

Viscoelastic Behaviour of Vinylic Copolymers of Cellulose and Their Glass Transition Temperature by DSC

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SYNOPSIS

The viscoelastic response of some vinylic copolymers of cellulose prepared with vinyl acetate–methyl acrylate mixtures and with Ce(IV) ion as initiator, and native cellulose, were studied at 110 Hz in a range of temperatures from -120 – 100°C .

The viscoelastic spectrum of cellulose shows the β -relaxation that is not shown in its vinylic copolymers. We observed the same effect in the dielectric β -relaxation.

For the vinylic copolymers of cellulose, one viscoelastic relaxation attributed to the α -relaxation of the grafted vinylic chains is observed. Some differences in the characteristics of this relaxation may be related to the composition of PVA/PMA vinylic side chains and to the ratio of cellulose in the copolymer. The plots of the Argand diagrams give us a better understanding of the viscoelastic behaviour of these materials. The results seem to indicate that the cellulose hinders the large-scale motions of the vinylic chains grafted onto it. The glass transition temperature (T_g) determined by differential scanning calorimetry (DSC) also shows the same fact: the T_g of the vinylic copolymers of cellulose are higher than both the T_g of polyvinyl acetate–polymethyl acrylate copolymers (PVA–PMA) without cellulose and the T_g of some blends of cellulose and the PVA–PMA whose composition was as similar as possible to the cellulosic copolymers. The importance of the covalent bonds between cellulose and the vinylic side chains in the structural transitions are revealed. The present results are compared with the dielectric α -relaxation that we described elsewhere. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

An understanding of the viscoelastic behaviour of polymeric materials is fundamental for the proper utilization of polymers. The time and temperature dependence of the mechanical properties of the polymeric materials allows us to compare them to other structural materials.

The viscoelastic behaviour of some materials under mechanical stress may be caused by both the deformation of inter- and intramolecular bonds and the slipping of one molecule over another. The viscoelastic relaxation can take place in both the crystalline and amorphous region of polymers. The chemical constitution of the macromolecular materials has a significant influence on the mechanical

properties, in particular modifying their glass transition temperature (T_g), which is usually related to the α -relaxation in amorphous and linear polymers since both involve large-scale structural rearrangements. Molecular weight, molecular interactions, chain flexibility, linear or branching structure, and cross-linking are some of the important factors that may influence both the mechanical properties and the T_g of the material. Therefore, if the material is a block or graft copolymer, as in the present work, some differences in their T_g or their viscoelastic α -relaxation may be observed.

The vinylic copolymers of cellulose considered in this paper are complex materials and there is little information about the dynamic mechanical properties of cellulose derivatives such as the copolymers considered in the present work,¹ although there is a little more about cellulose, polyvinyl acetate (PVA), and polymethyl acrylate (PMA),² which are the homopolymers that form part of these ma-

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terials. Therefore, it would be interesting to examine some factors such as the influence of cellulose, its ratio in the copolymer (or the percentage of grafting, %G) and the composition PVA/PMA of the grafted chains that may affect their viscoelastic behaviour and their T_g , and to compare it with the dielectric behaviour that we have considered in another work.³ We also examine the T_g of some blends of cellulose and vinylic copolymers PVA-PMA whose composition was similar to that of the cellulosic copolymers. The differences observed between the vinylic copolymers of cellulose and the blends is thought to be caused by the covalent bonds cellulose-vinylic chains in the cellulose copolymers, which do not exist in the blends.

EXPERIMENTAL

Materials

The vinylic copolymers of cellulose, the PVA-PMA copolymers, and the blends of cellulose with PVA-PMA copolymers were prepared as we described in a previous paper.¹

The vinylic copolymers of cellulose were prepared with cotton cellulose treated with NaOH solutions of different concentrations and using monomeric mixtures with different volumetric ratios of VA/MA. By this means we obtained copolymers with different cellulosic substrates, different grafting percentages (%G), different grafting frequencies (GF), and different viscosimetric average molecular weights (M_v) of the side vinylic chains. In the pres-

ent work we have selected the materials shown in Table I.

To prevent heat transfer problems in the material, the samples were pressed to give them better uniformity.

DSC Measurements

The T_g measurements were carried out by a TA 3000 METTLER thermoanalyzer with a DSC 30 differential scanning calorimetry cellule DSC 30, previously calibrated with indium, lead, and zinc standards. The heating rate was 10°C/min under nitrogen atmosphere.

Samples without moisture of about 10 mg sealed in an aluminium cell were taken in each experiment.

The T_g were evaluated according to the I.C.T.A. rules⁴ in which three regression lines are applied to the DSC curve: r1, r2, and r3, and three temperatures are defined: T_{g1} , T_{g2} , and T_{g3} , as is shown in Figure 1. The values of T_g in the present work correspond to the medium point.

The DSC curves of some of the materials considered in the present work showed the characteristic peak of the structural relaxation of the material. Since all the samples were submitted to the same thermal treatment, this peak may be due to the relaxation process that occurred during the storage time of the sample at r.t. before the calorimetric analysis was made. We can see it in the samples in which T_g is near the r.t. as a consequence of their chemical composition. The T_g evaluation may be more difficult when the relaxation peak is present.

Table I Materials Selected for the Present Work and Their Glass Transition Temperature

| | %G | %NaOH in Mercerized | V_{VA}/V_{MA} | T_g |
|----------------------|--------------------|------------------------|-----------------|-------|
| Cellulosic copolymer | | | | |
| CD1 | 305 | 20 | 80/20 | 31.3 |
| CD2 | 184 | 10 | 85/15 | 33.2 |
| CC1 | 170 | 15 | 80/20 | 31.0 |
| CB1 | 136 | 10 | 80/20 | 31.9 |
| CC2 | 53 | 15 | 85/15 | 31.5 |
| CC3 | 31 | 15 | 90/10 | — |
| PVA-PMA copolymer | | | | |
| CV1 | — | Without cellulose | 80/20 | 26.4 |
| CV3 | — | Without cellulose | 90/10 | 42.6 |
| PVA | — | Without cellulose | 100/0 | 41.8 |
| Blends | | | | |
| | %PAV-PMA Copolymer | | | |
| Cell. C+CV1 | 189 | 15 | — | 27.4 |
| Cell. C+CV1 | 170 | 15 | — | 26.7 |
| Cell. C+CV3 | 31 | 15 | — | 43.0 |

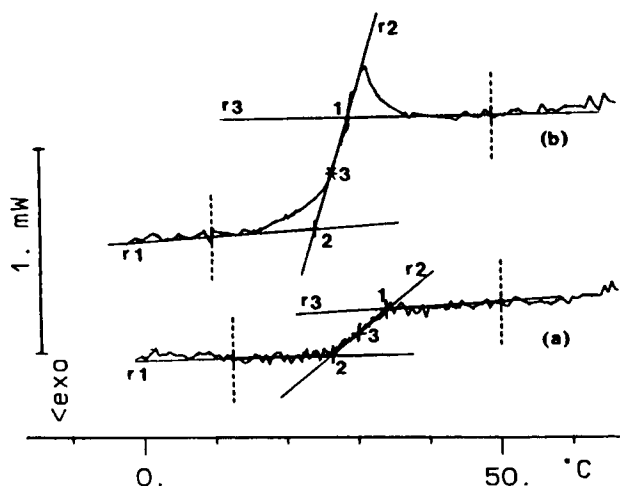


Figure 1 DSC curves of glass transition and evaluation of the characteristic temperature according to I.C.T.A. rules, (a) without relaxation enthalpy and (b) with relaxation enthalpy.

The T_{g1} , T_{g2} , and T_{g3} values may be different from those of the same material without a relaxation peak. T_{g3} is the least affected value, and therefore in the present work only the T_{g3} values are compared.

Viscoelastic Measurements

The samples, pressed to achieve better uniformity, were cut into strips of about 0.05 cm thickness and

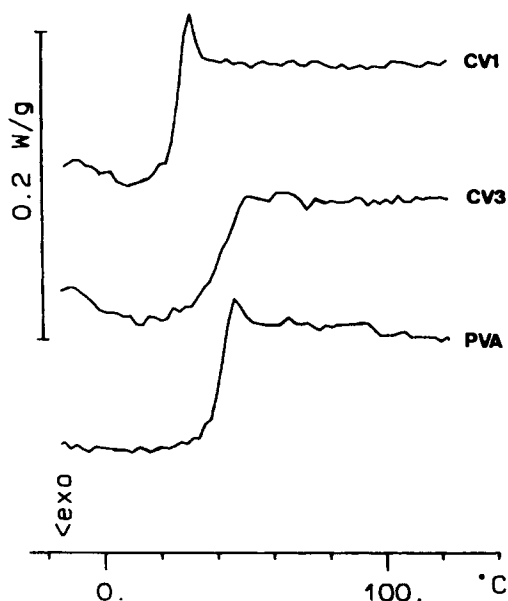


Figure 2 DSC curves of PVA-PMA copolymers and PVA.

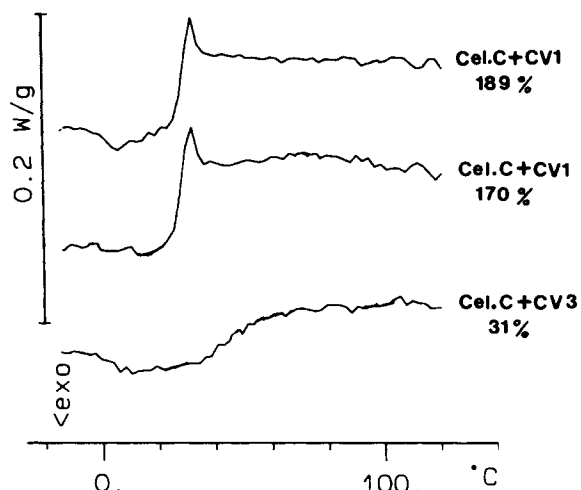


Figure 3 DSC curves of blends of cellulose with PVA-PMA copolymers.

2 or 3 cm length. For the viscoelastic analysis a DDV-II Rheovibron Viscoelastometer was used at the frequency of 110 Hz. For low temperature measurements (from -120 to about 0°C) a special camera cooled with liquid nitrogen was used and for temperatures higher than r.t. a furnace was adapted to the viscoelastometer. The differences between the two methods of varying temperatures leaves a range of temperatures (from about 0 - 20°C) where it is difficult to evaluate the $\tan \delta$, E' , and E'' parameters.

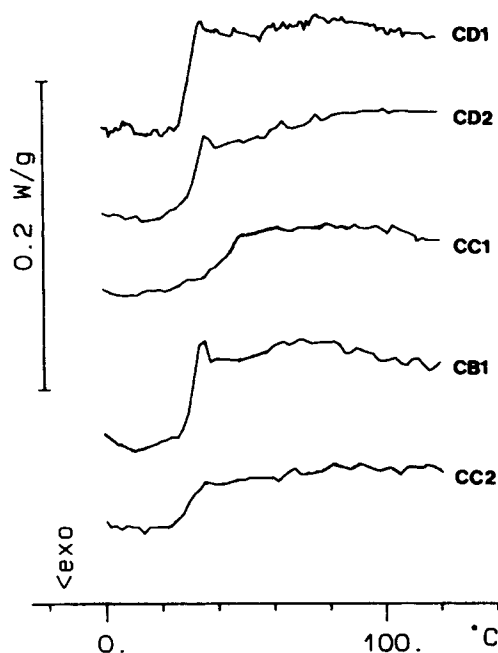


Figure 4 DSC curves of vinylic copolymers of cellulose.

RESULTS AND DISCUSSION

Glass Transition Temperature by DSC

To analyze the glass transition temperature of the vinylic copolymers of cellulose and to consider the possible influences of the cellulosic backbone and the PVA/PMA composition of the vinylic side chains, the following materials were submitted to thermal analysis by DSC:

1. Some copolymers of PVA-PMA without cellulose whose PVA/PMA composition is thought to be similar to that of the vinylic chains grafted onto cellulose. The PVA curves were also analyzed. These DSC curves are shown in Figure 2.
2. Some blends of cellulose and the copolymers PVA-PMA considered in 1.) (Fig. 2). The percentage of these samples was similar to the %G of some of the cellulosic copolymers

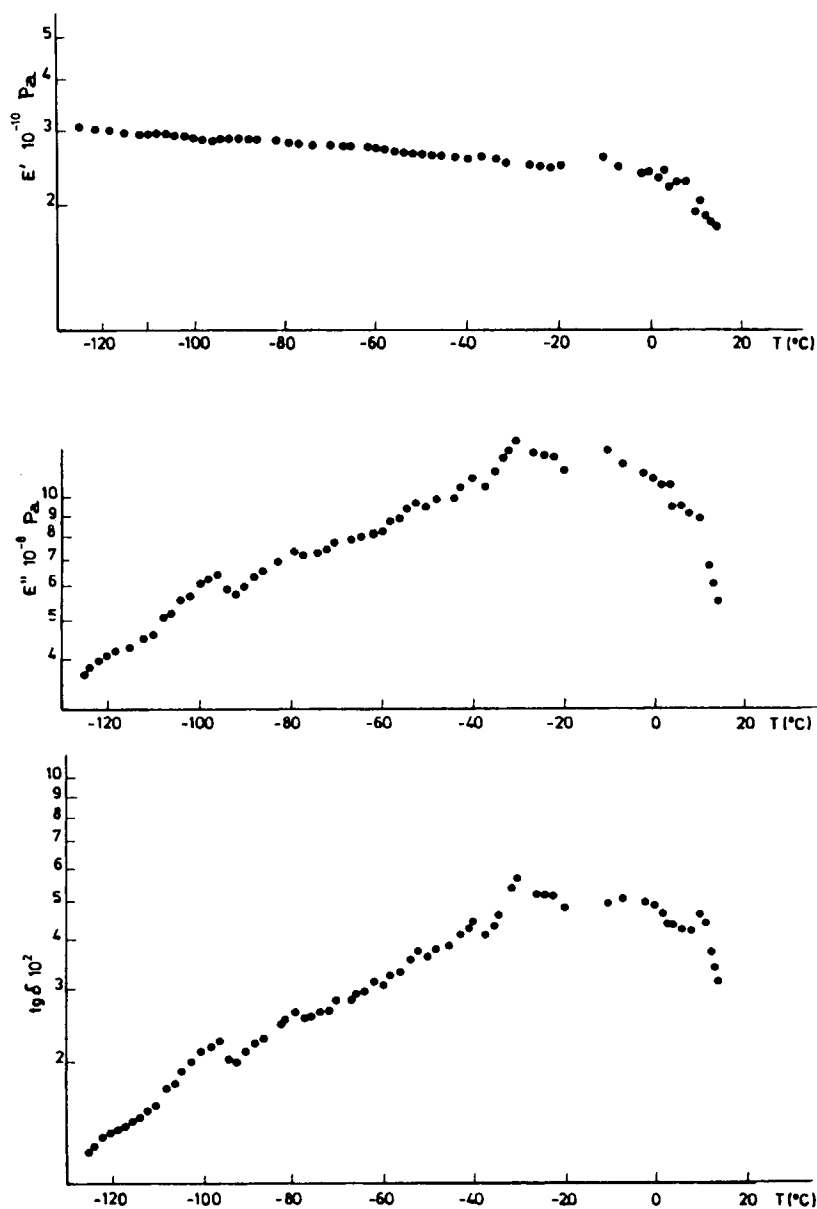


Figure 5 Viscoelastic spectrum of cellulose at 110 Hz vs. temperature in the low temperature range.

analyzed below. Figure 3 shows their DSC curves.

3. Vinyllic copolymers of cellulose. The T_g in the DSC curves was very confused and difficult to evaluate for the low %G copolymers. Therefore, only the high %G cellulosic copolymers are shown in Figure 4.

The glass transition temperature evaluated as we explained for all these materials is shown in Table I.

From the results obtained about glass transition it is possible to establish some important facts:

1. The T_g of PVA (41.8°C) is higher than the T_g of the PVA-PMA copolymer CV1 (26.4°C) that may be caused by the presence of the units of PMA, while

there is no significant difference from the CV3 copolymer ($T_g = 42.6^\circ\text{C}$), which may indicate that the ratio of PMA in this material may be very low. This hypothesis seems to agree with the fact that the CV1 copolymer was synthesized with a monomeric mixture VA/MA = 80/20, while for the CV3 the ratio was VA/MA = 90/10¹ and therefore less PMA may be incorporated in the vinyllic chain. It seems that the increased chain mobility arises from the incorporation of more flexible acrylate units into the polymer chain. The PVA-PMA copolymers of this work show only one T_g , which would indicate a greater degree of mixing between the two components and the length of PVA and PMA units in the polymeric chains must not be large.

2. The T_g of the blends of cellulose with PVA-PMA copolymers are approximately the same as the T_g of the PVA-PMA without cellulose. Therefore,

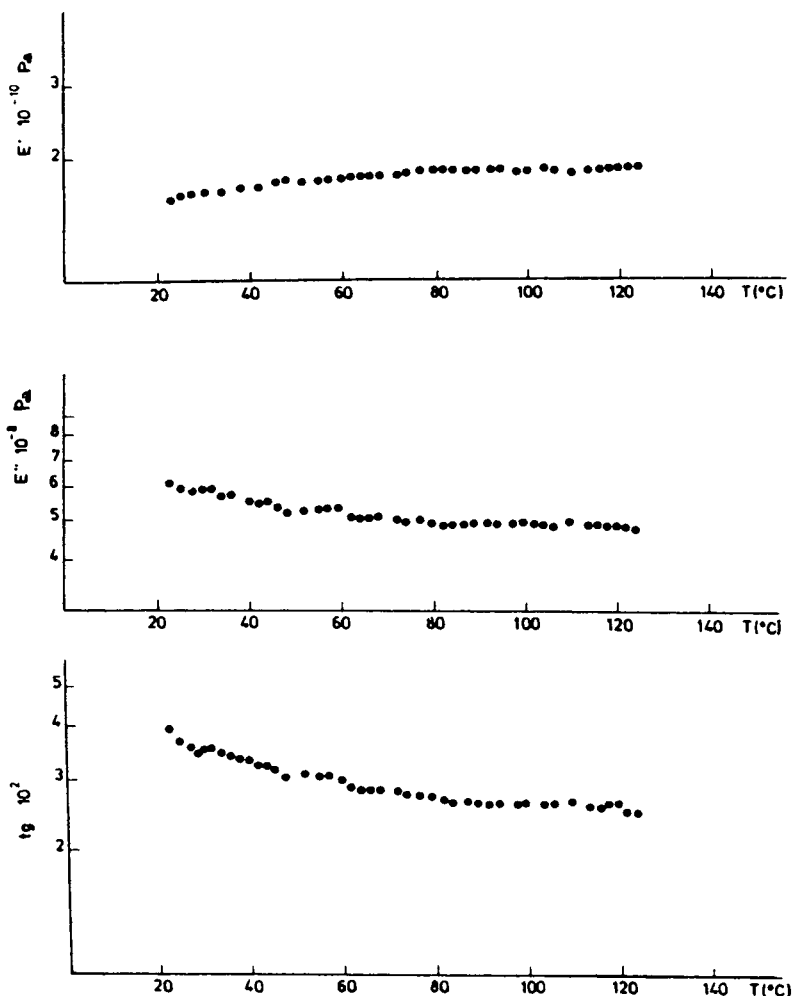


Figure 6 Viscoelastic spectrum of cellulose at 110 Hz in the high temperature range.

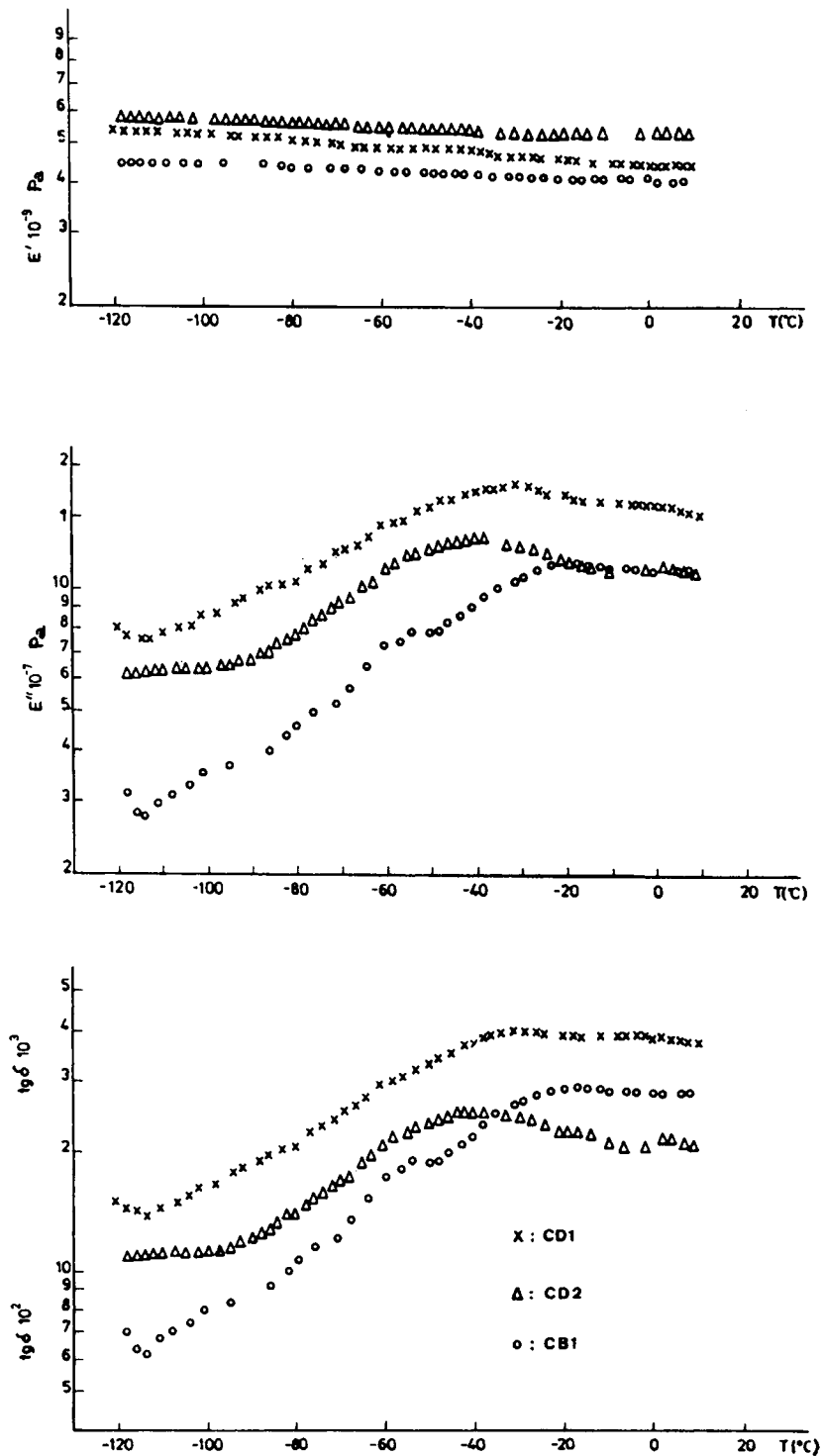


Figure 7 Viscoelastic spectrum at 110 Hz of vinylic copolymers of cellulose in the low temperature range.

it seems that the presence of cellulose has no influence on the motions of the PVA-PMA copolymer when they are blended.

3. In the vinylic copolymers of cellulose the T_g of the vinylic side chains is lower than the PVA glass transition temperature. This may be caused

by the incorporation of PMA units to the polymeric chain, as is shown in part 1.

4. The T_g of the cellulosic copolymer CC1, 170%G, is higher than the T_g of the blend with a similar composition Cell+CV1, 170% vinylic polymer. This may reflect the effect of the covalent bonds between the cellulose and the vinylic polymer, which hinder the motion of the vinylic chains, thus increasing their glass transition temperature. In the blends there are not these strong bonds, but only the weaker Van der Waals, hydrogen bond, and dipole-dipole. On the other hand, in the DSC curve of the cellulosic copolymer CC3, 31%G, the T_g was hardly observed and it was not possible to determine it, while it was observed in the blends of similar composition vinylic copolymer/cellulose (Cel.C+CV3, 31%).

5. The T_g of the vinylic side chains grafted onto cellulose seems to be unaffected by the ratio of cellulose in the material. Therefore, it is not possible to establish any relationship between the T_g and the %G or any other factors such as the grafting frequency (GF) or the molecular weight of the chains.¹

Viscoelastic Analysis of Cellulose

Many of the cellulose samples were broken during the experiment because of the slipping of the fibers over each other. To avoid this problem, a synthetic binder varnish was impregnated into the sample to increase stiffness and cohesion between fibers, but the viscoelastic spectrum was nearly plane and it was not possible to detect any transition. Therefore it was necessary to subject a large number of samples without the varnish to viscoelastic characterization.

The viscoelastic data of the storage modulus E' , loss modulus E'' , and tangent of loss angle, $\tan \delta$, at 110 Hz plotted against the temperature, are shown in Figures 5 and 6.

Figure 5 shows two main peaks of E'' and $\tan \delta$: at -96°C and -30°C . The first one is in good agreement with the dielectric results that we described elsewhere.³ This peak does not appear in the vinylic copolymers, as is shown below, and neither appears in the dielectric spectrum. In accordance with our dielectric data and with other works,⁶⁻⁸ we have assigned this peak to the β -relaxation of cellulose, which may be caused by motions of OH primary groups in the amorphous region of cellulose.³

The second peak at -30°C has been described by other authors,^{7,9-11} showing that it is highly influenced by the moisture absorbed in cellulose. This may indicate that the molecular motions involved

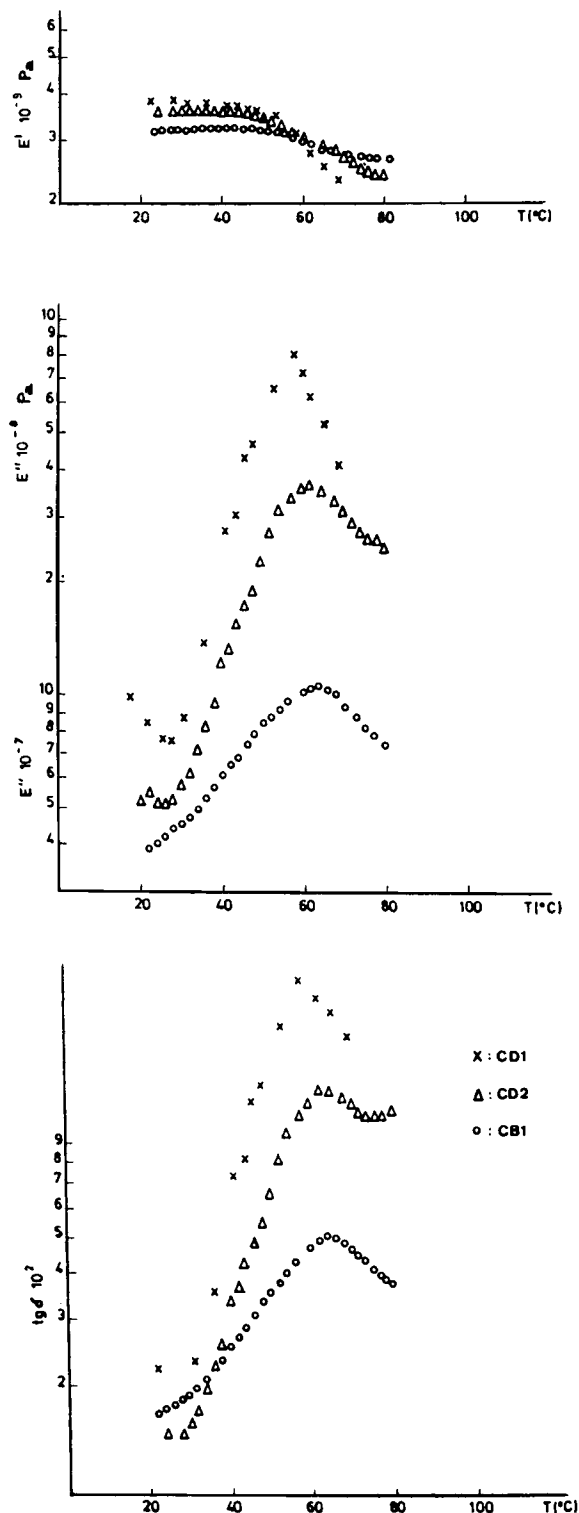


Figure 8 Viscoelastic spectrum at 110 Hz of vinylic copolymers of cellulose in the high temperature range.

in this relaxation may take place in the amorphous regions of cellulose, which are the ones accessible to the absorbed water, but its origin is not clear.

Table II Temperature of the E'' and $\tan \delta$ Maximum of the Viscoelastic Relaxation of Vinylic Copolymers of Cellulose

| Copolymer | %G | % Cellulose ^a | T_{\max} (°C) | $E''_{\max} \cdot 10^{-7}$ (Pa) | $\tan \delta$ |
|-----------|-----|--------------------------|--------------------|------------------------------------|---------------|
| CD1 | 305 | 24.69 | 58 | 80.9 | 0.255 |
| CD2 | 184 | 35.21 | 62 | 36.9 | 0.125 |
| CB1 | 136 | 42.37 | 64 | 14.2 | 0.050 |

Viscoelastic Analysis of the Vinylic Copolymers of Cellulose

Figures 7 and 8 show the results of the viscoelastic analysis of the vinylic copolymers of cellulose with high %G. The copolymers with low %G presented many difficulties because of the samples broken at temperatures slightly higher than r.t. This behaviour may be due to a decrease in the cohesive forces in the material because the graft is blocking some of the OH groups of the cellulose, which decreases the number of hydrogen bonds between the fibers. Therefore, there is a decrease in the strength of the material. When the %G is high enough, although the above effect also exists, the large amount of vinylic copolymer may prevent the breaking of the samples acting as a binder. Nevertheless, even the highest %G copolymer samples are broken for temperatures of about 70–80°C. This kind of problem

was also noted in copolymers of cellulose with PMMA.¹²

The plots of E'' and $\tan \delta$ in Figure 7 show a broad peak at about -50°C and in Figure 8 a more pronounced one at about 60°C . The cellulose peak is not shown at -96°C , which may be due to both the low percentage of cellulose in the copolymer and/or the difficulty in the motions of the OH groups of cellulose to which the transition is attributed caused by the grafted vinylic chains. The dielectric analysis of these copolymers showed a similar fact: the maximum dielectric loss constant ϵ'' and $\tan \delta$ in the cellulose at a low temperature range attributed to OH group motions did not appear in its vinylic copolymers.³

The peak at about -50°C (Fig. 7) in the copolymers considered may be due to the β -relaxation of the vinylic chains grafted onto cellulose, because the PVA shows a viscoelastic relaxation at 10 Hz and

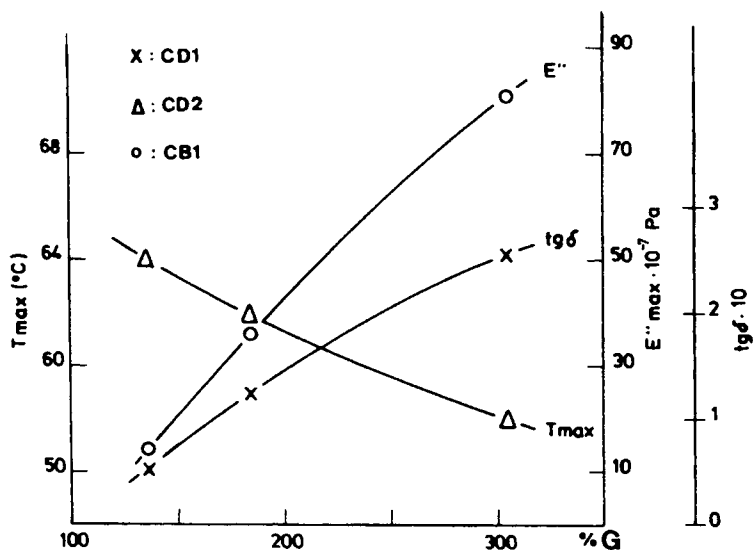


Figure 9 Temperature dependencies of the maximum E'' , $\tan \delta$, and temperature of the maximum, for vinylic copolymers of cellulose.

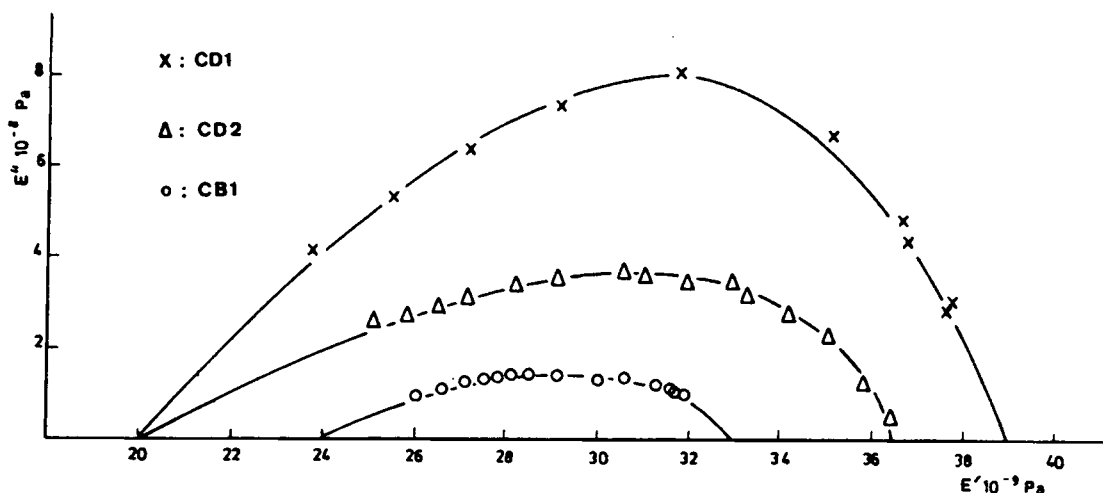


Figure 10 Argand arcs for vinyl copolymers of cellulose.

-30°C that is not shown in the dielectric spectra and PMA shows a mechanical relaxation at -120°C and 1 Hz.²

The peak at about 60°C (Fig. 8) may be attributed to the vinyl side chains, because it does not appear in the cellulose. This seems to be due to the α -relaxation,² but with the E'' and $\tan \delta$ maximum at a higher temperature than the homopolymers PVA and PMA. This may show the influence of cellulose on the large-scale motions of PVA-PMA grafted chains, as was shown in the T_g .

The temperature of the E'' maximum increases when the %G of copolymer decreases (Table II) and, therefore, when the percentage of cellulose in the material increases. Also the maximum E'' and $\tan \delta$ values increase with the %G. All of these facts may indicate that the cellulose hinders the viscoelastic relaxation of the vinyl chains grafted onto it.

There seems to be a linear relationship between the T_{\max} , E''_{\max} , and $\tan \delta$ values and the %G as shown in Figure 9. Therefore, the peak of E'' ($\tan \delta$) at about 60°C in the vinyl copolymers of cellulose may be due to the α -relaxation of the vinyl side chains under the influence of cellulose.

Argand Diagrams

The Argand diagrams are constructed by plotting E'' against E' , each point corresponding to one temperature and the frequency 110 Hz. Figure 10 shows the diagrams for the vinyl copolymers of cellulose.

In Figure 10 the points where the arc cuts the abscissa axis are obtained by extrapolation of the experimental curve. They represent the maximum (E'_0) and the minimum (E'_{∞}) values of the storage modulus E' . The difference between them is called the relaxation amplitude $\Delta E'$. The arcs are not a semicircle that should correspond to a single relaxation time model. They are slightly asymmetrical, being broader on the high-temperature side. Both the asymmetry and the width of the experimental arcs arise from the intrachain interactions and are thus characteristic of the long chain nature of the vinyl molecules. Cole and Cole² modified the single relaxation time expressions, introducing the empirical broad parameter $\bar{\beta}$ ($0 \leq \bar{\beta} \leq 1$). The arc height is directly related to the broad parameter $\bar{\beta}$, by the following equation:

$$\bar{\beta} = \frac{4}{\pi} \tan^{-1} \frac{2E''_{\max}}{E'_0 - E'_{\infty}} \quad (1)$$

Table III Viscoelastic Parameters of Vinyl Copolymers of Cellulose

| Copolymer | %G | E'_0 10^{-9} Pa | E'_{∞} 10^{-9} Pa | $\Delta E'$ 10^{-9} Pa | $\bar{\beta}$ |
|-----------|-----|------------------------|-------------------------------|-----------------------------|---------------|
| CD1 | 305 | 3.90 | 2.00 | 1.90 | 0.90 |
| CD2 | 184 | 3.62 | 2.05 | 1.57 | 0.56 |
| CB1 | 136 | 3.29 | 2.39 | 0.90 | 0.39 |

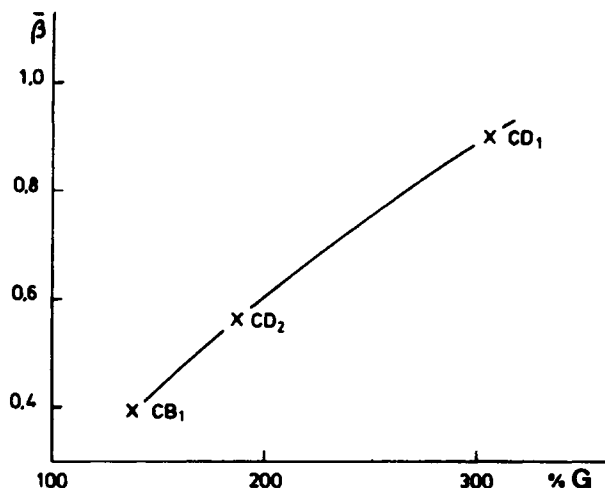


Figure 11 Grafting percentage of vinyl copolymers of cellulose dependent on the Cole-Cole parameter $\bar{\beta}$.

The numerical data for E'_0 , E'_∞ , $\Delta E'$ and the broad parameter of Cole-Cole $\bar{\beta}$ determined for the vinyl copolymers of cellulose are shown in Table III.

Table III shows that when the %G of the copolymer decreases:

1. the relaxation amplitude $\Delta E'$ decreases,
2. the whole arc is more depressed, and
3. the arc is more depressed when the E' values decrease and therefore when E' is going to its minimum value. The arcs become skewed.
4. The Cole-Cole parameter $\bar{\beta}$ decreases.

All these facts seem to confirm that the cellulose hinders the viscoelastic relaxation of the vinyl side chains grafted onto it. Besides, it seems likely that in these materials two or more discrete relaxations may be present, resulting in a broadening of the curve at high temperatures. The arc shape seems to indicate a broader distribution of relaxation time when the cellulose percentage in the copolymer increases (%G decreases) because they become more depressed and skewed when the %G decreases. In the same way, the $\bar{\beta}$ -parameter (which is related to the curve high, as we explained before) may show its relationship with the cellulose percentage: for the CD1 copolymer, whose percentage of cellulose is the lowest, $\bar{\beta}$ is close to the unit ($\bar{\beta} = 0.9$), which corresponds to a single relaxation time model.

Figure 11 shows that the $\bar{\beta}$ value increases with the %G, and therefore when the percentage of cel-

lulose decreases. So, the deviations from the single relaxation time are stronger with the increase in the cellulose ratio in the material, which seems to confirm that the cellulose hinders the relaxation process and also increases the relaxation time distribution.

The results of applying the Maxwell and Voigt models¹² did not agree with the experimental results, as was expected.

The dielectric analysis of these materials showed a relaxation in good agreement with the results of the present work. It was found that cellulose also hinders the dielectric relaxation of the vinyl side chains, making the temperature of the maximum dielectric loss modulus, ϵ'' , higher than that of the PVA and PMA. But it seems that the viscoelastic relaxation is more sensitive to the percentage of cellulose than the dielectric one is.³

CONCLUSIONS

1. The cellulosic backbone hinders the large-scale motions of the PVA-PMA chains when they are grafted onto it, as is shown by the increase in the temperatures of the viscoelastic α -relaxation and the T_g . This increase is not observed in blends.
2. The percentage of cellulose makes the viscoelastic α -relaxation more difficult, increasing the temperature of the loss modulus maximum and decreasing the Cole-Cole broader parameter ($\bar{\beta}$), and therefore increasing the deviations from a single relaxation time model.
3. The PMA incorporated in the PVA chain makes the polymeric chain more flexible because of the decrease in the T_g of the PVA-PMA copolymers (without cellulose) when the PMA increases in the chain.
4. The β -relaxation of cellulose attributed to the motion of the OH groups is not shown in the viscoelastic spectrum of the vinyl copolymers, as in the dielectric analysis, which may be due to both the small amount of cellulose in the material and the decrease in the number of free -OH groups that are replaced by the vinyl chain grafted onto the cellulose.

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