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Dynamic Mechanical Thermal Analysis Transitions of Partially and Fully Substituted Cellulose Fatty Esters

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ABSTRACT: The main transitions of cellulose fatty esters with different degrees of substitution (DSs) were investigated with dynamic mechanical thermal analysis. Two distinct main relaxations were observed in partially substituted cellulose esters (PSCEs). They were attributed to the glass-transition temperature and to the chain local motion of the aliphatic substituents. The temperatures of both transitions decreased when DS or the number of carbon atoms (n) of the acyl substituent increased. Conversely, all the transitions of fully substituted cellulose esters occurred within a narrow temperature range, and they did not vary significantly with n . This phenomenon was explained by the formation of a crystalline phase of the fatty substituents. The presence of few residual OH groups in PSCEs was responsible for a large increase in the storage bending modulus, and it eliminated the effect of n on damping.

Keywords: cellulose fatty esters; dynamic mechanical thermal analysis (DMTA); thermal mechanical analysis (TMA); glass transition; damping; Fox equation; biopolymers; structure-property relations

INTRODUCTION

The organic esters of cellulose are thermoplastic materials that can entirely be synthesized from natural, renewable products. Cellulose acetate, the most important commercial cellulose ester, requires, however, an external plasticizer for most thermomolding processes because it shows a high softening temperature. Longer linear acyl groups decrease the softening point of cellulose

esters. The lateral aliphatic chain acts as an internal plasticizer of the cellulosic polymer, as first demonstrated by Malm et al.¹ Since then, the relaxation processes of fully substituted cellulose esters, that is, with a degree of substitution (DS) value very close or equal to 3, have been widely studied with dielectric measurements,² viscoelastic properties in the molten state,³ dynamic mechanical thermal analysis (DMTA),^{4,5} and differential scanning calorimetry (DSC).⁶

In contrast, studies concerning partially substituted cellulose esters (PSCEs), that is, with a DS value distinctly inferior to 3, are less abundant. They principally concern biodegradation. For instance, Buchanan et al.⁷ showed that cellu-

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lose acetates are biodegradable if their DS value is 2.4 or lower. Beyond this value, the abundant substituents and crystallinity of the polymer interfere with the required access of cellulolytic enzymes to the glucosidic bonds, resulting in inhibition or retardation of the depolymerization process. Esters of cellulose with longer aliphatic groups have shown increased resistance to biodegradability in relation to both DS and substituent size.⁸

Biodegradability is not the only property that renders PSCEs interesting. It is well known that cellulose diacetate (DS = 2.4–2.5) exhibits the highest thermoplasticity. Indeed, cellulose triacetate cannot be processed as a thermoplastic because its softening temperature is too close to its decomposition temperature.

Despite their potential applications as thermoplastic materials, little information is available concerning the relaxation processes of PSCE. Most of the existing literature is limited to cellulose acetates.⁹ Only recently, Glasser et al.¹⁰ reported data of DSC transitions for cellulose propionate, cellulose hexanoate, and cellulose laurate with low DS.

In this work, we report the preparation of cellulose esters with DS values ranging from 1 to 3. The number of carbon atoms in the linear acyl group (n) was varied from 8 to 18. No cellulose solvent was used in the synthesis: it was carried out in a heterogeneous solid–liquid reaction medium. DMTA was used to investigate the properties of the purified obtained products. Dilatometric thermal mechanical analysis (TMA) was also used to confirm some hypotheses. We focused on the main transitions, that is, those associated with the loss of mechanical moduli, which have a direct impact on their processability. It is clear that the heterogeneous medium in which the synthesis of these derivatives was carried out caused heterogeneity in their substituent distribution; that is, cellulose fibers had *a priori* a higher local DS value on their surface or in their noncrystalline zones than in the whole mass. However, we think that this study is necessary to reveal trends and is a first step in promoting the development of such cellulose derivatives.

EXPERIMENTAL

Materials

α -Cellulose (4% pentosans) from Sigma France was the starting biopolymer for the synthesis of

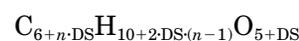
the cellulose esters. It was used after drying at 105 °C for 12 h. Fatty acid chlorides, pyridine, and other chemicals were reagent-grade. They were purchased from Aldrich France and used as received.

Synthesis of Cellulose Esters

A variant of the acid chloride/pyridine method was used. All of the samples were produced with the same temperature and reaction time to obtain similar degrees of polymerization. Only the amount of the acid chloride was varied to reach different DS values. Therefore, cellulose (10 g) was stirred in excess pyridine (250 mL) at 20 °C for 30 min. Fatty acid chloride (2, 1, and 0.5 equiv/OH) was poured into the reactor, and reflux was conducted at 130 °C for 2 h with mechanical stirring. After a period of cooling at 100 °C, 250 mL of 50% aqueous ethanol was added to consume the remaining acid chloride. The powder product was recovered by filtration over sintered glass and then thoroughly washed with ethanol and acetone. After further purification by Soxhlet extraction with acetone for 16 h, the cellulose ester was dried at 50 °C to a constant weight and stored in a desiccator at room temperature.

Determination of DS

DS of the purified and dried cellulose esters was determined by elemental analysis with the following formula in agreement with an earlier study:¹¹



Only in the case of fully substituted cellulose esters, the solubility of which in $CDCl_3$ was total, was ¹H NMR used to confirm the results obtained by elemental analysis.

Specimens

Cellulose esters were hot-compression-molded [30 °C above the glass-transition temperature (T_g)] between Teflon sheets in a laboratory press (4 ton) to obtain DMTA specimens of 30 mm × 12 mm × 3 mm. They were rapidly air-cooled to favor the amorphous state and stored in a room-temperature desiccator for 48 h before use. For TMA specimens, cellulose esters were molded at room temperature in a laboratory press (10 ton) with a standard KBr pellet maker to obtain compact,

Table 1. DS Values of Samples of Cellulose Fatty Esters Synthesized by the Fatty Acid Chloride/Pyridine Method

Substituent	<i>n</i>	ME	DE	TE
Caprylyl	8	1.04	2.23	3.00
Capryl	10	0.61	2.26	2.98
Lauryl	12	0.56	2.47	2.99
Myristyl	14	0.88	2.42	3.00
Palmityl	16	0.75	2.50	2.96
Stearyl	18	0.84	2.38	2.93
Average ± Standard Deviation		0.78 ± 0.18	2.38 ± 0.11	2.98 ± 0.03

uniform disks (10 mm in diameter and 3 mm thick) just before use.

DMTA Measurements

The dynamic bending storage modulus (E') and the loss factor ($\tan \delta$) were recorded with a DMTA Mk II analyzer (Rheometric Scientific) at 5 Hz at a heating rate of $4\text{ }^\circ\text{C} \cdot \text{min}^{-1}$. A single-cantilever bending module with a 14-mm span was employed.

TMA Measurements

Dilatometric transitions were detected in a Mettler thermomechanical analyzer (TMA 40) under a nitrogen atmosphere at a heating rate of $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$. The specimen was placed between two aluminum plates to distribute the probe's load uniformly.

RESULTS AND DISCUSSION

Fully substituted cellulose esters were obtained when 2 equiv of acid chloride/OH was used. PSCEs were obtained with 1 and 0.5 equiv of acid chloride/OH. The samples were classified into three nominal groups according to their bulk DS values (Table 1). For the sake of simplicity, in this work they are denoted monoesters (MEs), diesters (DEs), and triesters (TEs).

Assignment of Transitions

All of the cellulose esters, regardless of their DS value, presented DMTA curves that were characteristic of amorphous polymers (Fig. 1). Fully substituted cellulose esters showed a particular behavior that is discussed later. In the case of MEs

and DEs, two main peaks separated by at least $40\text{ }^\circ\text{C}$ were readily distinguished in the $\tan \delta$ curves. The relaxation at the higher temperature (α transition), which varied between 109 and $221\text{ }^\circ\text{C}$, was accompanied by the most important decrease of E' , and this indicated that it corresponded to the glass transition of the polymer. At temperatures higher than T_g , all specimens were severely distorted, and the DMTA signal became erratic; this made the detection of further relaxations (e.g., melting) impossible. Additional evidence on the assignment of T_g was obtained from the TMA of selected samples. An abrupt change in the expansion coefficient was observed in the dilatometric

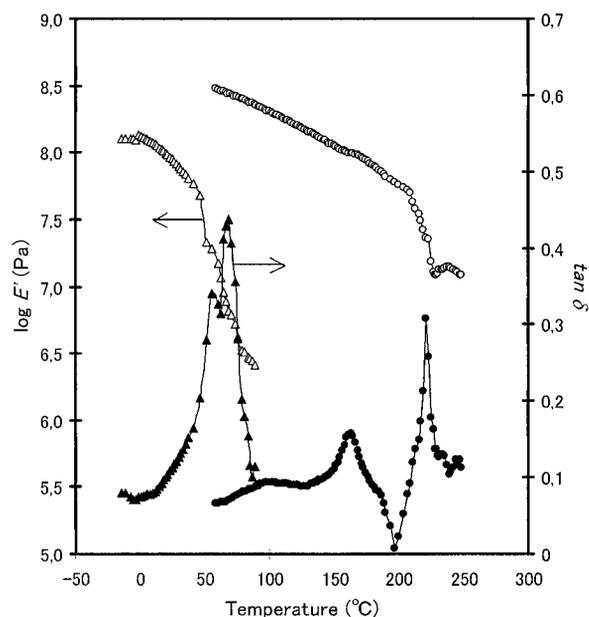


Figure 1. DMTA data recorded at 5 Hz for cellulose decanoates ($n = 10$): (Δ, \blacktriangle) $\log E'$ and $\tan \delta$ of TE (DS = 2.98) and (\circ, \bullet) $\log E'$ and $\tan \delta$ of ME (DS = 0.61).

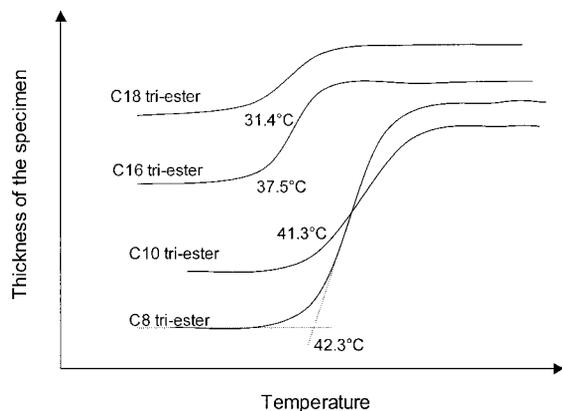


Figure 2. TMA dilatometric diagram of cellulose fatty TEs. The thermal expansion coefficient ($\partial V/\partial T$) at $T > T_g$ decreases with increasing n .

curve of cellulose esters as it occurred at the glass transition. As one can expect, the glass transitions determined with TMA were not the same as those determined by DMTA, but they agreed well for PSCEs (the differences were between 2 and 10 °C).

The DMTA transition at a lower temperature (β transition), which was as low as 37 °C for cellulose monostearate, was not observed in TMA dilatometric curves. The $\tan \delta$ magnitude of this relaxation was approximately half that of the α transition. It was first thought that it corresponded to a boat-chair configuration change of the glucopyranose ring. Such a transition occurs around 35–45 °C in cellulose triacetate and other TEs, as reported by other authors.^{12,13} This hypothesis was ruled out as the β transition was found to greatly depend on both the DS and the size of the lateral substituent. It shifted to temperatures as high as 192 °C in the case of cellulose monoctanoate. We assigned, therefore, the β transition to the local motion of the aliphatic substituents.

In the particular case of TEs, the DMTA T_g varied without a particular trend in a narrow range between 55 and 75 °C, and the β transitions varied between 42 and 53 °C. The proximity of the transitions caused both peaks to overlap, and sometimes they could not be clearly identified (shoulder peaks). The $\tan \delta$ magnitude of the β transition was higher in general than those of MEs and TEs, and this was particularly evident for cellulose trioctanoate. However, T_g 's of TEs determined by TMA decreased regularly from 42 to 31 °C when n increased (Fig. 2). A difference of at least 30 °C was, therefore, observed in comparison with DMTA values.

Table 2. DMTA Transitions of Fatty Cellulose Esters as a Function of DS and n

n	α Transition (T_g ; °C)			β Transition (°C)		
	ME	DE	TE	ME	DE	TE
8	220	189	64	192	122	53
10	221	157	69	163	76	55
12	208	160	75	129	70	52
14	203	128	66	113	51	43
16	188	136	56 ^a	62	53	— ^a
18	150	109	60	37	42	42

^a The resolution of the two transitions was not possible.

DMTA Transitions as a Function of n and DS

DMTA transitions of PSCEs were highly dependent on the size of the acyl groups (Table 2). A regular trend was observed for MEs and DEs: T_g decreased linearly with increasing n [Fig. 3(a)]. One of the possible explanations is the creation of

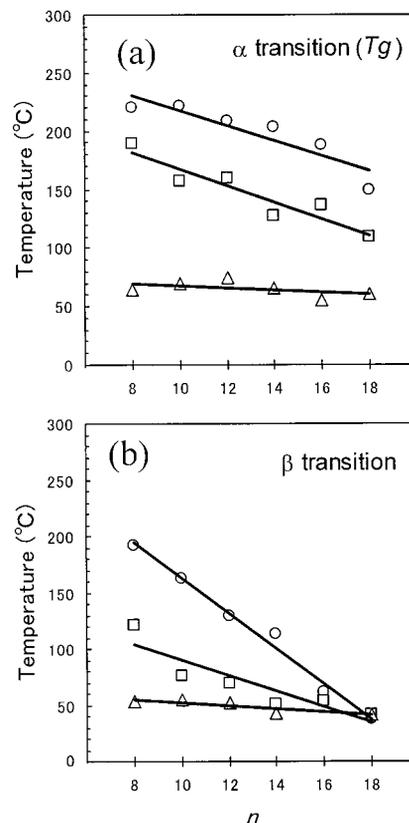


Figure 3. DMTA (a) T_g and (b) β transition of cellulose fatty esters as functions of the number of carbon atoms in the acyl substituent (n): (○) MEs, (□) DEs, and (△) TEs.

supplementary free volume as the fatty acid chains lengthen.^{14–16} The free-volume increase is more important when side chains are next to small hydroxyl groups, as in the case of PSCEs. This behavior is also well known for noncellulosic polymers bearing long flexible alkyl side groups, such as poly(*n*-alkyl methacrylates).^{17–19} However, T_g of TEs did not change significantly with n . This agreed well with Malm et al.¹ and Sealey et al.,⁶ who reported that cellulose TEs with short acyl groups show very high melting temperatures and T_g 's that decrease as n increases from C₂ to C₆, but they level off and start to increase when the substituent size increases from C₁₂ to C₂₀ (Fig. 4). Therefore, we can infer that a bulkier side chain reduces the cohesion between the cellulosic backbones so that lower temperatures are sufficient to make molecules flow (softening of the bulk material), but if the side chains become too long and numerous, they can accommodate in space and annihilate the effect of n .

If the free-volume argument is accepted, T_g data should fit the Fox equation,²⁰ which is based on this concept. Let us conceive the cellulose esters as a mixture of cellulose polymer and flexible fatty chains. The latter should be represented more precisely by the actually flexible methylene part of the acyl group, that is, R' in the following formula: R'CH₂C(O)—. The moieties closest to the cellulosic backbone, the ester and the first methylene groups, provide the main part of the steric hindrance. In light of these considerations, the cellulose fatty esters presented in this study contain from 30 to 70% mass of flexible fatty

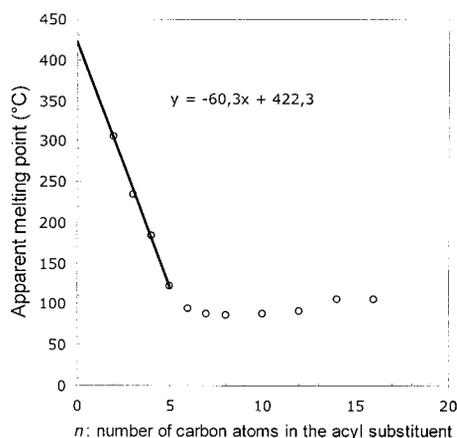


Figure 4. Apparent melting points of cellulose TEs with different numbers of carbon atoms in the acyl substituent (n) according to Malm et al.¹ The regression was calculated only with the first 4 points.

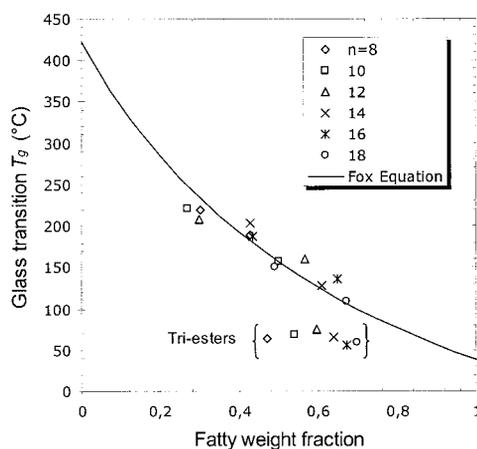


Figure 5. T_g 's of PSCEs and TEs as a function of the mass content of flexible fatty chains in the polymer [R' in R'CH₂C(O)—]. The line represents the calculated values obtained with the Fox equation.

chains. Figure 5 shows the glass transition plotted against the content of flexible fatty chains expressed as a mass fraction. The Fox equation line was obtained as follows:

$$T_g = \frac{1}{\frac{F}{(T_g)_F} + \frac{(1-F)}{(T_g)_C}}$$

where F is the mass fraction of the flexible fatty chains, $(T_g)_F$ is the glass transition of the fatty part of the polymer, and $(T_g)_C$ is the glass transition of the cellulose part of the polymer. Choosing values for the individual glass transitions is not so obvious in this case. The value for $(T_g)_C$ was chosen as the zero-extrapolated value of the softening temperatures of lower cellulose esters according to Malm et al.,¹ equal to 696 K (423 °C; Fig. 4). Conversely, it is not possible to assign *a priori* a specific value for the fatty part of the molecule. Attempts to consider it as an alkane or a methyl alkanoate are possible, but the relaxations of these substances are dependent on the number of carbon atoms (ca. 7 °C per additional carbon atom). Therefore, many values were tested, and the best agreement with the Fox equation was obtained when $(T_g)_F$ equaled 311 K (38 °C), which corresponds approximately to the melting point of a C₂₀ alkane.

It can be seen in Figure 5 that T_g 's of all of MEs and DEs were in good agreement with the Fox equation. TEs, however, did not behave in the same manner. We can also note that T_g of TEs did

not vary significantly when the nature of the fatty acyl substituent changed within the range studied [Fig. 3(a)]. This particular behavior of fully substituted cellulose esters is probably a reflection of a phenomenon previously described.⁶ When the acyl groups become long enough ($n \geq 8$) and when they are abundant (DS = 3), their mass represents at least 71% of the whole polymer (or 47% if calculated as the flexible methylene portion). Lateral chains can then readily associate with one another, creating local crystalline structures between the cellulosic backbones. An analogous behavior has also been observed in poly(*n*-octadecyl methacrylates).²¹ The cohesion of the cellulosic chains is then ensured exclusively by the interaction of the fatty chains. With an increasing temperature of the polymer, the local crystalline structures melt and cause a relaxation. The DSC endotherms for the melting of these local crystallites were described in a previous report.⁶ In DMTA testing, such a melting phenomenon appears to be the relaxation observed at the lower temperature (β transition). The lowest values obtained (Table 2) belong to the TEs bearing the longest side chains (ca. 40 °C). Surprisingly, such values agree with the best $(T_g)_F$ value found for the Fox equation.

It is clear that cellulose esters with longer aliphatic acyl groups (partially or fully substituted) can soften at lower temperatures than shorter chain cellulose esters (α transition). However, it is not clear why shorter side chains require a higher temperature to make evident their local motion than longer chains (β transition). Indeed, such a transition in MEs increases by about 150 °C when their acyl group length is reduced from C₁₈ to C₈. The natural folding of long chains is probably responsible. It is, therefore, possible to conceive that the thermal motion of the long chains is observed easily, that is, at lower temperatures, when they unfold and touch other molecules. For short chains, folding is less significant, and chains are more rigid; they protuberate and touch other molecules only punctually like the teeth of a comb. Their movement is more difficult to bring out, requiring higher temperatures to make it evident as a secondary transition. In other words, side chains not involved in crystalline domains would move but inside an unoccupied volume. Their movement would not, therefore, be detected, as it would not interact much with other molecular moieties.

This hypothesis is supported by the dependence of the β transition on DS [Fig. 3(b)]. The

local motion of lateral chains is revealed at lower temperatures when other side chains are close enough to interact (higher DS). Their contact is easily brought out, and the influence of the chain size becomes less important [the slope of the lines in Fig. 3(b) decreases with DS]. When cellulose is fully esterified (TEs), the interaction between side chains is maximal, and even if the aliphatic groups become more restricted in motion by entanglement with neighboring groups, their thermal movement is easily detected as a β transition.

We can notice in Figure 3 that both T_g and the β transition of TEs occurred at low temperatures but did not vary significantly with n in the studied range. However, most of all, their values were very close and sometimes overlapped. This suggests that the aliphatic local crystalline phases melt during heating from low temperatures and that the cellulosic chains gain mobility, giving rise almost simultaneously to both α and β relaxations. Such a phenomenon has also been observed in poly(*n*-alkyl methacrylates)²² and described as the coexistence of two dynamic glass transitions as a result of a nanophase separation.

Damping

Another surprising feature of TEs is revealed by a comparison of their damping curves. Figure 6 shows not only the dependence of T_g on n and DS but also the fact that the magnitudes of the damping peaks of MEs and DEs remained essentially constant (ca. 0.30) and independent of n . The same phenomenon occurred in the β transition of MEs and DEs (not shown), the $\tan \delta$ values of which were basically constant (0.16). By contrast, the damping magnitude of TEs varied significantly with n : cellulose trioctadecanoate showed a $\tan \delta$ value comparable to those of all of the MEs and DEs samples, but when the side-chain size decreased (cellulose trioctanoate), this magnitude increased twofold. Figure 7 summarizes the $\tan \delta$ values of all of the samples, illustrating the corresponding trends that seem to converge on the same $\tan \delta$ value (0.30).

In an attempt to explain the variable damping of TEs and the invariability of this parameter in MEs and DEs, the TMA transitions were investigated. The TMA T_g values paralleled the DMTA T_g values at about 10 °C lower. What is more interesting is that, at temperatures above T_g , the slopes of the dilatometric lines ($\partial V/\partial T$) varied with n (Fig. 2). The thermal expansion coefficient in the rubbery state decreased as the fatty side-

chain substituents became bulkier. This suggests that as the temperature increases, chains that are relatively short and stiff have less ability to adjust in space than longer and more flexible chains. The former, which protrude perpendicularly from the cellulosic chain, cause the thermal expansion to be directly translated into a magnified volume change, whereas longer aliphatic chains, which bend and accommodate themselves in more than one direction, possibly at the expense of free volume, cause a limited volume increase. This explanation is consistent with the interpretation of the observations on the β transition discussed previously. Moreover, it can account for the changes in the $\tan \delta$ values of TEs. The damping characteristics, that is, the energy that can be dissipated, vary with the length of the

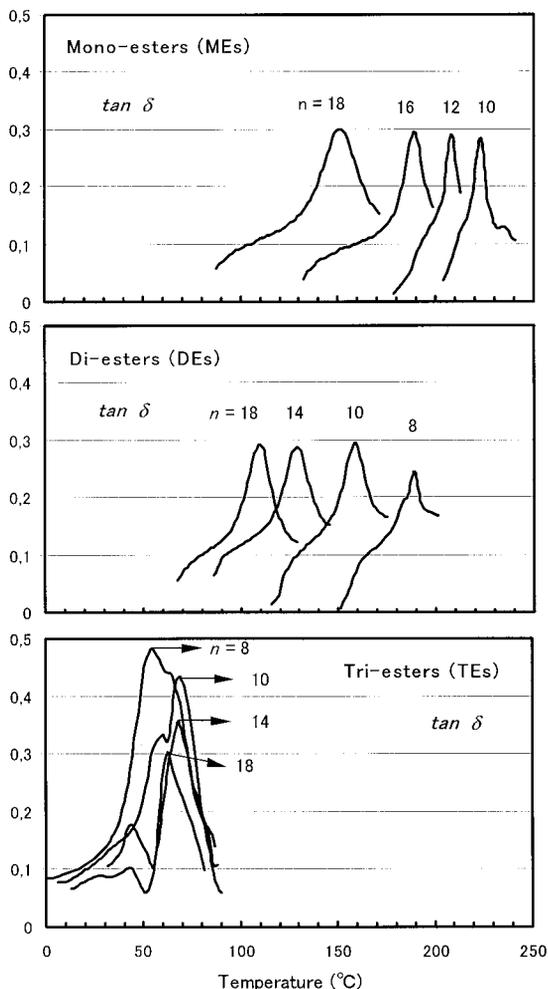


Figure 6. Damping ($\tan \delta$) curves for selected MEs, DEs, and TEs of cellulose with different fatty acyl substituents. Only the α transition (T_g) is shown for MEs and DEs.

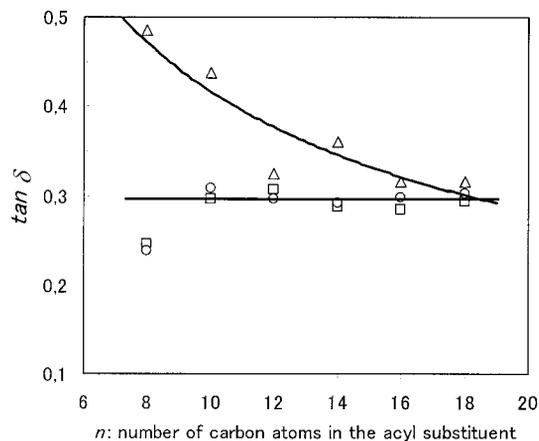


Figure 7. Damping ($\tan \delta$) magnitude of T_g for cellulose fatty esters: (○) MEs, (□) DEs, and (△) TEs.

side chains because the interaction between cellulosic molecules depends entirely on the aliphatic groups surrounding them. Cellulose TEs with relatively short aliphatic chains protruding from the cellulosic backbone possess more free volume than higher fatty esters. The former can, therefore, dissipate more energy. With increasing n , the free volume becomes occupied by a waxy mass, the material becomes more compact, and less energy is absorbed (lower damping). On the contrary, the molecular interactions in MEs and DEs depend not only on the chain length but also on the intermolecular and intramolecular hydrogen bonds. The OH functionality becomes the overriding factor in dictating the material properties of PSCEs.

E'

The E' data of the cellulose esters were collected from their DMTA curves below T_g (50 °C was the temperature for which common data were available). Figure 8 shows the behavior of $\log E'$ as a function of n for different values of DS.

It can be observed that the mechanical strength of the cellulose esters followed the same trend as the T_g behavior; that is, E' decreased with increasing n in MEs and DEs, but TEs kept relatively constant values. Furthermore, E' also decreased with increasing DS. It is interesting to note that the difference in the E' values observed between MEs (DS = 0.78 ± 0.18) and DEs (DS = 2.38 ± 0.11) was relatively small for an increase of 1.6 DS. When comparing the differences observed between DEs and TEs, we notice a higher variation of E' with an increase of only 0.6 DS, especially for low n values.

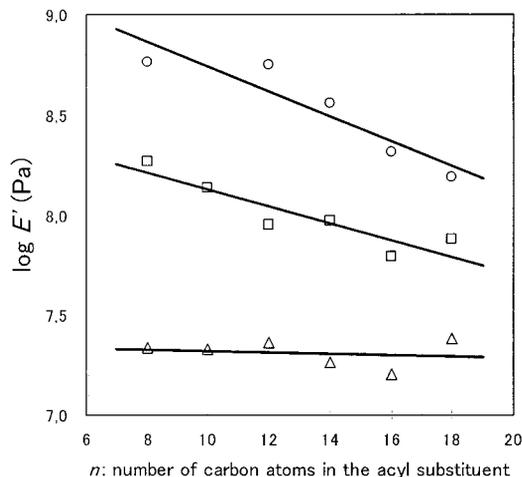


Figure 8. E' of fatty cellulose esters measured at 50 °C: (○) MEs, (□) DEs, and (△) TEs.

These data indicate that cohesion between cellulosic chains is substantially increased if at least a few hydroxyl groups (ca. 0.6 per anhydroglucose unit) remain unesterified. Larger quantities of free OH groups (ca. 2.2 per anhydroglucose unit) have only a moderate supplementary effect on cohesion. As far as mechanical properties are concerned, the interaction between cellulosic molecules by free hydroxyl groups in PSCEs is more important than the interaction due to the association of the fatty side chains in fully substituted cellulose esters. Consequently, TEs shows the lowest bending modulus. The practical importance of these observations is evident in choosing and processing a thermoplastic.

CONCLUSIONS

Cellulose fatty esters with different DS values, obtained by the acid chloride/pyridine method, show thermomechanical properties that depend on the length of the side chain and on the DS. An analysis of T_g , the thermal expansion coefficient, $\tan \delta$, and the dynamic elastic modulus shows that PSCEs behave in a very different way than fully substituted cellulose esters:

1. T_g and E' vary with n for PSCEs, whereas T_g and E' remains constant for cellulose fatty TEs.
2. Damping ($\tan \delta$) remains constant (independent of n and of DS) for PSCEs, but it varies with n for fully substituted cellulose esters.

The observed differences are mainly due to the interaction between the side chains in fully substituted cellulose esters and to the presence of unesterified OH groups in PSCEs, which increase the molecular interaction and dictate the mechanical properties of this kind of polymer.

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