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Cellulosic solid films exhibiting cholesteric liquid crystalline order:

Part II *Static tensile, dynamic mechanical and stress relaxation properties of ethyl cellulose films*

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Static tensile, dynamic mechanical, and stress relaxation properties of ethyl cellulose (EC) films cast from liquid crystalline and non-liquid crystalline solutions at various conditions were determined.

EC films exhibited a marked tensile yield behaviour at room temperature. The yield stress depended on strain rate and an activated volume *V* could be evaluated from the data of the yield stress. The dependence of *V* obtained from the yield behaviour on the casting conditions was almost the same as that from creep behaviour.

There was a phenomenological correlation between the dynamic modulus E' and the activated volume *V*: the higher the value of E', the lower the value of *V*; but there was no clear correlation between the relaxation modulus and *V*. From the stress relaxation behaviour, *V* was also evaluated; however, the dependence of *V* evaluated from the stress relaxation data on the casting conditions was not similar to that from the creep or yield stress data.

1. Introduction

This is Part II of a two-part series which studies the mechanical properties of cellulosic solid films cast from liquid crystalline solutions. In Part I, we examined the creep behaviour of the cast films of ethyl cellulose (EC) and hydroxypropyl cellulose (HPC) and reported activated parameters, in particular the activated volume *V* on the basis of the Eyring process. Unfortunately, we have not evaluated the value of *V* at lower temperatures than 50 °C due to the uncertainty in the accuracy of our measurements. The data around room temperature are needed for practical application. Some researchers [2–6] have reported that the Eyring process [7] can be applied to the yield stress behaviour of glassy thermoplastics. Roetling [2] has compared the activated parameter (activated energy) obtained from the creep and yield stress measurements on the basis of the Eyring process and has shown that the values of activated energy agreed fairly well at a limited temperature range. This suggests that the Eyring approach can be applied to both creep and yield stress behaviour. In this paper, therefore, we determined the tensile properties of the cast films, analysed the yield stress behaviour on the basis of the Eyring process, and evaluated the activated volume at room temperature.

Generally, liquid crystalline fibres are characterized by those of higher modulus [8]. The cast films which remain the liquid crystalline order also should exhibit a higher modulus than non-liquid crystalline films. Then, we determined the dynamic mechanical and stress relaxation properties of the EC films cast at different conditions and discussed the difference between the elastic properties of amorphous EC and liquid crystalline EC films from the standpoint of the difference of the activated volume. Finally, we attempted to evaluate the activated volume from the stress relaxation behaviour according to the method proposed by Kubat *et al.* [9, 10].

2. Experimental procedure

2.1. Samples

Ethyl celluloses (ECs) and solvents used in this study were the same as those in Part I [1]. In this study, commercial reagent grade n-butanol (Wako Pure Chemical Ind. Ltd.) was added to the solvents. The solution of EC in n-butanol did not form liquid crystals, as well as the solution of EC in benzene. In this study, we prepared 30 wt % solution of EC (polymer code: EC-2; in Table I in Part I [1]) in n-butanol.

2.2. Preparation of film specimen for each test

Solid films were cast by the same process as in Part I [1]. In this study, EC-B (m-cresol, at 25 °C) and EC-D (benzene, at 25 °C) films were mainly used. In addition, three EC films were used: films cast from 50 wt % m-cresol solution (polymer code: EC-2 in Table I in Part I [1]) at − 18 and 50 °C, and from 30 wt % n-butanol solution at 25 °C. They were abbreviated as

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EC-B′, EC-B″, and EC-E, respectively. Test specimens were cut along a line parallel to a long side of the cast films, similar to the specimen for creep test in Part I [1].

2.3. Static tensile properties

Static tensile properties of film specimens (size: 3 cm long × 0.15 cm wide × ~ 0.01 cm thick) were determined by using a Tensilon VIM-IV-500 (Toyo Baldwin Co. Ltd.) at room atmosphere (~ 23 °C, 60% RH). An interval between chucks of 2 cm was chosen. The crosshead speed was changed from 5 to 500 mm min^{-1}. Three measurements were performed and the mean was obtained at each crosshead speed. The reproducibility of the yield stress was better than 8%.

2.4. Dynamic mechanical properties

Dynamic mechanical measurements were carried out with a Rheovibron DDV-II-C (Toyo Baldwin Co. Ltd.) in the temperature range from 10 to ~ 130 °C at a heating rate of ~ 0.5 °C min^{-1} and a constant frequency of 110 Hz. The size of film specimen was 3 cm long × 0.3 cm wide × ~ 0.005 cm thick.

2.5. Stress relaxation in simple extension

Stress relaxation data were obtained using an apparatus constructed in our laboratory. The schematic diagram of the apparatus is shown in Fig. 1. The specimen (size: 2 cm long × 0.13 cm wide × ~ 0.005 cm thick) was set between the fixed jaws and was kept at a given temperature for 30 min. The sample chamber was thermostatically controlled and the temperature was maintained constant at 90, 130, and 150 ± 0.5 °C. Then, we extended the specimen by pulling down the extention rod made of brass (6 mm diameter) and kept the extension constant with rod stopper. The extension was measured by means of a dial gauge. The initial strain was ~ 0.03. Stress was measured directly with strain gauge. The output from the strain gauge was amplified and was recorded continuously as a function of time. The relaxation modulus $G(t)$ was calculated by

$$G(t) = \sigma(t)/\varepsilon_0 \qquad (1)$$

where $\sigma(t)$ is stress as a function of time, and ε_0 is initial strain. The reproducibility of the data was better than 7%.

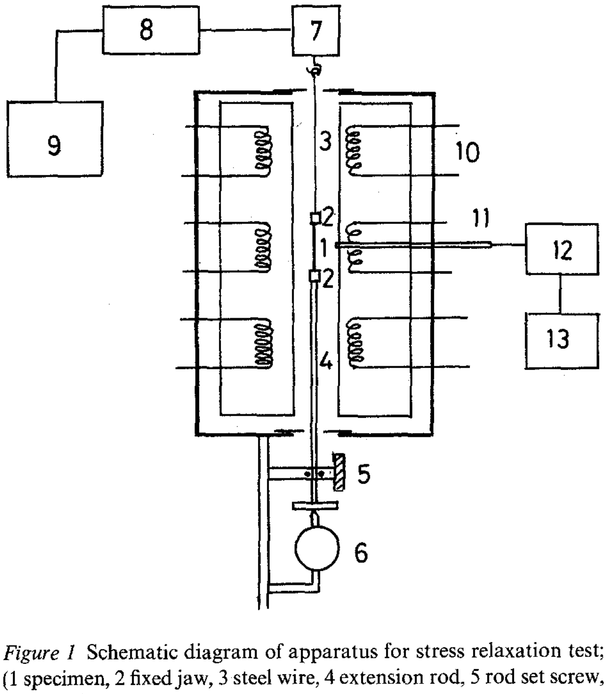

Figure 1 Schematic diagram of apparatus for stress relaxation test; (1 specimen, 2 fixed jaw, 3 steel wire, 4 extension rod, 5 rod set screw, 6 dial gauge, 7 strain gauge, 8 strain amplifier, 9 strain recorder, 10 heater, 11 thermosensor, 12 temperature controller, 13 temperature recorder).

3. Results and discussion

3.1. Tensile properties

Our main objective of this work is to evaluate the activated volume V from the yield behaviour. The yield stress measurement at a constant strain rate is analogous to the creep rate measurement at a constant applied stress. Then, the Eyring activated process [7] can be applied to the yield stress behaviour with some modifications. In a special case: high stresses; Bauwens *et al.* [5, 6] have derived the following equation

$$\sigma_y/T = \Delta U/VT + (R/V)\ln 2\dot{\varepsilon}/\dot{\varepsilon}_0 \qquad (2)$$

where σ_y is yield stress, T absolute temperature, ΔU activated energy, V activated volume, R the gas constant, $\dot{\varepsilon}$ strain rate, and $\dot{\varepsilon}_0$ a constant. Equation 2 suggests that a plot of σ_y/T against ln $2\dot{\varepsilon}$ is a straight line of slope R/V. Consequently, we can evaluate the value of V at given temperature, when Equation 2 is valid for our films. This is the reason that we focus on the yield stress behaviour in this study.

Fig. 2 shows the stress–strain curves for each film at different conditions. Each curve exhibited a marked yield stress. The range of strain rate for EC-B was different from that for EC-B′ and EC-D. This was because the marked yield behaviour was not exhibited at relatively low strain rate for EC-B′ and EC-D. According to Equation 2, when σ_y/T is plotted against the logarithm of strain rate, a straight line of a slope of R/V should be obtained. Then, we show the plot of σ_y/T against log $\dot{\varepsilon}$ for each film in Fig. 3. The solid lines were drawn by the least-squares method. Despite some scatter of the plots, the trend agreed that σ_y/T increased linearly with log $\dot{\varepsilon}$. The activated volumes calculated from the slopes are shown in Table I. The values of V for each film obtained from the creep data are also shown in the same table. The values of V at 23 °C for EC-B and EC-D were almost the same and were of the order of 1 nm^3. It was noteworthy that the value of V for EC-B′ was much smaller than those for EC-B and EC-D. This agreed with the result obtained for hydroxypropyl cellulose film [1, 11]. As discussed in the preceding paper in this issue [1], this finding means that the activated event for the liquid crystalline film cast at lower temperature becomes more localized than that cast at higher temperature.

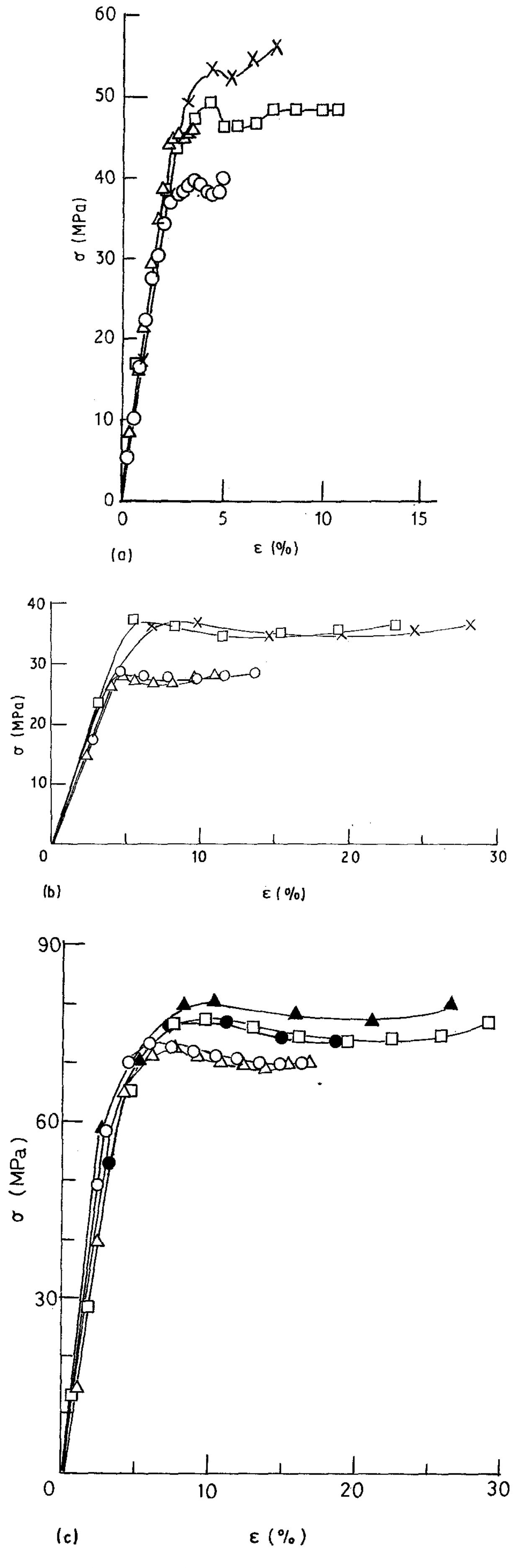

Figure 2 (a) Stress–strain curves for EC-B film at given strain rates. (Strain rate: ○ 0.399 s^{-1}, △ 0.443 s^{-1}, □ 0.959 s^{-1}, × 3.58 s^{-1}, (b) stress–strain curves for EC-B′ film at given strain rates. (Strain rate: ○ 4.34 s^{-1}, △ 9.16 s^{-1}, □ 25.6 s^{-1} × 32.4 s^{-1}. (c) Stress–strain curves for EC-D film at given strain rates. (Strain rate: ○ 9.92 s^{-1}, △ 10.27 s^{-1}, □ 21.5 s^{-1}, ● 24.7 s^{-1}, ▲ 35.3 s^{-1}).

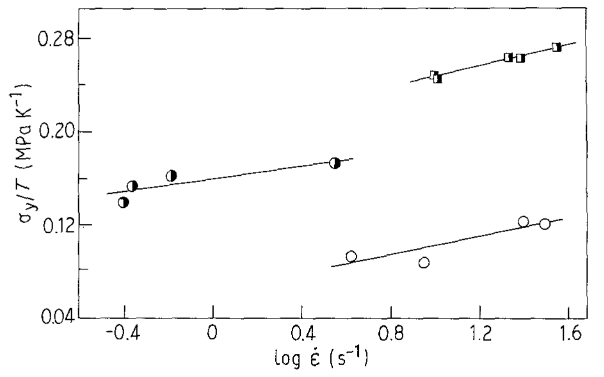

Figure 3 Ratio of yield stress to temperature as a function of logarithm of strain rate for EC films. (○ EC-B′, ◑ EC-B, ◨ EC-D).

TABLE I Activated volume evaluated from yield stress or creep data for ethyl cellulose films

	V(nm^3)			
	Yield stress	creep		
Sample	23 °C	50 °C	70 °C	90 °C
EC-B	1.226	0.849	1.796	3.042
EC-B′	0.163^a	–	–	–
EC-D	1.265	2.245	3.821	4.321

^{a} 25 °C

Now we compare the values of V evaluated from the data of yield stress with those evaluated from the data of creep for EC-B and EC-D. The data shown in Table I are represented in Fig. 4. The value of V for EC-D, which was amorphous [1], decreased linearly with decreasing temperature and interestingly the decrease in the value of V with decreasing temperature was continuously linear irrespective of the method by which the value of V is evaluated. On the other hand, with respect to EC-B, which was liquid crystalline [1], the data evaluated from creep behaviour were discontinuous to the data from yield behaviour: the value of V from yield behaviour was greatly larger than that estimated by extrapolating the data evaluated from creep behaviour. Ward and Wilding [12] have noted that the value of V from creep behaviour was consistent with that from yield behaviour for oriented amorphous polymers, but was smaller than that from yield behaviour for crystalline polymers. This was in fair agreement with our findings shown in Fig. 4. Our findings suggest that the value of V for liquid crystalline polymers depends on the approaches by which the value of V is evaluated, but the value of V for the amorphous polymers does not.

Additionally, we show the other tensile properties. Young's modulus was 3 to 6 × 10^4 MPa, tensile strength at break was 30 to 80 MPa, which was almost the same as the yield stress, and elongation at break was 3 to 18%. The strain rate dependence of Young's modulus was not remarkable in our experimental range, however, tensile and elongation at break tended to increase with increasing strain rate, shown in Fig. 2. The modulus for EC-B was greater that those for EC-B′ and EC-D. Young's modulus should be dependent on the value of V [12], but the dependence

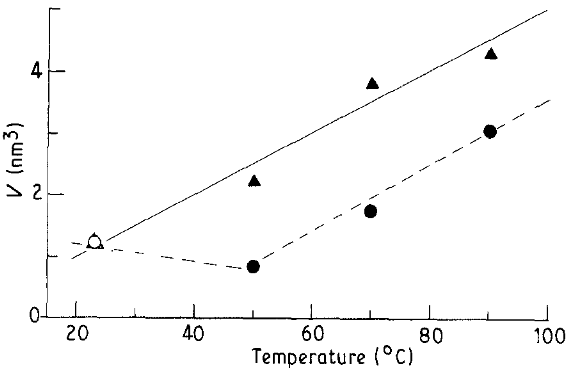

Figure 4 Activated volume as a function of temperature for EC-B (○, ●) and EC-D (△, ▲); (○, △): V from yield stress data, (●, ▲): V from creep data.

was not remarkable for our films. Interestingly, the tensile strength at break for EC-D (amorphous) was greater than that for EC-B′ (liquid crystalline).

4. Dynamic mechanical properties

Fig. 5 shows the temperature dependence of dynamic modulus E' and loss tangent $\tan\delta$ for EC-B, EC-D, and EC-E. Over the temperature range, E' for EC-B was greater than that for the other films. As noted previously, EC-D and EC-E were amorphous, whereas EC-B remained the cholesteric liquid crystalline order [1]. Our results showed that liquid crystalline films exhibited a higher modulus than non-liquid crystalline films, as expected.

Fig. 6 shows the dependence of E' and $\tan\delta$ on temperature for EC-B, EC-B′, and EC-B″. This shows the effect of the casting temperature on those properties. E' and $\tan\delta$ did not depend on the casting temperature in our experimental range: − 18 to 50 °C. This was partially because the solution prepared in this study was single-phase liquid crystalline and the structure of the liquid crystal at each temperature was almost the same.

Now we compare the values of V and E' for the films. We showed the values of V at 23 °C for EC-B, EC-B′, and EC-D in Table I. Apparently, the films showing a higher value of V exhibited lower E': EC-B exhibited higher E' than EC-D and the value of V for EC-B was smaller than EC-D; EC-B′ exhibited higher E' around 30 °C than EC-B and the value of V for EC-B′ was smaller than EC-B. This agreed with the finding by Ward *et al.* [12]: V decreases with increasing modulus.

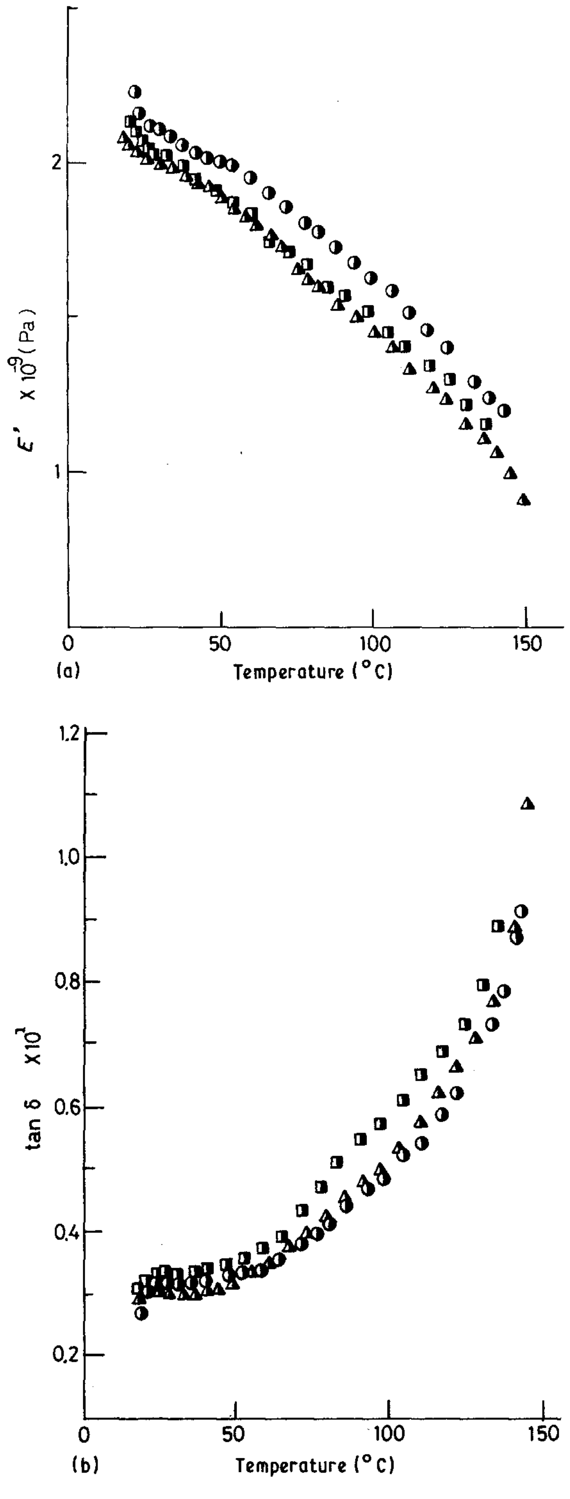

Figure 5 (a) Dynamic modulus as a function of temperature for EC films. (◑ EC-B, ▲ EC-E, ◧ EC-D). (b) Loss tangent $\tan\delta$ as a function of temperature for EC films. (◑ EC-B, ▲ EC-E, ◧ EC-D).

5. Stress relaxation behaviour

Fig. 7 shows the stress relaxation modulus $G(t)$ for EC-B at each temperature. The initial strains at 90, 130, and 150 °C were 2.1, 3.4, and 2.8×10^{-2}, respectively. At short time, the modulus at each temperature was of the order of 10^8 Pa. The order was the same and the shapes of curves were very similar irrespective of whether or not the film remained the liquid crystalline order.

Fig. 8 shows the effect of the casting temperature on the relaxation modulus at 90 °C for EC films cast from liquid crystalline solution. Within our experimental range, in short times, the modulus for EC-B′ tended to be larger than that for EC-B or EC-B″. No marked tendency for the effect of the casting temperature on the modulus for the films was, however, observed; at other temperatures than 90 °C, the modulus for EC-B′ was not always larger than EC-B.

A comparison of the moduli at 90 °C for the films cast from different solvent systems at room temperature is made in Fig. 9. The modulus for EC-E (n-butanol) appeared to be larger than that for EC-D (benzene) or EC-B (m-cresol) in our experimental

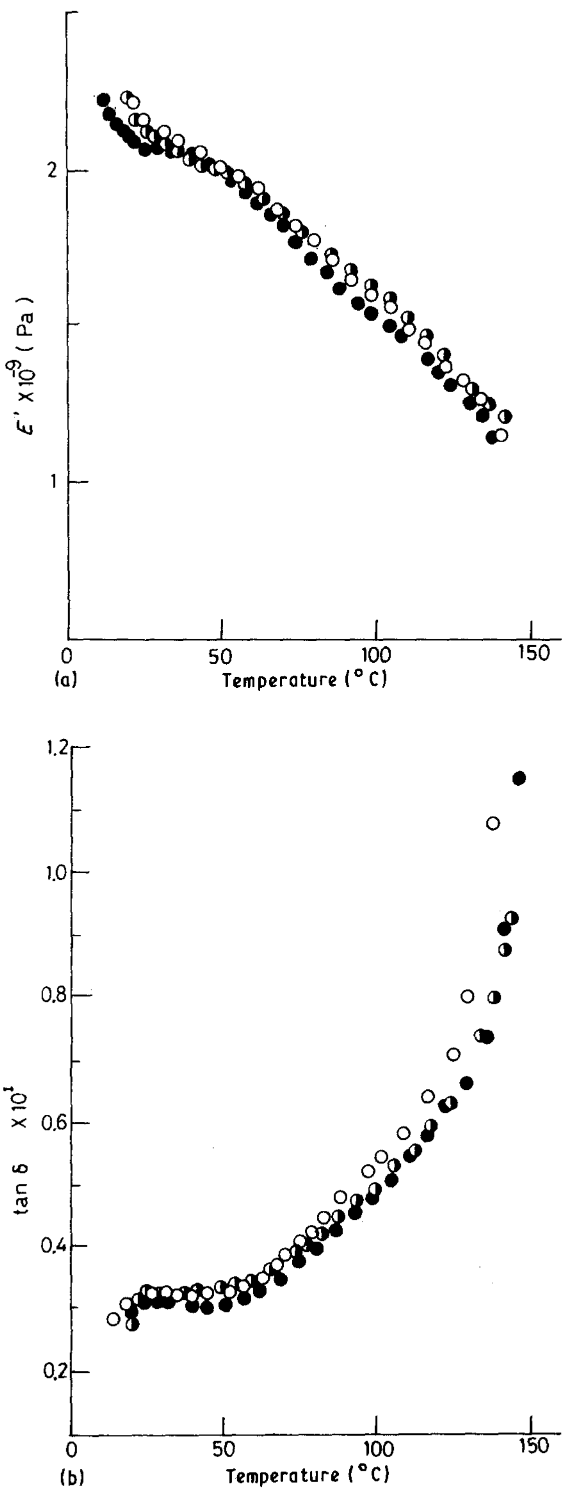

Figure 6 (a) Dynamic modulus as a function of temperature for EC films. (○ EC-B′, ◑ EC-B, ● EC-B″). (b) Loss tangent tanδ as a function of temperature for EC films. (○ EC-B′, ◑ EC-B, ● EC-B″).

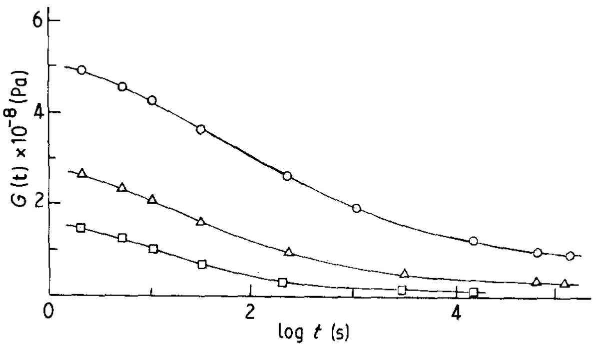

Figure 7 Stress relaxation modulus as a function of logarithm of time for EC-B film at given temperature. (Temperature: ○ 90 °C, △ 130 °C, □ 150 °C).

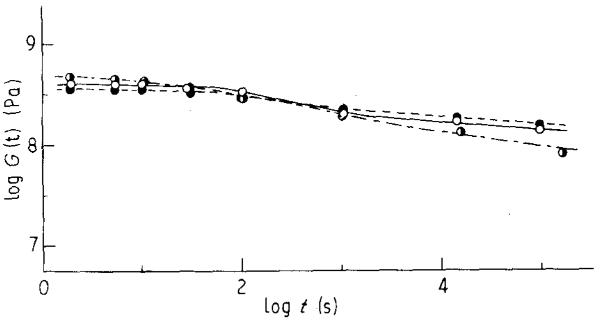

Figure 8 Stress relaxation modulus at 90 °C as a function of logarithm of time for EC films. (○ EC-B′, ◑ EC-B, ● EC-B″).

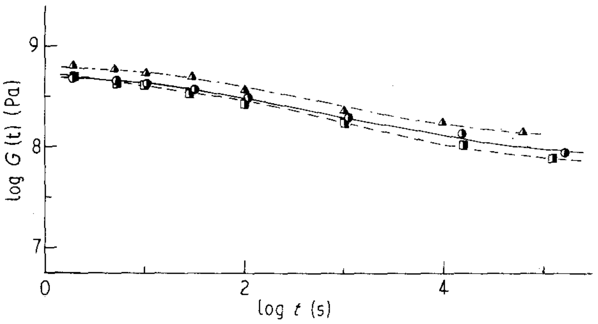

Figure 9 Stress relaxation modulus at 90 °C as a function of logarithm of time for EC films. (◑ EC-B, ▲ EC-E, ◨ EC-D).

range of time and this trend was observed at other temperatures (130 and 150 °C). The feature shown in Fig. 9 was little different from that shown in Fig. 5a and from that observed for creep compliance [13]: liquid crystalline films exhibited a higher modulus than non-liquid crystalline ones for the dynamic mechanical properties and creep behaviour, but not for the relaxation behaviour. Generally the interconversion of creep compliance $J(t)$ and relaxation modulus $G(t)$ for linear viscoelastic materials is comparatively simple [14]

$$G(t) = (\sin m\pi)/m\pi J(t) \qquad (3)$$

where m is the slope of the doubly logarithmic plot of $G(t)$.

Consequently, at least between the creep and relaxation data a simple trend of higher modulus with higher liquid crystallinity must be observed. This was not, however, valid for our films. The reason for the disagreement in the trends for creep and relaxation is not clear.

Our main objective of this study is to evaluate the activated volume V. Kubat *et al.* [9, 10] have proposed a method for evaluating V from the stress relaxation data. When the logarithm of stress is plotted against the logarithm of time, the maximum slope of the curves, F, defined as $(-\mathrm{d}\sigma/\mathrm{d}\ln t)_{\max}$, is equal to kT/V

$$F = (-\mathrm{d}\sigma(t)/\mathrm{d}\ln t)_{\max} = kT/V \qquad (4)$$

where k is the Boltzmann constant and T absolute temperature. We attempt to apply the method to our relaxation measurements. Approximate stress relaxation spectra H can be usually obtained according to the following equation [15]

$$(-\mathrm{d}G(t)/\mathrm{d}\ln t)_{t=\tau} = H(\tau) \qquad (5)$$

The value of $\mathrm{d}\sigma(t)/\mathrm{d}\ln t$ can be obtained in a similar manner to $H(\tau)$. The curves shown in Fig. 7 are then drawn as a plot of $\sigma(t)$ against $\ln t$. The $(-\mathrm{d}\sigma(t)/\mathrm{d}\ln t)$ was calculated at every time ($\mathrm{d}\ln t = 1$) and then the maximum slope obtained. Following this procedure, the value of F for each temperature and film, and therefore V, could be evaluated according to Equation 4. The values of V for each film are shown in Table II and were of the order of 1 nm^3, which was the same as for the values evaluated from creep data. The value of V increased with temperature, except for the cases of EC-B′ and EC-B at 130 °C. This was similar to the trend of data obtained from creep and yield behaviour. A comparison between the values of V for EC-B, EC-B′, and EC-B″ at given temperatures revealed, however that the value of V decreased with increasing casting temperature. This trend was different from that obtained from creep and yield behaviour. Furthermore, the values of V for EC-B were larger than those for EC-D or EC-E: the value of V for liquid crystalline films was larger than that for non-liquid crystalline films. This was also in disagreement with the results obtained from creep and yield behaviour.

The value of V obtained from stress relaxation data was greatly dependent on the initial stress σ_0 and on the effective stress which was equal to $(\sigma_0 - \sigma_\infty)$; σ_∞ is the stress remaining after infinite time [9, 10]. In our experimental range, σ_0 could be obtained for each film at each temperature, but σ_∞ could not be obtained at 150 °C. Our data shown in Table II were not ones at the same conditions of the effective stress, therefore, before comparisons between the values of V from creep or yield behaviour and stress relaxation behaviour are performed, we need to confirm the applicability of the method proposed by Kubat *et al.* [9, 10] to our relaxation measurements.

TABLE II Activated volume evaluated from stress relaxation data for ethyl cellulose films

	V (nm^3)		
Sample	90 °C	130 °C	150 °C
EC-B′	4.350	3.720	9.090
EC-B	4.274	3.755	6.131
EC-B″	2.194	3.690	5.175
EC-D	1.999	3.090	6.167
EC-E	2.502	3.240	4.207

6. Conclusions

EC films cast from both liquid crystalline and non-liquid crystalline systems exhibited a tensile yield behaviour. The activated volume V could be evaluated from the dependence of the yield stress on strain rate for each film. The dependence of V on the casting temperature tended to be similar to that obtained from the creep behaviour.

The film cast from liquid crystalline solution at lower temperature exhibited a higher dynamic modulus E' than the film cast at higher temperature and than the film cast from non-liquid crystalline solution. The phenomenological correlation between E' and V was in agreement with the data reported by Ward *et al.* [12]: the activated volume decreased with increasing modulus.

The relaxation modulus $G(t)$ for the film cast from liquid crystalline solution did not depend markedly on the casting temperature and was not always larger than that for the film cast from non-liquid crystalline solution. Then, the $G(t)$ for each film was not correlated to V. This was different from the findings obtained for the creep and dynamic mechanical behaviour. V was also evaluated from the stress relaxation data in accordance with the method proposed by Kubat *et al.* [9, 10], however, the temperature dependence of V evaluated from stress relaxation data was different from that evaluated from the creep data.

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