properties of nylon 6 and calculating the activation energy of relaxation.

EXPERIMENTAL

Materials

Nylon 6 fibers were converted to powder form as previously described [9]. The powder produced was sieved to a particle size ranging from 0.1 to 1.0

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mm. The samples were purified and dried at 70°C under vacuum before any measurements.

Measurements

The TG, DTG and DTA measurements were carried out at 25–550°C. using an M.O.M. (Budapest) Derivatograph. The experimental technique was as previously described [10]. The rate of heating was adjusted to 5°C min^{-1}.

The dielectric constant, ϵ', and the dielectric loss, ϵ'', were measured over the frequency band 0.2–10 MHz and the temperature range 10–80°C. The apparatus and the technique were as previously described [9]. The apparatus consisted of a Multidekameter (WTW type DK06) and an MFM 5T type cell. The cell was modified for the measurements of dry samples under a vacuum [11]. The accuracy in the thermal measurements was $\pm 0.5\%$ and that in the measurement of the dielectric constant was $\pm 5\%$ [9].

The degree of crystallinity of the samples was determined by the infrared absorption method [12]. Bands at 935 and 990 cm^{-1} were considered in accordance with Sandeman and Keller [13] as crystalline and non-crystalline bands, respectively, and the baseline method developed by Heigl and White [14] was applied to determine the absorbance ratio of the two bands, which in turn was taken as a measure of the degree of crystallinity of the sample under investigation.

RESULTS AND DISCUSSION

The results of the sieve analysis and the degree of crystallinity for the nylon samples under investigation are given in Table 1. The thermal decomposition curves of the samples are shown in Figs. 1, 2 and 3.

The TG curves in Fig. 1 show that the thermal decomposition of nylon 6 takes place in three distinct stages. In the first stage, up to a temperature of about 150°C, only a slight loss in weight is observed which can be attributed

TABLE 1

The characterization of the samples

Sample No.	Particle size (mm)	Degree of crystallinity
1	-0.2 $+0.1$	1.0714
2	-0.3 $+0.2$	1.0869
3	-0.5 $+0.4$	1.1221
4	$-0.75+0.5$	1.1390
5	-1.0 $+0.75$	1.1800

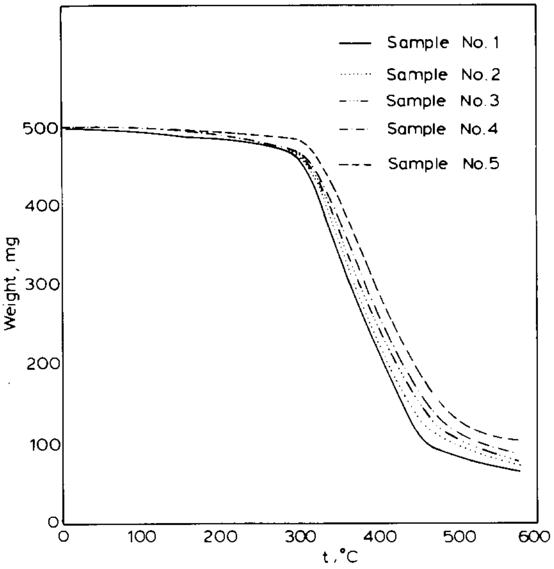

Fig. 1. TG curves of nylon 6.

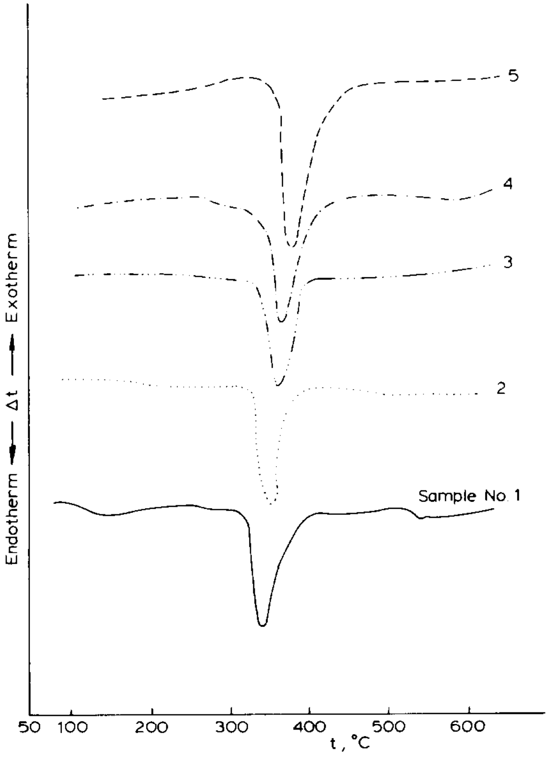

Fig. 2. DTA curves of nylon 6.

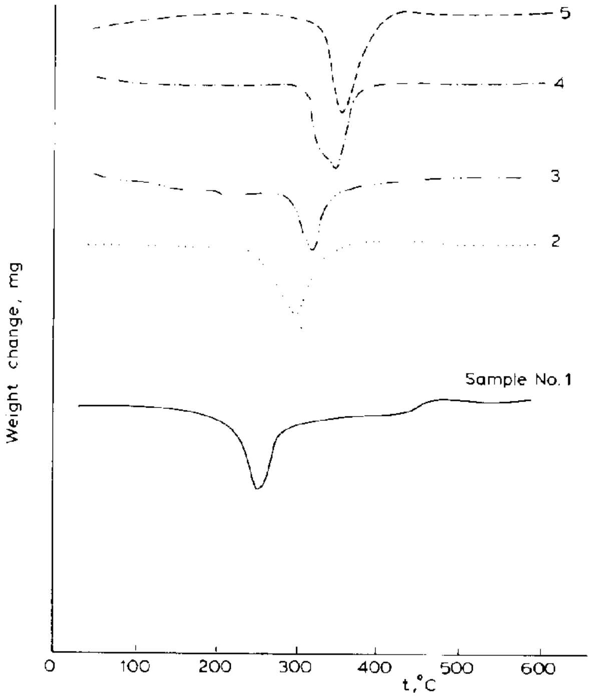

Fig. 3. DTG curves of nylon 6.

to the removal of the absorbed water. During the second stage, in a temperature range of 280–450°C, most of the decomposition of the nylon takes place. During the third stage, at a temperature of > 450°C, the undecomposed nylon and other impurities are lost. The shapes of the TG curves for all samples are very similar with some shift in the borders of these three stages.

The second stage, which is characteristic to the nylon 6 decomposition, was analyzed for the calculation of the kinetic parameters. From the weight

TABLE 2

The kinetic parameters of nylon 6 samples

Sample No.	Specific rate constant (min^{-1})	Activation energy (kcal mol^{-1})
1	2.55	38.86
2	2.87	43.16
3	3.06	45.68
4	3.15	51.98
5	3.56	52.32

loss–time relation the kinetic parameters were calculated (Table 2) as used in the previous investigation [10]. The results indicate that nylon 6 degrades in a first-order reaction with a small deviation in the initial stage of decomposition with a specific rate constant, k, of 2.55 min^{-1} for the finest sample (No. 1) and reaching 3.56 min^{-1} for the coarsest sample (No. 5).

According to the Arrhenius equation, the activation energy, E_a, of the samples is calculated in Table 2. It is found that the value of E_a increases from 36.63 to 50.71 kcal mol^{-1} when the degree of crystallinity increases from 1.07 to 1.18. These values are in agreement with the literature values [1]. The difference between the highest and the lowest value of the activation energy for the samples is 14.08 kcal mol^{-1}. This energy difference is considered to be consumed in the breaking of the crystalline parts of nylon to produce finer molecules.

From another viewpoint, it is clear that sample No. 1 (with degree of crystallinity = 1.0714) starts to decompose at 280°C, while sample No. 5 (with degree of crystallinity = 1.180) starts to decompose at 315°C. This indicates that as the degree of crystallinity increases the sample starts to decompose quickly.

From the value of the activation energy and the initial temperature of the decomposition for the different samples, it is clear that the thermal stability of nylon 6 increases with increasing degree of crystallinity.

The DTA curves (Fig. 2) of all the samples exhibit an endothermic peak; at ~ 350°C for sample No. 1, and increasing gradually to reach ~ 377°C for sample No. 5. The endotherm indicates that a condensed phase reaction is

TABLE 3

The variation of the dielectric constant, ϵ', and the dielectric loss, ϵ'', with temperature at different frequency for nylon 6

f(MHz)	10°C		20°C		30°C		40°C	
	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
0.2	3.096	0.293	3.152	0.278	3.193	0.273	3.270	0.269
0.5	3.064	0.335	3.104	0.307	3.152	0.301	3.213	0.296
1.0	3.035	0.325	3.074	0.342	3.110	0.335	3.165	0.335
2.0	3.010	0.314	3.039	0.335	3.086	0.342	3.132	0.342
5.0	2.949	0.296	2.990	0.317	3.080	0.333	3.069	0.336
10.0	2.888	0.270	2.910	0.280	3.076	0.296	2.997	0.301
	50°C		60°C		70°C		80°C	
	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
0.2	3.298	0.265	3.439	0.261	3.648	0.244	3.772	0.235
0.5	3.302	0.292	3.376	0.287	3.546	0.268	3.656	0.262
1.0	3.251	0.328	3.343	0.321	3.491	0.310	3.600	0.297
2.0	3.193	0.337	3.273	0.332	3.421	0.326	3.526	0.310
5.0	3.122	0.352	3.202	0.346	3.320	0.340	3.436	0.327
10.0	3.05	0.332	3.110	0.359	3.221	0.358	3.397	0.353

taking place between the flame retardant and the sample. This reaction, although it does not alter the decomposition products, has a marked effect on the decomposition temperature; it is obvious from the lowering of the endotherm temperature with the decrease in the degree of crystallinity.

The DTG curves (Fig. 3) showed that there is a maximum peak at ~ 360°C for sample No. 1 and the intensity of this peak increases as the degree of crystallinity decreases.

The variation of the dielectric constant, ϵ', and the dielectric loss, ϵ'', with temperature and frequency for nylon 6 (sample No. 1) are given in Table 3. The results indicate that the value of ϵ' increases with increasing temperature over the entire frequency range. This increase may be attributed to a decrease in the effect of the environment as the temperature is increased. This decrease enhances rotation and polarization of the side groups and the other flexible units in the nylon 6 chain [9].

Figure 4 represents the variation of ϵ'' with frequency at different temperatures. The figure shows that there is a flat maximum which shifts towards a higher frequency with less broadening when the temperature is increased. The shift of the maximum loss, ϵ''_m, with temperature for the sample proceeds as follows:

t (°C)	10	20	30	40	50
$\log f_m$	5.66	5.95	6.20	6.30	6.50

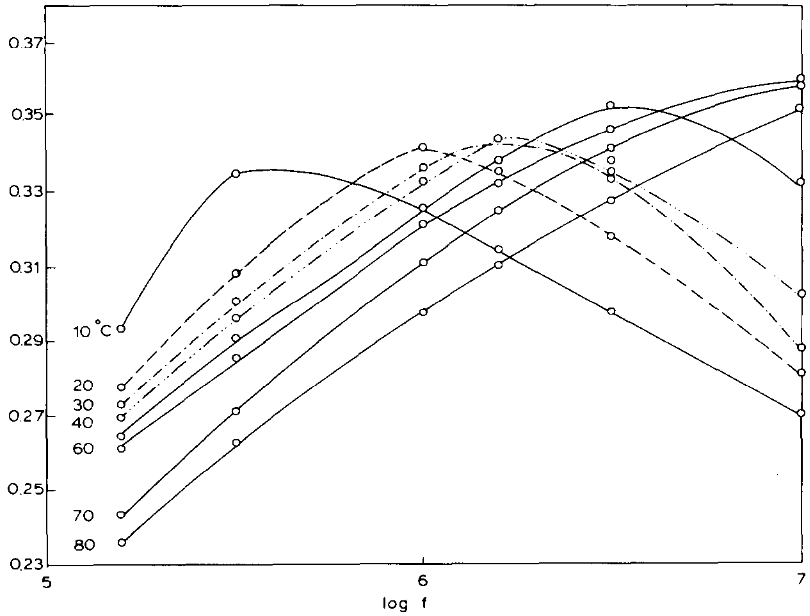

Fig. 4. The variation of ϵ'' with frequency at different temperatures.

From the shift of $\log f_\mathrm{m}$ with temperature, the apparent activation energy of the relaxation process, ΔH_ϵ, was calculated according to the following equation [15]

$$\Delta H = \frac{2.303\, R \mathrm{d} \log f_\mathrm{m}}{\mathrm{d}\left(\frac{1}{T}\right)}$$

The value of ΔH_ϵ is 8.9 kcal mol^{-1}. This value is in agreement with the value obtained by other authors [16] and attributed to the polarization of the side groups of the polymer, *β*-relaxation process.

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