

# Viscoelastic properties of cellulose derivatives: 2. Effect of diethylphthalate on the dynamic mechanical relaxations of cellulose acetate

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The dynamic mechanical spectra of cellulose acetate (CA) with various amounts of diethylphthalate (DEP), from 3 to 50 wt%, have been obtained over a range of temperatures ( $-130^{\circ}\text{C}$  to  $240^{\circ}\text{C}$ ) and frequencies (0.1 to 30 Hz). The effect of DEP addition on the main ( $\alpha$ ) relaxation is to shift the dispersion and corresponding modulus drop to lower temperatures. The depression of the transition temperature is smaller than commonly found for polymer-diluent mixtures. The influence of DEP on the secondary  $\beta$  and  $\gamma$  relaxations is quite different: while the low-temperature  $\gamma$  dispersion is progressively depressed by DEP addition, the intensity of the  $\beta$  relaxation increases strongly at DEP contents higher than 15%. The dynamic modulus increases with  $\gamma$  peak depression and shows a more intense drop with the strengthening of the  $\beta$  relaxation. The activation energy of the  $\beta$  dispersion remains fairly constant up to 15% DEP content, then increases to approach, at 50% DEP, the  $\Delta H$  value of the  $\alpha$  relaxation of the pure diluent. At high DEP contents, active participation of the diluent molecules in the motion responsible for the  $\beta$  relaxation is suggested.

(Keywords: cellulose acetate; diethylphthalate; dynamic mechanical relaxations; plasticizer effect)

## INTRODUCTION

A number of papers concerning plasticized cellulose derivatives, in particular the influence of diluents on the dilatometric<sup>1,2</sup>, dielectric<sup>3,4</sup> and dynamic mechanical<sup>2,5,6</sup> properties, have been reported in the literature. While the 'plasticizing' effect of the diluent on the polymer glass transition is a feature common to all systems investigated, rationalization of the results of the diluent effect on sub- $T_g$  transitions is difficult.

In a previous paper<sup>7</sup> the viscoelastic and calorimetric properties of cellulose acetate were discussed. It was found that, besides the main ( $\alpha$ ) relaxation corresponding to the glass transition, three secondary dispersions, named  $\beta^*$ ,  $\beta$  and  $\gamma$  in order of decreasing temperature, are present in the dynamic mechanical spectrum. The  $\beta^*$  process was attributed to loss of moisture from the samples, while the  $\beta$  and  $\gamma$  relaxations were tentatively assigned to motions of the glucopyranose rings in the main chain ( $\beta$ ) and of complex units formed by interaction of the unesterified methylols of CA and absorbed water ( $\gamma$ ). In an attempt to improve the identification of the molecular groups responsible for the viscoelastic relaxations of cellulose acetate, the present study on the effect of increasing amounts of diluent on the relaxation spectrum of CA was undertaken.

A phthalic ester commonly used as a plasticizer for cellulose acetate, diethylphthalate, was chosen as diluent and a large number of different polymer-diluent compositions were examined. The dynamic mechanical measurements were carried out as a function of temperature at a number of selected frequencies: this allows calculation of the activation energy of the viscoelastic

relaxations, a parameter that may be very helpful in the assignment of the dynamic mechanical absorptions.

## EXPERIMENTAL

The cellulose acetate (CA), degree of substitution 2.4, and the plasticizer, diethylphthalate (DEP), purity 98%, used in this work were commercial products supplied by Mazzucchelli Celluloide S.p.A. and Fluka, respectively. Cellulose acetate/diethylphthalate mixtures with DEP contents up to 50 wt% were investigated.

Appropriate amounts of DEP were added to the CA powder in order to obtain the required polymer/plasticizer composition and the mixture was subjected to dry blending at  $100^{\circ}\text{C}$  for 30 min. The dry blend was then fed to the mixing cup of a Mini Max Molder (Custom Scientific Instruments), a miniature mixing/injection-moulding machine. The temperature was set to the lowest possible value allowing injection moulding: this value was lower the higher the DEP content, starting from about  $250^{\circ}\text{C}$  for pure CA. The samples were stored under normal room conditions of temperature and humidity.

The dynamic mechanical measurements were carried out by means of a dynamic mechanical thermal analyser (DMTA, Polymer Laboratories), using the dual cantilever geometry. A wide range of temperatures ( $-130^{\circ}\text{C}$  to  $+240^{\circ}\text{C}$ ) and frequencies (0.1 to 30 Hz in six steps) were investigated at a constant heating rate of  $3^{\circ}\text{C min}^{-1}$ . A strip of glass fibre paper (Whatman GF/C) was used as an impregnating support for the pure plasticizer, diethylphthalate being a liquid at room temperature.

The calorimetric measurements were performed by means of a Perkin-Elmer DSC2, equipped with a scan-

ning autozero and a liquid N<sub>2</sub> subambient accessory, at a heating rate of 20°C min<sup>-1</sup>.

## RESULTS AND DISCUSSION

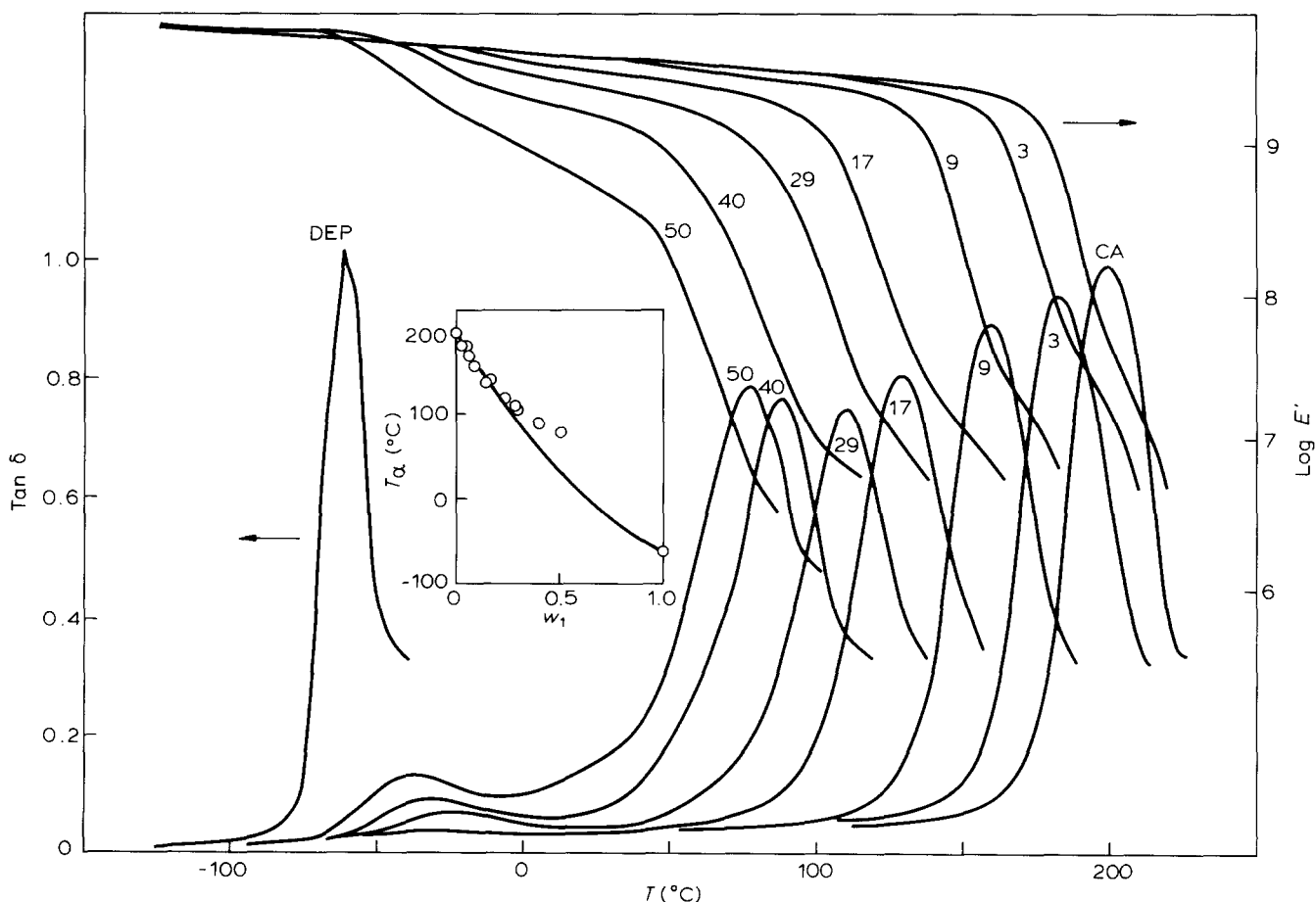
The effect of the plasticizer on the dynamic mechanical spectrum of cellulose acetate is summarized in *Figure 1*, where the loss tangent and storage modulus as functions of temperature for various CA/DEP mixtures and for the pure components are shown. For the sake of clarity, only selected polymer-diluent compositions are reported in the figure. It can be observed that the  $\alpha$  relaxation of cellulose acetate, which corresponds to the glass-to-rubber transition<sup>7</sup>, is shifted to lower temperatures by increasing amounts of DEP. Unfortunately, the limited compatibility of DEP with CA<sup>8</sup> prevents the study of plasticizer concentrations higher than 50%. Also the modulus drop accompanying the main transition undergoes the same low-temperature shift with increasing plasticizer content. Owing to the appearance of a relaxation of increasing intensity below room temperature, it is seen that the modulus value at the beginning of the glass transition is lower the higher the diluent content, especially for high DEP concentrations. The insert in *Figure 1* shows the dependence of the peak temperature  $T_x$  on DEP concentration together with a curve connecting the  $T_x$  values of the pure components (CA,  $T_x = 197^\circ\text{C}$ ; DEP,  $T_x = -63^\circ\text{C}$ ); the curve has been calculated by means of the following equation<sup>9</sup> containing a single

adjustable curvature parameter ( $k = 0.83$ ):

$$\ln T = \ln T_2 + \frac{\ln(T_1/T_2)}{1 + kw_2/w_1} \quad (1)$$

where  $w_1$  and  $w_2$  are the weight fractions and  $T_1$  and  $T_2$  the peak temperatures (K) of diluent and polymer respectively. It can be observed that the curve correctly describes the experimental decrease of  $T_x$  only up to DEP concentrations of about 15%, the  $T_x$  values deviating from the predicted behaviour at higher diluent contents. Similar observations were previously reported<sup>1,5</sup> for a number of plasticized cellulose esters that showed  $T_g$  depressions smaller than expected.

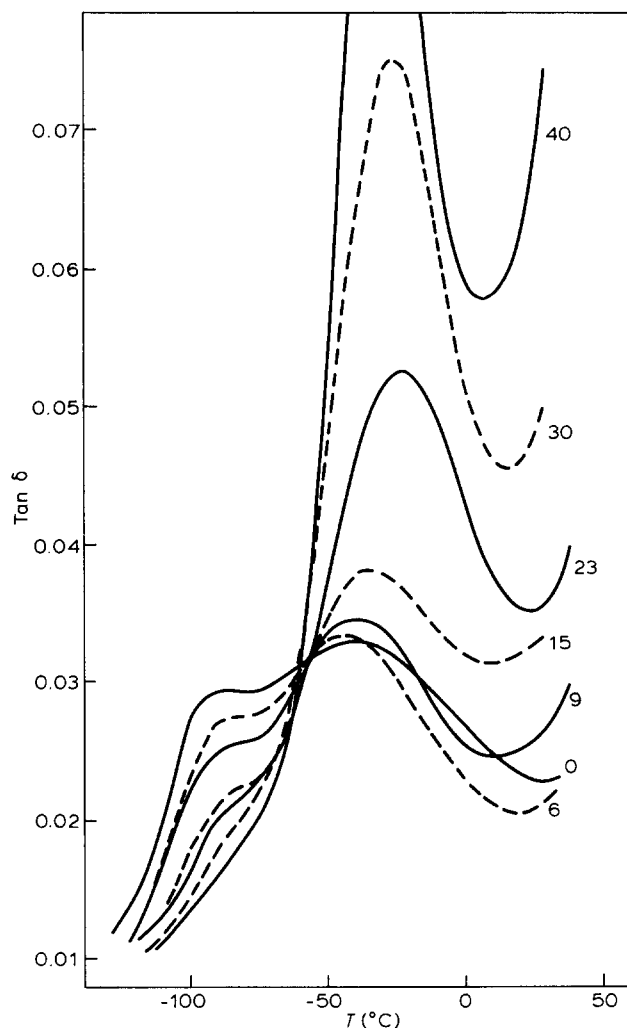
Since cellulose acetate is a partially crystalline polymer, the possible influence of crystallinity on the observed anomalous decrease of  $T_x$  is briefly discussed. It is known that only the amorphous fraction of partially crystalline polymers is involved in the transition from the glassy to the rubbery state. If cellulose acetate retains its crystallinity after mixing with the diluent, the concentration of DEP in the amorphous regions of CA should be different from the nominal composition of the mixture. In particular, the 'true' DEP concentration should be higher than the nominal one. Moreover, if the degree of crystallinity of cellulose acetate is altered by the effect of solvation—a rather controversial point for cellulose esters<sup>1,10,11</sup>—the differences between 'true' and nominal composition should also change over the range of mixtures examined.



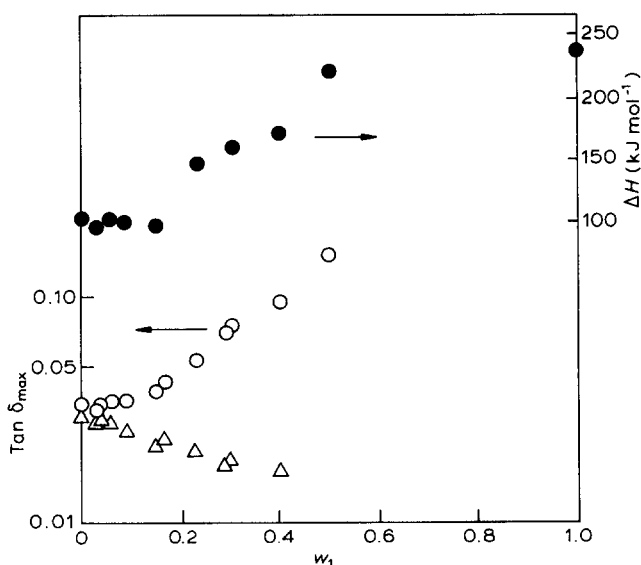
**Figure 1** Dynamic mechanical properties of cellulose acetate/diethylphthalate mixtures: loss tangent ( $\tan \delta$ ) and dynamic storage modulus ( $E'$ ) as functions of temperature at 3 Hz. Numbers on the curves indicate the diluent content (%). Insert: peak temperature of the main  $\alpha$  relaxation as a function of DEP content:  $\circ$ , experimental values; —, calculated according to equation (1)

It may be supposed that, while small amounts of diluent only solvate the amorphous regions, higher amounts also penetrate the crystalline fraction of the polymer. As a consequence, the difference between 'true' and nominal composition would decrease with increasing DEP content, tending to become nil at high DEP concentrations, where the whole sample could be assumed to be uniformly diluted, owing to complete solvation of the crystalline fraction. This argument may be applied to the experimental results of *Figure 1* by considering, for example, the 50% DEP sample as homogeneously solvated, in contrast to the lower concentrations whose 'nominal' composition would variously underestimate the 'real' situation in the amorphous regions. In the insert of *Figure 1* it may be noted that the experimental  $T_x$  value for the 50% DEP mixture is above the straight line connecting the  $T_x$  values of the pure components. This observation would consequently indicate that the 'true' compositional dependence of  $T_x$  ought to be convex, a very unusual behaviour only occasionally found for mixtures of organic solvents<sup>12</sup>. It seems therefore that the unusually small depression of the  $\alpha$  peak temperature of cellulose acetate shown in *Figure 1* cannot be related only to the semi-crystalline character of the polymer. Unfortunately, the limited compatibility of the CA/DEP system hinders further investigations on DEP-rich mixtures. It is known<sup>13</sup> that when a polymer-diluent system reaches its compatibility limit, as a consequence of further diluent addition the glass transition temperature remains constant and pure diluent appears as a separate phase. As regards the present system, it can be confidently assumed that no phase separation occurs up to the DEP concentrations investigated, since no pure diluent—characterized by a very sharp calorimetric  $T_g$ —nor a constant value of the  $\alpha$  peak temperature—corresponding to a hypothetical constant composition mixture—are found. On the contrary, in *Figure 1* the dynamic mechanical  $\alpha$  peak is clearly seen to shift to lower temperatures at all concentrations examined up to 50% DEP. Apart from the effect on the main  $\alpha$  relaxation discussed above, *Figure 1* shows diluent effects also on the curves of the storage modulus at low temperatures where a modulus drop, whose strength increases with increasing diluent content, is observed. At the highest DEP concentration (50%), the dynamic storage modulus decreases by about one order of magnitude. Correspondingly, the loss tangent shows a dispersion of increasing intensity in the temperature region where the secondary  $\beta$  ( $-38^\circ\text{C}$  at 3 Hz) and  $\gamma$  ( $-88^\circ\text{C}$  at 3 Hz) relaxations—not visible in the figure due to the low resolution of the  $\tan \delta$  scale—are found in the spectrum of pure cellulose acetate<sup>7</sup>. A magnification of the low-temperature region of the absorption spectrum is shown in *Figure 2*, where the loss tangent,  $\tan \delta$ , is plotted as a function of temperature and diluent content for selected CA/DEP mixtures, at constant frequency (3 Hz). With increasing diluent concentration, the intensities of the two relaxation maxima undergo a strikingly opposite change: while the  $\gamma$  peak is gradually depressed down to complete suppression, a large increase of the  $\beta$  peak intensity is observed.

The dependence of the peak intensities (at 3 Hz) on diluent content for all the mixtures examined is plotted in *Figure 3*. It is observed that, while the  $\gamma$  peak is progressively depressed over the whole concentration range explored, the  $\beta$  peak intensity apparently shows two

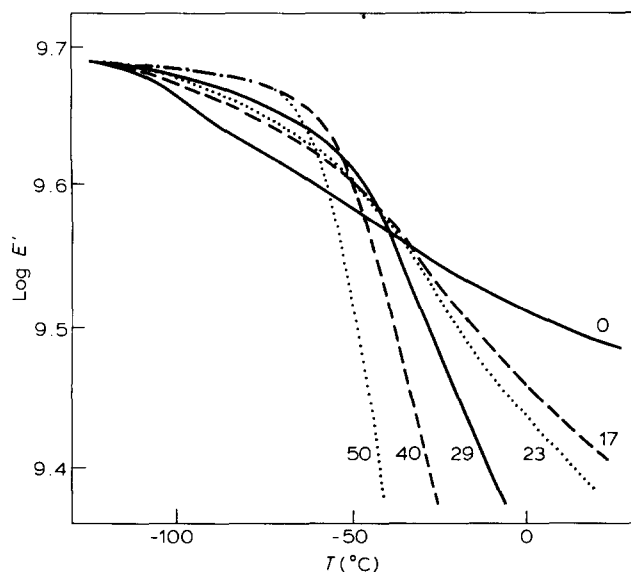


**Figure 2** Loss tangent as a function of temperature at 3 Hz, for CA/DEP mixtures whose DEP content (%) is shown



**Figure 3** Dependence of the  $\beta$  and  $\gamma$  peak parameters on DEP content: ●, activation energy of the  $\beta$  peak; ○, intensity of the  $\beta$  peak; △, intensity of the  $\gamma$  peak, taken as the  $\tan \delta$  value at  $-88^\circ\text{C}$

regimes of concentration dependence: quasi-constancy up to about 15% DEP, and strong increase (four-fold) from 15 to 50%. As already pointed out, the increase of the  $\beta$  peak intensity corresponds to an intensification of the related modulus drop. Conversely, as shown in *Figure 4*,



**Figure 4** Dynamic storage modulus as a function of temperature at 3 Hz, for selected CA/DEP mixtures. The DEP content (%) is shown. For clarity of presentation, the small experimental scatter of the absolute values of the modulus has been eliminated by means of small vertical shifts of the curves, so as to bring to coincidence the modulus values at  $-130^{\circ}\text{C}$

the depression of the  $\gamma$  relaxation is paralleled by a progressive elimination of the modulus decrease accompanying the transition. A recent paper<sup>6</sup> on nitrocellulose plasticized with nitroglycerine reports modifications of the dynamic mechanical spectrum of nitrocellulose with increasing plasticizer content analogous to those presently found for plasticized cellulose acetate: depression of a  $\gamma$  dispersion located at  $-80^{\circ}\text{C}$ , increase of the intensity of a  $\beta$  relaxation located at  $-50^{\circ}\text{C}$ , decrease of the  $\alpha$  peak temperature and changes in the storage modulus *versus* temperature curves.

In a previous paper<sup>7</sup> the  $\gamma$  relaxation of cellulose acetate was found to be moisture-dependent—sample drying caused a decrease of the peak intensity—and was tentatively attributed to motions involving water associated with the unesterified methylol groups of CA. It was found that the moisture content of CA samples stored under normal room conditions was about 3%, slightly lower than that corresponding to a 1:1 molar ratio of water to the available unesterified hydroxyl groups in the cellulose acetate employed. Within the framework of the assignment mentioned, an interpretation of the effect of DEP on the intensity of the  $\gamma$  relaxation is attempted. It may be assumed that during sample preparation (extrusion at high temperatures) no moisture is present, so that no interaction may occur between water and CA. The plasticizer, on the contrary, can interact with the polymer and give rise, for example, to hydrogen-bond formation between the unesterified hydroxyls of CA and the polar ester groups of DEP. When the temperature is lowered, the CA/DEP mixture is frozen in the glassy state; though hydrogen bonding of water to the hydroxyls of the polymer would be certainly favoured with respect to the interaction displayed by the organic solvent, water absorbed from the environment is able to interact only with the remaining 'free' hydroxyls. As already mentioned, the intensity of the  $\gamma$  relaxation of cellulose acetate at low moisture contents depends on the amount of absorbed water<sup>7</sup>: if the above interaction scheme is not too far from being correct, the intensity of the  $\gamma$  relaxation in the

CA/DEP mixtures may be regarded as indicative of the number of interacting sites (hydroxyls) not yet occupied by DEP molecules.

It appears that, while diluent addition progressively hinders the motion that originates the  $\gamma$  relaxation, the units responsible for the  $\beta$  dispersion remain free to relax. As already seen in Figure 3, the intensity of the  $\beta$  relaxation changes with DEP content, a dual concentration dependence being observed below and above 15–20% diluent concentration. A crude estimate of the diluent/polymer molar ratio shows that 20% DEP concentration corresponds to 0.3 diluent molecules per monomer unit of cellulose acetate, this value being equal to one-half of the average number of unesterified hydroxyl groups present in each monomer unit of CA (degree of substitution 2.4).

At high DEP contents, the increase of the  $\beta$  peak intensity is so strong and the corresponding modulus drop becomes so marked that active participation of the diluent molecules in the motion responsible for the  $\beta$  relaxation is clearly suggested. Support for this hypothesis comes from examination of the variations with plasticizer of the apparent activation energy of the  $\beta$  absorption ( $\Delta H$ ), derived from the frequency dependence of the peak temperature, shown in Figure 3. As already found for the peak intensity, the activation energy of the  $\beta$  relaxation also remains fairly constant up to a DEP content of about 15%; further diluent addition increases the  $\Delta H$  value from the original  $100\text{ kJ mol}^{-1}$  of pure CA to  $222\text{ kJ mol}^{-1}$  of the 50/50 sample. The latter value is only slightly lower than the activation energy of the  $\alpha$  relaxation of the pure diluent ( $239\text{ kJ mol}^{-1}$ ). The concentration dependence of  $\Delta H$ , i.e. the increase from values typical of secondary dispersions to high values usually associated with main  $\alpha$  transitions, agrees with the hypothesis of an increasing participation of the diluent molecules in the motions responsible for the  $\beta$  dispersion.

A recent review on secondary relaxation in glassy polymers by Kolarik<sup>14</sup> classifies the diluent-related relaxations as due either to motions of the diluent molecules themselves—rather independently of existing molecular mobility of the host polymer—or to more complex motions of the diluent molecules associated with the motion of some part of the polymer main or side chains. As regards the present  $\beta$  absorption of plasticized cellulose acetate, it may be noted that: (a) the peak temperature is at least  $25^{\circ}\text{C}$  higher than that of the main transition of the pure diluent, even at the highest DEP concentration examined; (b) the peak magnitude is not proportional to the diluent content over the whole range of diluent concentrations (being roughly constant up to 15% DEP); and (c) in the 0–15% concentration range, the peak activation energy also remains equal to that characterizing the  $\beta$  relaxation of pure cellulose acetate. These observations suggest that the dispersion is not a totally new diluent peak superimposed on the original  $\beta$  relaxation but rather is a modification of the pre-existing cellulose acetate  $\beta$  absorption, due to a polymer–diluent interaction that probably yields a change in bulkiness of the relaxing units and becomes effective above a certain diluent content. It is difficult to compare this latter point with previous results, since the available data<sup>5,6</sup> only consider polymer–diluent mixtures containing more than 10% diluent. In a previous paper<sup>7</sup> the  $\beta$  relaxation of cellulose acetate was tentatively attributed to local mo-

tions of the polymer main chain, i.e. of the sugar rings. In the range of DEP contents where the strengthening of the  $\beta$  relaxation is presently observed, it is possible that, besides the DEP-hydroxyl interaction suggested above, the polymer-diluent interaction also involves 'looser' bonding of DEP to the glucopyranose rings through the acetate groups. This may lead to an increase in size of the motional units responsible for the  $\beta$  absorption, as suggested by the increase of activation energy experimentally observed.

In this connection it is worth recalling previous work by the authors<sup>15</sup> on a naturally occurring polymer, the protein elastin, diluted with ethylene glycol, where a diluent-induced behaviour similar to that presently observed for the  $\beta$  relaxation of cellulose acetate was reported. In the work mentioned a  $\beta$  relaxation, attributed to local main chain motions in the undiluted polymer, underwent transformations with increasing diluent concentration analogous to those of the CA/DEP system presently described. In the case of glycol-swollen elastin, the modifications of the  $\beta$  dispersion were attributed to interaction between the macromolecules and the low-molecular-weight substance, leading to an increase in size of the complex polymer-diluent relaxing units. Calorimetric measurements at low temperatures give support to the hypothesis of a large contribution of the solvent molecules to the low-temperature relaxation of highly solvated CA. Figure 5 shows the broad specific-heat increment that appears in the low-temperature region of the d.s.c. curve of the 50% DEP sample, compared to the glass transition of pure DEP. Only the 40 and 50% DEP mixtures show such a feature in the d.s.c. curve, the thermogram for the lower concentrations being flat in this temperature region. As pointed out earlier, the d.s.c. curve of the 50/50 mixture shown in Figure 5 does not show evidence of phase separation of the pure diluent: the specific-heat increment associated with the glass transition of pure DEP is extremely sharp (4°C), while the one characterizing the low-temperature transition of the 50% DEP sample is 10 times broader (40°C) and begins at a higher temperature (-82°C vs. -93°C of DEP, baseline deviation). Nevertheless, the appearance of a calorimetric transition corresponding to the intense  $\beta$  relaxation of highly diluted CA indicates the occurrence of a motion that involves rather large relaxing units, in accordance with the high values of the characteristic parameters of the dynamic mechanical dispersion: intensity, magnitude of the modulus drop and activation energy.

The results of the present work agree with a previous tentative assignment of the dynamic mechanical relaxations of cellulose acetate<sup>7</sup>. However, to make possible a conclusive correlation between loss peaks and mole-

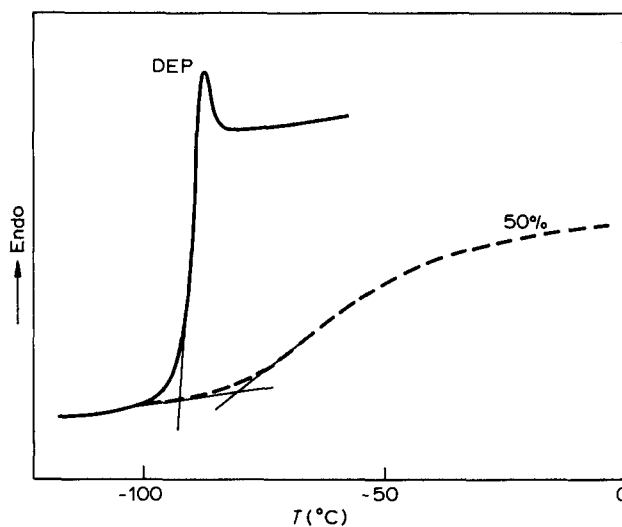


Figure 5 D.s.c. curves for pure DEP and the CA/DEP mixture containing 50% DEP, from -120°C to 0°C

cular motions, especially for the low-temperature relaxations, further investigations are needed. Along these lines, cellulose derivatives where type and degree of substitution are systematically changed are currently being investigated in our laboratory.

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