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Transitions of Cellulose Acetate

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ABSTRACT

The transitions of cellulose acetate (40% acetyl) have been
studied by differential scanning calorimetry (DSC) and dynamic
mechanical analysis (DMA). Two distinct transitions, one at
63°C and the other at 218°C, have been observed. An exothermic
peak at 234°C is attributed to crystallization and is analyzed by
the Kissinger and the Ozawa methods for calculating the various
kinetic parameters.

INTRODUCTION

Mandelkern and Flory [1] have reported transitions at 30 and 105°C
in dilatometric studies of cellulose triacetate (44.8% acetyl) and at 60
and 120°C for cellulose acetate (38.2% acetyl). Nakamura [2] ob-
served transitions at 30 and 105°C in dilatometric studies of cellu-
lose triacetate (44.8% acetyl). Russell and Van Kerpel [3] have
observed the transitions at 40, 120, and 155°C for cellulose triacetate
(44.8% acetyl) and at 55 and 115°C for cellulose acetate (37.5% acetyl)
from dilatometric measurements. From mechanical measurements
they observed the second-order transition at 175°C in the case of
cellulose triacetate and at 195°C in cellulose acetate (37.5% acetyl).
From their dilatometric measurements Sharples et al. [4] have
reported that cellulose triacetate (44.8% acetyl) exhibits three

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transitions (46, 112, and 157°C) and have assigned the highest one to be the glass transition (T_g). Daane and Barker [5] observed four transitions (15, 50, 90, and 114°C) for cellulose acetate (40.3% acetyl) from dilatometric measurements.

Nakamura et al. [6] have reported the glass transition temperature to be 153°C for cellulose triacetate (44.8% acetyl) from DSC measurements. Cowie and Ranson [7] have reported the glass transition temperature to be 178-205°C from DSC measurements and the melting temperature to be 304-309°C for cellulose acetate samples of varying acetyl content. Seymour and Johnson [8] from DSC measurements noted that cellulose acetate (40% acetyl) shows one transition due to softening at about 50-80°C and decomposition peak at about 350-380°C. They have not observed the glass transition temperature.

Thus it is to be noted that the existing data [1-8] on the transitions of cellulose acetate of varying acetyl content do not agree. In the present study we have used DSC and DMA techniques for studying the transitions of cellulose acetate (40% acetyl).

It is known that the kinetic parameters derived from the DSC measurements are generally based on 1) the peak temperature-heating rate relationship [9-11], 2) the shape of the heat flow curve obtained [12], and 3) the derivative of the peak [13]. Some of these methods assume either zero or first-order kinetics while others provide calculation of the reaction order [10-15]. In the present work the results obtained from DSC thermograms scanned at a heating rate of 10 to 50°C/min are treated in light of the Ozawa [10] and the Kissinger [9] methods for calculating the various kinetic parameters.

EXPERIMENTAL

Materials

The cellulose acetate (40% acetyl) used in the present study was obtained from Eastman Kodak Chemicals, U.S.A. The dynamic mechanical measurements were performed on a film prepared from acetone solution of the polymer over a mercury surface. The solvent was removed by controlled evaporation and then leaching the film into water for 8 h. The film was dried under vacuum at 50°C for several days until the weight of the film was constant.

DSC Measurements

A DuPont DSC Model 900 was used in the present study. The thermograms of cellulose acetate were obtained by using heating rates ranging from 10 to 50°C/min in air. The heating rate as well as thermal lag corrections were applied to the results.
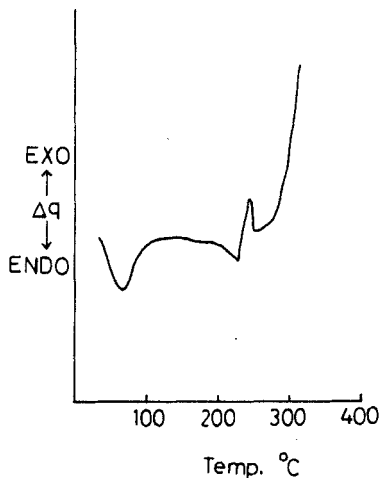
FIG. 1. The DSC thermogram of the cellulose acetate (40% acetyl) sample.

Dynamic Mechanical Measurements

The dynamic mechanical measurements were carried out with the help of a DuPont Model 981 Dynamic Mechanical Analyzer based on resonance frequency.

Thermogravimetry

The thermogravimetry (TG) of the cellulose acetate sample was carried out with the help of Linseis thermobalance at a heating rate of 5°C/min in air.

RESULTS AND DISCUSSION

The DSC thermogram of cellulose acetate (40% acetyl) obtained at a heating rate 10°C/min is shown in Fig. 1. The transition at 63°C can probably be attributed to a conformational change in the glucose ring, while the transition at 218°C is attributed to the glass transition temperature (T_g). An exothermic peak also appeared at 234°C, and it will be discussed later.

From the results of dynamic mechanical analysis (DMA) of cellulose acetate film the resonant frequency (f) and the damping signal of the sample were converted to Young's modulus (E) and the mechanical loss factor (tan δ) by using the following Eqs. (1) and (2), respectively.

E (Nm^{-2} or Pa)

$$= \left[\frac{(4\pi^2 f^2 j - K)}{2W(L/2 + D)^2} \left(\frac{L}{T} \right)^3 \right] \left[1 + 0.71 \left(\frac{2T}{L} \right)^2 - 0.1 \left(\frac{2T}{L} \right)^3 \right] \quad (1)$$

where f = DMA resonant frequency (Hz)
    j = moment of inertia of arm (1.58×10^{-3} kg·m^2)
    K = spring constant of pivot (0.356 Nm/rad)
    D = sample clamping distance (9.6×10^{-3} m)
    W = sample width (m)
    L = sample length (m)
    T = sample thickness (m)

and

$$\tan \delta = CV/f^2 \quad (2)$$

where V = DMA damping signal (mV)
    C = system constant (0.231 Hz^2/mV)

The typical experimental data on a cellulose acetate film sample are shown in Table 1 with details of the sample dimensions.

Young's modulus E and $\tan \delta$, calculated from Eqs. (1) and (2), are plotted against temperature in Fig. 2. As is found for all viscoelastic materials, the modulus which is high at low temperature, drops appreciably in the glass transition region, and attains a minimum value in the rubbery state at high temperature.

The value of $\tan \delta$ shown in Fig. 2 goes through a maximum as the temperature is raised. It is well known that molecular motions of macromolecules as well as motions of certain segments give rise to dissipation of energy during mechanical experiments. This results in the occurrence of maxima in the frequency and temperature depend-ence of the mechanical loss factor, $\tan \delta$. From Fig. 2 it is seen that $\tan \delta$ attains a maximum temperature around 210°C. This can be regarded as the glass transition temperature, T_g, of cellulose acetate. This value of T_g is in excellent agreement with that obtained from DSC measurements.

In comparing the glass transition temperature of our cellulose acetate sample (cf. Table 2) obtained from DSC measurements with that reported by Cowie and Ranson [7], it may be concluded that the transition temperature decreases with increasing acetyl content. This is also in agreement with the results reported by Nakamura [2].

TABLE 1. DMA Data on Cellulose Acetate (40% acetyl) Sample[a]

Temperature (°C)	Frequency (f, Hz)	Damping (V, mV)
40	15.20	60
60	14.90	56
90	14.30	51
100	14.20	50
120	13.90	45
140	13.30	44
150	12.90	46
155	12.70	47
160	12.40	48
165	12.10	49
170	11.85	50
180	11.10	54
185	10.60	58
190	9.70	66
192.5	9.20	70
195	8.65	73
197.5	8.00	75
200	7.10	74
202.5	6.15	70
205	5.15	60
207.5	4.40	48
210	3.30	34
212.5	2.65	14

[a]Sample dimensions: $T = 5.1 \times 10^{-3}$ m, $W = 0.435 \times 10^{-3}$ m, $L = 11.2 \times 10^{-3}$ m. Heating rate = 5°C/min.
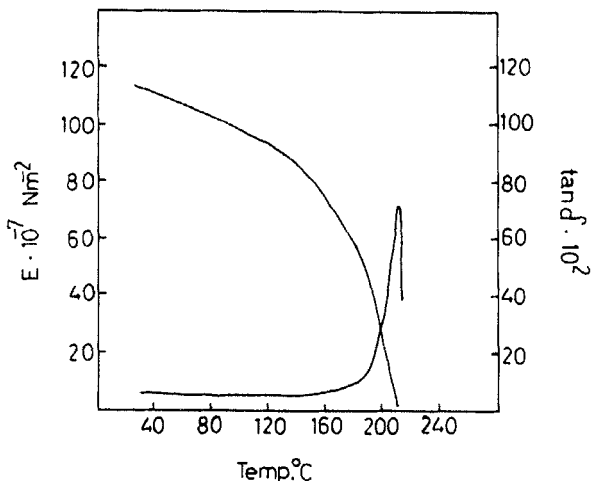
FIG. 2. The dynamic mechanical data of modulus E and tan δ as a function of temperature for cellulose acetate (40% acetyl) film sample

In addition to the first two transitions (viz., at 63 and 218°C) discussed above, we have also observed one exothermic peak at 234°C (cf. Fig. 1). It is noted from the TG measurements (Fig. 3) that decomposition takes place in the temperature range 276-430°C. Thus the exothermic peak in the DSC thermogram (Fig. 1) at 234°C may be attributed to the crystallization peak. This exothermic peak is confirmed by cooling the same sample in the DSC cell to room temperature after heating to 240°C and then rescanning under the same conditions. X-ray data [16] indicate that cellulose triacetate (CTA) is a highly crystalline material. The cellulose acetate sample under investigation contains some amount of CTA and hence the exothermic peak observed at 234°C is ascribed to the presence of CTA.

In the present work the DSC measurements of the cellulose acetate (40% acetyl) sample have been carried out using heating rates of 10 to 50°C/min. The values of the exothermic peak temperatures obtained are reported in Table 3. The data of the exothermic peak temperatures were utilized for the application of the Ozawa and the Kissinger methods in order to evaluate the kinetic parameters.

According to the Ozawa method [10], the log heating rate (log β) vs the reciprocal exothermic peak temperature (°K) is plotted as shown in Fig. 4. The slope of the plot obtained is used to calculate the activation energy by using the relation

$$E \cong 2.19R \frac{d \log \beta}{d (1/T)} \tag{3}$$

TABLE 2. Transition Data of Cellulose Acetate (CA)

| Sample	T_1 (°C)	T_2 (°C)	T_3 (°C)	T_4 (°C)	Measurements	Ref.
CA (44.8% acetyl)	30	105	-	-	Dilatometric	1
CA (38.2% acetyl)	60	120	-	-	"	1
CA (44.8% acetyl)	30	105	-	-	"	2
CA (44.8% acetyl)	40	120	155 (T_g)	-	"	3
CA (37.5% acetyl)	55	115	-	-	"	3
CA (44.8% acetyl)	-	-	175 (T_g)	-	Mechanical	3
CA (37.5% acetyl)	-	-	195 (T_g)	-	"	3
CA (44.8% acetyl)	46	112	157	-	Dilatometric	4
CA (40.3% acetyl)	15	50	90	114	"	5
CA (44.8% acetyl)	-	-	153 (T_g)	-	DSC	6
CA (43.1–44.8% acetyl)	205–178 (T_g)		304–320 (T_m)	-	"	7
CA (40% acetyl)	50–80 (softening temperature)		350–380 (decomposition temperature)	-	"	8
CA (40% acetyl)	63	218 (T_g)	234 (T_c)	-	"	Present work
CA (40% acetyl)		210 (T_g)			DMA	Present work
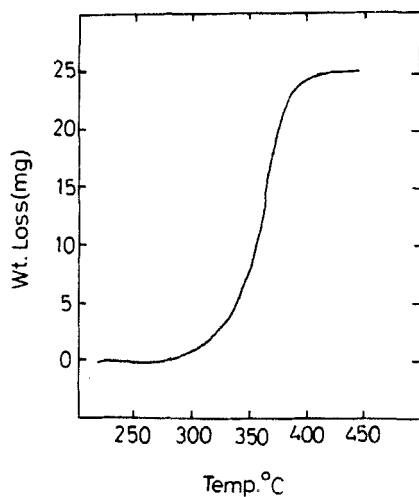
FIG. 3. The TG thermogram for the cellulose acetate (40% acetyl) sample.

TABLE 3. Values of the Kinetic Parameters for CA (40% acetyl)

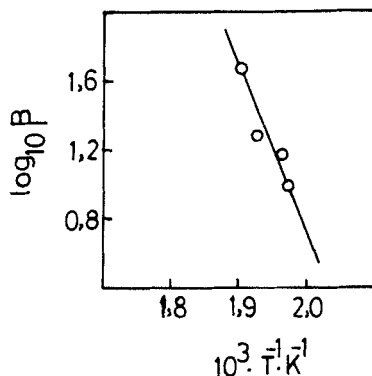| Heating rate, β ($°C/min$)	Exothermic peak temperature ($°K$)	Ozawa method: E = 165.43 kJ/mol E = 39.53 kcal/mol $Z = 8.1 \times 10^{16}$ min^{-1}		Kissinger method: E = 166.28 kJ/mol E = 39.74 kcal/mol $Z = 9.9 \times 10^{16}$ min^{-1}	
		k (min^{-1})	$t_{1/2}$ (h)	k (min^{-1})	$t_{1/2}$ (h)
10	507	0.75	0.93	0.74	0.93
15	511	1.01	0.68	1.01	0.68
20	520	1.99	0.35	1.99	0.35
50	527	3.30	0.21	3.32	0.21

FIG. 4. The Ozawa plot, of log heating rate vs reciprocal peak temperature, for the cellulose acetate (40% acetyl) sample.

where E = activation energy, J/mol (cal/mol).
        R = gas constant, 8.314 J/mol·K (1.987 cal/mol·K)
        β = heating rate, K/min (deg/min)
        T = exothermic peak temperature, °K

   The value of E is found to be 165.4 kJ/mol (39.53 kcal/mol). An alternative method for the calculation of the activation energy is based on the method of Kissinger [9], according to which a plot of ln (β/T^2) vs 1/T is plotted as shown in Fig. 5. The slope of this plot is used to calculate the activation energy E with the help of following equation:

$$\frac{d \ln (\beta/T^2)}{d (1/T)} = - \frac{E}{R} \qquad (4)$$

The activation energy for the sample is found to be 166.3 kJ/mol (39.74 kcal/mol).
   The preexponential factor (Z) is evaluated from

$$Z = \frac{\beta E e^{E/RT}}{RT^2} \qquad (5)$$

The average values of Z found on the basis of the Ozawa and the Kissinger methods are 8.1×10^{16} and 9.9×10^{16} min^{-1}, respectively.
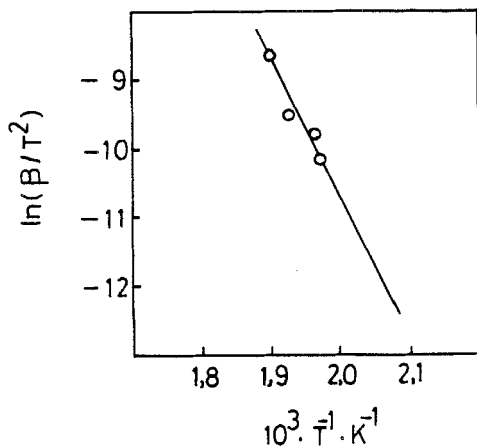
FIG. 5. The Kissinger plot of $\ln(\beta/T^2)$ vs $(1/T)$ for the cellulose acetate (40% acetyl) sample.

The value of the rate constant is obtained from the Arrhenius equation:

$$k = Ze^{-E/RT} \tag{6}$$

The values of the rate constants obtained for cellulose acetate (40% acetyl) by the Ozawa and the Kissinger methods are tabulated in Table 3. From the calculated values of the rate constants, the half-life ($t_{1/2}$) was also calculated from the relation

$$t_{1/2} = 0.693/k \tag{7}$$

The half-life values obtained are also given in Table 3. It is seen from this table that the values of the rate constant and the half-life values obtained by the Ozawa and the Kissinger methods are almost constant. It may also be noted that as the heating rate increases, the rate constant increases and the half-life decreases.

ACKNOWLEDGMENT

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