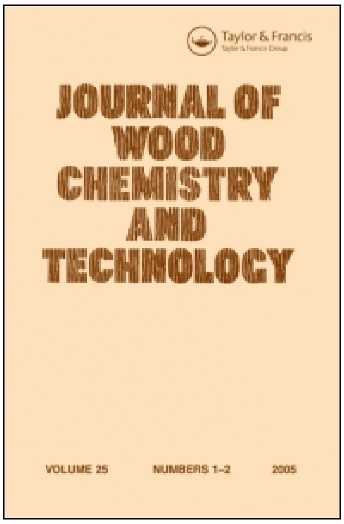

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EFFECT OF THE EXPLOSION PRETREATMENT ON THE THERMAL SOFTENING AND MELTING OF ESTERIFIED WOOD

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SYNOPSIS

The explosion treatment has been used with the objective of increasing the accessibility of wood. After the explosion treatment wood meal was esterified. Acyl groups introduced were acetyl, caproyl and lauroyl. Caproylation was carried out by three different methods - PCA catalyst method, TFAA catalyst method and DMF/PY/acid chloride method. The PCA catalyst method was not used for lauroylation since it is not an effective procedure for introducing higher acyl groups. The DMF/PY/acid chloride method could not be used successfully for acetylation. Thermal softening and apparent melting behaviour of the exploded-esterified wood meal was studied by following the collapse of a column of powder under a constant load in a glass capillary tube 3 mm in diameter at a programmed rate of heating.

Samples exploded at various conditions and esterified by the DMF/PY/acid chloride method showed thermal flow in nearly the same temperature range. The thermal flow was observed at considerably lower temperature for the corresponding samples acylated by TFAA catalyst method. Also, the thermal softening or apparent melting

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temperature (flow temperature) of the samples acylated by TFAA method was found to be dependent on the condition of explosion. The more severe the explosion treatment, the lower was the flow temperature. In other words, an increase in the explosion temperature or duration at a particular temperature resulted in a decrease in the thermal softening or melting temperature. This fact has been attributed to the loosening of wood texture in combination with the action of trifluoroacetic acid (TFA) formed during the acylation by the TFAA method.

The larger the size of the acyl group introduced the lower the flow temperature became.

INTRODUCTION

Nowadays increasing shortages demand an effective utilization of organic resources. As far as the forest industry is concerned, total utilization of wood waste products such as saw dust and wood remnants from the forest is desirable. And with irregular supplies of petroleum and oil, efforts need to be directed towards developing new or modifying existing plastics in order to at least in part, replace or reduce the dependence on petroleum-based plastics.

In our previous work[1)] we have reported on the thermoplasticization of cellulose and wood by graft copolymerization and acylation in combination with graft copolymerization. We have also reported on the thermoplasticization of wood by chemical modifications using non-aqueous cellulose solvents and special solvent systems like N_2O_4-DMF-pyridine[2,3)] and DMSO-PF[4)]. The chemically modified wood was shown to flow under heat and pressure. The present work was aimed to enhance the thermoplastic properties of wood. It is known that any treatment that changes the state of interpolymer bonds among wood components and, at the same time, reduces the crystallinity of cellulose in wood results in remarkable thermoplasticization of wood. The chemical modifications do achieve this purpose. It was thought that a treatment which results in the loosening of the morphological texture of wood, in combination with chemical modifications, might improve the thermoplastic properties of wood.

Wayman and Lora[5)] extensively studied the autohydrolysis of wood with steam at elevated temperatures. The autohydrolysis of wood is catalyzed by the organic acids formed from the wood components during the hydrolysis. The temperature and duration of autohydrolysis of wood determine the changes taking place in the main constituents of wood. A small part of cellulose is rendered water soluble. Hemicelluloses are degraded to soluble sugars and under more drastic conditions partly converted to furfural and hydroxymethyl furfural by dehydration. Lignin, at the initial stages, is depolymerized to oligomers which can be extracted by using organic solvents. However, under prolonged duration these oligomers repolymerize and form highly condensed unextractable lignin. There is an optimum time at each autohydrolysis temperature for maximum lignin solubility. They are about 80 min at 175°C, 60 min at 185°C, 25 min at 195°C and 16 min at 205°C and 4 min at 215°C.

We have used the IOTECH explosion process[6)], but at milder conditions, to increase the accessibility of wood towards chemical reactions. In light of Wayman and Lora's results, it can be said that the explosion treatment employed in the present work involves mainly the first fast reaction — the breaking of lignin - carbohydrate bonds as well as the depolymerization of lignin thus resulting in the loosening of wood texture. This has been supported by our recent work[7)]. Thus, it was anticipated that the exploded wood meal with its modified morphology would allow smooth and uniform introduction of acyl groups.

EXPERIMENTAL

Explosion Treatment The wood species used in the present research was White Birch (Betula platyphylla var. japonica). Since our aim was to render the whole wood thermoplastic, the wood meal without any pretreatment was subjected to explosion process. We preferred wood meal to wood chips because at lower temperature and shorter durations the latter did not result in a powder of a size suitable for subsequent chemical modification. Wood meal of

40 - 80 mesh was steam exploded at arbitrarily determined temperatures for definite times with a rapid decompression. Temperatures selected were 210°C, 190°C and 170°C for four different durations 15, 10, 5, and 2 min at each temperature. After explosion the whole of the sample including water formed from the steam used for explosion was collected, without isolating or removing any fraction, and then freeze-dried.

Acylation by PCA Catalyst Method The exploded – freeze dried samples were further dried in a vacuum oven at 40°C for 24 h. The completely dried wood meal was pretreated with a mixture of acetic acid and acetic anhydride at room temperature for 15 h. The acylating mixture containing aliphatic acid anhydride and catalyst PCA (perchloric acid) was added and allowed to stand at room temperature for 1 h followed by shaking at 35°C for 3 h. The reaction was stopped by adding an acetic acid solution of potassium carbonate (1.03%) and shaking at 35°C was continued for a further 30 min. The esterified wood meal was recovered and dried.

Acylation by TFAA Catalyst Method Acylation by TFAA (trifluoroacetic anhydride) catalyst method was carried out in the same manner as described in a previous report8) except that no solvent was used in the present case.

Acylation by DMF/PY/Acid Chloride Method Caproylation and lauroylation of wood meal were carried out at 100°C for 7 h, using DMF (dimethylformamide) as a solvent. The reaction products were recovered and dried. Other experimental conditions were similar to those described in an earlier report9).

Determination of Thermal Softening and Apparent Melting Point (Flow Temperature) About 20 mg of the exploded-esterified-dried wood meal was used for this purpose. Thermal softening and apparent melting point (flow temperature) were observed as the collapse of a column of powder under a constant pressure of 3 kg per square centimeter at a programmed rate of heating 1°C/min. The thermomechanical analyzer used was Sinku Rico Co. Ltd., TM 3000. The measurements were conducted automatically at temperatures ranging from 20 to 350°C.

Crystallinity Measurements Portions (0.5g) of the exploded-dried samples were compressed under 3.0 ton/cm^2 pressure to give pellets of 2.0 cm diameter. The diffraction patterns, using these pellets, were measured from 40° to 3° values of 2 θ with Ni-filtered Cu-Kc radiation at 35 kV and 20 mA. The instrument used was Rigaku Denki Geiger Flex 2011 B wide-angle X-ray diffractometer. The operating conditions were the same as described in a previous report$^{10)}$.

Crystallinity indexes were calculated from the diffractograms by an empirical method based on that of Segal et al.$^{11)}$ In this method, the diffractogram height at the position of the 002 peak (2 θ = 22.6°) and at suitable locations for the amorphous background (2 θ = 19.0°) were used to calculate the percentage of crystalline material from the relation.

$$\% \text{ Cr} = \frac{I_{002} - I_{am}}{I_{002}} \times 100$$

This method gives only a relative set of values, but is useful in rating a series of samples with respect to one another.

RESULTS AND DISCUSSION

The results obtained can be divided into three groups depending upon the method of acylation as shown in Table 1. None of the samples esterified with PCA catalyst method show a complete thermal flow except the one which was exploded at 210°C for 15 min and acetylated. Fig. 1A shows thermograms of the samples exploded at 210°C for 15 and 10 min and acetylated, along with the one exploded at 210°C for 15 min and caproylated. These thermograms were obtained by plotting deformation of the sample against temperature. Only in the case of the sample exploded at 210° for 15 min and acetylated did the deformation reach a value of 1.0 which means a complete flow occurs. The PCA catalyst method of acylation is a mild one and is known as an inadequate procedure for introducing

TABLE 1

Flow temperature (^{o}C) of the exploded-acylated wood meal

Explosion temp. ^{o}C		$210^{o}C$				$190^{o}C$				$170^{o}C$			
Explosion duration min.		15	10	5	2	15	10	5	2	15	10	5	2
Acetylation	PCA method	300	300*	310*	305*	295*	295*	300*	—	305*	300*	326*	—
	TFAA method	290	295	290	290	285	280	285	275	280	285*	285*	285*
Caproylation	PCA method	320*	325*	330*	330*	320*	335*	320*	320*	315-340*	320*	305*	295*
	DMF/PY/Acid choride method	246	250	255	255	260	260	270	270	260	260	275	270
	TFAA method	135	145	160	185	185	185	195	195	—	200	200	205
Lauroylation	DMF/PY/Acid chloride method	200	200	195	200	200	200	195	215	210	215	205	210
	TFAA method	120	125	145	160	150	160	170	180	170	185	180	185

• indicates incomplete flow

higher acyl groups. This has been confirmed by determining the degree of substitution. First, the samples were analyzed for ester content[12)] and using this value the degree of substitution was calculated assuming that one gram of the wood meal contains 13 mMol of hydroxyl groups[13)]. The degree of substitution was found to be 76% and 40% for the acetylated and caproylated samples, respectively. That is why, the sample exploded at 210°C for 15 min and caproylated does not show flow behaviour though the sample exploded under the same condition and acetylated flows at around 300°C. Hence, this method was not used for introducing lauroyl groups. Fig. 1B shows the plots of deformation rate against temperature for the same samples.

Malm and co-workers[9)] prepared a series of organosoluble cellulose esters from the propionate through the palmitate by the acid chloride-pyridine procedure. They used 1,4 dioxane as a solvent and carried out the reactions at steam-bath temperatures for 20-24 hr. Sufficient analytical data were furnished to show that the higher homologues of cellulose esters thus prepared were fully esterified and had substantially the same degree of polymerization as the original cellulose. However, it is known that the use of acetyl chloride and pyridine does not yield satisfactory cellulose acetates, because of side reactions. Acetyl chloride and pyridine react to form a stable addition compound which takes part in the subsequent reaction resulting in the introduction of chlorine and nitrogen into the final product. Hence, acetylation by the pyridine-acetyl chloride method was not attempted. The lauroylation and caproylation was carried out at 100°C for 7 h as described in the experimental section. Samples caproylated or lauroylated by this method showed a complete flow. However, the flow temperature of all the samples, though it depends upon the size of acyl group introduced, was only slightly affected by the explosion conditions. For the caproylated samples it ranges from 245°C (for the sample exploded at 210°C for 15 min) to 275°C (the sample exploded at 170°C for 5 min) and for the lauroylated samples it ranges from 195°C to 215°C. To illustrate this, the

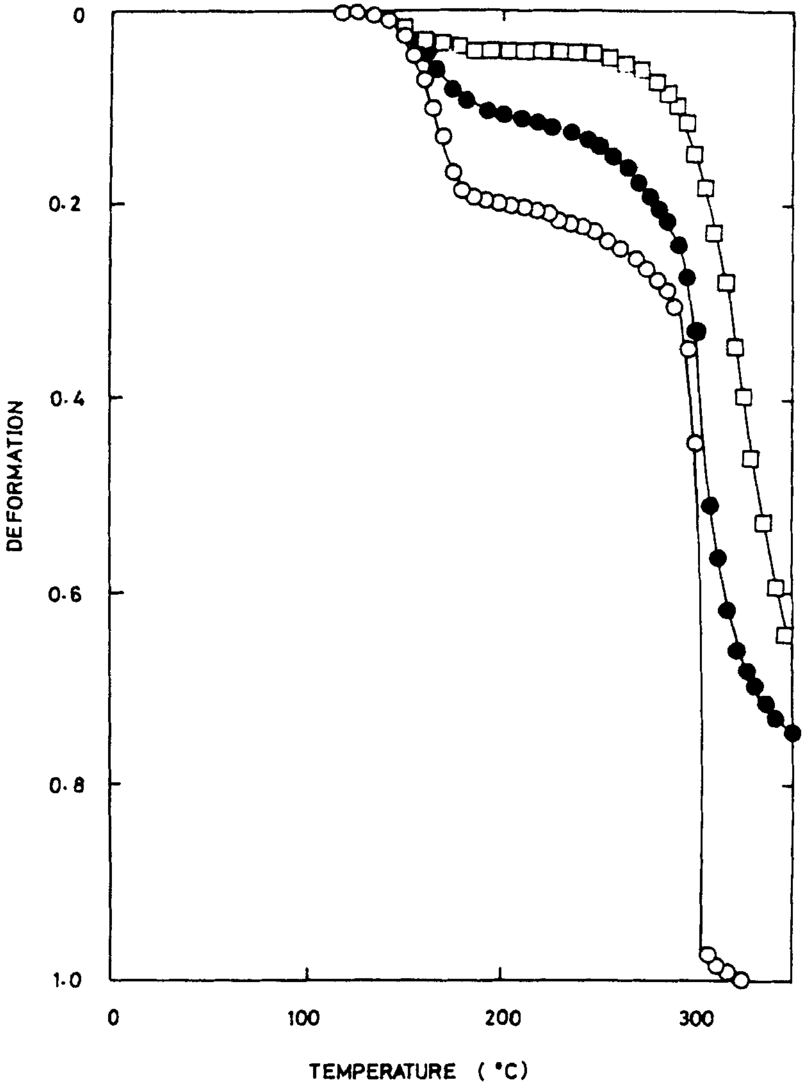

Fig. 1A Deformation as a function of temperature for the samples acylated by PCA method. o exploded at 210°C for 15 min—acetylated; ● exploded at 210°C for 10 min—acetylated; □ exploded at 210°C for 15 min—caproylated

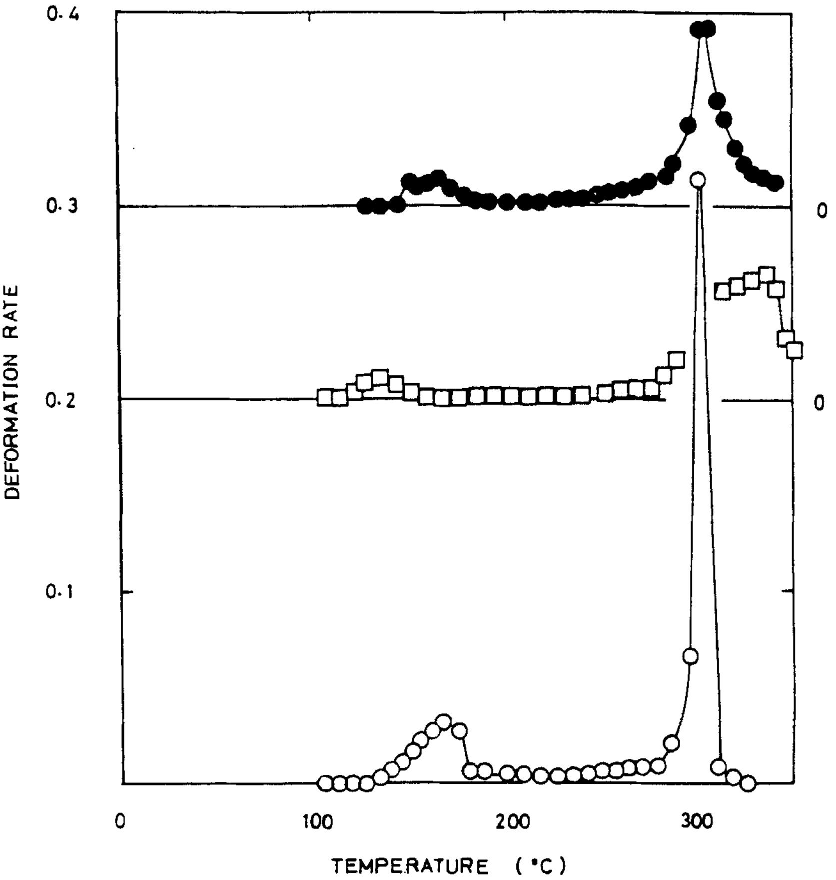

Fig. 1B Deformation rate as a function of temperature for the samples shown in Fig. 1A

thermograms of the samples exploded at different conditions and lauroylated are shown in Fig. 2A (deformation against temperature) and 2B (deformation rate against temperature). From these figures and Table 1 it can be said that though the flow temperature is in the same range irrespective of the explosion conditions it tends to decrease slightly as the explosion becomes more severe. But the effect of explosion conditions on the thermal behaviour of the samples exploded and esterified by DMF/PY/acid chloride method is not conspicuous.

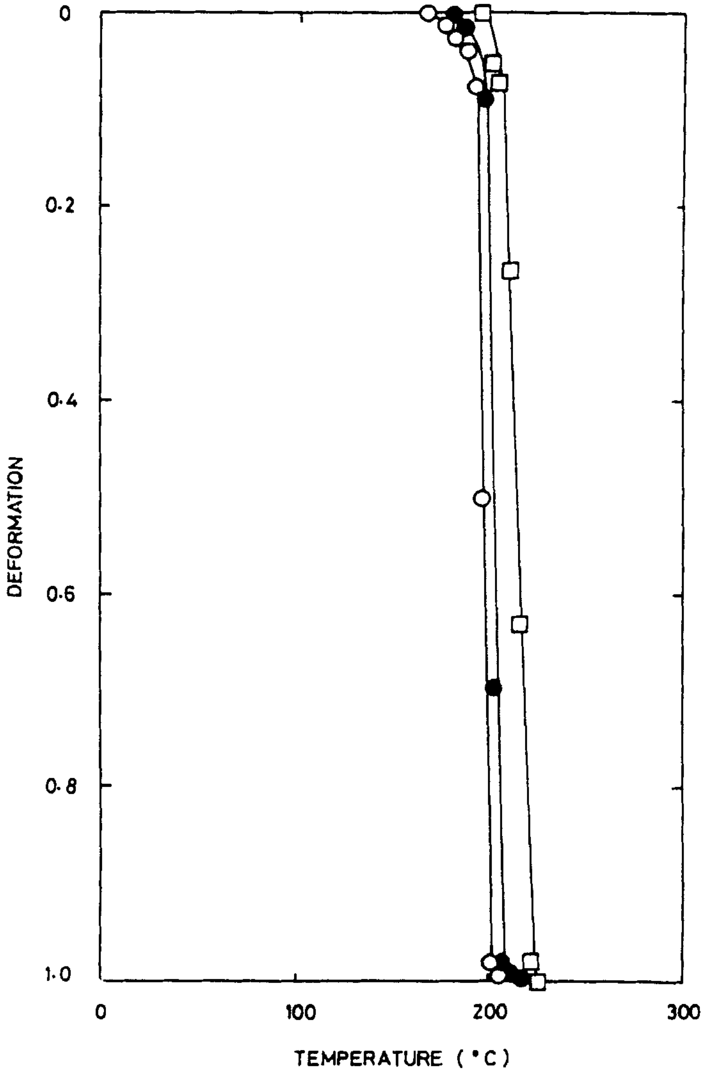

Fig. 2A Deformation as a function of temperature for the samples lauroylated by DMF/PY/acid chloride method. Explosion conditions were o 210°C/5 min, ● 190°C/10 min and ☐ 170°C/10 min

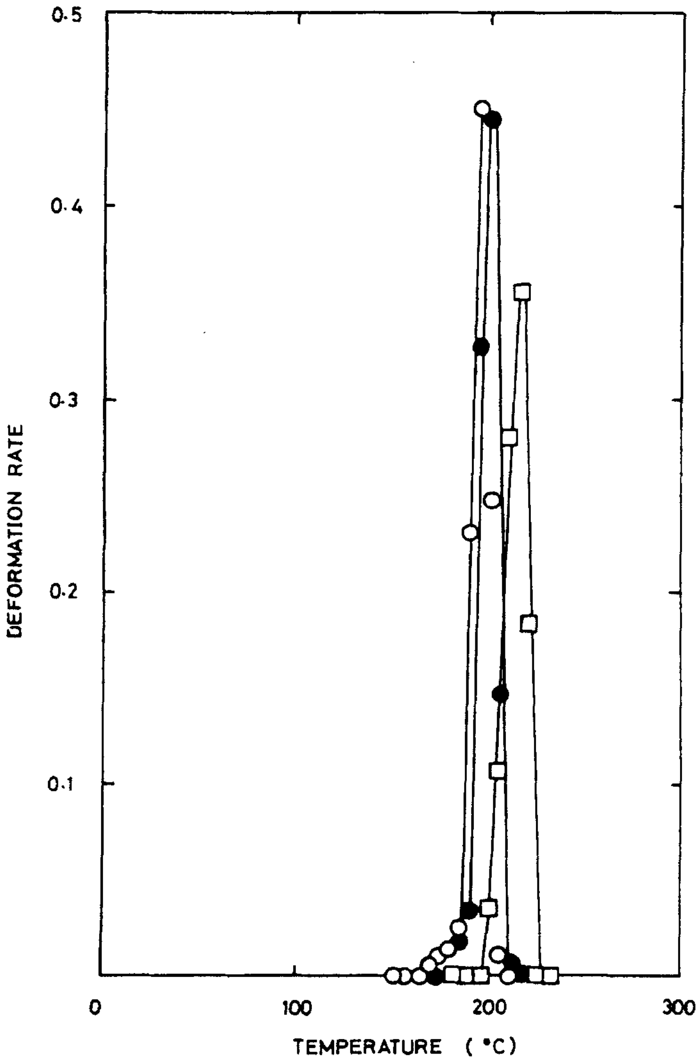

Fig. 2B Deformation rate as a function of temperature for the samples shown in Fig. 2A

All samples acetylated by the TFAA method showed a complete flow except the samples exploded at the milder conditions of 170°C for 5 and 2 min (Table 1), and the flow occured in the relatively small range of 275°C to 290°C. On the other hand, the flow temperature of the samples caproylated and lauroylated by TFAA method seems to be affected by the explosion conditions. That is, as the explosion condition became more severe the sample melted at lower temperature. This phenomenon is shown in Fig. 3A and 3B. Fig. 3A shows the plots of deformation against temperatures for products exploded at 210°C, 190°C and 170°C but for same duration — 15 min, followed by lauroylation with TFAA method. In all cases the deformation reaches a value of 1.0 indicating a complete flow. But the flow temperature was different in all these three cases. It was 120°C, 150°C and 170°C for the samples exploded at 210°C, 190°C and 170°C, respectively. This means, there is a steady decrease in the flow temperature as the explosion is carried out at increasing temperature. Thermograms obtained by plotting deformation rate against temperature for the same samples are shown in Fig. 3B. The explosion duration also plays a similar role in determining the flow temperature in case of the samples caproylated or lauroylated by TFAA method. The results are shown in Fig. 4A and 4B. Fig. 4A shows the plots of deformation against temperature while deformation rate against temperature is depicted in Fig 4B for the samples which were exploded at 210°C for different durations 15, 10, 5 and 2 min followed by lauroylation with TFAA method. The flow temperature seems to be inversely related to the explosion duration. It was 120°C, 125°C, 145°C and 160°C for the samples exploded at 210°C for 15, 10, 5 and 2 min, respectively. Thus, it seems that, for the samples caproylated (Table 1) or lauroylated (Fig. 3A, 3B, 4A, 4B and table 1) by TFAA method, there is a steady decrease in flow temperature at increasing explosion temperature or longer duration at a particular temperature.

The above experimental results obtained on the thermal behavior of the wood acylated by the TFAA method can be explained in terms of the effects of the explosion pretreatment and also in terms of the apparent melting temperatures of acylated wood components. As was shown in our previous report7), the explosion pretreatment employed in the present work results in the loosening of wood texture. Baldwin and Goring14) also showed that steam-cooked chips yielded thermomechanical pulp with a low glass transition temperature, and the action of steaming was interpreted as loosening the interpolymer bonds between cellulose, hemicellulose and lignin macromolecules in wood. Wayman and Lora5) have studied the autohydrolysis of aspen wood meal over a wide range of temperature (175-215°C) for varying duration, as mentioned in the introduction section. Our conditions of explosion treatment would cause considerable breaking of lignin-carbohydrate bonds and also depolymerization, especially of hemicellulose and lignin within the wood. Because of chemical degradation of hemicellulose and lignin caused by the explosion treatment, the apparent melting temperature of the acylated wood thus prepared tends to be governed by that of the cellulose acylate as the major component in the acylated wood. This trend becomes more conspicuous as the conditions of the explosion treatment became more severe. Then, accordingly, a conspicuous difference was noted between the thermal behavior of acetylated wood and caproylated or lauroylated wood. In the case of acetylated wood, the apparent melting temperature of cellulose acetate gave the highest value among the acetylated wood components. In fact, the apparent melting point of cellulose triacetate is around 300°C, whereas that of acetylated hardwood lignin and acetylated hemicellulose (xylan) are 140 °C and 210°C, respectively15). This is the reason why a series of samples acetylated by TFAA method have almost the same apparent melting temperature in the range of 275-295°C. The slight lowering in the melting temperature compared with that of cellulose acetate, in this case, is considered to be caused from the "external plasticization" effect of degraded and acetylated lignin. The occurence of mutual interaction and plasticization among acetylated wood components has already been proved15). On the other hand, in the cases of caproylated and lauroylated wood, the apparent melting

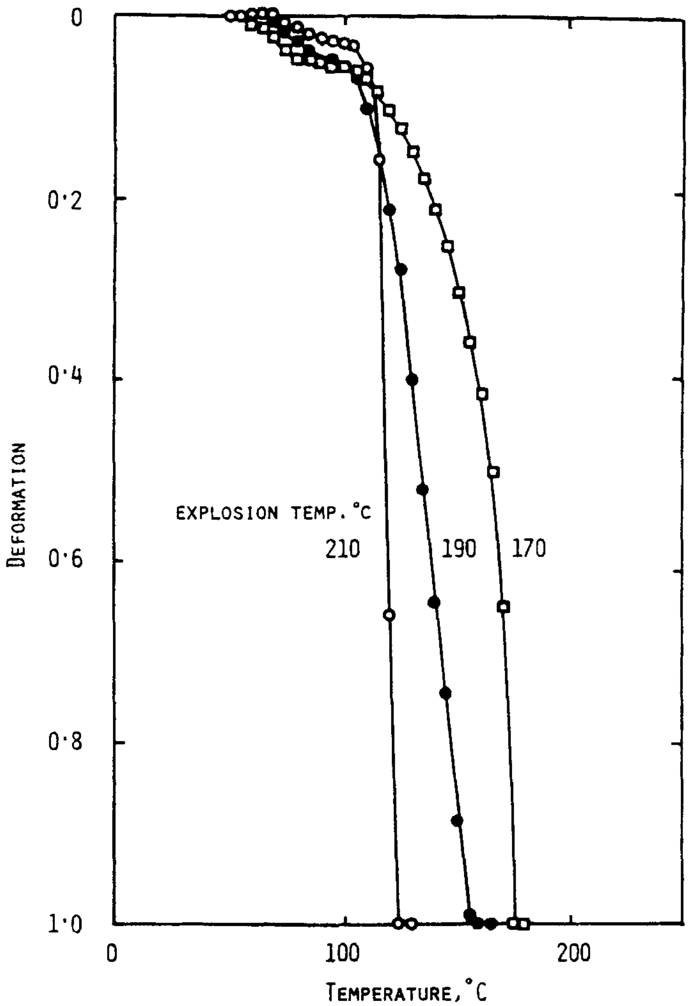

Fig. 3A Effect of the explosion temperature on the thermal behaviour of the samples lauroylated by TFAA method. Explosion duration : 15 min, explosion temperature : o 210°C, ● 190°C and □ 170°C

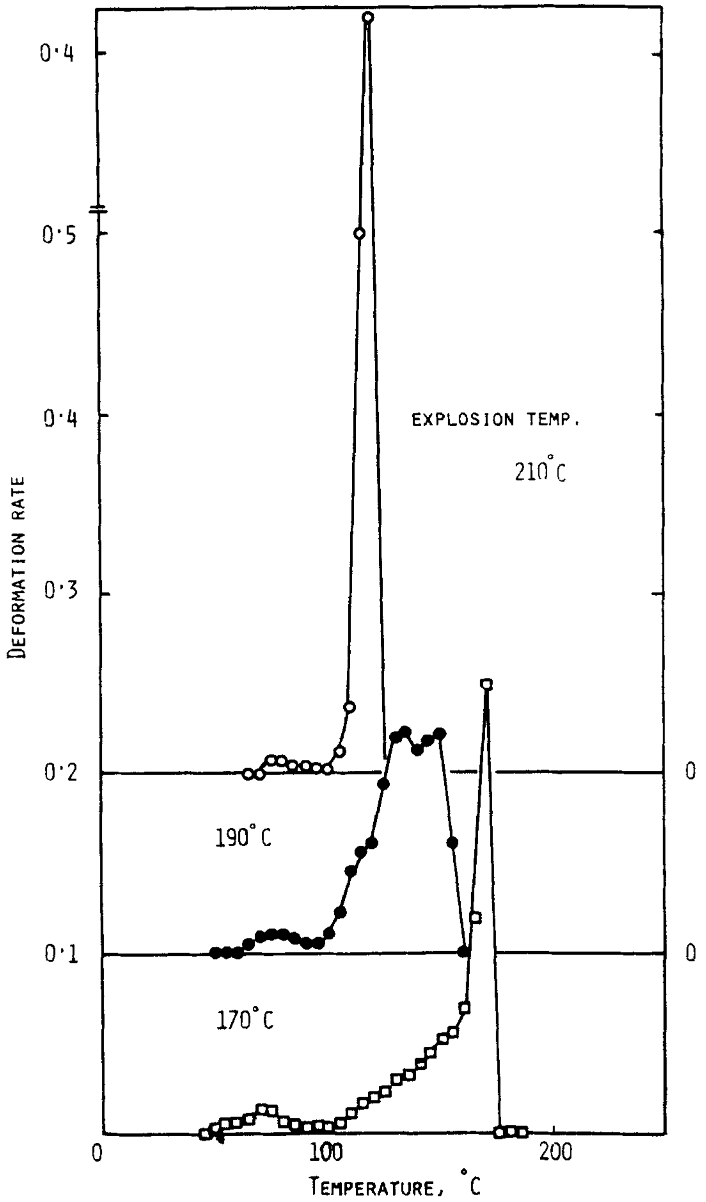

Fig. 3B Deformation rate as a function of temperature for the samples shown in Fig. 3A

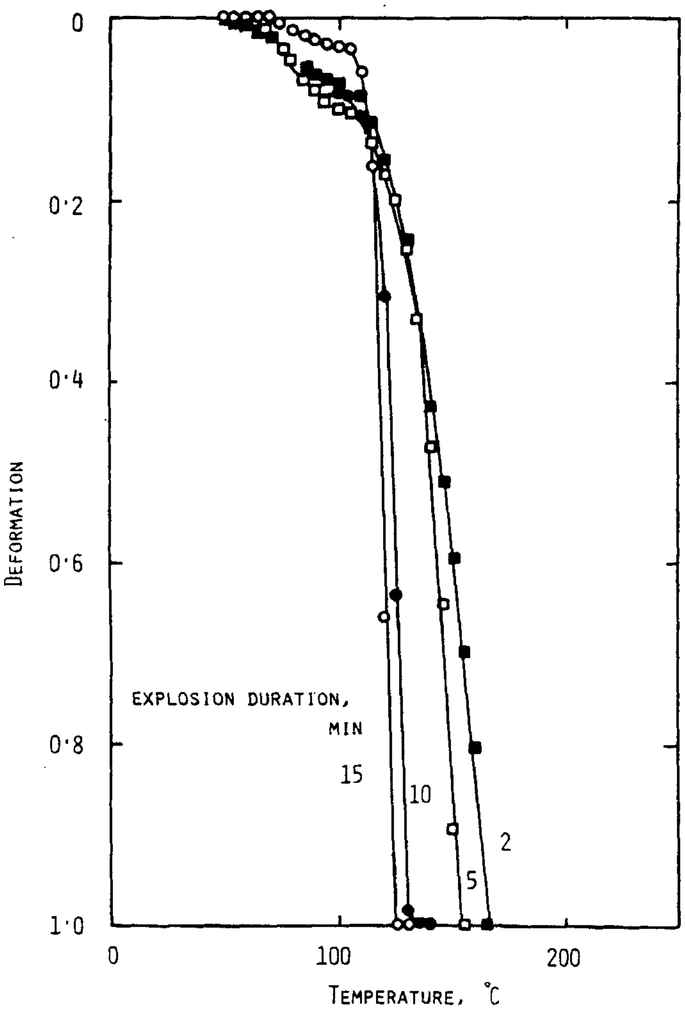

Fig. 4A Effect of the explosion duration on the thermal behaviour of the samples lauroylated by TFAA method. Explosion temperature : 210°C, explosion duration : ○ 15 min; ● 10 min; □ 5 min and ■ 2 min

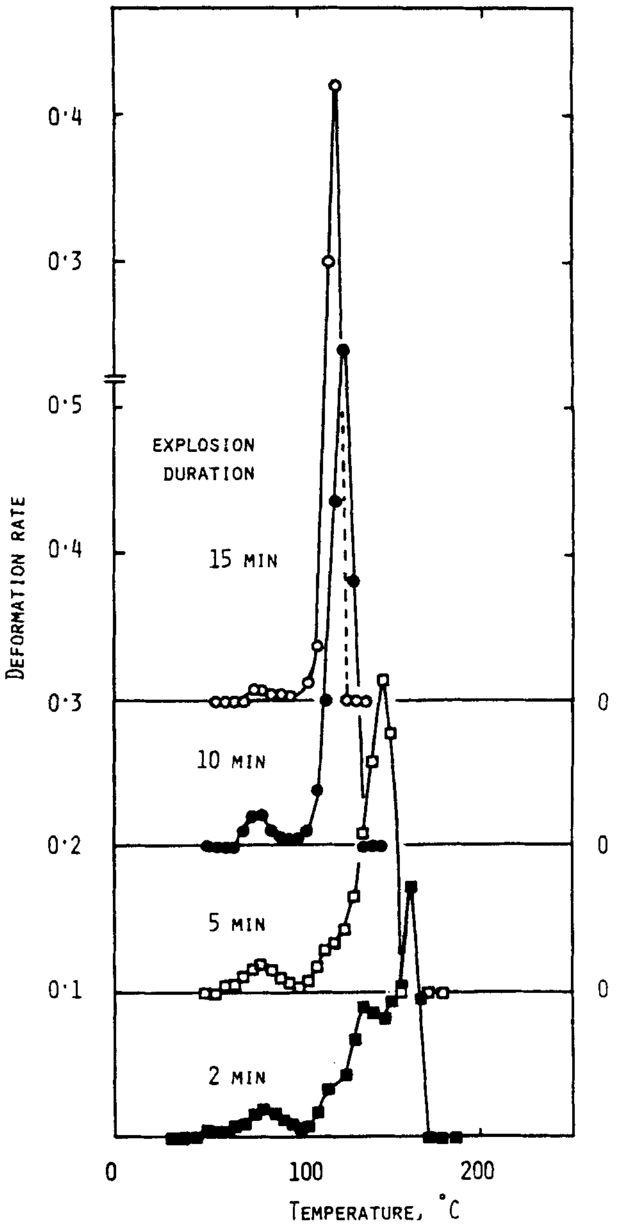

Fig. 4B Deformation rate as a function of temperature for the samples shown in Fig. 4A

temperatures of the cellulose acylates gave lower values than those of the corresponding acylated lignins. Actually, the apparent melting points are in the vicinity of 110°C and 115°C for cellulose tricaproate and cellulose trilaurate, respectively[16)]. These values are lower than any of the apparent melting temperatures of the corresponding caproylated or lauroylated woods, found in this study (Table 1). This proves that the apparent melting temperatures of these cellulose acylates are lower than those of the corresponding acylated lignin. This is the reason why samples caproylated or lauroylated by TFAA method after the explosion pretreatment show a steady decrease in flow temperature with increasing explosion temperature or duration at temperature.

There is another apparent anomaly in the effect of the explosion conditions on the thermal softening or melting temperature of exploded-acylated wood meals. The samples exploded and caproylated or lauroylated by DMF/PY/acid chloride method show no significant difference in their apparent melting temperature. On the other hand, the flow temperature of the samples exploded and caproylated or lauroylated by TFAA method depends upon the explosion conditions. Because in both reaction systems, the explosion conditions were the same, this apparent anomaly can be attributed, at least, to the action of trifluoroacetic acid formed in the reaction medium during acylation by TFAA method.

The effect of the explosion conditions on the thermal softening and flow temperature of the samples acylated by TFAA method is, in fact, a combined effect of the explosion treatment and the action of trifluoroacetic acid formed during the subsequent acylation by TFAA method. Trifluoroacetic acid is known to cleave benzyl-aryl ether bonds in addition to ester bonds. Marsh and Goodman[17)] have reported on the selective fission of the benzylaryl ether bonds by the action of trifluoroacetic acid at room temperature. Hence, it might be possible that the O-benzyl aryl groups present in lignin, that is, α-O-4 bonds, are cleaved by trifluoroacetic acid which results in further loosening of wood texture. Trifluoroacetic acid also acts as a solvent for cellulose and cellulose acylate[18) and also for the degraded and acylated lignin. Hence, the acid causes partial dissolution of acylated wood components during the acylation, resulting in the separation of wood components and increased loosening of wood texture.

In fact, the apparent melting temperature of the samples exploded at the most severe condition (210°C and 15 min) and acylated by the TFAA method approached that of the corresponding cellulose acylate. Furthermore, as the explosion condition became more severe, due to the loosening of morphological texture, wood became more susceptible to the action of trifluoroacetic acid. Thus, due to the combined effect of the explosion pretreatment and trifluoroacetic acid, samples exploded at 210°C for 15 min and caproylated or lauroylated by TFAA method, have apparent melting temperatures as low as 135°C and 120°C, respectively.

It might be possible that lignin oligomers formed during the explosion treatment undergo a recondensation reaction initiated by the acidic medium of the acylating system. In an earlier report we have shown that the addition of nucleophiles in the acylating system inhibits the recondensation of lignin oligomers and the resultant exploded-acetylated wood meal showed flow properties[19). Wayman and Lora[5) have also found recondensation reactions of lignin oligomers during the acidic medium of the autohydrolysis treatment. The amount of solvent extractable lignin was increased by the addition of some nucleophiles which inhibit the recondensation reaction. Hence, this could be one of the reasons for the higher flow temperature of samples esterified by DMF/PY/acid chloride method even though they were exploded under more severe conditions. However, in the case of samples esterified by TFAA method, the recondensation reactions of lignin oligomers are overcome by the action of trifluoroacetic acid.

It was of interest to find out that whether the loosening of morphological texture of wood caused by the explosion treatment is accompanied by an increase in the accessibility of cellulose. This aspect has been studied by the X-ray diffractograms obtained on the series of samples exploded under the same conditions used above,

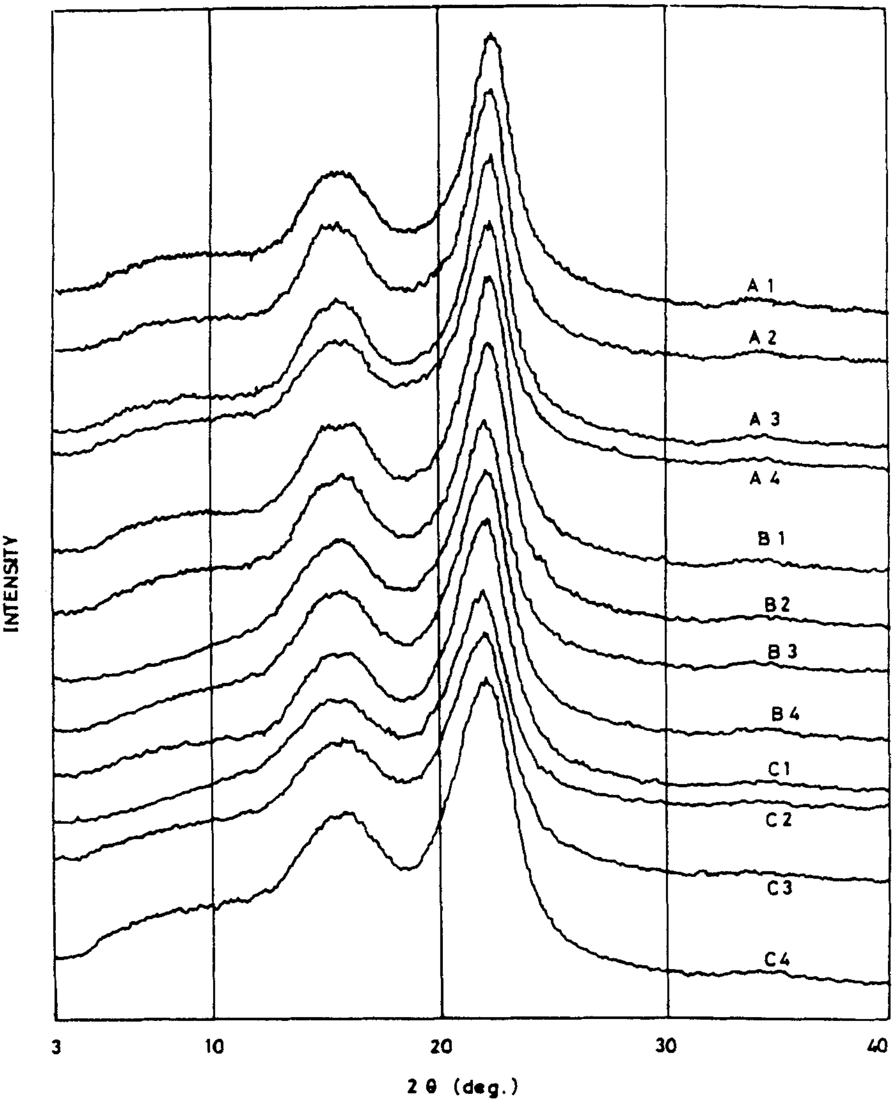

Fig. 5 X-ray diffractograms of the sample exploded under varying conditions. Explosion temperature : A-210°C; B-190°C; C-170°C, explosion duration : 1-15 min; 2-10 min; 3-5 min; 4-2 min

TABLE 2

Influence of explosion conditions on crystallinity of cellulose in wood

Explosion temp. °C	Explosion duration min	Cr%
170	2	51.78
	5	42.0
	10	46.0
	15	50.41
190	2	47
	5	50.9
	10	54.03
	15	54.23
210	2	47
	5	59.39
	10	62.01
	15	61.36

freeze dried without removing any fraction and dried further in a vacuum oven at 40°C. Fig. 5 shows the X-ray diffractograms of these samples. Crystallinity indexes were calculated from the diffractograms as described in the experimental section and are shown in Table 2. The crystallinity index is directly related to the explosion temperature and time at temperature and ranges from 42.0 to 62.01 for the samples exploded at 170°C for 5 min and at 210°C for 10 min, respectively. This means that the explosion treatment causes both loosening of wood texture as well as an increase in crystallinity of cellulose. This result is somewhat surprising, but similar results were recently reported by Tanahashi et. al.[20, 21] They also found that the average width of microfibrils of wood exploded under 28 kg/cm^2 for 8 min was about 63 Å. This value is almost twice that of untreated wood which is 32 Å. Hence, it is possible that the paracrystalline region rearranges, due to the plasticizing action of water during the high temperature and pressure of the steaming resulting in the increase in crystallinity of cellulose.

CONCLUSION

The explosion treatment resulted in loosening of the morphological texture of wood accompanied by an increase in the crystallinity of cellulose. Thus the overall effect of the explosion treatment on the flow temperatures of the samples acylated by DMF/PY/acid chloride method was insignificant. However, when the samples were acylated by TFAA method, the joint effect of the explosion treatment and trifluoroacetic acid formed during the acylation, was very conspicuous. Thus, modified wood meal flowable at temperatures as low as 120°C could be obtained.

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