

Dynamic Viscoelastic Properties in the Molten State for Cellulose Acylates and (Cellulose Oligo-Oxymethylene Ether) Acylates

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Synopsis

The dynamic viscoelastic properties of cellulose acylates, its mixed acylates, and (cellulose oligo-oxymethylene ether) acylates (COM acylates) have been measured in the molten state over wide ranges of frequency and temperature. The $\log G'$ vs. $\log \omega$ curves as well as the similar curves for the loss modulus G'' at various temperatures for cellulose acylates could not be superposed into respective master curves by use of the time-temperature superposition principle. This is considered to be caused from the orientation of cellulose acylates' main chain in the molten state. In the case of cellulose mixed acylates, rheological simplicity was found but this was only the case on selected combinations of acyl groups. Most cellulose acylates, which were introduced oxymethylene chains (OM chains) in between glucopyranose ring and the acyl group, behaved as thermorheologically simple materials in the molten state. When the acyl groups become large, however, it is necessary to introduce long OM chains in order to get thermorheologically simple COM acylates in their molten state. Several studies have been made concerning the behavior of side chains, both the OM and the acyl chains, of COM acylates in the molten state.

INTRODUCTION

Recently, one of the authors and others^{1,2} have found that wood can be converted to thermoplastic materials by simple chemical modifications, such as esterification and etherification. As one of the extensions of the study,³ the rheological properties in the molten state were studied for several blends composed of butyrylated, caproylated, or lauroylated wood and synthetic polymers. The results of viscoelastic measurements gave excellent time-temperature superposition for most of the blends examined. This fact suggests mutual plasticization among the derivatized wood components and synthetic polymers in the blends. However, the superposition was not possible for blends with more than 90% of esterified wood or for mere esterified wood. On the other hand, a series of aliphatic acid esters of cellulose are known to be partially crystalline polymers. Since they are crystalline polymers, no detailed investigation has been made concerning the rheological properties of cellulose acylates in the molten state.

In the present study, we did measure the dynamic viscoelastic properties of the cellulose acylates in the molten state and tried to convert the cellulose acylates to amorphous and nonorientable materials. Some inquiries were made

to elucidate the roles of side chains to give cellulose derivatives crystalline or amorphous nature.

EXPERIMENTAL

Preparation of Samples

Preparation of Cellulose Acylates. Whatman cellulose powder CF-11 (DP = 300–400) was peresterified without degradation by a conventional method utilizing trifluoroacetic anhydride-fatty acid system (TFAA method).⁴

Preparation of Cellulose Mixed Acylates. Daicel acetate flakes (cellulose acetate with DS = 1.8; DP = 120) was used as a starting material, and was further esterified by the TFAA method to get cellulose mixed acylates.

Preparation of (Cellulose Oligo-Oxymethylene Ether) Acylates. Two methods were used to prepare (cellulose oligo-oxymethylene ether) acylate (COM acylates) differing in the method for the preparation of cellulose solution. One is to dissolve cellulose (Whatman cellulose powder CF-11) in paraformaldehyde (PF)/dimethyl sulfoxide (DMSO) solution at high temperatures (115–130°C) for certain durations.⁵ The other is to dissolve cellulose by bubbling formaldehyde vapor to its DMSO suspension at an intermediate temperature (85°C).⁶

The acylation of COM is similar to that reported in the previous article.⁷ That is, triethylamine (6 mol/glucose unit of cellulose) and one of a series of aliphatic anhydride from butyric anhydride to dodecanoic anhydride (6

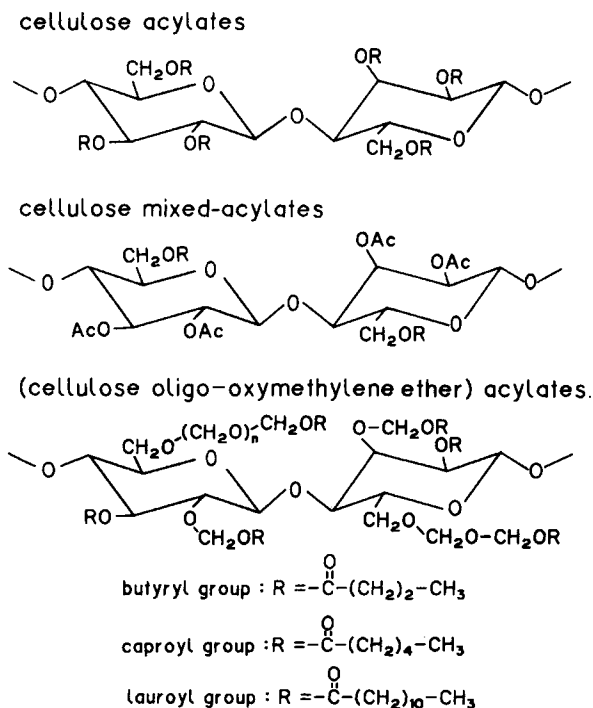


Fig. 1. Chemical structures of cellulose acylates, cellulose mixed acylates, and COM acylates.

mol/glucose unit of cellulose) were added to the cooled cellulose solutions obtained as described above with continuous stirring. For the preparation of COM laurate, an adequate amount of toluene was added so as to prevent gel formation during the reaction. After the reaction mixtures were allowed to stand at room temperature for 5–16 h, it was poured into suitable precipitants to obtain the sample. The sample was completely peracylated without degradation. It was reported by Johnson et al.⁶ that COM acetate even prepared after dissolving through the bubbling method contains no contamination of polyoxymethylene (POM) after purification.

Characterization of the Samples

The degree of substitution of the samples was determined by use of Fourier transform infrared (FTIR) spectrometry. All the samples were found to be almost completely substituted.

Calculation of the average length of oligo-oxymethylene chains (I/E) and of the molar substitution (MS) was achieved by use of ¹H nuclear magnetic resonance (NMR) data in line with that reported by Miyagi et al.⁵

In Figure 1, are shown schematically the chemical structures of cellulose acylates, cellulose mixed acylates, and COM acylates. X-ray diffractograms were obtained in the same way as described in the previous report.⁸

Measurements of Dynamic Viscoelastic Properties

The measurements of dynamic viscoelastic properties were carried out with a Rheometrics Mechanical Spectrometer RMS-605 with parallel plate geometry. The samples were molded into disks, 1.6 mm in thickness, 25 mm in diameter. For the dynamic measurements, sinusoidal varying angular displacement with a strain amplitude of 10% was imposed on the sample through the upper plate and the resulting torque acting on the surface of lower plate was measured by a transducer. The viscoelastic functions, the storage shear modulus G' , and the loss modulus G'' were calculated from the amplitude

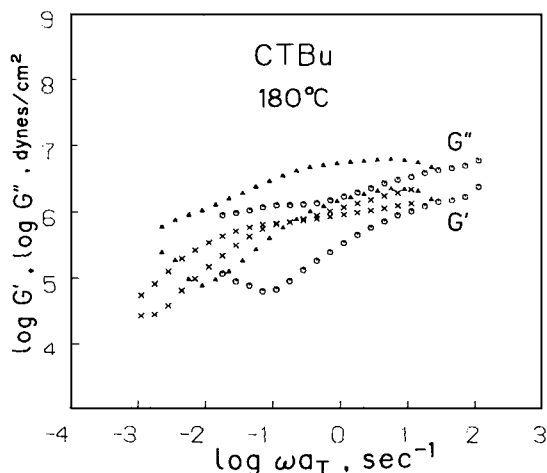


Fig. 2. Frequency dependencies of G' and G'' for CTBu. \circ = 180°C; \blacktriangle = 185°C; \times = 190°C.

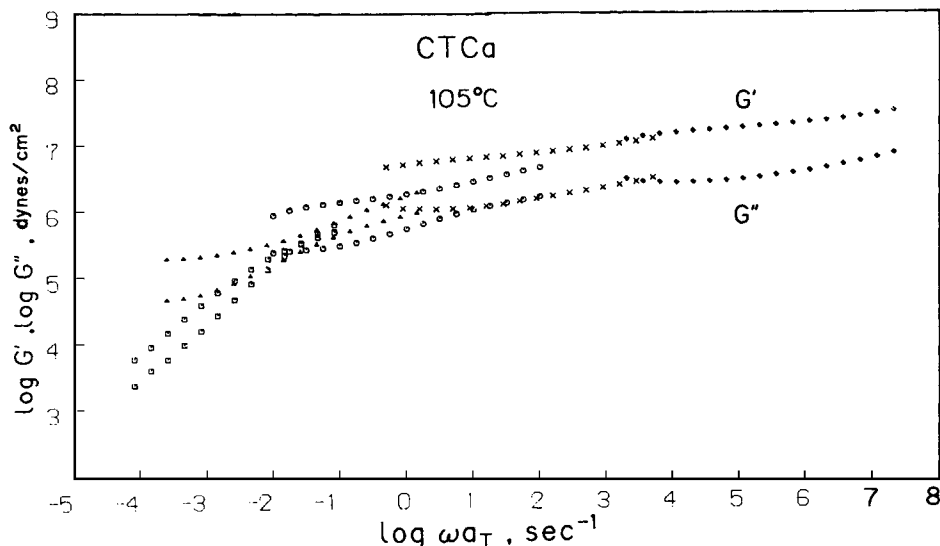


Fig. 3. Frequency dependencies of G' and G'' for CTCa. \diamond = 90°C; X = 100°C; \circ = 105°C; Δ = 110°C; \square = 115°C.

ratio and the phase difference between the strain and the torque by a computer. G' and G'' were logarithmically plotted against angular frequency ω which covered the range from 10^{-1} to 10^2 radian/s at various temperatures. The measuring temperatures ranged from 60°C to 225°C.

RESULTS AND DISCUSSION

Dynamic Viscoelastic Properties for Cellulose Triacylates

Viscoelastic properties in the molten state have been measured for cellulose-tributyrate(CTBu), -tricaproate(CTCa), and -trilaurate(CTLa), and the results of their time-temperature superposition trials are shown in Figures 2, 3 and 4, respectively. From these figures, the trials of the time-temperature superposition are found to be unsuccessful, showing that the viscoelastic properties of these samples are not thermorheologically simple. That is, these cellulose triacylates behave rheologically markedly different from amorphous polymers in the molten state. This is considered to be caused by orientation of the main chain in its longitudinal axis, due to the fact that cellulose main chain is rigid and has difficulty in bending energetically because of bulkiness of the component segment and that cellulose triacylates have stereotacticity.

Figure 5 shows the logarithmic plots of G' and G'' for CTCa measured repeatedly at 100°C against angular frequency. It can be seen that the values of G' and G'' measured secondarily are evidently larger than those measured first throughout the whole region of frequency. This result indicates a formation of an oriented structure in the molten state during the measurement and that the oriented structure is not an inherent character to the system but is largely dependent on the history of mechanical treatment to which the system has been subjected thus far.

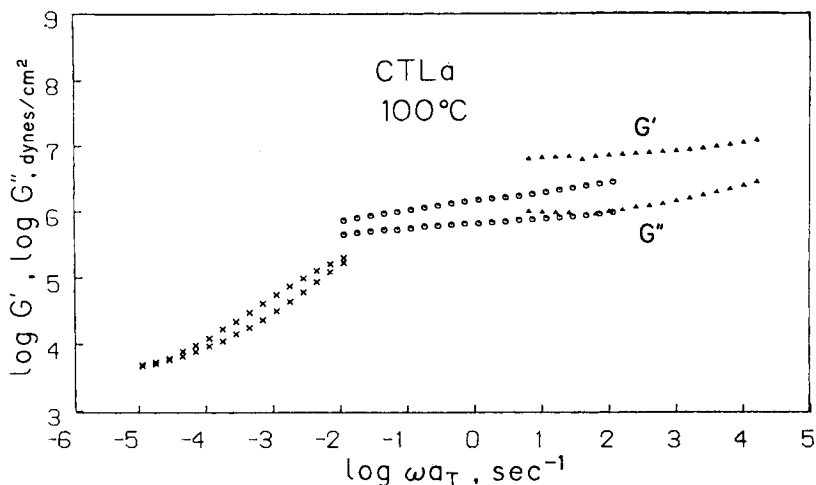


Fig. 4. Frequency dependencies of G' and G'' for CTL α . Δ = 80°C; \circ = 100°C; X = 110°C.

From the comparison of individual data shown in Figures 2-4, it can be pointed out that the degree of the orientation of the main chain becomes less when the molecular volume of the acyl group introduced becomes larger. That is, introduction of bulky side chains weaken the interchain cohesive force among main chains of cellulose acylates.

It can be said, however, that even though a bulky acyl group like lauroyl is introduced, the cellulose acylate substituted with the same acyl group has a tendency to orient in its molten state.

Dynamic Viscoelastic Properties for Cellulose Mixed Acylates

In the previous section, cellulose acylates composed of the same side chains were shown to be polymeric materials which reveal an orientation property in the molten state. The physical properties of cellulose derivatives are consid-

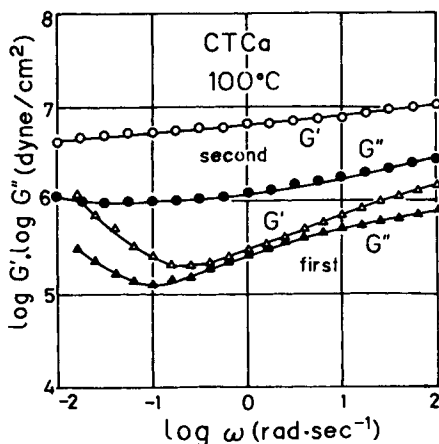


Fig. 5. Logarithmic plots of dynamic moduli G' , G'' against angular frequency ω for CTC α repeatedly measured at 100°C. Δ : first measurement. \circ : second measurement.

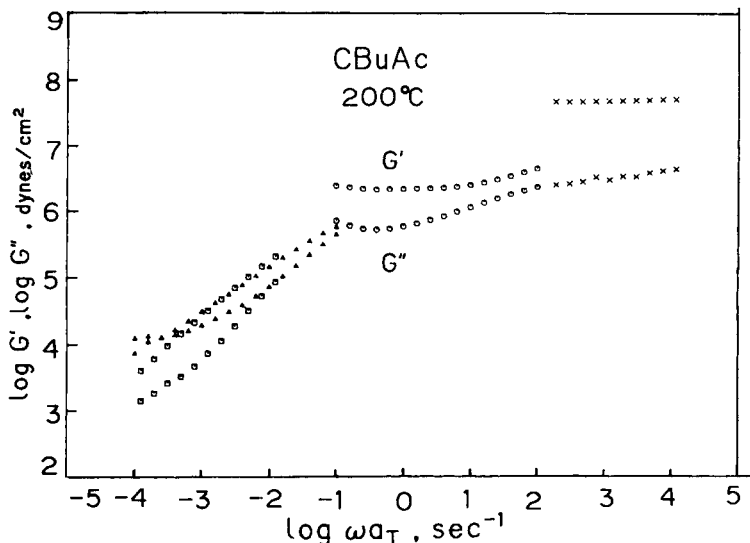


Fig. 6. Frequency dependencies of G' and G'' for CBuAc. X = 180°C; ○ = 200°C; ▲ = 210°C; □ = 225°C.

ered to alter depending on the properties and substituting situation of side chains.

Next, several cellulose mixed acylates which have nonuniformity or heterogeneity of side chains have been prepared and their viscoelastic properties in the molten state have been investigated. What is interesting is whether or not the additional internal plasticization caused by a method which is not so different from the mere acylation can convert the cellulose acylates to amorphous polymers in their molten state.

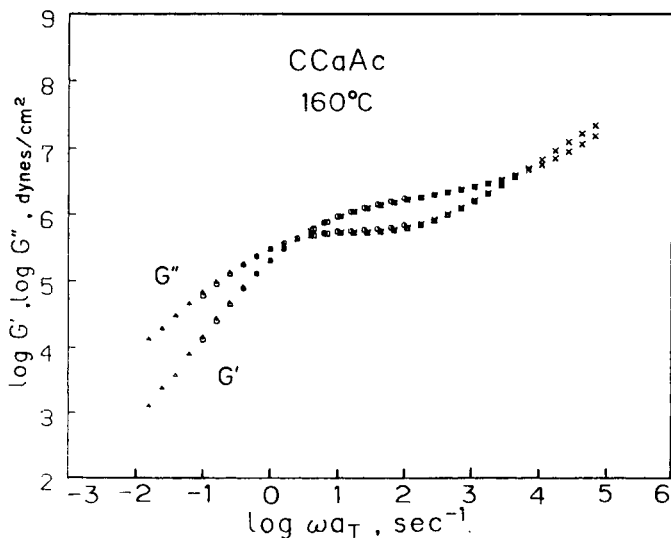


Fig. 7. Frequency dependencies of G' and G'' for CCaAc. The reference temperature is 160°C. X = 130°C; □ = 140°C; ○ = 160°C; Δ = 180°C.

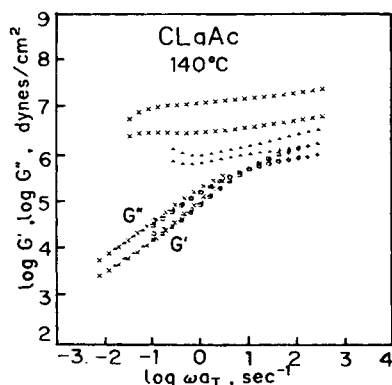


Fig. 8. Frequency dependencies of G' and G'' for CLaAc. X = 135°C; Δ = 136°C; O = 140°C; \square = 150°C; X = 160°C.

The dynamic viscoelastic properties for cellulose acetate-butyrate (CBuAc), cellulose acetate-caproate (CCaAc), and cellulose acetate-laurate (CLaAc), all of which contain the degree of acetyl substitution of 1.8, are shown in Figures 6, 7 and 8, respectively. It is known from Figure 6 that viscoelastic data for CBuAc cannot be superposed into a master curve. This result implies that a combination of the two resemble small acyl groups does not give amorphous character to the cellulose derivative in the molten state.

The results of a viscoelastic measurement for CCaAc expressed as master curves are shown in Figure 7. The abscissa of the figure is the reduced angular frequency ωa_T , and the reference temperature is 160°C. From this figure, it is known that in the case of CCaAc the $\log G'$ vs. $\log \omega$ curve as well as the similar curve for the loss modulus G'' at various temperatures can be superposed into respective master curves, and the curves of G' and G'' are apparently similar in shape to those of the ordinary amorphous polymers in the molten state. The log-log plot of G' vs. ωa_T shows a straight line with a slope of almost 2 and the curve of G'' with a slope of nearly unity in the low frequency region. From these features of the master curves, flow of CCaAc sample can be said to be confirmed.

From the above results, it can be said that the crystallinity of cellulose acylates is reduced by the mixed acylation with an adequate combination of acyl groups like acetyl and caproyl, yielding amorphous cellulose derivatives in the molten state. That is, mixed esterifications of cellulose introducing acyl groups adequately different in molecular size can result in cellulosic polymers which reveal viscoelastic properties of amorphous polymers in the molten state.

The shift factor a_T , determined upon the time-temperature superposition of the viscoelastic data for CCaAc, is plotted against the reciprocal value of the absolute temperature in Figure 9 (Arrhenius plot). From the slope of this plot, an apparent activation energy (H_a) for the flow behavior of CCaAc was calculated to be 67.85 kcal/mol.

Figure 8 shows viscoelastic properties for CLaAc. The $\log G'$ vs. $\log \omega$ curves as well as the similar curves for G'' measured at temperatures higher than 140°C can only be superposed into respective master curves. From this result,

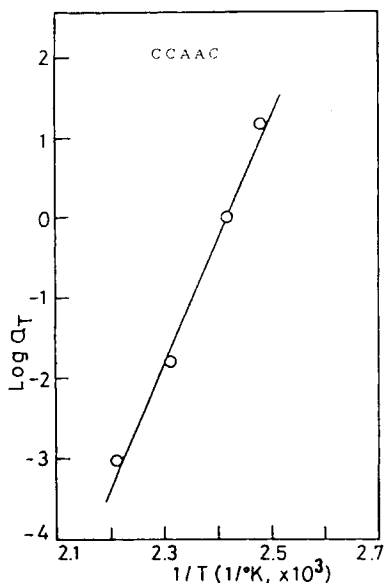


Fig. 9. Arrhenius plot for CCAc.

it can be said that CLaAc is more amorphous compared with CTLa but still has an essentially crystalline nature. In this case, the molecular size of the mixed acyl groups, acetyl, and lauroyl, are too different to effect nonuniformity in the side chain of cellulose, resulting in a not so amorphous polymer.

It was shown that among the mixed esters of cellulose used, only the CCAc was found to behave as an amorphous polymer in the molten state and to reveal successful time-temperature superposition. From this, it can be said that there is a certain range of appropriate pairing of acyl groups, in order to convert the viscoelastic properties of cellulose acylate to those of amorphous polymers.

Dynamic Viscoelastic Properties of (Cellulose Oligo-Oxymethylene Ether) Acylates

In the previous section, it was shown that cellulose acylates can be converted to cellulosic polymers, which can behave rheologically as amorphous polymers in the molten state, by appropriate mixed acylation. In this case, however, the requirement for the combination of acyl groups was found to be severe.

On the other hand, a PF/DMSO solution was recently found to be a nonaqueous cellulose solvent.⁹ The mechanism by which cellulose dissolves in the PF/DMSO mixture was shown to involve the formation of cellulose hydroxy oligo-oxymethylene ether mainly at C-6 hydroxyl group of the anhydrous glucose ring of cellulose, but considerable substitution occurs also at the C-2 and C-3 secondary hydroxyl groups depending on the conditions of the dissolution.^{5,6,9-11} The obtained cellulose hydroxyl oligo-oxymethylene ether has unstable hemiacetal parts but can be converted to stable compounds through acetalation of its hemiacetal units. The oligo-oxymethylene chain

(OM chain) parts thus introduced have the following characteristics: (1) Flexible because of its ether bond. (2) High polarity because of the large difference in electronegativity between carbon and oxygen atoms.

The length of the OM chains attached to the cellulose backbone can be adjusted by the dissolution conditions.⁵ As described above, the OM chain is not introduced equally to C-2, C-3, and C-6 hydroxyl groups. That is, the addition of formaldehyde (methylolation) of cellulose occurs selectively at the C-6 position at the initial stage of dissolution and then, along with the enlargement of OM chain at the C-6 position, substitution occurs also at the C-2 and C-3 position, followed by propagations of the OM chains. At the same time, demethylolation, that is, breakdown of side chain occurs by use of higher dissolution temperature or prolonged heating. Selectivity of the demethylolation at C-6 hydroxyl position also accompanied this case.

The extents of the introduced OM chain, that is MS, and the average OM chain length (I/E) for each dissolution stage and conditions can be obtained by the ¹H NMR analysis of the acylated samples.⁵

As has been described, the side chain of COM acylate can be brought to considerably complex states. COM acylates can be recognized as internally plasticized materials of cellulose acylates through intervention of OM chains in between the glucopyranose ring and the acyl group.

From this point of view, three kinds of COM acylates differing chiefly in OM chain length have been prepared in this investigation.

- A. COM acylates with prolonged side chain prepared by use of an appropriate dissolution temperatures and durations.
- B. COM acylates with short side chain, especially at C-6 hydroxyl position, prepared through dissolution using prolonged heating at rather high temperature.
- C. COM acylates with a considerably long side chain prepared by the bubbling method as described in the experimental section.⁶

The results of the characterization of these samples through ¹H NMR analysis are shown together with their dissolution conditions in Table I.

TABLE I
Cellulose Dissolution Conditions and Characterization of (Cellulose Oligo-oxymethylene Ether) Acylates Prepared

Dissolution type	Cond. for dissolution		CBuOM		CLaOM	
	PF/cell (g/g)	Temperature (°C) program	MS	I/E	MS	I/E
A-1	2.0/1.0	90-115/9 min 115 + 1/13 min	4.47	2.17	7.65	1.60
A-2	2.0/1.0	90-120/13 min 120 + 1/5 min	3.15	1.79	—	—
A-3	2.0/1.0	90-125/10 min 125 + 1/4 min	2.34	1.36	—	—
B	2.0/1.0	99-130/28 min 130 + 1/20 min	0.44	0.92	0.73	0.67
C	10.0/1.0	85 + 1/120 min	11.3	4.30	20.32	3.25

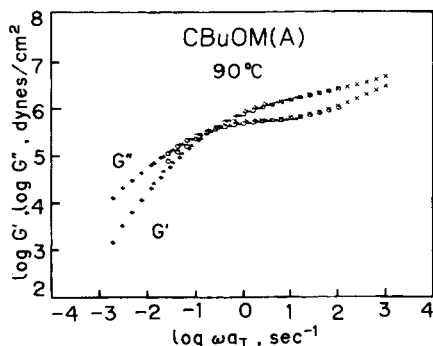


Fig. 10. Frequency dependencies of G' and G'' for COM butyrate (A). The reference temperature is 90°C . X = 70°C ; o = 90°C ; Δ = 110°C ; \diamond = 130°C .

Internal Plasticization of Cellulose Butyrate by Intervention of OM Chains

The dynamic viscoelastic properties in the molten state were measured for COM butyrate (A) with an intermediately long OM chain at various temperatures and superposition into master curve was attempted. The results are shown in Figure 10. The results of the viscoelastic measurements give excellent time-temperature superposition and the master curve obtained reveals the flow phenomenon within the range of the measurement, showing typical viscoelastic behavior starting from rubbery plateau to the flow region.

The successful time-temperature superposition suggests that by introducing a long OM chain having an average chain length of 2.4, to an extent of MS of 4.47, to cellulose prior to butylation, the butyrate becomes a material which cannot behave as a crystalline polymer, that is, an amorphous polymer, in the molten state.

Because the introduction of a long OM chain was found to be quite effective for internal plasticization of cellulose butyrate, then, the effects of the OM chain length and the conformation of side chain on the dynamic viscoelastic properties were investigated. The results of measurements for all the COM butyrates shown in Table I gave excellent time-temperature superposition. It is interesting to note that even in the case of COM butyrate (B), which was

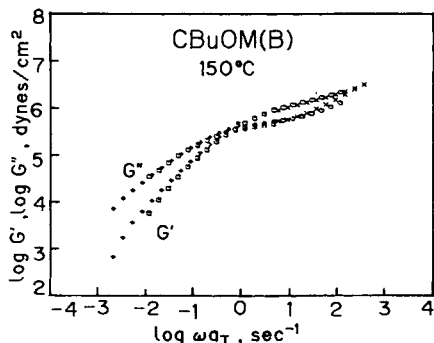


Fig. 11. Frequency dependencies of G' and G'' for COM butyrate (B). The reference temperature is 150°C . X = 130°C ; o = 150°C ; \square = 170°C ; \diamond = 190°C .

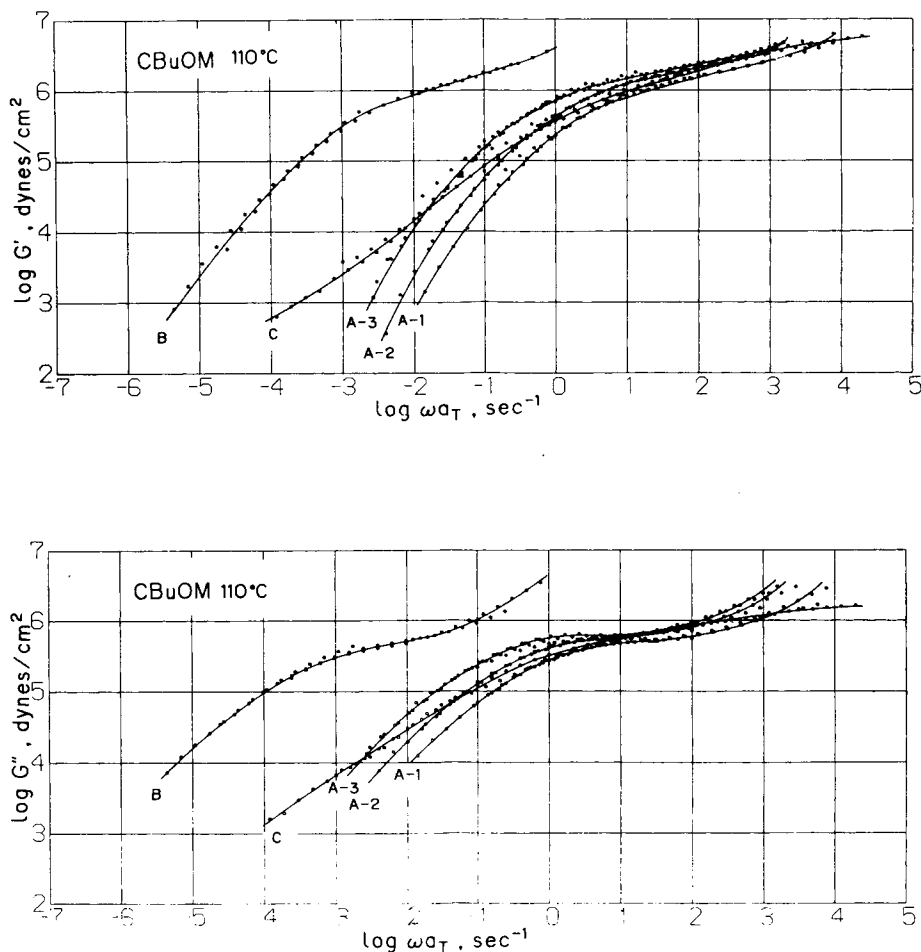


Fig. 12. Master curves of G' and G'' for COM butyrates having different MS. The reference temperature is 110°C .

introduced to only 0.44 unit of OM chain per anhydride glucose unit and has short OM chain (i.e. $I/E = 0.92$) the viscoelastic behavior of this sample did not indicate the nature of crystalline polymers but was similar to that of amorphous polymer in the molten state (Fig. 11). This result leads us to think that even in the case of COM butylate (B) whose acyl group is comparatively small, a small intervention of OM chain between glucopyranose ring and the acyl side group could bring about considerable decrease in crystallinity of CTBu. Figure 12 shows a grouping of the master curves of G' and G'' for these COM butyrates. The reference temperature is 110°C . The MS range of the samples for OM chain is 0.44(B) to 11.3(C). As may be seen from Figure 12, all of the master curves include not only the flow region or the terminal zone but also the rubbery region. As regards A-1, 2, 3, and B, that is, the MS of OM chain ranging from 0.44 to 4.47, the terminal zone shifts progressively to the low frequency side as the MS decreases, but both the length and the height of the rubbery plateau seem to be almost constant, independent of MS. As long

TABLE II
The Apparent Activation Energy of COM Butyrates

Sample	ΔH_a (kcal/mol)
A-1	30.61
A-2	29.90
A-3	33.57
B	56.12
C	48.53

as the MS is not too large, it can be said that intermolecular force of cellulose main chain is weakened with increasing the MS and the I/E of OM chain. The apparent activation energy of these samples is shown in Table II. It may be seen from this table that the more the terminal zone shifts to the low frequency, the greater the value of ΔH_a becomes. We can understand these relationships between ΔH_a and thermal flow in viscoelastic consideration.

On the other hand, the master curves of G' and G'' in the temperature range 60–160°C for COM butyrate (C), which introduces fairly long OM chains, are somewhat different from those of other COM butyrates. It is found that the slope of G' and G'' in the flow region of Figure 12 is small in the case of COM butyrate (C) and this sample is less temperature sensitive than others. In addition, ΔH_a of this sample is large, 48.53 (kcal/mol). These results indicate that internal plasticization of CTBu by OM chain is not so simple as expected. Taking into consideration the fact that these results were caused from intervention of fairly long OM chains, it may be thought in this case that interaction among oligo-oxymethylene chains brings about ordered structures with longer relaxation times.

In Figure 13 are shown X-ray diffractograms of COM butyrates measured at 25°C. It is evident from this figure that the intervention of OM chain

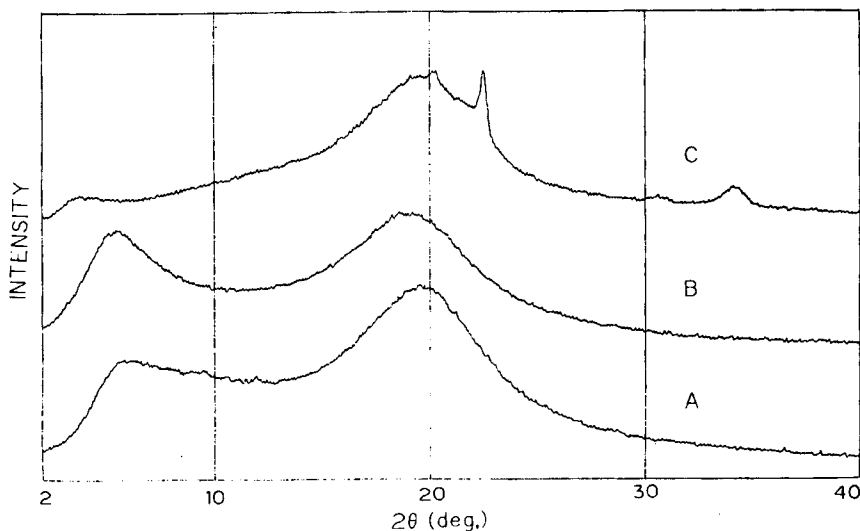


Fig. 13. X-ray diffractograms of COM butyrates, (A, B, and C) with different MS.

TABLE III
The Lattice Spacings for COM Butyrate(C) and POM

2θ	CBuOM	POM	
	d (Å)	d (Å)	I
34.3°	2.61	2.60	S
22.7°	3.92	3.90	VS
20.4°	4.35	4.34	W

converts cellulose from a crystalline polymer to an amorphous one and that three novel peaks at $2\theta = 20.4^\circ$, 22.7° , and 34.3° appeared on the spectrum of COM butyrate (C) having fairly long OM chains. The lattice spacings calculated from these values are shown in Table III. In this table, reported lattice spacings for crystalline polyoxymethylene (POM) are also shown.¹² As may be seen from Table III, the spacings for COM butyrates with fairly long OM chains agree well with the reported values for POM. Therefore, it can be said that the OM chains in between the glucopyranose ring and the acyl side group have a tendency to orient themselves in the same way as POM does when the OM chain parts have enough length. However, it can be said that the effect of the crystallinity of the OM chains on the dynamic viscoelasticity in the molten state is not so important, because its time-temperature superposition is successful.

Dynamic Viscoelastic Properties for Other COM Acylates

The logarithmic plots of G' and G'' against angular frequency ω at various temperatures for valerilated, caproylated, as well as caproylated COM can also be superposed into respective master curves just as the cases with COM butyrate. That is, the COM acylates with acyl groups having up to eight carbon atoms are confirmed to be thermorheologically simple, and behave viscoelastically as amorphous polymers in the molten state.

On the other hand, when acyl groups larger than the capryl group were introduced into COM, somewhat different phenomena have been obtained. Dynamic viscoelastic properties in the molten state were measured for COM laurates with different OM chain length. Superposition of the logarithmic plots of G' and G'' against angular frequency ω obtained at various temperatures for these samples were attempted and the results are shown in Figures 14–16.

From these figures it can be recognized that the time-temperature superposition becomes unsuccessful as the OM chain length shortens. Actually, in the case of COM laurate (B), the trials of the superposition are not so successful. The lauroyl group is composed of twelve carbon atoms and is nonpolar. Since the group is fairly large, OM chain intervention between cellulose and acyl group must be of a certain length in order to effect the internal plasticization and result in amorphous COM laurates. That is to say, when the acyl group introduced is large, the introduction of OM chains with certain large length is necessary in order to give enough irregularities to the side chain. It can be pointed out, however, that orientability shown for COM laurate (B) is small compared with that for CTLA.

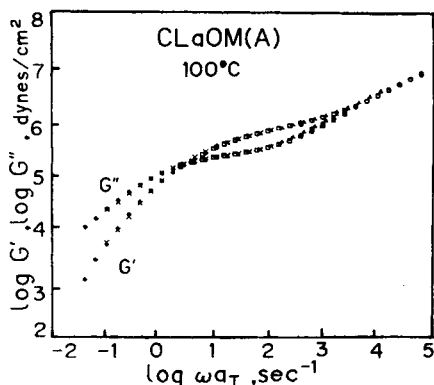


Fig. 14. Frequency dependencies of G' and G'' for COM laurate (A). The reference temperature is 100°C. \circ = 60°C; Δ = 70°C; \square = 80°C; \times = 100°C; \diamond = 120°C.

X-ray diagrams obtained for A, B, and C types of COM laurates are shown in Figure 17. It is apparent from the figure that a fairly large diffraction peak appears at a smaller angle of $2\theta = \text{ca. } 3^\circ$ (larger interplanar spacing) in the case of the B-type sample, which does not show successful time-temperature superposition of the viscoelastic data, whereas the strength of the peak weakens in the case of the C-type sample which shows successful superposition of the data. The strength of the peak for A-type sample appears as an intermediate one. Okamura et al.¹³ studied the change of X-ray diffraction peaks in aliphatic cellulose ester homologues and reported that their largest X-ray diffraction peak, which corresponds to the above-mentioned peak, always moves toward smaller angle as the number of carbons in the acyl group was increased. For example, the interplanar spacing of cellulose propionate was 1.17 nm while it reached about 2.99 nm in the case of CTLA. The significance of the shift of the peak is not known, but the authors presumed that the values must somehow be related to the distance between the

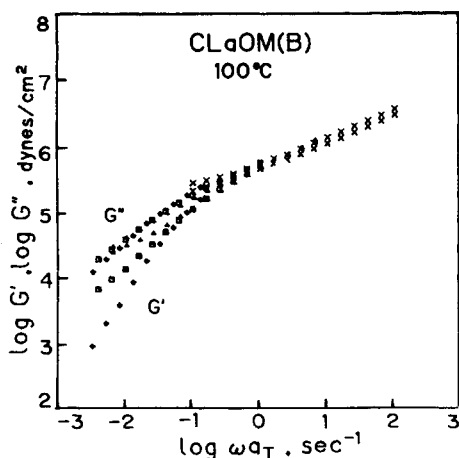


Fig. 15. Frequency dependencies of G' and G'' for COM laurate (B). The reference temperature is 100°C. \times = 100°C; \circ = 105°C; \square = 110°C; \diamond = 120°C.

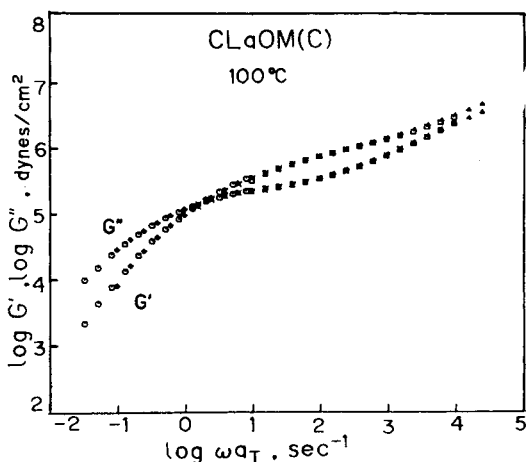


Fig. 16. Frequency dependencies of G' and G'' for COM laurate (C). The reference temperature is 100°C. Δ = 60°C; \square = 70°C; \times = 80°C; \diamond = 100°C; \circ = 120°C.

neighboring two cellulose chains in unit lattice, which increases as the length of acyl group becomes longer.

Thus, from Figure 17 and the above statement, the introduction of longer OM chains can be said to complicate the state of the side chain and prevent a formation of lattice structure of cellulose acylate having large acyl groups.

The peaks attributable to the lattice formation of OM parts of side chain can also be found in the diffraction curve for the type C sample. Even though the presence of this aggregate structure of the part of the side chain,

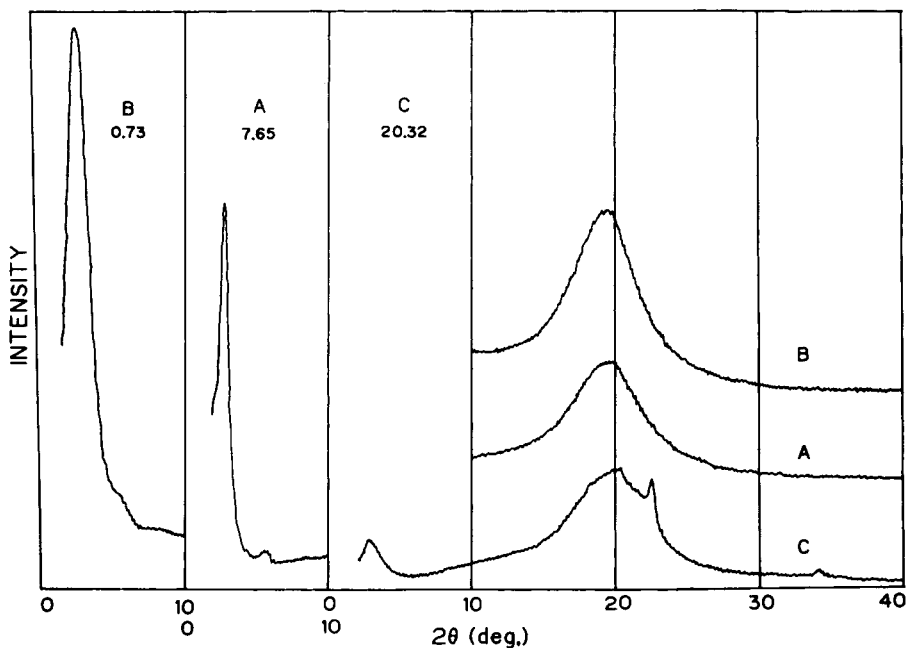


Fig. 17. X-ray diffractograms of COM laurates (A, B, and C) having different MS.

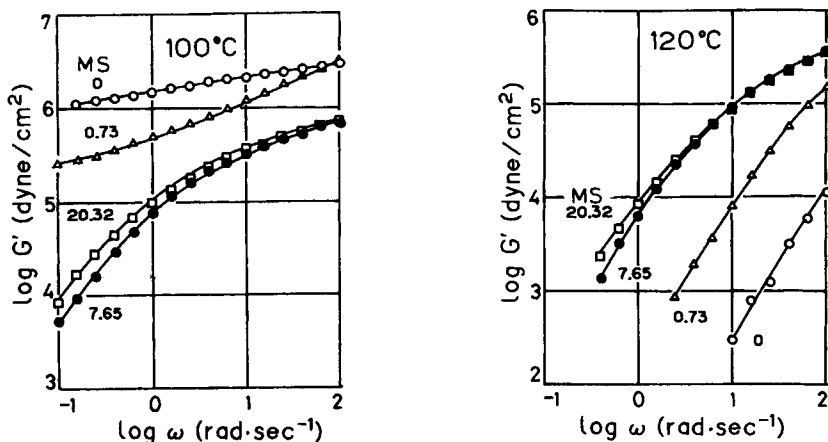


Fig. 18. Plots of $\log G'$ against $\log \omega$ for COM laurates ($MS = 0.73, 7.65, 20.32$) and CTLA ($MS = 0$) measured at 100°C and 120°C .

time-temperature superposition is possible for viscoelastic data of the type C. This might mean that the molecular force for making up the aggregate structure of OM chain parts no longer works in the molten state. The type A sample shows an intermediately strong peak at the smaller angle of its X-ray diffraction curve, showing a formation of the interplanar structure of cellulose chain, but it is rheologically simple so far as the melt phenomena are concerned.

Since the B-type sample [COM laurate (B)] which is not rheologically simple is included, comparison among the type A, B, and C samples through their master curves are not possible. Then, by use of the $\log G'$ vs. $\log \omega$ curves measured at 100°C and 120°C as shown in Figure 18, the three samples were compared. The MS values of the type A, B, and C are 7.65, 0.73, and 20.32, respectively, and CTLA ($MS = 0$) was also used as a control.

From the figure it is known that, at 100°C , the value of G' obtained for the samples decreases with an increase in the MS value up to that of 7.65 but the curve for the type C sample which has extremely large value of MS (20.32) is situated a little above the curve of G' for the type A sample ($MS = 7.65$). The latter fact can be explained in terms of the aggregate structure formation of the long OM chain parts of the side chain. The same trends could be obtained when the logarithmic plots of G'' against angular frequency measured at 100°C are compared.

On the other hand, the value of G' obtained for the samples at 120°C increases with an increase in the MS value. The trend is reverse to the previous finding measured at 100°C . All the samples reveal flow behavior at 120°C , and the sample which has longer OM side chain is known to have larger resistance to flow. It can be said that the introduction of long OM chains makes the sample amorphous and that more complex entanglement due to the hydrophobic aggregation of lauroyl groups occurs for the amorphous cellulosic polymers than the case with crystalline ones. It might be further said that introduction of longer OM chains would permit increased freedom of

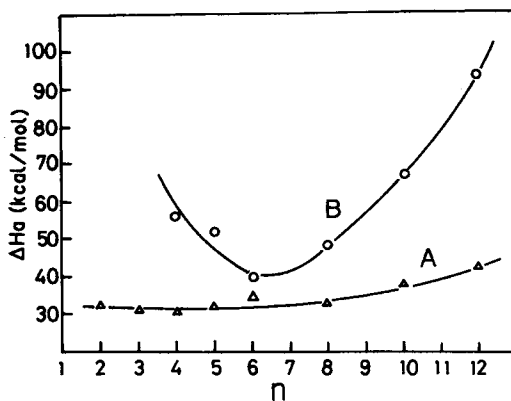


Fig. 19. Carbon number dependencies of the apparent activation energy (ΔH_a) for COM acylates employed in this study.

movement for lauroyl parts, which facilitates the formation of the hydrophobic aggregates. Similar but somewhat obscured results could be observed also for COM caprate.

In Figure 19 are shown apparent activation energy ΔH_a for a series of COM acylates investigated in the present study, plotted against carbon number of acyl group (n).

The upper curve indicates ΔH_a of COM acylates (B), which has fairly short OM chains and whose physical properties are close to those of cellulose acylates. The lower curve shows ΔH_a of COM acylate (A), in which intermediately long OM chains intervene in between glucopyranose ring and the acyl groups. The curve of ΔH_a for B type has its minimum around COM caproate ($n = 6$). Malm et al.¹⁴ reported that the apparent melting temperature for cellulose acylates shows a minimum value when plotted against n . Their explanation for this phenomenon is as follows. First, cellulose is internally plasticized by introduction of acyl groups. While the introduced acyl group is small in molecular size, this internal plasticization effect works as a predominant effect. Second, long acyl groups have a tendency to aggregate rather than separate main chains. When the acyl group becomes long or large in molecular size, this aggregation effect works somewhat more than the above-mentioned plasticization effect. The superposition of this effect yields a minimum in the apparent melting temperature vs. n curve.

In this connection, it can be said that the dependence of ΔH_a for COA-acylate (B) on n is comparable to those for the cellulose acylates. The increase in the ΔH_a value found with COM acylates (B) having larger acyl groups than caproyl should be ascribed to the hydrophobic aggregation of the acyl group which results in orientation of main chains. This assumption can be supported by the comparison of the X-ray diffractogram of COM butyrate (B) with that of COM laurate (B) shown in Figures 13 and 17 and the related discussion on Figure 17.

On the other hand, it is also shown in Figure 19 that the value of ΔH_a for COM acylate (A) is less sensitive to the carbon number of acyl groups. The slope of the ΔH_a vs. the carbon number of the acyl group is small but positive. From this observation, it can be pointed out, first, that introduction of the

long OM chain can result in enough internal plasticization even with the COM acetate (A). Second, it is also possible to say that even though the acyl groups introduced become large and long, the orientation of main chains coming from the hydrophobic aggregation seems to be hindered because of the intervention of long OM chains in the side chains of COM acylates (A). This second argument can be also confirmed by the comparison of the X-ray diffractogram of COM butyrate (A) (Fig. 13) with that of COM laurate (A) (Fig. 17).

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