Viscoelastic properties of cellulose derivatives: 1. Cellulose acetate

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The dynamic mechanical spectrum of cellulose acetate (CA) from − 130°C to 240°C has been determined at different frequencies (from 0.1 to 30 Hz). Three relaxations, designated α, β and γ in order of decreasing temperature, and one shoulder (β^*) above room temperature were found. Comparison with calorimetric and thermogravimetric measurements yields the conclusion that the α relaxation (197°C at 3 Hz) is related to the glass-to-rubber transition and the β^* shoulder (50°C–100°C) is due to loss of moisture. The β relaxation (−38°C at 3 Hz, $\Delta H = 100$ kJ mol^{-1}) is tentatively assigned to local motions of the main chain (glucopyranose rings). The low-temperature γ relaxation (−88°C at 3 Hz, $\Delta H = 46$ kJ mol^{-1}) is humidity-dependent: its intensity decreases when the samples are dried to moisture contents lower than that obtained by normal room conditioning (about 3%). Higher water contents shift the relaxation to lower temperatures without increasing the intensity of the mechanical loss. It is suggested that water associated with the unesterified methylol groups of cellulose acetate is responsible of the dynamic mechanical γ dispersion.

(Keywords: cellulose acetate; dynamic mechanical spectrum; thermal analysis; moisture)

INTRODUCTION

A number of papers have been devoted to the study of the transitions and relaxations of cellulose and its derivatives. Early investigators mainly used specific volume–temperature measurements[1–3] to determine the glass transition as well as one or two additional second-order transitions whose molecular origin, however, remained unclear. On the basis of results on cellulose derivatives with different types and degrees of ester substitution, dielectric and n.m.r. studies by Mikhailov *et al.*[4,5] attributed the low-temperature relaxation of the cellulose esters to motions of the ester side chains. Recently, dynamic mechanical and dielectric studies on cellulose acylates[6,7] reported more than one relaxation process below room temperature, depending on the chain length of the ester group. One of the dielectric relaxations present in all acylates from acetate to stearate was assigned to motion of the oxycarbonyl group in the side chain. Also the influence of water has been extensively studied, especially in connection with the parent polymer, cellulose[8–10], due to the importance of the interaction of water with the hydroxyl groups of the polysaccharide. Most attention has been focused on the dielectric relaxation occurring below room temperature, whose origin has been attributed either solely to the presence of water[9] or to the association of water with side groups of the polymer giving rise to a coupled motion[8,10]. The role of water is still controversial, though Crofton[10] recently suggested that two regimes of hydration—relative to low or high water contents—are involved, giving rise to relaxations of different molecular origin. Compared with the amount of dielectric data, few dynamic mechanical studies have been carried out, especially on the acetate ester of cellulose[2,11]. As regards the influence of water on the dynamic mechanical spectrum, Seymour *et al.*[11], in an investigation on a series of cellulose esters (mainly acetate–butyrate and acetate–propionate), report a small effect on the dynamic mechanical loss spectrum as opposed to a strong effect of water on the dielectric properties. To our knowledge the available dynamic mechanical studies on cellulose acetate investigate rather wide temperature ranges, but only report single frequency measurements[2,11].

The aim of the present work is to determine the dynamic mechanical properties of cellulose acetate over a wide range of temperatures and frequencies in order to correlate the relaxation regions of the viscoelastic spectrum with the molecular motions responsible for the mechanical dispersions. The determination of the activation energy of the individual relaxations, made possible by multifrequency scans, is expected to contribute—through comparison with literature data for relaxations already assigned to specific molecular motions—to the clarification of the molecular origin of the dynamic mechanical dispersions of cellulose acetate.

EXPERIMENTAL

The cellulose acetate (CA), degree of substitution 2.4, used in this work was a commercial product (Mazzucchelli Celluloide S.p.A., Castiglione Olona). The CA powder was introduced into the mixing cup of a Mini Max Molder (Custom Scientific Instruments), a miniature mixing/injection-moulding machine supplied with a rectangular mould (30 × 8 × 1.6 mm) especially designed to deliver suitable specimens for the dynamic mechanical measurements. The temperature of the Mini Max machine was set to the lowest possible value allowing injection moulding, i.e. about 250°C.

The dynamic mechanical measurements were carried out by means of a dynamic mechanical thermal analyser (DMTA, Polymer Laboratories), using the dual cantilever

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geometry. A wide range of temperatures (−130°C to +240°C) and frequencies (0.1 to 30 Hz in six steps) were investigated at a constant heating rate of 3°C min^{-1}.

The calorimetric measurements were performed by means of a Perkin–Elmer DSC1B. The glass transition temperature, T_g, was determined at a scanning rate of 16°C min^{-1} by the method of baseline deviation.

Thermogravimetric analysis was carried out with a Mettler 3000 apparatus from room temperature to 400°C at a heating rate of 16°C min^{-1}. A step analysis of the weight losses was also performed by means of the computing programs of the TA3000 system.

RESULTS AND DISCUSSION

The calorimetric curve of cellulose acetate from room temperature to 350°C is shown in *Figure 1* for a typical injection-moulded sample to be used in the dynamic mechanical measurements. The original CA powder shows analogous calorimetric behaviour. The thermogram is rather complex and shows several endo- and exothermal phenomena, among which a poorly defined glass transition can be identified in the vicinity of 200°C. This transition is followed by an exothermal effect probably due to crystallization and by a subsequent melting endotherm.

A thermogravimetric analysis has also been carried out in order to elucidate the origin of the complex endo/exothermal effects that appear in the high-temperature region of the calorimetric curve. From the t.g.a. curve shown in *Figure 1* it is readily seen that a substantial weight loss begins in the temperature range where the endo/exothermal phenomena appear, suggesting that the polymer undergoes thermal decomposition at temperatures higher than 300°C, in accordance with previous results[12,13].

An improvement in the resolution of the glass transition region can be obtained by appropriate quenching from about 220°C, as shown in *Figure 2*. Comparison of the first d.s.c. curve with that recorded during the second run clearly shows that both the broad endotherm preceding and the exotherm following the glass transition have disappeared. The easily detectable specific-heat increment that appears in the second scan has a value of 0.27 J g^{-1} °C^{-1} and the temperature corresponding to the onset of the transition is 190°C. This glass transition temperature falls reasonably into the range of expected values for cellulose acetate with degree of substitution 2.4 (ref. 14). As a matter of fact, the very high glass transition of cellulose is decreased by esterification, being lower the longer the aliphatic chain in the acyl group and the higher the degree of ester substitution[6,11].

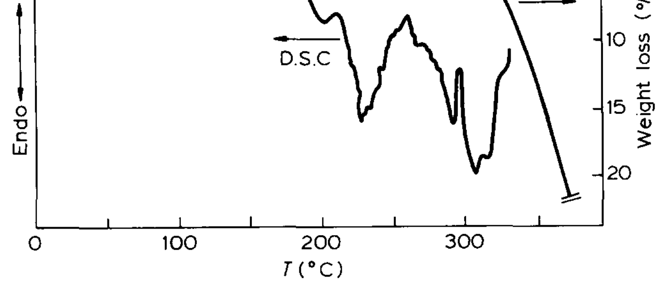

Figure 1 D.s.c. and t.g.a. curves of cellulose acetate

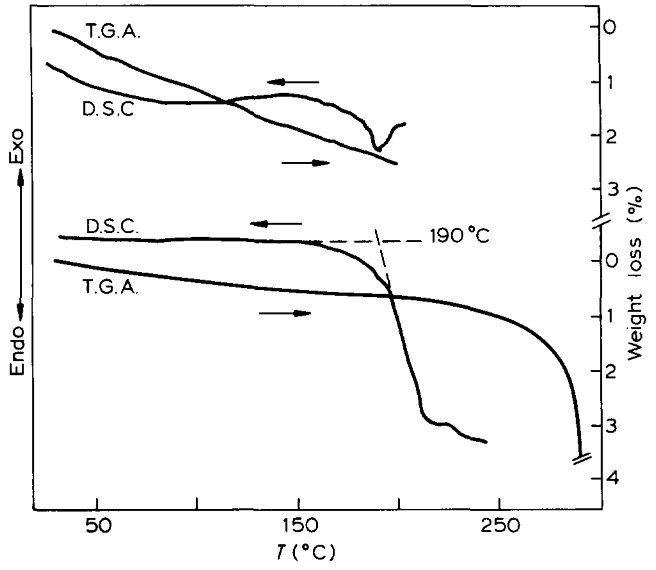

Figure 2 Consecutive d.s.c. and t.g.a. scans of cellulose acetate: upper curves, first run from room temperature to 220°C; lower curves, second run after quenching from 220°C

The dynamic mechanical spectrum of cellulose acetate stored under normal room conditions is shown in *Figure 3*, where loss tangent (tan δ) and storage modulus (E') are plotted as functions of temperature at two frequencies, 0.33 and 30 Hz. The loss tangent shows three frequency-dependent absorption peaks and one shoulder centred at about 80°C, the absorption regions being named α, β^* (shoulder), β and γ in order of decreasing temperature. The main α relaxation, which occurs in the same temperature range as the calorimetric glass transition, shows a very intense absorption maximum associated with a very steep modulus drop. The partially overlapping β and γ peaks, in contrast, are secondary relaxations of moderate intensity, associated with a fairly small decrease of the storage modulus.

As expected, the temperature shift produced by a change in test frequency is larger for the low-temperature relaxations than for the main transition; interestingly, the shoulder above room temperature (β^*) does not seem to be affected by the frequency parameter. The apparent activation energy (ΔH) of the dynamic mechanical relaxations has been determined from the frequency dependence of the peak temperature by means of an Arrhenius-type equation. The ΔH values are reported in *Table 1* together with the peak temperatures and intensities at a selected frequency (3 Hz). Although the Arrhenius relationship appropriately describes only the temperature–frequency dependence of secondary viscoelastic relaxations, in the present case a satisfactory linear ln ν vs. $1/T$ plot is also obtained for the main α relaxation whose ΔH value is therefore included in *Table 1*.

In *Figure 3* it can be observed that the intensity of the dynamic mechanical α dispersion barely reaches tan $\delta = 1$; moreover, the width at half-height ($\Delta T_{1/2}$) is as large as 31°C (at 3 Hz). These values of the peak parameters reflect—in accordance with the present calorimetric results and with previous investigations[12,15]—the partially crystalline character of cellulose acetate. They may be

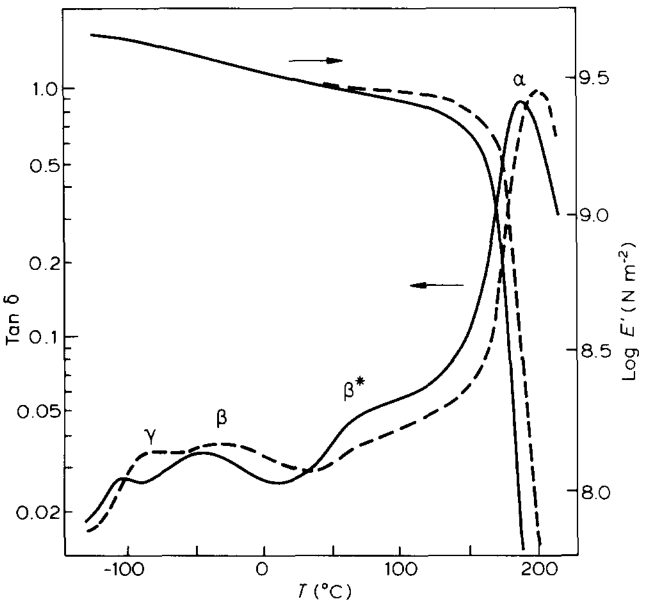

Figure 3 Dynamic mechanical spectrum of cellulose acetate at different frequencies: ——, 0.33 Hz; – –, 30 Hz

Table 1 Parameters of the dynamic mechanical relaxations of cellulose acetate

Peak	T_{max}[a] (°C)	$\tan \delta_{max}$[a]	ΔH (kJ mol^{-1})
α	197	0.970	573
β	−38	0.033	100
γ	−88	0.030	46

[a] Values at 3 Hz.

conveniently compared with those typical of amorphous or slightly crystalline polymers such as polystyrene and poly(vinyl chloride), respectively[16]: $\tan \delta_{max} = 2$ and $\Delta T_{1/2} = 12°C$ for polystyrene; $\tan \delta_{max} = 1.2$ and $\Delta T_{1/2} = 14°C$ for poly(vinyl chloride). Also the high ΔH value reported in *Table 1* (573 kJ mol^{-1}) suggests the presence of a substantial crystalline fraction that hinders the motions occurring at the glass-to-rubber transition.

As regards the largely overlapping β and γ relaxations, it has to be pointed out that, in a range of temperatures and frequencies comparable to those of the present work, previous studies report a single, very broad, low-temperature dynamic mechanical and dielectric relaxation for cellulose acetate[2,11,17] as well as a single n.m.r. relaxation for cellulose triacetate (CTA)[5]. Only very recently, two low-temperature relaxations have been reported[6,7] for cellulose triesters of varying chain length, a single low-temperature absorption, however, being reported for cellulose acetate[7]. The activation energy value commonly accepted for the low-temperature dispersion of cellulose acetate—attributed to motions of the ester side chains—is that given by Mikhailov[5] for the triacetate, i.e. 46 kJ mol^{-1}, identical to the activation energy of the γ relaxation reported in *Table 1*. From the available temperature-frequency data[5,10], it is possible to calculate the temperature at which the acetate side-chain relaxation is expected to occur at a frequency of 3 Hz. A peak temperature of −55°C to −58°C is predicted, a value that does not compare with either of the present low-temperature relaxations, being halfway between T_γ and T_β.

It is worth pointing out that the dynamic mechanical spectra of cellulose acetate samples stored under normal temperature and humidity conditions (hereafter called room conditions) show good reproducibility, with respect to both intensity and temperature location of the absorption peaks. We have found, however, that it is possible to induce substantial modifications in the secondary relaxation regions of CA through variations in the humidity content of the samples. The reproducibility of the spectra of CA stored under room conditions indicates, therefore, that the amount of moisture absorbed in these conditions is practically constant.

Figure 4 shows the loss tangent as a function of temperature at 3 Hz for three subsequent scans on the same CA sample: (1) sample stored in room conditions for several months; (2) immediately re-run (under dry nitrogen purge) after quenching from 130°C; (3) following scan number 2, after 4 days room storage. It is observed that the heat treatment to 130°C (compare runs 1 and 2) mainly modifies the γ and β^* regions of the loss spectrum. As a consequence of the heat treatment, the dynamic storage modulus (not shown in the figure) increases in the temperature range of the β^* shoulder. Subsequent room storage tends to reproduce the initial relaxation spectrum (third scan): the longer the room storage, the closer to run number 1 is the spectrum obtained.

It is interesting to compare the dynamic mechanical loss behaviour in the β^* shoulder region to the d.s.c. and t.g.a. curves reported in *Figure 2*. In the temperature range of interest, the first d.s.c. and t.g.a. scans are characterized by a broad endotherm and 3% weight loss respectively, these phenomena being absent from the second thermal scans. The process is totally reversible: after room storage, d.s.c. and t.g.a. curves analogous to those found during the first scan are obtained. It may be observed that, while the d.s.c. and t.g.a. heat treatments need to be carried out up to 220°C, a scan to 130°C is sufficient to suppress the β^* shoulder from the dynamic mechanical spectrum. This apparent disagreement may be accounted for by the different heating rates employed (16°C min^{-1} vs. 3°C min^{-1}, respectively).

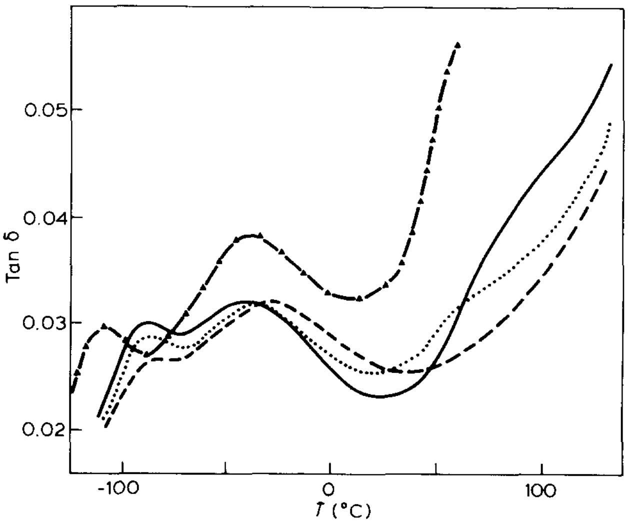

Figure 4 Effect of moisture level on the low-temperature relaxations of cellulose acetate (same sample tested at 3 Hz): ——, stored under room conditions for several months; – –, immediately re-run after quenching from 130°C; ·····, 4 days room storage after previous run; –▲–, hydrated by storage in water-saturated atmosphere for one week

It is clear that the dynamic mechanical β^* shoulder and the related calorimetric phenomena are due to the presence of absorbed moisture and specifically to evaporation of water from the samples. Such a conclusion is also supported by a dynamic mechanical measurement carried out on a strip of glass fibre paper impregnated with water, which in identical experimental conditions showed a very intense absorption maximum in the range 70°C–90°C. The mentioned increase of the storage modulus after elimination of the β^* shoulder from the spectrum of CA is therefore due to increased rigidity of the sample caused by loss of the plasticizing agent (water). Moreover, the intensity and temperature location of the β^* shoulder in the third scan of *Figure 4* indicate that the moisture absorbed between scans 2 and 3, besides being less than that present in the original sample, has a higher mobility, i.e. is more superficially absorbed. It is worth recalling also that previous dynamic mechanical studies on cellulose acetate[2,11] revealed a shoulder above room temperature, which was difficult to resolve owing to its proximity to the α relaxation. No assignment of the mechanical loss was made, except for the observation by Seymour *et al.*[11] of a resemblance to the relaxation of the ester side groups in methacrylate polymers, a hypothesis that does not gain support from the above experimental evidence. On the other hand, the present assignment agrees with that relative to an analogous dispersion found in the spectrum of several polysaccharides, including regenerated cellulose[8], whose origin was attributed to loss of moisture rather than to a true mechanical transition.

There has been much debate over the origin of water-related relaxations in polymers[18]. In particular, the effect of water on the dielectric and mechanical relaxations of cellulose and its derivatives is still controversial[8–11,19]. As far as the present γ relaxation is concerned, *Figure 4* shows that the loss of moisture resulting from heat treatment at 130°C carries as a consequence a decrease of the peak intensity. The differences in magnitude are small (note the highly magnified tan δ scale) but larger than the experimental error. Hydration of a cellulose acetate sample to a water content higher than that typical of room conditioning was carried out by keeping the sample in a water-saturated atmosphere for one week. The amount of water additionally absorbed, determined gravimetrically, was 10%. *Figure 4* shows that, contrary to the simple expectation of an increase in the peak intensity, a dispersion located about 20°C lower than the original γ relaxation appears in the spectrum of the hydrated sample. The intensity of the new dispersion is comparable to that of the original γ peak, confirming that no simple relationship exists between the amount of absorbed water and the magnitude of relaxation.

It has already been pointed out that, though the activation energy of the γ peak reported in *Table 1* is equal to that of the relaxation previously attributed[5,10] to motions of the acetate side chains in CA and CTA, the γ peak temperature is well below the expected value (−83°C vs. about −55°C). Since not all the hydroxyl groups of the glucopyranose rings of CA are acylated, a possible contribution to the water-dependent γ relaxation from hydrophilic units such as unesterified methylol groups must be taken into consideration. In order to check the likeliness of such a hypothesis, the expected location of a relaxation attributed to motions of the methylol units in the spectrum of cellulose[5,10] has been calculated and compared with the present γ peak temperature. A peak temperature of −86°C at 3 Hz is obtained for the $-CH_2OH$ relaxation of cellulose ($\Delta H = 54$ kJ mol^{-1})[5], in good agreement with the T_γ value of *Table 1*. It has been shown[10] that small amounts of water increase the magnitude of the hydroxyl side-group motion of cellulose, while further addition shifts the loss to lower temperatures. As regards cellulose acetate, the effect of water has been explained[10] assuming the existence of a dual regime of hydration, involving binding of water to specific polymer sites at low water contents (up to about 4.5%) and loss of specificity of the binding sites at higher water contents. Gravimetric determination of the water content of the CA samples presently studied—relative to the same samples assumed 'dry' after storage in a desiccator under vacuum over P_2O_5 up to constant weight—yielded the following values: room conditioned, 3%; hydrated, 13%, i.e. below and above the reported water monolayer formation[10] respectively. The tentative assignment of the γ relaxation of cellulose acetate to motions of water–methylol complex units is corroborated by preliminary measurements on room-conditioned tri-substituted cellulose acetate, whose dynamic mechanical spectrum shows no dispersions in the temperature range of the γ relaxation.

As regards the β relaxation, only the hydrated CA sample shows an evident increase in the magnitude of dispersion. This effect may be due either to a real increase in the β relaxation strength or to simple superposition with the much stronger α relaxation, whose temperature location appears to be downshifted by plasticization. Water evaporation corresponding to the very intense β^* absorption makes the α transition shift back to high temperatures. Involvement of the acetate side chains in the motion responsible for the β relaxation cannot be excluded *a priori*, since the only low-temperature relaxation that occurs in the mentioned dynamic mechanical spectrum of CTA seems to correspond to the present β relaxation. However, as already observed, comparison with previous results[5,10] shows that none of the peak parameters of the cellulose acetate β dispersion agree with those of the acetate-related relaxation. In this connection, a few general considerations may be put forward. The temperature of the β relaxation (−38°C at 3 Hz) is high not only when compared with that expected[5,10] for the $-COOCH_3$ relaxation of CA and CTA (about −55°C) but also (and to a larger extent) when the acetate side-chain relaxation of the simplest acetate-containing polymer, poly(vinyl acetate) (about −100°C at 1 Hz[20,21]), is considered. Also the activation energy of the present β relaxation is twice as high (100 vs. 40–50 kJ mol^{-1}) as expected for the acetate motion.

A semiempirical relationship for secondary relaxations, derived from the Arrhenius equation and assuming a linear dependence of the activation energy on $T_{\max}$ (K) at a given frequency[22,23], predicts a ΔH value of 60–70 kJ mol^{-1} for a secondary relaxation located in the temperature range of the β dispersion of CA. If the assumptions on which such a relationship is based are correct, the experimental value of the activation energy (100 kJ mol^{-1}) appears to be high for a typical secondary relaxation. It is of interest to recall that, unlike the investigations discussed above[5,10], a relaxation appearing in the spectrum of several cellulose esters in the range of the present β dispersion was assigned by Seymour *et al*[11] to motions of the glucopyranose rings in the polymer main chain. No activation energy was reported, although a relatively high value may be expected for a motion of the polymer backbone involving a ring structure. The present ΔH data seem to be consistent with the assignment of the β relaxation of cellulose acetate to main-chain motions, though the absence of a clearly identifiable dynamic mechanical relaxation related to the motion of the acetate side groups is a rather puzzling result. A contribution of such groups to the β relaxation cannot, however, be excluded, since the motion may involve rather complex relaxing units.

It has to be emphasized that the identification of the molecular groups responsible for the low-temperature relaxations of cellulose acetate is made particularly difficult by the complex molecular structure of the polymer and the unavoidable inhomogeneities in ester substitution. It is expected that a better understanding will be obtained from further investigations on cellulose derivatives where the type of substituent and degree of substitution will be systematically changed, as well as from the results of the following paper[24] on the influence of increasing amounts of diluent on the dynamic mechanical spectrum of cellulose acetate.

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