

# Dielectric investigation of some oxyviscoses

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## Abstract

The dielectric properties of oxyviscose samples prepared with different oxidizing agents were investigated. The results obtained are interpreted and compared from the viewpoint of the modifications that occur in the structure of the fibres during the oxidation processes. These modifications were determined by infra-red spectroscopy, X-ray diffraction, degree of polymerization, copper number, total carbonyl content and carboxyl content. The relative permittivity and loss index were measured over a frequency range from 0.1 to 100 kHz and temperature range from  $-50$  to  $100^{\circ}\text{C}$ . The dipolar group involved in the secondary relaxation processes was concluded to be the methylol group in the non-crystalline regions. © 1998 Elsevier Science Ltd. All rights reserved.

*Keywords:* Dielectric measurements; Oxyviscose; Thermal transition

## 1. Introduction

The existence of several relaxations in cellulose and its derivatives was observed when these materials were investigated by dielectric and dynamic mechanical measurements [1–18]. Analysis of the results obtained with celluloses of different degrees of order, cellulose derivatives and polysaccharides of structure similar to that of cellulose (dextran and pullulan) reveals no closer assessment of the molecular mechanism of the relaxation processes observed. In such polymers, a variety of submolecular and side-group motions are expected to occur as a result of thermal activation, so that the molecules could acquire various configurational states. For example, Muus [1] ascribed the dielectric loss absorption to orientation polarization of the hydroxyl group in crystalline and non-crystalline regions, while others [2] suggested that dipoles in the non-crystalline regions provide the chief contribution to the relaxation process observed. Also, movement of the methyl group in the non-crystalline regions [3–6,8,10,15,16,18], torsional vibrations of the cellulose molecules [7] and motion of the whole anhydroglucose ring [11,13,17,18] have all been suggested to be the molecular mechanism responsible for the relaxation process. Some investigators [5,9,14] centred their discussion around the contribution of water.

In view of the fact that the molecular mechanism of the

relaxation processes observed in cellulose fibres and its derivatives has not yet been clarified, together with a lack of work concerning the dielectric behaviour of oxycelluloses, it seemed worthwhile to perform a further dielectric investigation on viscose fibres in the native and oxidized states as well as on hydroviscose. To achieve this aim, use was first made of specific as well as non-specific oxidizing agents to oxidize the methylol or secondary alcoholic groups, and changes in the characteristic properties of the resulting oxyviscoses were followed, prior to dielectric measurements, by different types of measurement: degree of polymerization, X-ray crystallinity, copper number, total carbonyl and carboxyl contents and infra-red spectra.

## 2. Experimental and results

### 2.1. Preparation of samples

The oxyviscose samples examined were prepared from viscose fibres under mild conditions of oxidation by using different oxidizing agents. Fibrous product or solid powder insoluble in water or dilute alkali was obtained.

#### 2.1.1. Hydrogen peroxide oxyviscose

A 10 g sample of viscose fibres was treated with 250 ml of hydrogen peroxide ( $\approx 30\%$  w/v) in a stoppered bottle for 5 h at room temperature. The sample was washed with distilled water and dried.

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Table 1  
Some characteristics of viscose fibres, hydroviscose and oxyviscose samples

Sample	DP	% Cr	Copper no. (g/100 g)	Total carbonyl (mmol/100 g)	% COOH
Viscose	465	40	0.63	6.0	0.17
Peroxide oxyviscose	400	41	0.99	18.0	0.50
Hypochlorite oxyviscose	50	88	1.37	32.8	1.14
Nitric acid oxyviscose	43	93	3.79	41.6	2.93
Periodate oxyviscose	43	diffuse	8.42	22.8	0.03
Hydroviscose	45	70	1.73	9.8	0.08

### 2.1.2. Sodium hypochlorite oxyviscose

A viscose sample weighing 20 g was treated in a stoppered bottle with 200 ml of N/25 sodium hypochlorite at room temperature in the dark, with occasional shaking, for a period of 1 month. The product was washed with distilled water, dilute acid and again with water, and then dried.

### 2.1.3. Nitric acid oxyviscose

A 25 g sample of viscose was heated with 75 g of nitric acid ( $d, 1.3 \text{ g cm}^{-3}$ ) in a water bath for 1 h. The residue was washed with distilled water and then dried.

### 2.1.4. Periodate oxyviscose

A 20 g sample of viscose was steeped in 1 l of a solution of 0.01 M potassium periodate and 0.005 M sulfuric acid. The mixture was kept in the dark with occasional shaking for 20 days at room temperature. The residue was washed with water, sodium thiosulfate and water again, and dried. This sample was found to be free from inorganic contamination as judged from its undetectable ash content.

### 2.1.5. Hydroviscose

This was prepared by the hydrolysis of viscose fibres using 1 N HCl (1:50) at about 100°C for 5 h. The residue was washed with water until free from acid and then dried.

## 2.2. Measurements

The characteristic properties — i.e., the degree of polymerization (DP), percentage crystallinity, copper number, and total carbonyl and carboxyl contents — of the prepared oxyviscose samples, together with corresponding values for native viscose and hydroviscose samples, are listed in Table 1. The degree of polymerization was calculated from viscosity measurements of cuoxam solution using sodium sulfite as antioxidant [19]. The percentage crystallinity was estimated from X-ray diffraction as described before [20]. The micro-technique of Heyes [21] was used for determination of the copper number. The total carbonyl content was determined by the hydroxylamine method [22], and the carboxyl content by using the procedure of Neale [23].

The infra-red (i.r.) spectra of viscose fibres, hydroviscose and the oxyviscose samples were recorded in the 1500–4000  $\text{cm}^{-1}$  region under identical conditions. The spectra obtained are presented in Fig. 1.

Dielectric measurements were performed with a Polymer Laboratories dielectric thermal analyser (PL-DETA, UK). The dielectric constant,  $\epsilon'$ , and the dielectric loss,  $\epsilon''$ , were measured over the frequency range from 0.1 to 100 kHz at temperatures from  $-50$  to  $80^\circ\text{C}$ , or up to  $100^\circ\text{C}$  in some cases. Measurements were taken on discs of 33 mm diameter and 0.7–0.9 mm thickness under dry conditions. These discs were prepared by moulding the samples, which were in the form of powder in all cases except for hydrogen

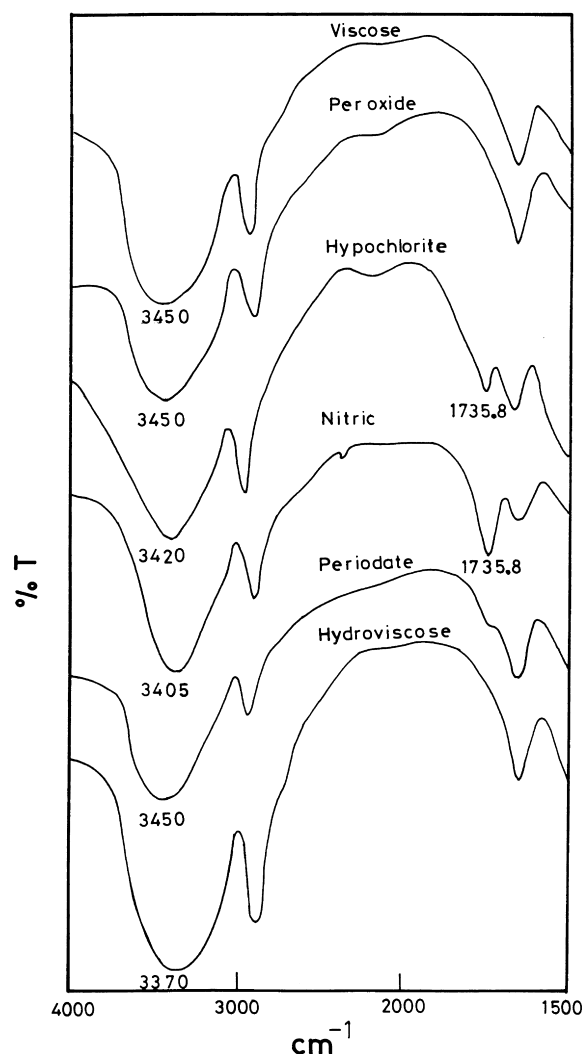


Fig. 1. I.r. absorption spectra between 1500 and 4000  $\text{cm}^{-1}$  of viscose fibres, hydroviscose and the examined oxyviscoses.

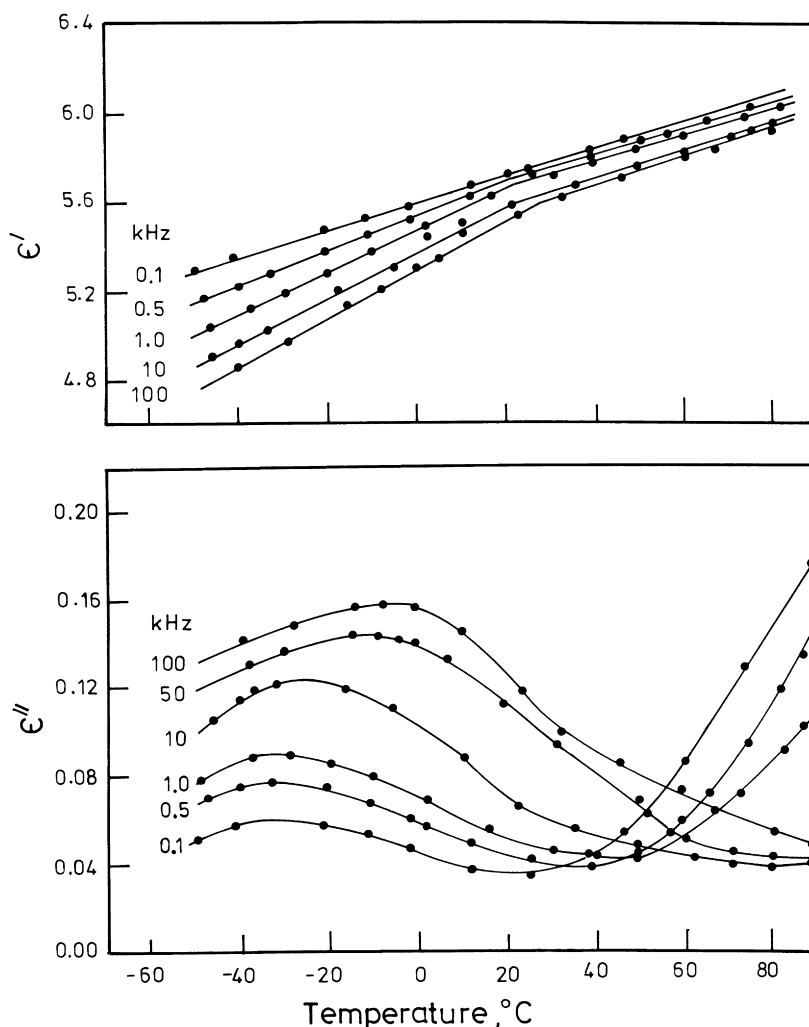


Fig. 2. Temperature dependences of  $\epsilon'$  and  $\epsilon''$  at various frequencies for viscose rayon.

peroxide oxyviscose, which was fibrous. Good contact between the surfaces of the discs and the electrodes was ensured to avoid the error arising from air gaps.

The temperature dependences of the dielectric constant,  $\epsilon'$ , and the dielectric loss,  $\epsilon''$ , at various frequencies for the samples are given in Figs 2–7.

### 3. Discussion

The oxidation of cellulosic fibres is a complicated process, wherein the different parts of a cellulose fibre possess different accessibilities and also the different types of oxidizing agent behave in different ways. Therefore, the various samples of oxyviscose prepared were expected to differ widely in their properties.

#### 3.1. Hydrogen peroxide oxyviscose

The oxidation here is non-specific, where the reagent attacks any of the hydroxyl groups throughout the molecular

chain. The process is accompanied by chain scission and results in depolymerization of the viscose fibres, from  $DP = 465$  to 400 as shown in Table 1. The action of the oxidizing agent does not initially lead to rupture of the chain molecules, but reaction takes place at centres adjacent to the glycosidic linkage [24] which leads to a lowering of  $DP$  and the formation of more ketonic groups compared with the original viscose (as evident from the increase in total carbonyl content, see Table 1). Such oxidation also results in a slight increase in: (1) the copper number, which may be due to a lowering of the  $DP$  or to the formation of new aldehydic groups; and (2) the carboxyl content (see again Table 1).

The i.r. spectrum of hydrogen peroxide oxyviscose, Fig. 1, shows no carbonyl band. In addition, no shift in the OH stretching vibration band is observed compared with the original fibres.

It is clear from the above that partial oxidation of viscose fibres by hydrogen peroxide modifies the fine structure and chemical composition of the fibres.

As regards the dielectric properties, the results plotted in

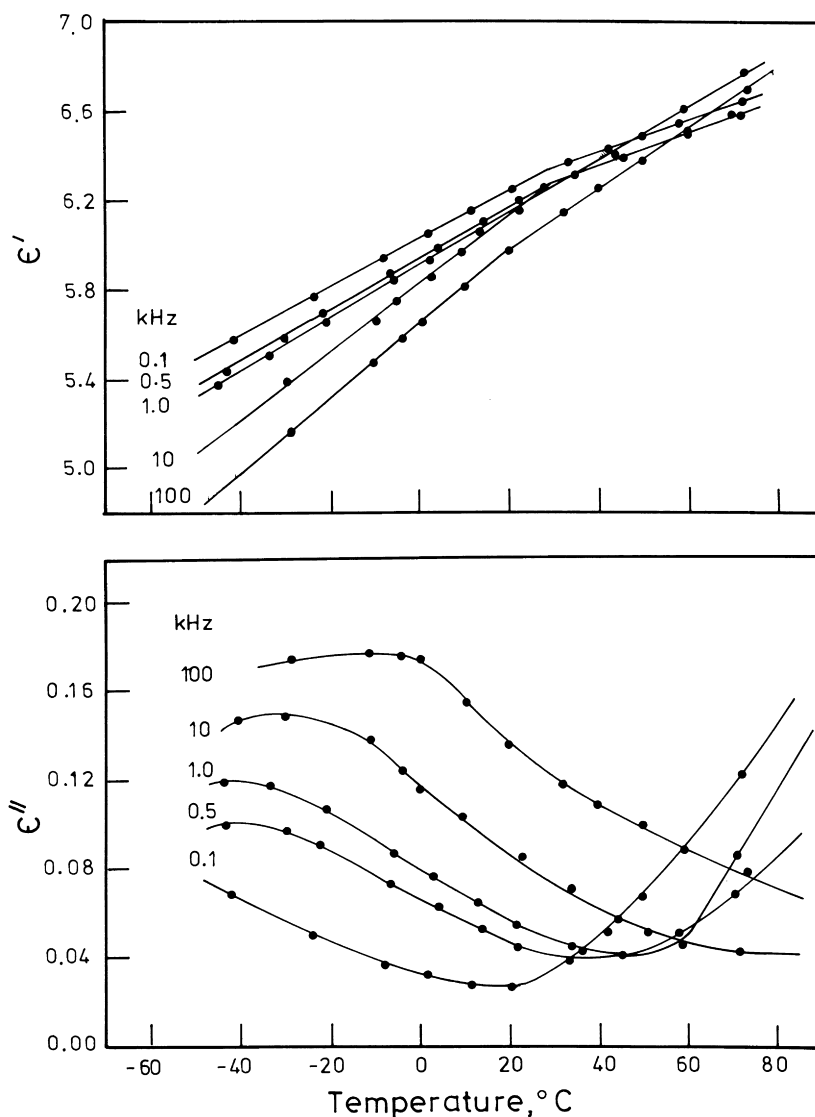


Fig. 3. Temperature dependences of  $\epsilon'$  and  $\epsilon''$  at various frequencies for hydrogen peroxide oxyviscose.

Figs 2 and 3 reveal that: (1) there is a secondary relaxation process in both viscose and hydrogen peroxide oxyviscose within the experimental temperature and frequency ranges applied; (2) a broadening of the absorption takes place as a consequence of oxidation; (3) an increase in the dielectric loss values occurs at lower frequencies and higher temperatures in both samples; (4) the relative permittivity is higher in the oxidized sample than in the original; and (5) the transition temperature of viscose fibres, observed in the temperature dependence of the dielectric constant plots, is still retained in the peroxide oxyviscose sample.

These findings can be explained as follows. The relaxation process obtained with oxyviscose is characterized by an activation energy of  $25 \text{ kcal mol}^{-1}$ , which is comparable to that obtained for native viscose ( $\Delta E = 24 \text{ kcal mol}^{-1}$ ), suggesting that the same molecular relaxation mechanism — which is local in nature — probably takes place in the two samples. The greater

broadening of the absorption bands in the oxidized sample might lead one to suggest that the orienting dipolar group involved in this relaxation is subject to an inner viscosity varying from one microregion to another, so that there is a distribution of relaxation times. Furthermore, the increase of the dielectric loss with increase of temperature at lower frequencies might be attributed to direct current (DC) conduction which is mainly intrinsic in nature, since the samples examined are free from inorganic impurities as judged from the negligible ash content. Also, the increase of the dielectric constant upon oxidation confirms the formation of more polar groups, i.e., carboxylic groups (see Table 1), which could not be detected in the i.r. spectra.

On the other hand, the thermal transition observed at  $30^{\circ}\text{C}$  (as shown in Figs 2 and 3) is a property of hydrogen bonding [25], and can be attributed to the breaking of some weak hydrogen bonds in the dry sample with the increase of thermal energy. Such a transition is retained in hydrogen

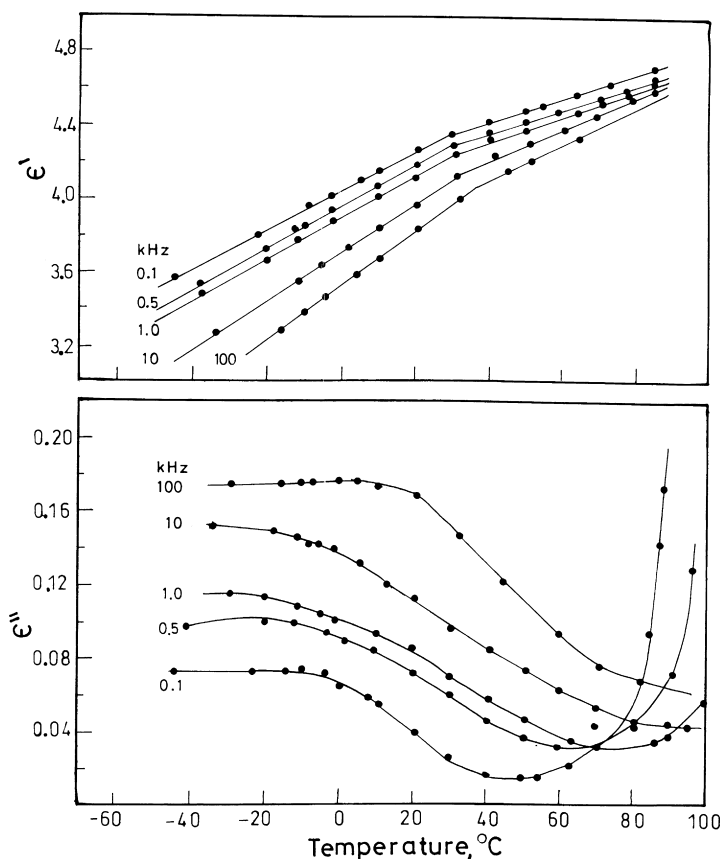


Fig. 4. Temperature dependences of  $\epsilon'$  and  $\epsilon''$  at various frequencies for sodium hypochlorite oxyviscose.

peroxide oxyviscose, indicating that this sample still contains weakly hydrogen-bonded regions. These regions were confirmed by i.r. spectra, where practically no shift in the OH stretching vibration band was detected upon oxidation of viscose.

### 3.2. Hypochlorite oxyviscose

The oxidation reaction with hypochlorite is non-specific, similar to that with peroxide, and the chemical changes taking place are similar but with different extents of oxidation. The results listed in Table 1 reveal that the oxidation with hypochlorite is accompanied by vigorous degradation, the  $DP$  decreasing from 465 to 50 and the crystallinity increasing from 40 to 88%. The main functional groups formed are ketonic groups, as evidenced from the higher carbonyl content. Some aldehydic and carboxylic groups are also formed. The i.r. spectrum (see Fig. 1) of the resulting oxyviscose sample shows a carbonyl band at  $1735.8\text{ cm}^{-1}$ , and a shift in the OH stretching vibration band to a lower frequency of  $3420\text{ cm}^{-1}$  from  $3450\text{ cm}^{-1}$  in viscose, indicating a strengthening in the degree of hydrogen bonding. However, this degree is not as high as in the case of hydroviscose of comparable  $DP$  ( $= 45$ ), where the OH stretching vibration band is shifted to  $3370\text{ cm}^{-1}$ .

In view of these findings it seems of interest to compare the dielectric properties of the hydrogen peroxide oxyviscose

(Fig. 3) and hypochlorite oxyviscose (Fig. 4) samples with those of viscose (Fig. 2) and hydroviscose (Fig. 5). It is evident that: (1) in all cases there is a broad secondary relaxation process in the lower temperature range and the broadening is greater in the oxidized samples than in viscose or hydroviscose; (2) the dielectric constant values of the hypochlorite oxyviscose sample are less than those of viscose and peroxide oxyviscose but higher than those of hydroviscose; (3) in all samples there is an increase in the dielectric loss with increase of temperature in the lower frequency range; and (4) the thermal transition observed in the temperature dependence of the dielectric constant in viscose is retained in peroxide and hypochlorite oxyviscoses but not in hydroviscose.

The magnitude of the shift in the OH fundamental arising from hydrogen bonding could be used as a measure of the strengthening in the degree of hydrogen bonding [26]. During oxidation, which occurs in the highly accessible regions, destruction of weak hydrogen bonds is expected to take place. At the same time, new hydrogen bonds are formed between the resulting carbonyl or carboxyl groups and OH groups, leading to a sample of fine structure differing from that of both the original viscose and the resulting hydroviscose. Accordingly, the disappearance of the transition in the case of hydroviscose indicates strengthening in the degree of hydrogen bonding in such a sample, and its existence in the case of hypochlorite oxyviscose, of low  $DP$ ,

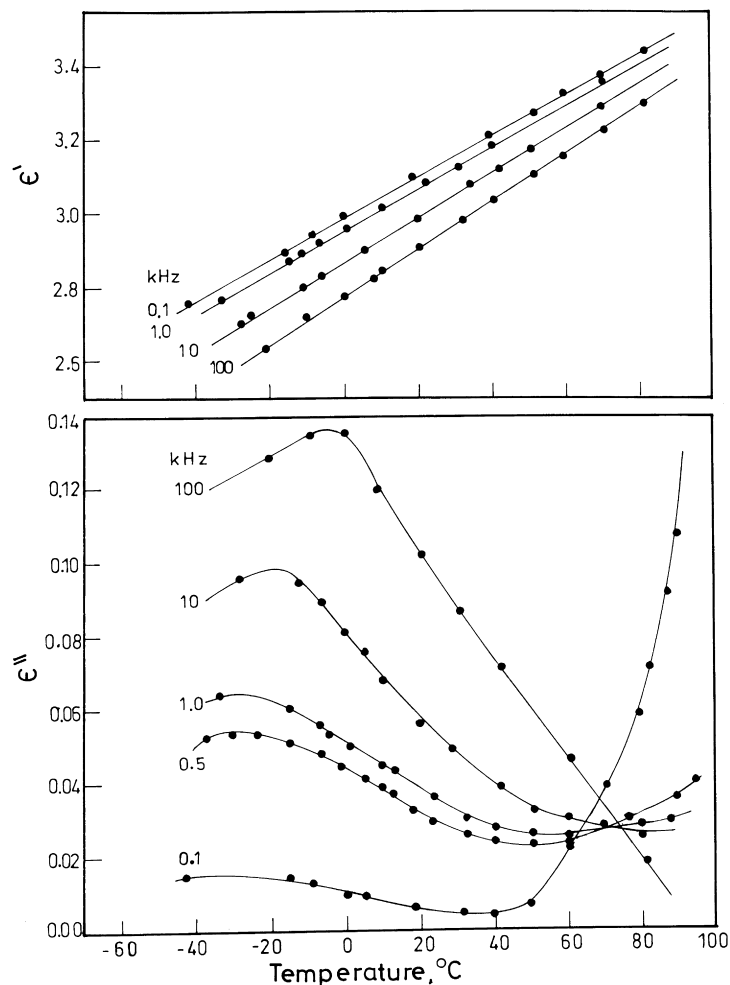


Fig. 5. Temperature dependences of  $\epsilon'$  and  $\epsilon''$  at various frequencies for hydroviscose.

shows that this sample still possesses regions of weak hydrogen bonds. This, in turn, implies that such oxyviscose is of more open structure compared with hydroviscose, which is characterized by a compact structure [27]. In addition, the presence of more polar carboxyl groups in hypochlorite oxyviscose is reflected in a greater dielectric polarization, thus leading to an increase of the dielectric constant, and also in more conduction, which gives rise to an increase in the dielectric loss in the lower frequency range. Further, the variation in the inner viscosity from one microregion to another leads to a distribution of relaxation times which, in turn, causes broadening of the absorption bands as pointed out above. Also, the relaxation process observed in all samples with an activation energy of 24–25 kcal mol<sup>-1</sup> implies that this process is local in nature. However, in view of these results, one cannot deduce the molecular mechanism of the group responsible for such relaxation.

### 3.3. Nitric acid oxyviscose

The oxidation of cellulose with nitric acid results in preferential attack of the primary hydroxyl groups [28].

Treating viscose fibres with such an oxidizing agent results in a vigorous disintegration as well as oxidation of the primary alcoholic groups to aldehydic and carboxylic groups. The results in Table 1 reveal that nitric acid oxyviscose has  $DP = 43$  and 93% crystallinity, whereas the corresponding values for viscose are 465 and 40%, respectively. Also, when compared with peroxide and hypochlorite oxyviscose samples, the nitric acid oxyviscose sample appears to be of higher carboxyl and carbonyl contents. The same can be said with respect to the aldehyde content, as revealed by the higher copper number. The infrared spectrum of this sample (Fig. 1) shows a very sharp and intense carbonyl band at 1735.8 cm<sup>-1</sup> and a shift in the OH stretching vibration band from 3450 to 3405 cm<sup>-1</sup>, indicating a great strengthening in the degree of hydrogen bonding upon oxidation.

On the other hand, it is evident from Fig. 6, which presents the temperature dependence of the real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of the complex permittivity, that the dielectric relaxation process observed in the original viscose, peroxide and hypochlorite oxyviscoses and hydroviscose samples disappears in nitric acid oxyviscose. These results might, therefore, lead one to infer that the group

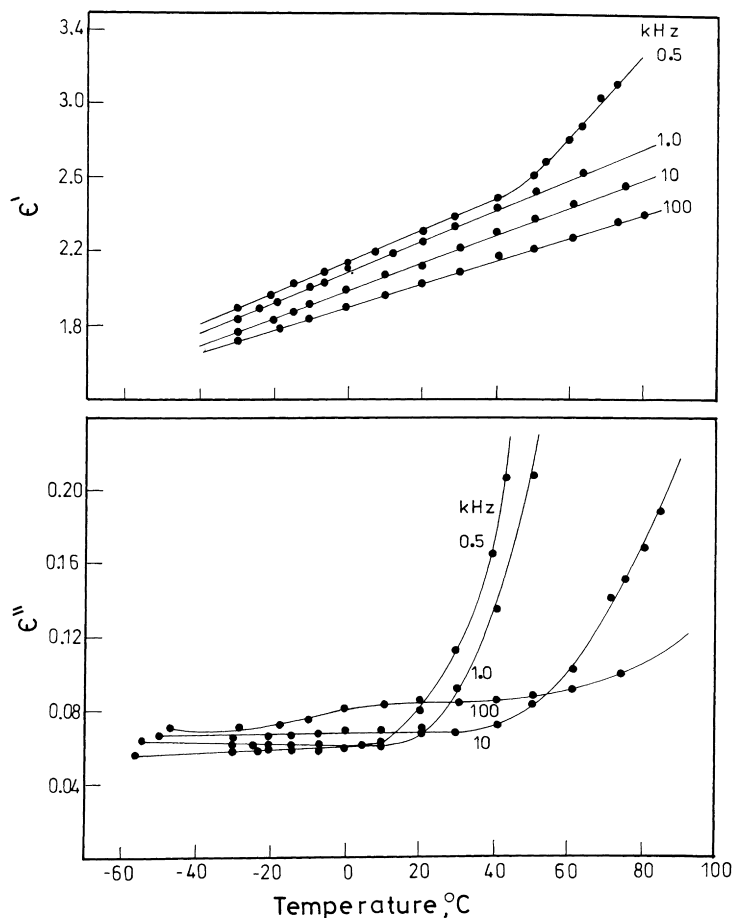


Fig. 6. Temperature dependences of  $\epsilon'$  and  $\epsilon''$  at various frequencies for nitric acid oxyviscose.

responsible for such a secondary relaxation process, which will be denoted as  $\beta$ , are most probably the methylol groups, most of which have been oxidized by the nitric acid. Such an oxidation also results, as pointed out above, in a rapid increase in the degree of crystallinity. This increase may be due either to the dissolution of the highly accessible regions or the aggregation of some of the particles split off from these regions, a consequence of which is that the groups involved in the observed relaxation process in the other samples are in the non-crystalline regions. The experimental fact [28] that the methylol groups in the inaccessible regions resist oxidation with nitric acid, and the disappearance of this dielectric  $\beta$ -relaxation in such an oxidized sample, are in conformity with the previous suggestion [3–6,8,10,15,16,18] that this relaxation occurs in the non-crystalline regions.

In addition, Fig. 6 reveals that the relative permittivity values of nitric acid oxyviscose at a given temperature are less than the corresponding values of the original fibres as well as those of the other samples investigated, although the former sample contains much more carboxylic groups which are more polar than the hydroxyl groups or carbonyl groups. This might be accounted for by the rapid increase in the degree of crystallinity (Table 1) together with the

formation of ester groups as a result of the reaction of carboxylic groups in the nitric acid oxyviscose residue with unreacted hydroxyl groups. The partial conversion of carboxylic groups into esters was confirmed previously [28,29], which is a drawback in the method of determining the carboxyl groups in cellulose by cation exchange [28]. Accordingly, the nitric acid oxyviscose is expected to be more crosslinked and of more ordered structure, thus leading to hindrance of the mobility of the polar groups and, hence, to a decrease in the relative permittivity.

On the other hand, increase of temperature reduces the intermolecular forces and favours the formation of open structure, together with enhancing the ionization of both the carboxylic and the remaining hydroxyl groups. Thus an increase in the loss index is expected with increase of temperature, particularly at lower frequencies, as is observed. Also, the sharp rise in the dielectric constant as the temperature increases above 50°C at low frequency (0.5 kHz), which takes place exponentially, is attributed to increased polarization in the sample studied.

Finally, the disappearance of the thermal transition — which is usually observed at about 30°C in the temperature dependence of the dielectric constant plots (Fig. 6) — implies that, as a consequence of oxidation of viscose fibres

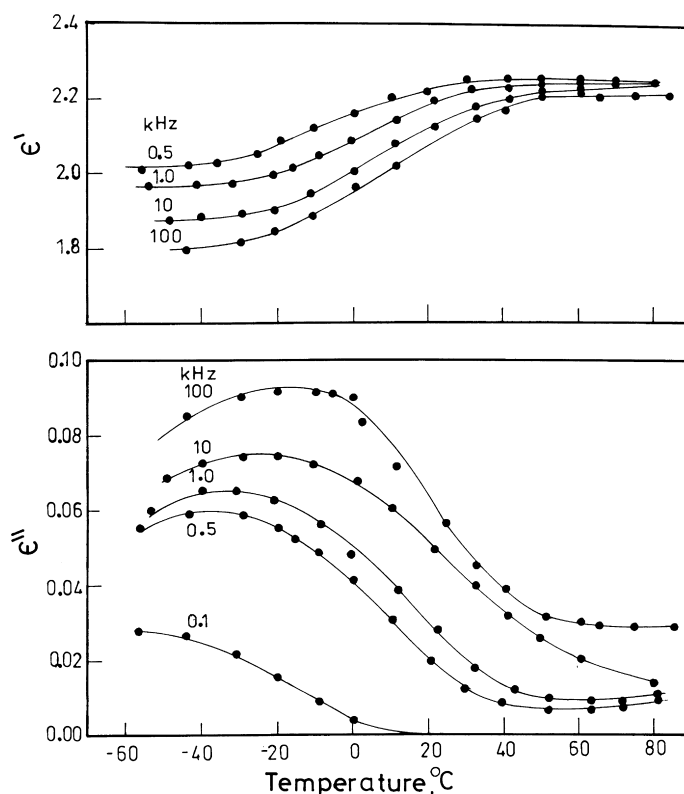


Fig. 7. Temperature dependences of  $\epsilon'$  and  $\epsilon''$  at various frequencies for periodate oxyviscose.

by nitric acid, strengthening of the intermolecular hydrogen bonding has taken place.

#### 3.4. Periodate oxyviscose

The oxidation of viscose with periodate proceeds via cleavage of the bonds between the second and third carbon atoms of the anhydroglucose unit, thus transforming the secondary hydroxyl groups into aldehyde groups, together with the formation of dialdehyde cellulose [30–34]. The results obtained in Table 1 show that oxidation of the original fibres with periodate decreases the degree of polymerization from 465 to 43. At the same time a diffuse X-ray diffraction pattern is obtained, indicating the formation of a non-crystalline material. During oxidation the crystalline portion of the fibres becomes dispersed and accessible to the oxidizing agent leading to a high carbonyl and aldehyde contents, but practically no carboxylic groups are formed.

It is clear from the above results that use of such a specific oxidizing agent retains the primary alcoholic groups, but to a lesser extent owing to the degradation process. In spite of the presence of high contents of carbonyl and aldehyde groups, no absorption bands were observed within their absorption ranges in the i.r. spectrum (see Fig. 1). One can also note that no shift in the OH stretching vibration band of this sample was observed by comparison with the spectrum of the original fibres. But there was a shift to higher frequency with respect to the spectrum of hydroviscose of comparable *DP*, indicating that the

periodate oxyviscose still possesses weak hydrogen bonds. The absence of free aldehyde groups in periodate oxyviscose was explained previously [24,35] by the formation of hemiacetal groups or the hydration of aldehyde groups.

In view of the above modification of the structure of viscose fibres caused by the oxidation with periodate, the dielectric results, which are given in Fig. 7, might be explained as follows. The occurrence of a single relaxation process in the lower temperature range at frequencies from 0.1 to 100 kHz, with an activation energy of  $\sim 26 \text{ kcal mol}^{-1}$ , indicates that this relaxation is similar to the one observed in the other samples investigated except for the nitric acid oxyviscose. As regards the molecular mechanism of this secondary relaxation process, the methylol groups in the non-crystalline regions were suggested above to be the dipolar group involved in this process. A justification of this conclusion is the observation that the periodate oxyviscose, which still retains such groups (not oxidized by periodate), exhibits the same dielectric relaxation process, whereas the sample oxidized by nitric acid and lacking the methylol groups in the non-crystalline regions does not exhibit such a relaxation. It may be added that the decrease in the dielectric permittivity of the periodate oxyviscose may be due to hemiacetal formation [24], which constitutes a form of covalent crosslinking. Also, such interaction might lead to the absence of free ions and subsequently to the disappearance of the DC loss at low frequencies and high temperatures, as is observed in Fig. 7.

Finally, two thermal transitions have been observed in the



temperature dependence of the dielectric constant for this sample as shown in Fig. 7: one in the neighbourhood of  $-20^{\circ}\text{C}$  and the other at about  $35^{\circ}\text{C}$ . Such transitions might be associated with rupture of the weak hydrogen bonds in the non-crystalline regions, in which an ensemble of energetically non-equivalent hydrogen bonds may exist.

#### 4. Conclusion

1. One of the useful procedures for assigning the molecular relaxation processes of macromolecules in general is through altering chemical constituents systematically.
2. The dielectric properties of viscose fibres change considerably upon oxidation. No molecular mechanism could be deduced in the case of oxidation with non-specific oxidizing agents (peroxide and hypochlorite), whereas for specific oxidation (nitric and periodate) the molecular mechanism could be clarified.
3. The dielectric relaxation observed in all of the samples examined, except the nitric acid oxyviscose sample, is due to the orientation of the methylol group in the non-crystalline regions.

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