

Thermal Softening and Melting of Esterified Wood Prepared in an N₂O₄-DMF Cellulose Solvent Medium*

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Synopsis

The thermal softening and melting of a series of esterified wood samples, whose preparation has previously been described,⁴ have been studied by measuring the deformation of the samples under constant load at a constant heating rate. The introduction of acyl groups into wood including part of the original crystal structure in cellulose makes the modified wood meal conspicuously thermoplastic. While untreated dry wood shows a thermal softening point (T_s) of ca. 260°C, esterified wood meal samples with acyl groups larger than caproyl have a T_s of around 100°C or less, and appeared to melt over the temperature range of 220° to 250°C. In this case, the melting occurs even with wood meal samples esterified with appropriate acid chlorides in an N₂O₄-DMF-pyridine medium only for 30 min at room temperature. This might be the first finding that wood meal is converted, as a whole, into a thermoplastic material which can melt without any accompanying detectable degradation.

INTRODUCTION

Although shortage of forest resources has become a matter of great concern these days, a way for effectively utilizing wood waste products has not been developed. For example, in spite of the fact that saw dust is an abundant by-product of the wood products industry, it is simply treated as waste material. To find a way for the effective utilization of saw dust, the thermal softening of isolated lignin, hemicellulose, and cellulose as well as wood^{1,2} together with the thermoplasticization of wood³ have been studied. In the previous investigation,^{1,2} the softening temperatures of lignin were found to range from 127° to 193°C, while hemicellulose softened in the region of 167° to 181°C and cellulose softened at temperatures greater than 240°C. Wood tended to soften at higher temperatures than 200°C. Goring¹ attributed the softening phenomenon to the fact that wood is not a random mixture of cellulose, hemicellulose, and lignin. Softening of wood is thus affected by the morphological arrangement of and chemical interconnection between the wood components.² In particular, it can be pointed out that cellulose plays an important role in the thermoplasticization of wood, and the crystalline nature of cellulose makes a large contribution to its higher softening temperature. Therefore, it can be postulated that chemical processes which can change the state of the interpolymer bond between wood components and, at the same time, reduce the crystallinity of cellulose in wood can bring about appreciable thermoplasticization of wood.

In this research, the thermal softening as well as the melting of a series of es-

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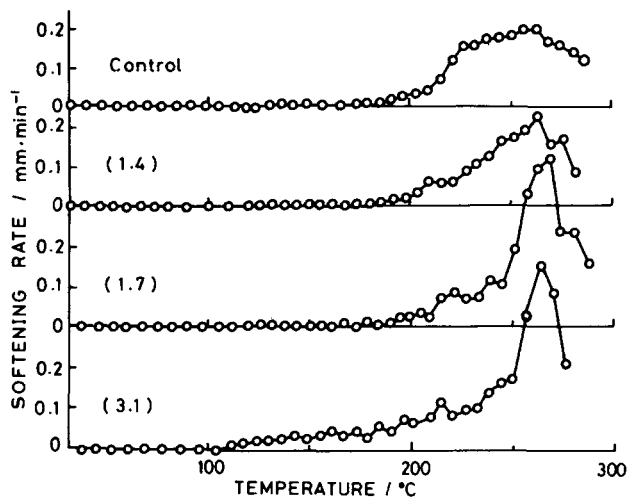


Fig. 1. Thermal softening curves for *n*-butyrylated wood samples prepared by reaction of wood meal with *n*-butyric anhydride in an N_2O_4 -DMF-pyridine medium. Numerical values in parentheses represent the substituent molality.

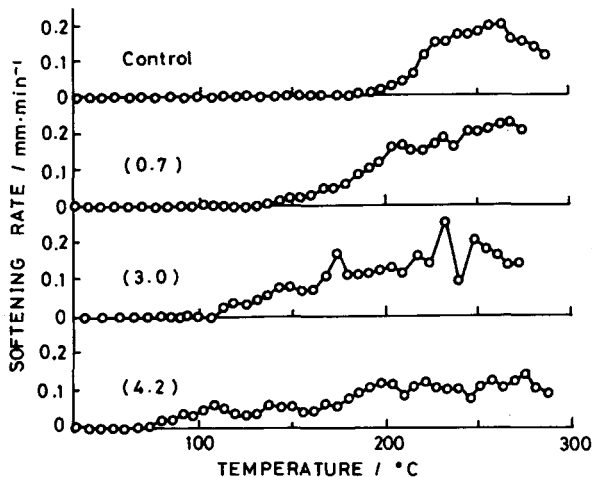


Fig. 2. Thermal softening curves for caproylated wood samples prepared by reaction of wood meal with caproic anhydride in an N_2O_4 -DMF-pyridine medium. Numerical values in parentheses represent the substituent molality.

terified wood samples, prepared as reported in the preceding paper,⁴ were studied.

EXPERIMENTAL

Samples

The samples used are a series of esterified wood meal samples (60–80 mesh) whose preparation has previously been described.⁴ These samples include a homologous series of fatty acid esters of wood from the propionate to the caproate and those from the caproate to the stearate. The former group was prepared by the reaction of wood samples with the appropriate acid anhydride in an

N_2O_4 -DMF-pyridine medium, and the latter was prepared with the acid chlorides in the same reaction medium.

Measurement of Thermal Softening and Melting

A softening temperature apparatus similar to that of Goring¹ and Chow² was used. Thermal softening and melting were observed as the collapse of a column of powder under a constant load in a heated glass capillary tube 3 mm in diameter. The measurement was conducted over the temperature range from room temperature to 300°C or to the melting temperature, at a constant heating rate of 3°C/min. The other experimental details were the same as those described by Goring.¹ The treatment of data was also based on the method of the previous example.¹

RESULTS AND DISCUSSION

Thermal Softening of a Series of Esterified Wood Samples from the Propionate to the Caproate Prepared by Reacting with Acid Anhydrides in an N_2O_4 -DMF-Pyridine Medium

As shown in the preceding paper,⁴ the reactivity of acid anhydrides toward wood is not large; but by virtue of the presence of an N_2O_4 -DMF mixture as the reaction medium, fairly permanent decrystallization is attained in the esterified wood. Therefore, some significant differences can be expected between the thermal softening behavior of esterified wood samples and that of untreated wood.

Typical thermal behavior for the chemically modified wood prepared by esterification with acid anhydrides in an N_2O_4 -DMF-pyridine medium is shown

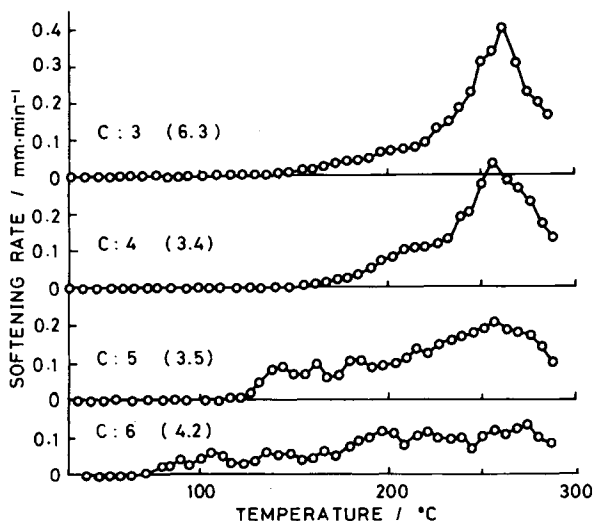


Fig. 3. Thermal softening curves for a series of esterified wood samples from the propionate to the caproate prepared by reacting with acid anhydrides in an N_2O_4 -DMF-pyridine medium: C:3, propionylated wood; C:4, isobutyrylated wood; C:5, valerylated wood; C:6, caproylated wood. Numerical values in parentheses represent the substituent molality.

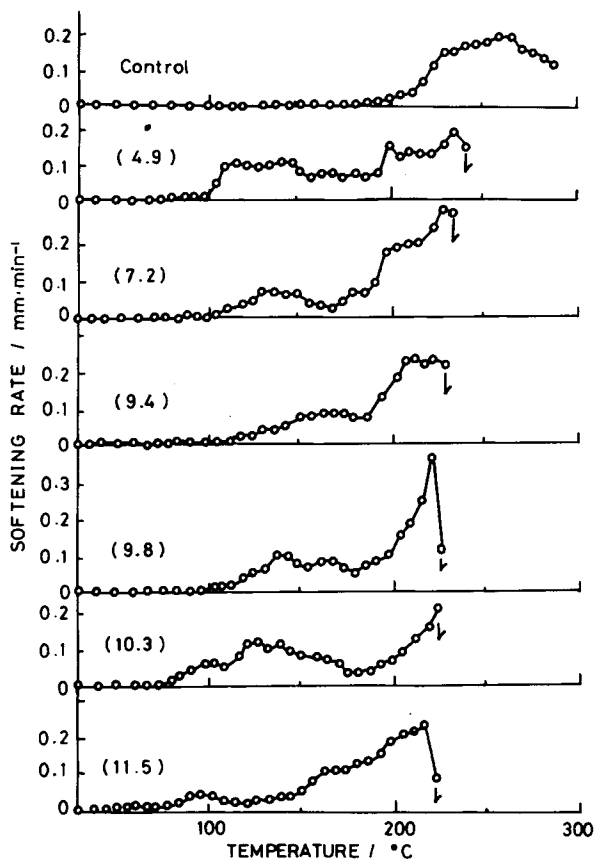


Fig. 4. Thermal softening curves for lauroylated wood samples prepared by reaction of wood meal with lauroyl chloride in an N_2O_4 -DMF-pyridine medium. Numerical values in parentheses represent the substituent molality.

TABLE I
Melting Points for a Series of Esterified Wood Samples from Caproate to Stearate Prepared by Reacting with Acid Chlorides in N_2O_4 -DMF-Pyridine Medium

Acyl chloride	Number of carbon atoms	Molarity of substituent	Melting point, °C
Caproyl	6	10.6	252
Capryloyl	8	10.5	250
Caprinoyl	10	9.4	240
Lauroyl	12	11.1	224
Palmytoyl	16	8.5	240
Stearoyl	18	9.2	224

in Figures 1 and 2. Oven-dry wood meal from the sapwood of Mankanba (*Betula maximowicziana* Regel) starts to soften near 190°C with a maximum softening peak at 270°C . On the other hand, in the cases of thermal behavior for esterified wood samples, the starting temperature of the thermal deformation decreases and the absolute softening grows larger with increasing substituent molality (ester content) and number of carbon atoms in the acyl group. The latter is confirmed in Figure 3 where the thermal behavior is compared for the homologous series of fatty acid esters of wood in which approximately 25–45% of the hydroxyl group

in wood is substituted. The trend can be considered reasonable if the change in the melting points of the corresponding cellulose esters as well as the degree of decrystallization are taken into account. These results show that even a comparatively small degree of cellulose esterification using low molecular weight acyl groups (less than six carbon atoms) can produce significant internal plasticization and thus a significant effect on thermal plasticization.

Thermal Softening of a Series of Esterified Wood Samples from the Caproate to the Stearate Prepared by Reaction with Acid Chlorides in an N_2O_4 -DMF-Pyridine Medium

Figure 4 shows the thermal softening behavior of lauroylated wood samples prepared by the reaction of wood samples with lauroyl chloride in an N_2O_4 -DMF-pyridine medium. Relatively small softening peaks, presumably made from the superposition of many peaks, appear at temperatures below $200^\circ C$. These peaks can be attributed to the melting of lauroyl cellulose with various degrees of substitution within the wood structure. There is a marked lowering of the softening temperature with increase in the ester content.

What is important, however, is that there is a second softening peak ending with the thermal melting of the sample. An arrow is used in the figure to designate the melting point of the sample. The starting point of the second softening peak also decreases with increasing ester content, but the melting temperature only decreases until a constant value of $225^\circ C$ is attained. It is also important to note that the melting can be observed with a sample having the

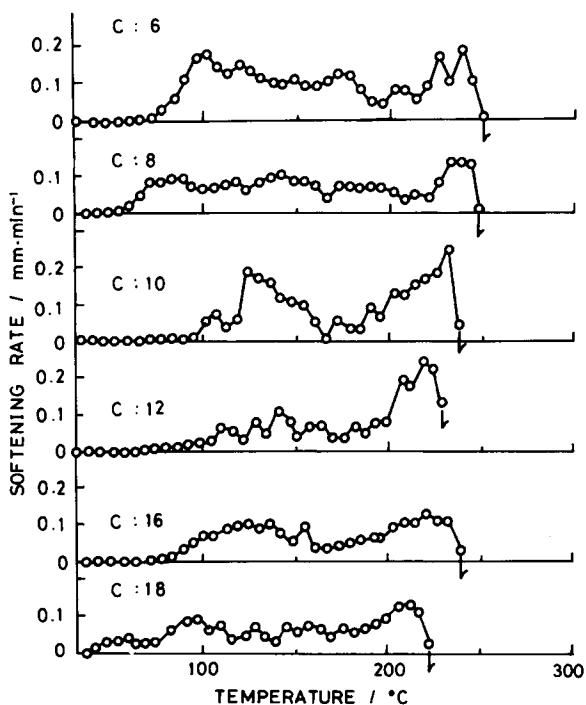


Fig. 5. Thermal softening curves for a series of esterified wood samples from the caproate to the stearate prepared by reacting with acid chlorides in an N_2O_4 -DMF-pyridine medium: C:6, caproylated wood; C:8, capryloylated wood; C:10, caprynoylated wood; C:12, lauroylated wood; C:16, palmytoylated wood; C:18, stearoylated wood.

lowest value of the substituent molality of 4.9. As known from the preceding paper,⁴ the lauroylated wood with the substituent molality of 4.9 can be prepared by reacting wood samples with lauroyl chloride in an N_2O_4 -DMF-pyridine medium only for 30 min at room temperature. This might be the first finding that wood meal is converted, as a whole, into a thermoplastic material which can melt at temperatures around 230°C.

The thermal behavior of a series of esterified wood samples from the caproate to the stearate having almost the same degree of substitution is shown in Figure 5. Table I shows the data characterizing the samples and the melting point observed. The pattern of the thermal behavior is similar for these samples showing very low starting points for thermal softening and final melting. The melting temperature decreases with increase in the number of carbon atoms in the acyl group. Anyway, the occurrence of the melting of the sample is quite different from the results of the preceding section and suggests a possible way of effectively utilizing wood waste products such as saw dust in molding composites or hot melt adhesives.

Degradation of Esterified Wood During Chemical Processing and Thermal Treatment

There is a possibility of chemical wood degradation during the esterification process with acid anhydrides or acid chlorides in an N_2O_4 -DMF-pyridine medium. There is the further possibility that some degradation might occur during the thermal treatment. If the melting of the chemically modified wood, found in the preceding section, is chiefly caused by these kinds of degradation, the phenomenon of melting is not worthy of further study. Based on this, therefore, the occurrence of degradation during the chemical modification and thermal melting processes has been examined briefly.

First, esterified samples having a substituent molality of 3.45 or 7.51 were saponified with 0.5*N* alcoholic alkali for 22 hr at room temperature and the

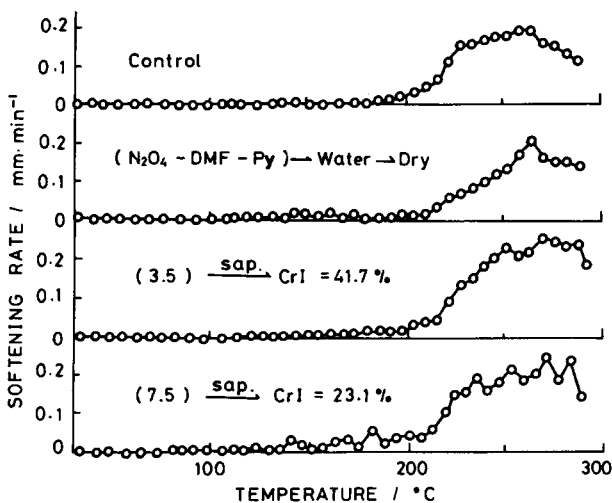


Fig. 6. Comparison of thermal softening curves for saponified wood samples with those for a decrystallized and an untreated sample. Lauroylated wood samples having a substituent molality of 3.45 and 7.51 were saponified with 0.5*N* alcoholic alkali. Decrystallization was made by using an N_2O_4 -DMF-pyridine solution.

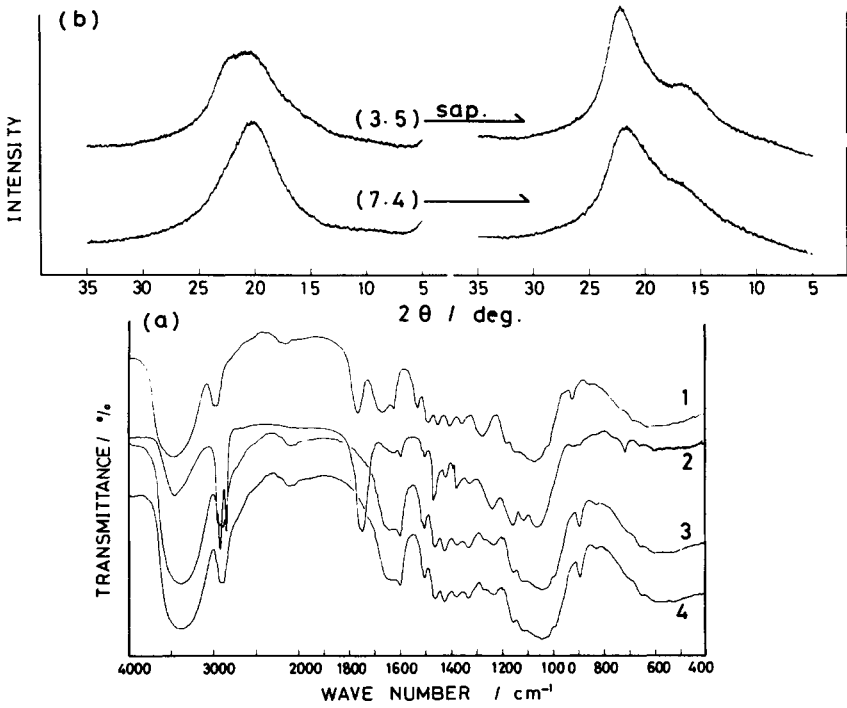


Fig. 7. Comparison of (a) IR spectra and (b) x-ray diffraction curves for saponified wood samples with those for the corresponding lauroylated wood. (a) 1, untreated wood; 2, lauroylated wood having the substituent molality of 7.51; 3, saponified wood from untreated wood; 4, saponified wood from lauroylated wood. (b) Numerical values in parentheses represent the substituent molality.

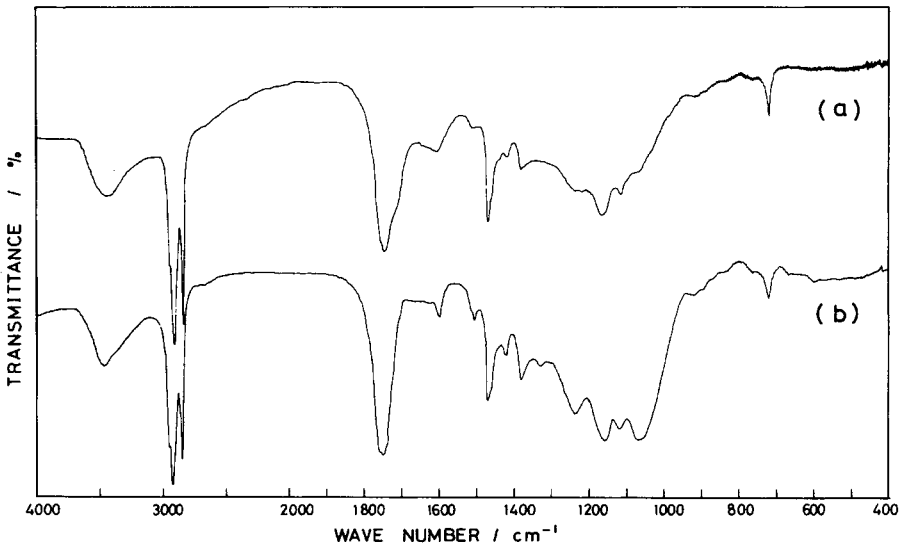


Fig. 8. Comparison of IR spectrum for (a) stearylated wood after heat treatment up to 290°C with that for (b) lauroylated wood without heat treatment. The substituent molality of both samples are almost the same.

thermal behavior of the saponified wood samples was studied. In Figure 6, the resultant thermal softening of the saponified wood samples is compared with that of untreated wood and decrystallized wood. All of these wood samples show essentially the same pattern. As shown in Figure 4, lauroylated wood having a substituent molality more than 4.94 (an ester content of more than 90.4%) appears to melt. However, these samples, after saponification, do not show any melting behavior and have almost the same pattern of deformation against temperature as that of untreated wood after saponification (Fig. 6).

That the complete removal of the acyl group by this saponification had occurred was proved by IR spectroscopy as shown in Figure 7(a). Also in this figure, a comparison of curve 3 with that of 4 indicates that the esterification procedure utilizing acid chlorides as acylating agents and an N_2O_4 -DMF-pyridine solution as the reaction medium does not cause any detectable degradation. On the other hand, from Figure 7(b) it is found that cellulose I diffraction at 22 and 15 to 16 degrees reappears in the saponified samples, although corresponding lauroylated wood samples exhibit x-ray diffractograms characteristic of fairly advanced decrystallization of cellulose which is appreciably superimposed with the cellulose laurate pattern.

In conjunction with results from thermal softening analysis, IR spectra, and x-ray diffractions, the chemical procedure for obtaining esterified wood utilizing acid chlorides and the cellulose solvent was found to cause neither detectable physical nor chemical changes. On the other hand, in connection with these experiments, it is noteworthy that even higher aliphatic acid esters of wood such as lauroylated wood can be saponified completely by reacting with dilute alcoholic alkali solution (0.5N KOH) for 22 hr at room temperature. This finding that higher esters of cellulose can be saponified within the wood cell wall structure is interesting because saponification of the corresponding higher esters of isolated cellulose is almost impossible under these conditions.

Figure 8 shows an IR spectrum for stearylated wood after it was heated up to 290°C, at which temperature the sample melted. An IR spectrum for lauroylated wood without any heat treatment is also shown in the same figure for comparison. There are no meaningful changes in major peaks at 3400 (OH stretching), 2900 (CH stretching) and 1750 (C=O stretching) cm^{-1} between the spectra. That is, upon heating to the melting point, the IR spectrum of esterified wood shows essentially the same spectrum as that at room temperature. This result indicates that no evident degradation occurs even after heating the esterified wood at 290°C for a short time (3 min).

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