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# **Studies on Development of Lignocellulosic and Cellulosic Plastics**

**1999**

**Mariko Yoshioka**

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# Chapter 1

## Introduction

During the past fifty years, synthetic polymers utilizing petroleum as their raw material have been advanced and a wide variety of plastic materials are now being used commercially, that support our daily life with considerable comfort. Even plastics which have properties similar to those of metals have appeared as engineering plastics.

Before the start of the synthetic polymer industry, there were a number of attempts to obtain moldable materials from natural polymers, mainly from cellulose. Trials of developing cellulose derivatives to industrially acceptable materials,<sup>1)</sup> as well as efforts to identify excellent plasticizers for cellulose acetate (CA),<sup>2, 3)</sup> provide good examples. However, these efforts became unpopular with the start-up of the industrialization of petrochemistry.

Actually, many synthetic polymers exhibit properties that polymers of natural origin do not possess, especially in relation to melt-processability. Many opinions expressed in textbooks claim that cellulose has such a rigid backbone that it cannot be converted to plastic materials. Because of these circumstances, it becomes understandable that attempts to develop plastics from natural origin have been deemphasized during the past half century.

Recently, however, several changes have occurred and provided motivation for the authors to start and continue studies on the conversion of biomass into plastics. The first change concerns the discovery from the authors' group that wood could be converted into thermally flowable materials by chemical modification, such as esterification and etherification. This discovery implies that plastics can be obtained from such low cost materials as wood wastes. There are actually almost no sophisticated methods or technologies available that can make use of biomass wastes for the purpose of adding satisfactory value. Thus, this kind of work, that is, wood plasticization, can be considered as one of the attempts for pursuing recycling technology, and this is the one that should be developed.

The second motivation results from a recently occurring requirement for

developing biodegradable plastics. To meet this need, development of biodegradable plastics from natural polymers becomes attractive, together with that of bacterial polyesters as well as synthetic polymers (aliphatic polyesters and water soluble polymers).

Much interest has recently focused on biodegradable plastics. At present, investigations in the field of bacterially-produced polymers as well as synthetic polymers are more actively and extensively pursued compared to the case of polymers from natural origin. However, it can be concluded overall that the investigations on biodegradable polymers have not arrived to the stage of commercialization. It is pointed out that it will take five to ten more years before the development of biodegradable polymers reaches a practical level.<sup>4)</sup>

In the case of the utilization of polymers from natural origin, attempts to develop biodegradable polymers have been focused chiefly on the utilization of starch. Relatively few studies have been conducted on the conversion of cellulose or lignocellulosics into biodegradable polymers up to recently. One reason for this is that cellulose diacetate is not considered a biodegradable polymer, at least not as recently as 1993. In 1993, as described in a later chapter, Buchanan and co-workers<sup>5)</sup> demonstrated that cellulose acetates are biodegradable when their degrees of substitution are less than 2.5. Thus, it can be said that systematic and novel studies on the preparation of biodegradable plastics from cellulose and lignocellulosics are just starting, although several practical proposals for biodegradable plastics from cellulose diacetates, prepared by simple blending with low molecular weight plasticizers, have recently been announced. These will be described later.

In contrast to the observation mentioned above, that cellulose has an intrinsically rigid main chain, Kamide has shown that cellulose behaves almost as a freely rotating chain when it is dissolved in a hypothetical nonpolar solvent.<sup>6)</sup> In other words, cellulose may intrinsically be very flexible according to Kamide's claim, and the low degree of flexibility of the cellulose chain, deduced from the physical properties of the solution and the solid, is caused by solvation or intra- and intermolecular hydrogen bonds.

With this background, studies on the thermoplasticization of wood had already been started when the author joined the Professor Shiraishi's group. Thus,



the author started her studies as a new-comer on the subject of thermoplasticization of wood by acetylation. More precisely, it was an attempt to obtain an acetylated wood with enhanced thermoplasticity by use of trifluoroacetic acid pretreatment. Its details are contained in Chapter 2.

Actually, by using trifluoroacetic acid as pretreatment, the resulting acetylated wood can reveal flow behavior at a temperature as low as 190 °C, which is almost 80 °C lower than the apparent flow temperature of cellulose diacetate. This means that acetylated wood becomes an easily flowable material. However, it still presents some problems as a plastic material. That is, the pretreatment agent is expensive, the fluidity is not completely satisfactory, physical and mechanical properties of the moldings are insufficient, and so forth.

Among the cellulose derivatives, benzyl cellulose is known as a material revealing good plasticity. Actually, benzyl cellulose is generally called cellulose plastics. It was therefore the author's interest to explore benzylated wood in a subsequent stage. The mechanical properties of benzylated wood and its blends with some synthetic plastics had already been described at that time by author's colleague belonging to Professor Shiraishi's laboratory.<sup>7)</sup>

Subsequent to these preliminary studies, the author examined the flow properties of benzylated wood in an attempt to improve the fluidity by blending with polycaprolactone, which is one of the known biodegradable plastics. Moldings were prepared from the benzylated wood-polycaprolactone blends, and their biodegradability was examined. The results are presented in Chapter 3.

The results of Chapter 3 revealed that benzylated wood, especially its blends with polycaprolactone, can behave as an excellent plastic material with biodegradability. Although these facts are extremely fascinating as a subject for academic studies, the benzylation is considered to be impractical, at least at present, because the reagent for benzylation, benzyl chloride, is a serious poison, and it is explosive. Benzyl cellulose is therefore not industrially produced in western or advanced countries.

It appears that an extensive development effort is required before a practical production technology can be defined. From this point of view, the author decided to focus further attention on wood acetylation. In order to simplify the problem and to take advantage of published information, the author decided to

concentrate on advancing the conversion of cellulose acetates (CAs) into effective and genuine plastics. This decision was also motivated by the fact that CAs have been the most widely produced industrial cellulose derivatives, and that CAs having degrees of substitution of  $\leq 2.5$  have been demonstrated to be biodegradable. In this regard, it should be noted that CAs are processed chiefly through dissolution in certain solvents, that is, dry molding processes are not so often adopted in the industry. This is caused by the fact that present plasticization technologies for CA are still unsatisfactory.

As stated earlier, there are numerous studies on the plasticization of CA from around the 1940's, and this attention has decreased until recently. However, recent development studies on biodegradable plastics have again drawn attention to plasticization studies concerning CA, especially since the biodegradability of CA was demonstrated. Most of these studies have dealt with blends of CA with low molecular weight plasticizers, such as diethyl phthalate, triacetine, polycaprolactone (with molecular weight around 300), etc. Other attempts often found today concern blends of CA with bacterially produced or synthetic polyesters, using polymer plasticizers. All of these studies involve external plasticization.

Two types of cellulosic biodegradable polymers have been announced in newspapers within the past two years, one of which was proposed in the USA and the other originated in Japan. Both are produced in a commercial scale. They involve the use of triacetine (USA) and polycaprolactone (Japan) as external plasticizers for CDA.

Considering the present situation, the author has focused on the development of an internal plasticization methodology, that is, chemical modification techniques, along with appropriate external plasticization, in order to develop biodegradable polymers from cellulose which have plastic properties.

In this approach, it is best to consider first the cost of the final product, because the biggest obstacle to the development of biodegradable plastics today is that the polymers hitherto proposed are too expensive compared with the prices of plastics of general use. With this goal in mind, the author started a study on plasticizing CA by a kneading reaction using reactive plasticizers.

Attempts were made to react CA with dibasic acids and with monoepoxides

within a batch kneader. This is a kind of reactive processing approach. Thus, the processing is said to be very similar to that of blending low molecular weight plasticizers with CA, and this reduces the processing costs.

The formation of oligoesters chains as grafted branches of CDA, together with homo-oligomers, during the processing is described in Chapters 4 and 5. Although the presence of homo-oligomers enhances the thermoplasticity of the products, it also causes "bleeding", especially when the amount of grafting is insufficient (Chapter 4). This kind of plasticizer loss is considered to be caused by a lack of miscibility. To make two immiscible polymers, A and B (or polymer A and oligomer B), miscible, a compatibilizer is often added. As one type of compatibilizer, A-B block or graft copolymers have been found to be effective. Therefore, a large amount of oligoester side chains attached to CA molecules can be expected to enhance the affinity between the modified CAs and the homo-oligomer. The results concerning this aspect are discussed in Chapter 5.

The biodegradability of representative samples obtained was examined by a soil burial test in a controlled environment (30 °C , 80%RH) as well as by the measurement of oxygen consumption in a closed system where test samples were exposed to standard activated sludge. The latter test method is adopted from methodology advocated by JIS. The results of these trials are presented and discussed in Chapter 5.

In order to prevent the bleeding of homo-polymer, more effective grafting methods have been studied. "Effective grafting" thereby includes all those reactions that produce more grafting and enhanced grafting efficiency within a short reaction period. It was a requirement that the grafted products, (that is, grafted CDA,) were biodegradable.

The accomplishments of this study are summarized in Chapter 6. This describes methods based on plasticizing CDA by graft copolymerization using  $\epsilon$ -caprolactone (CLN) and/or lactide (LA). The reactions developed greatly improved the processability of CA by reducing its flow temperature to a value ranging from 60 to 150 °C. This was achieved within short reaction time of 3 to 20 min at 110 - 160 °C. The grafted CDAs exhibited a wide range of physical properties, from vitreous state to rubbery. Those properties could be controlled by changing reaction time, temperature, the liquid ratio (ratio of cyclic esters to

CDA), and the reagent ratio of LA to CLN.

Reactive processing by using a twin-screw extruder was also pursued. Practical conditions were defined under which high grafting results were achieved with low liquid ratios. The conversion and graft efficiency was found to be related to the polymerization mechanism.

The biodegradability of grafted CDAs was confirmed by several methods, the features of which are resemble quite well to those in Chapter 5.

Thus, this series of studies led to the following conclusions.

The ring opening graft copolymerization using CLN and/or LA in the presence of Tin( II ) 2-ethylhexanoate as a catalyst is a very effective method for enhancing the processability of CDA. The application of this reaction to the reactive processing technique using the twin-screw extruder is expected to help advance the commercialization of thermoplasticized CDA. A low liquid ratio contributes to a high biomass content in the finished product and short reaction times are economically attractive. Moreover, the products are known to be more easily degraded by bacteria and fungi than synthetic polymers under several test conditions. They can therefore be considered as promising candidates for biodegradable materials of low cost that are competitive with recently developed biodegradable plastics from other sources.

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## Chapter 2

# Plasticization of wood by acetylation with trifluoroacetic acid pretreatment<sup>1, 2)</sup>

### 2-1 Introduction

There are basic differences between plastics and wood. Most plastics can flow by heating or by being exposed to mechanical force, and they can be dissolved in some organic solvents. On the contrary, wood is a non-flowable and insoluble material.

However, we found recently that wood can be converted into plastic materials by chemical modification, such as esterification and etherification. This fact can most simply be explained by the mechanism of internal plasticization due to derivatization. Thus, the introduction of substituents with large molecular size can confer thermoplasticity to wood. For example, acylation with higher aliphatic acids as well as benzylation resulted in modified woods possessing thermofluidity.<sup>3-10)</sup>

On the other hand, when the molecular size of substituent groups decreases or polarity increases, the corresponding chemically modified woods do not necessarily reveal thermofluidity. Even in these cases, however, additional external plasticization, for example by blending with appropriate plasticizers and/or synthetic polymers, has been found to result in thermally flowable modified wood products. For example, the conventional allylation, carboxymethylation, acetylation and so forth can not cause sufficient internal plasticization and hence can not confer thermoplasticity to wood, but the addition of adequate external plasticizers can meet the purpose.<sup>5, 10-12)</sup>

From the findings above, it can be said, in principle, that, irrespective of the molecular size of the substituent group introduced, wood can be conferred with thermoplasticity by internal plasticization, that is, chemical modification,

supplemented, if necessary, by external plasticization.

The chemically modified wood has also been found to be soluble in some appropriate solvents.<sup>6-13)</sup> Even solutions with concentrations higher than 70% have been obtained and its application to the preparation of wood-based adhesives, molded materials, foams, and so forth has been investigated successfully.<sup>13, 14)</sup>

The present study is concerned with the enhancement of thermoplasticity of chemically modified wood. In order to make feasible the preparation of thermoplastic resins from wood with or without blending with synthetic polymers, the thermofluidity of chemically modified wood should be enhanced as much as possible. In this study, an attempt has been made to obtain thermally flowable acetylated wood by using a pretreatment with trifluoroacetic acid (TFA).

## **2-2 Experiment**

### **2-2-1 Materials**

Makanba (birch: *Betula maximowiczii Regel*) wood meal (sapwood, cold water extracted, 20 - 80 mesh) was used for acetylation. All the chemicals used for the derivatization, extraction and others in this experiment were of "extra-pure" grade or "guaranteed reagent" grade and were used without further purification.

### **2-2-2 Pretreatment**

Dried wood meal (3 g) was pretreated with a mixture of acetic acid (5.28 ml) and acetic anhydride (0.84 ml) or that of trifluoroacetic acid (6.9 - 13.8 ml) and acetic anhydride (0.84 ml) at room temperature for 2 - 12 hrs.

### **2-2-3 Acetylation**

The acetylating mixture, containing acetic anhydride (17.8 ml), acetic acid (9.6 ml) and perchloric acid catalyst (PCA 0.038 ml) which was previously cooled to ca. -10°C, was added after pretreatment and the reaction vessel was kept shaking at room temperature for 1 hr. Then, the reaction temperature was raised to 30 - 50°C within 30 min. At this temperature, the reaction was continued for a definite period (2 - 6 hrs). The reaction was ceased by adding a solution of 0.0309g potassium carbonate in 3 ml acetic acid and shaking at 35 °C was continued for further 30 min. After this neutralization process, the whole reaction mixture was poured into an excess (ca. 600 ml) of deionized water and allowed to

stand for 2 hrs. Then, the product, acetylated wood, was collected by filtration. It was repeatedly washed with deionized water and dried.

#### **2-2-4 Characterization**

##### ***Measurements of thermal softening and melting :<sup>4, 5, 10)</sup>***

Thermal softening and melting of the acetylated wood was observed by using a thermomechanical analyzer (SHINKU RIKO Co. Ltd., TM-3000) in which a column of the sample collapsed under a plunger which supported a constant load of 0.3 MPa. Heating rate was 1°C/min.

##### ***Methanol extraction of acetylated wood :***

Dried acetylated wood (0.8 g) was extracted with methanol (450 mL) with stirring at room temperature for a prescribed duration. After the extraction, the acetylated wood samples and the extracts were collected and dried, or the solvent was driven off by evaporation.

##### ***Delignification of acetylated wood :***

Acetylated wood was delignified by the peracetic acid method,<sup>15)</sup> a typical delignification method for wood.

##### ***FTIR and GPC measurements :***

A HITACHI EPI-G3 grating double beam spectrometer was used for IR spectroscopic measurements. The KBr disk technique was employed to prepare samples for IR measurements. The molecular weight distribution of the methanol extracts as well as the delignified residues of the acetylated wood were measured by gel permeation chromatography (GPC). A Waters HLC 6000A with a Shodex GPC A-80M column (SHOWA DENKO Co. Ltd.) was used with chloroform as eluent at 1.0 mL/min flow rate at room temperature. Calibration was done using a series of polystyrene standards with different molecular weights.

### **2-3 Results and Discussion**

Fig. 2-1 shows the thermal behavior of three kinds of acetylated wood prepared at different reaction temperatures for the same reaction time of 6 hrs after an overnight pretreatment at room temperature with acetic acid (1.76 mL/g



wood)-acetic anhydride (0.28 ml/g wood) mixture. The results are compared with those obtained with untreated wood meal. In this figure, deformation of the samples ( $\Delta$ ) under a constant load at a programmed heating rate is plotted against temperature (T). When apparent melting takes place, a sudden fall in the curve occurs and the  $\Delta$  value moves to 1.0. From this figure, it is evident that none of these curves show real melting behavior. Acetylation increases the thermoplasticity of wood but complete flow does not occur.

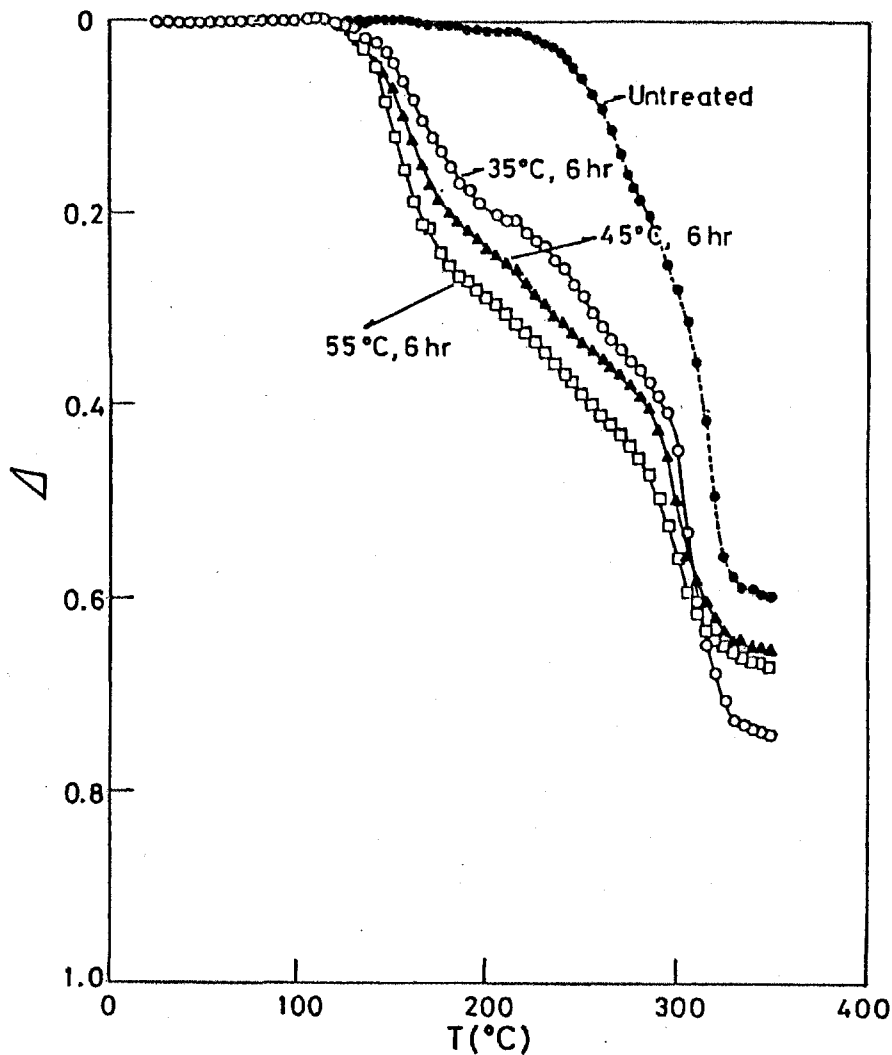


Fig. 2-1. Thermograms of untreated wood and wood acetylated by the conventional perchloric acid catalyst method.

Notes: Acetylation temperature and time are shown in the figure. Pretreatment: acetic acid (1.76 ml/g wood) - acetic anhydride (0.28 ml/g wood), room temperature, 12 h.

It has been already reported the influence of acetylation on thermoplastic properties of wood.<sup>5,10)</sup> It was found that peracetylated or highly acetylated wood prepared by the conventional methods, including those using the acetic anhydride-pyridine or triethylamine system, the acetic anhydride-acetic acid-sulfuric acid or perchloric acid system, etc., failed to reveal melting.

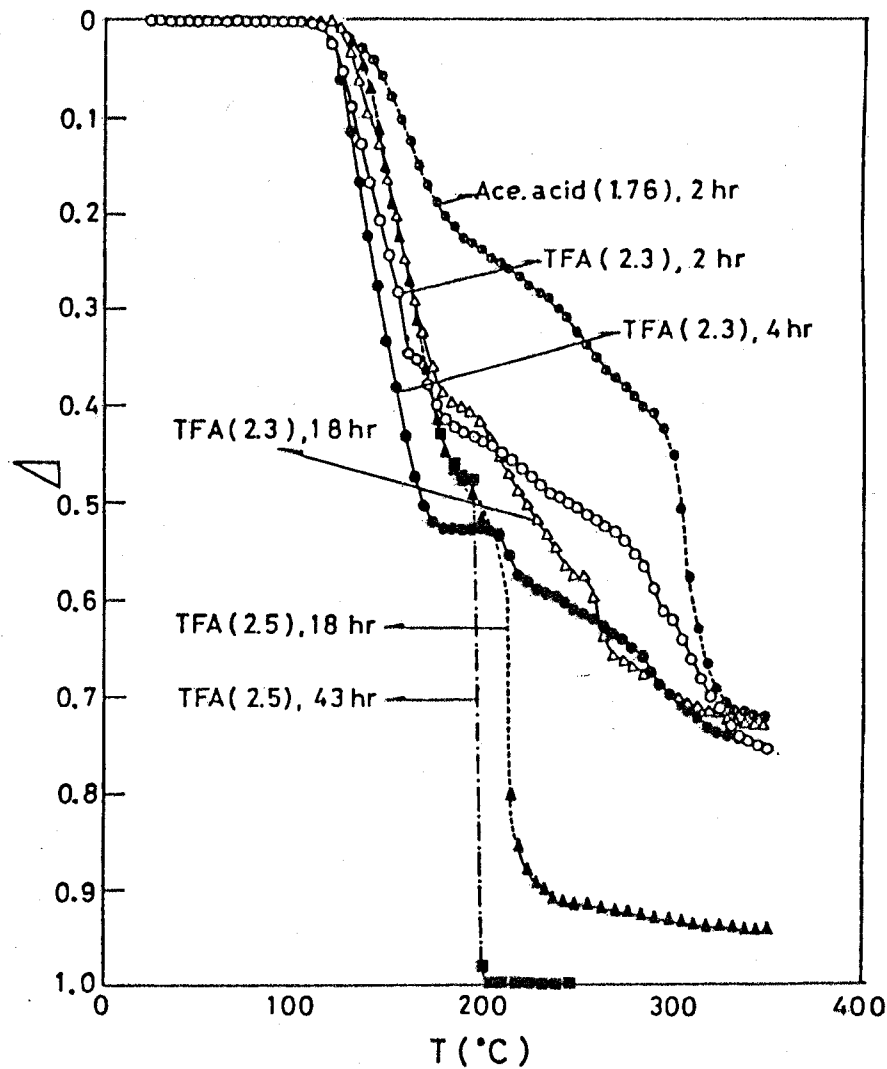


Fig. 2-2. Thermograms of acetylated woods prepared after pretreatment with TFA-acetic anhydride systems and acetic acid-acetic anhydride system (control).

Notes: Pretreatment: TFA (2.3 or 2.5 ml/g wood) - acetic anhydride (0.28 ml/g wood), 25 °C, 2-43 h; Acetylation: 50 °C, 3 h.

There was only one exception, and this, was that of the wood acetylated in a trifluoroacetic anhydride (TFAA)-acetic acid mixture at 30°C or 0°C (TFAA method). Wood samples acetylated by the TFAA method clearly melted at 320°C under a pressure of 0.3 MPa.<sup>4,5,10)</sup>

Based on these findings, an attempt was made to adopt the TFAA method to this experiment. That is, in order to confer thermofluidity to acetylated wood, acetic acid used in the conventional pretreatment was replaced by trifluoroacetic acid (TFA). It is known that TFA is formed continuously in the reaction medium as acetylation by the TFAA method proceeds.

In Fig. 2-2, the thermal behavior of acetylated wood prepared after pretreatment with TFA-acetic anhydride is shown. Two different quantities of TFA were used: equimolar, (2.3 ml TFA per gram of wood), or 8% excess molar quantity, (2.5 ml TFA per gram of wood), to that of acetic acid used in the preparation of the samples in Fig. 2-1. Other conditions for pretreatment are 2 to 43 h of treatment time at 25°C. After the pretreatment, acetylation was achieved at 50°C for 3 h using the perchloric acid catalyst as described in the Experimental Section. Fig. 2-2 also includes, for comparison, the thermal behavior of acetylated wood prepared after pretreatment with a mixture of acetic acid (1.76 ml/g wood)-acetic anhydride (0.28 ml/g wood).

From Figure 2-2, it is found that a small increase in the quantities of TFA as well as an extension of the pretreatment period can confer enhanced thermoplasticity to acetylated products. Even complete flow is observed for acetylated woods following the severest conditions of pretreatment in Fig. 2-2.

In consideration of these results, the author tried to develop more effective pretreatment conditions. First, the effect of increasing the quantity of TFA was examined. When the amount of TFA was raised up to two-fold the molar quantity of acetic acid, that is, 4.6 ml of TFA and 0.28 ml of acetic anhydride per gram of wood, respectively, the resulting thermal softening and flow curves of the acetylated products revealed excellent flow (Fig. 2-3). It was found (a) that even 2 h of pretreatment causes considerable thermoplasticization of acetylated wood, and (b) that a pretreatment period of 18 hrs confers complete thermal fluidity to the acetylated wood.

Next, the effect of pretreatment temperature on the thermoplastic properties

of the final products was studied. In this case, the quantity of TFA was fixed to two times of the standard amount, the same as for the experiment of Fig. 2-3, and the pretreatment period was held constant at 2 h. The experimental results are shown in Fig. 2-4. From Fig. 2-4, it is found that the thermoplasticity of the acetylated wood increases and that the flow temperature decreases with the increase in pretreatment temperature. That is, when the pretreatment temperature is 50°C, acetylated wood with high thermoplasticity can be obtained within two

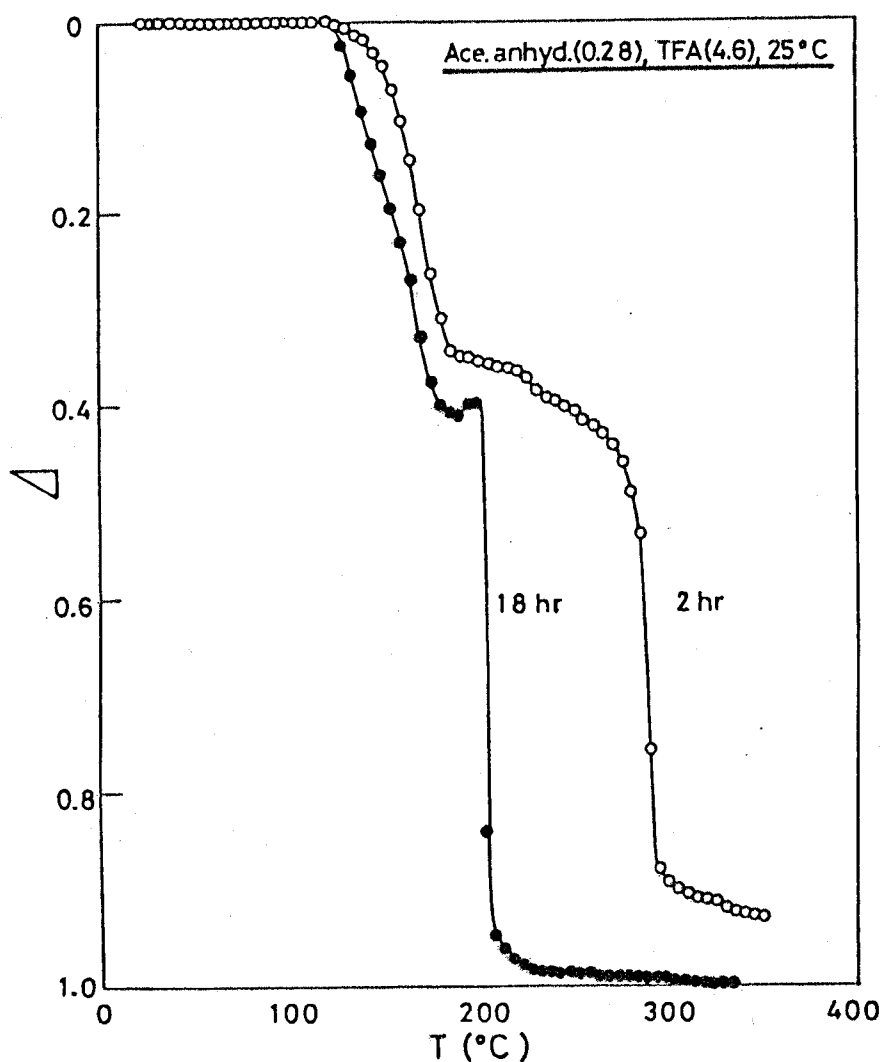


Fig. 2-3. Thermograms of acetylated woods prepared after pretreatment with a TFA - acetic anhydride system.

Notes: Pretreatment : TFA (4.6 ml/g wood) - acetic anhydride (0.28 ml/g wood), 25°C, 2-18 hrs (shown in the figure); Acetylation: 50°C, 3 hrs.

hours of pretreatment. However, a small portion of unflowable parts was detected in this case.

Then, the effect of pretreatment period at 50°C was investigated in order to define adequate conditions for the generation of acetylated wood with complete thermofluidity. The results are shown in Fig. 2-5.

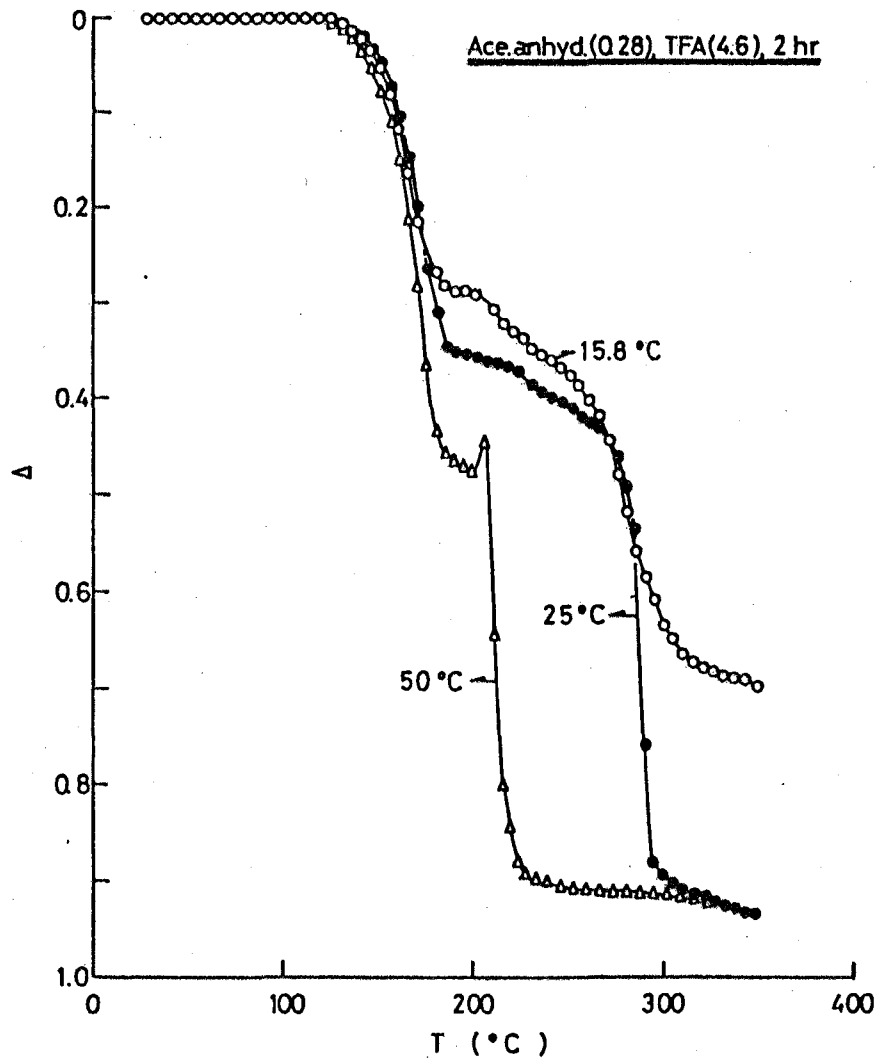


Fig.2-4. Effect of pretreatment temperatures on thermal softening and flow behavior of acetylated wood.

Notes: Pretreatment: TFA (4.6 ml/g wood) - acetic anhydride (0.28 ml/g wood), 15.8, 25 and 50°C, 2 h ; Acetylation: 50°C, 3 h.

It is clear that samples acetylated after pretreatment with a sufficient amount of TFA at 50°C for more than 4 h reveal complete thermofluidity.

It is most interesting that the acetylated wood obtained shows an apparent melting point of about 210°C. This has already been shown in Fig. 2-3. That is, although the pretreatment temperature is as low as 25°C, the acetylated product reveals an apparent melting temperature of about 205°C, when the pretreatment

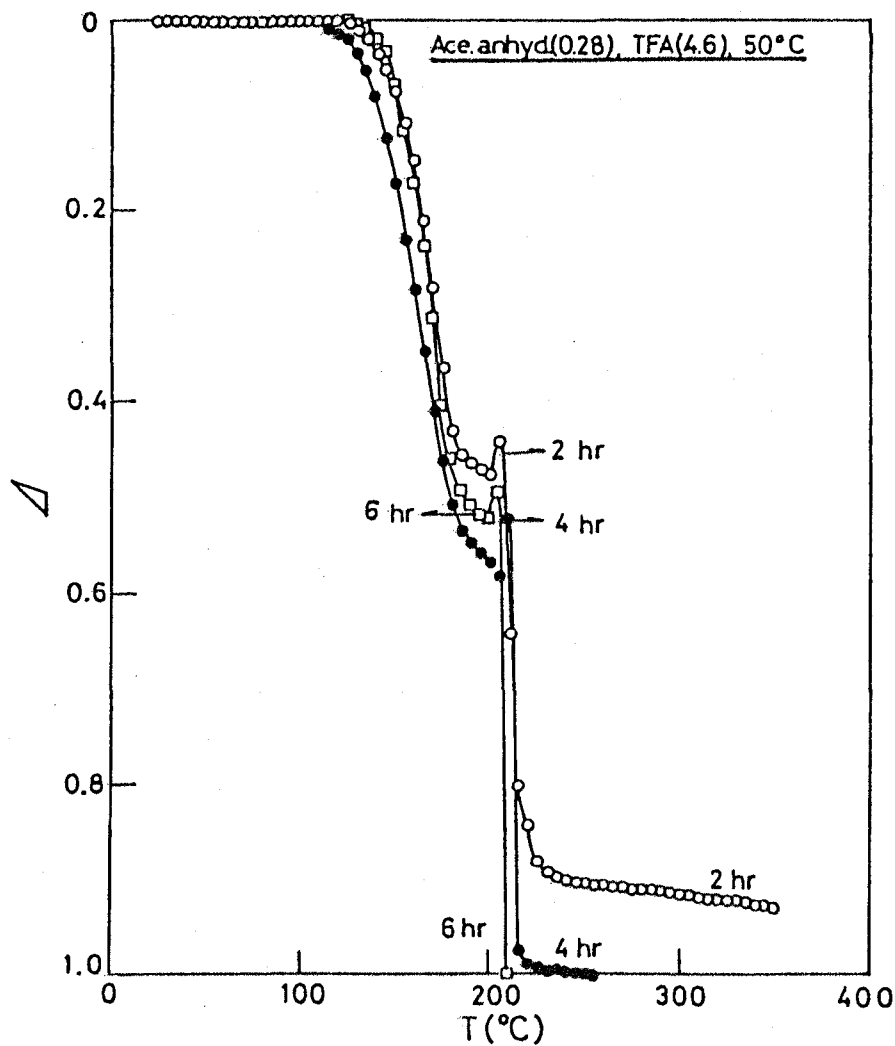


Fig. 2-5. Effect of pretreatment time on thermal softening and flow behavior of acetylated wood.

Notes: Pretreatment: TFA (4.6 ml/g wood) - acetic anhydride (0.28 ml/g wood), 50°C, 2 - 6 h; Acetylation: 50°C, 3 h.

period is as long as 18 h. The same phenomenon is also found in Fig. 2-2 with a sample acetylated after sufficient pretreatment. All the samples shown in Figs. 2-2, 2-3 and 2-5 were found to be highly acetylated wood (IR spectroscopic examination).

These flow temperatures of 205-210 °C are about 90 °C lower than that of flowable wood acetylated by the TFAA method, or that of cellulose triacetate. In fact, the apparent melting temperature of cellulose triacetate is almost 300°C (Fig. 2-6).

Fig. 2-6 shows the differential thermomechanical diagram for a series of fractionated cellulose triacetates ranging in weight average molecular weight from  $6.1 \times 10^3$  to  $5.39 \times 10^4$ . The apparent melting temperature is indicated by the peak at the higher temperature. It is found that the apparent melting temperature does not reveal a significant molecular weight dependence, and that even the cellulose triacetate with very low molecular weight flows at around 300°C.

In this connection, it can be said that the findings in the previous figures (i.e., that the acetylated wood shows apparent melting temperatures of about 205-210°C) are quite interesting. One of the reasons for this observation could be that wood components degraded, especially cellulose. However, this does not seem to be likely from the following observation.

First, the decrease in the degree of polymerization of cellulose during acetylation by the TFAA method was studied previously,<sup>16)</sup> and when Whatman cellulose powder (0.3 g) was used, the degradation of cellulose during the acetylation (TFAA: 5 ml, acetic acid: 2.5 ml,  $\text{CHCl}_3$ : 20 ml, at 50°C) was not observed during reaction times of up to 5 h, and then, a slight decrease in the degree of polymerization was detected up to a reaction time of 12 h. That is, the original number average degree of polymerization ( $\bar{P}_n$ ) for the Whatman cellulose was 228 and the value fell to 150 in between 5 and 12 h, after which the value of  $\bar{P}_n$  remained constant.

Second, both the acetylated woods prepared after pretreatment by the conventional method (with acetic acid and acetic anhydride; 25°C, 2 h) and by the method with a mixture of TFA (double the standard molar quantity) - acetic anhydride (50°C, 2 h) were delignified and the residue, acetylated holocellulose, was characterized by GPC analysis. The weight average molecular weight

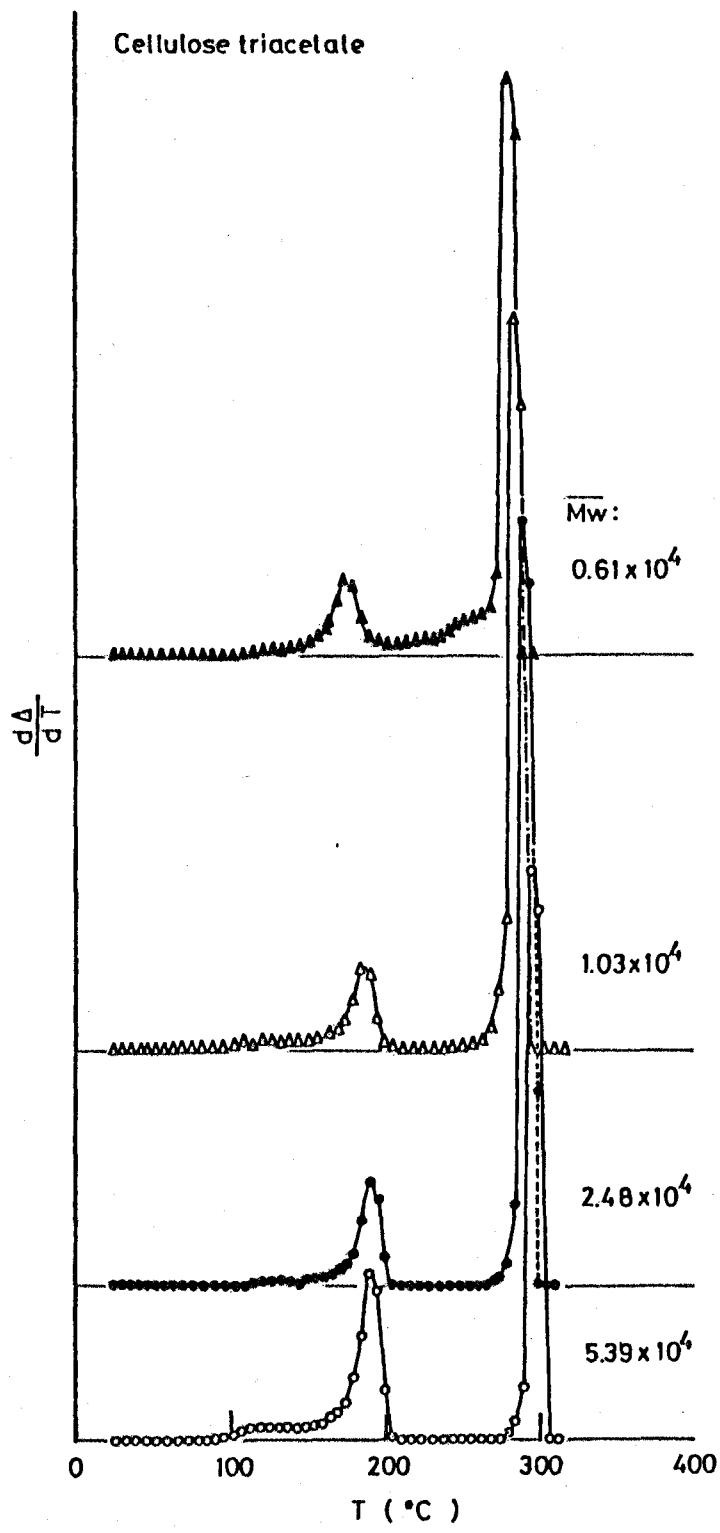


Fig. 2-6. Differential thermomechanical diagrams for a series of fractionated cellulose triacetate.



(based on standard polystyrene calibration) of the former sample was found to be  $2.51 \times 10^5$ , and that of the latter was  $2.13 \times 10^5$ . Then, it can be said, that cellulose triacetate in acetylated wood can remain as a high polymer even after being pretreated with TFA at  $50^\circ\text{C}$ .

On the other hand, the shift of flow temperature in some multicomponent polymers, is generally attributed to the compatibility and/or mutual plasticization among the component polymers. Then, plasticization of cellulose acetate by the interaction with acetylated lignin and hemicellulose could be postulated, and this would account for the above mentioned shift of the flow temperature of the acetylated wood to about  $205 - 210^\circ\text{C}$ .

Actually, the flow temperatures of acetylated MWL (milled wood lignin) and hemicellulose (xylan) are  $135^\circ\text{C}$  and  $210^\circ\text{C}$ , respectively, as shown in Fig. 2-7. Judging from these observed values, acetylated lignin is considered to play a greater role than acetylated hemicellulose in decreasing the apparent flow temperature of the acetylated wood.

In order to confirm the plasticization of cellulose acetate mainly by acetylated lignin in the acetylated wood, the acetylated lignin was extracted stepwise from the acetylated wood with methanol at room temperature, and the variation in the thermofluidity of the acetylated wood was measured in relation with the extraction time.

The results are presented in Figs. 2-8 and 2-9. In Fig. 2-8, the curve on the extreme left is for acetylated wood, prepared after being pretreated in the presence of TFA at  $25^\circ\text{C}$  for 18 h, before methanol extraction. In this case, the sample shows flow at  $205^\circ\text{C}$ . In contrast, the curve in the extreme right is for a completely delignified sample. It behaves almost like cellulose triacetate. The thermomechanical diagrams for the acetylated wood partially delignified by methanol extraction fall between the two extremes. Almost the same is found in Fig. 2-9 which shows the samples acetylated after TFA - acetic anhydride pretreatment at  $50^\circ\text{C}$  for 4 h. The flow temperatures obtained from these thermograms do not show a significant dependence on extraction period in the range of 12 to 120 h.

However, this can be explained by the data of Table 2-1 where only a very small change in the extraction amount with extraction time in the range of 12 to

120 h is seen for the above mentioned two kinds of samples.

The table also reveals that the extractable parts, which can act as plasticizer within the acetylated wood, have a high extractability and amount to about 30 wt% of the whole acetylated wood. This value is slightly higher than that of acetylated lignin within acetylated wood.

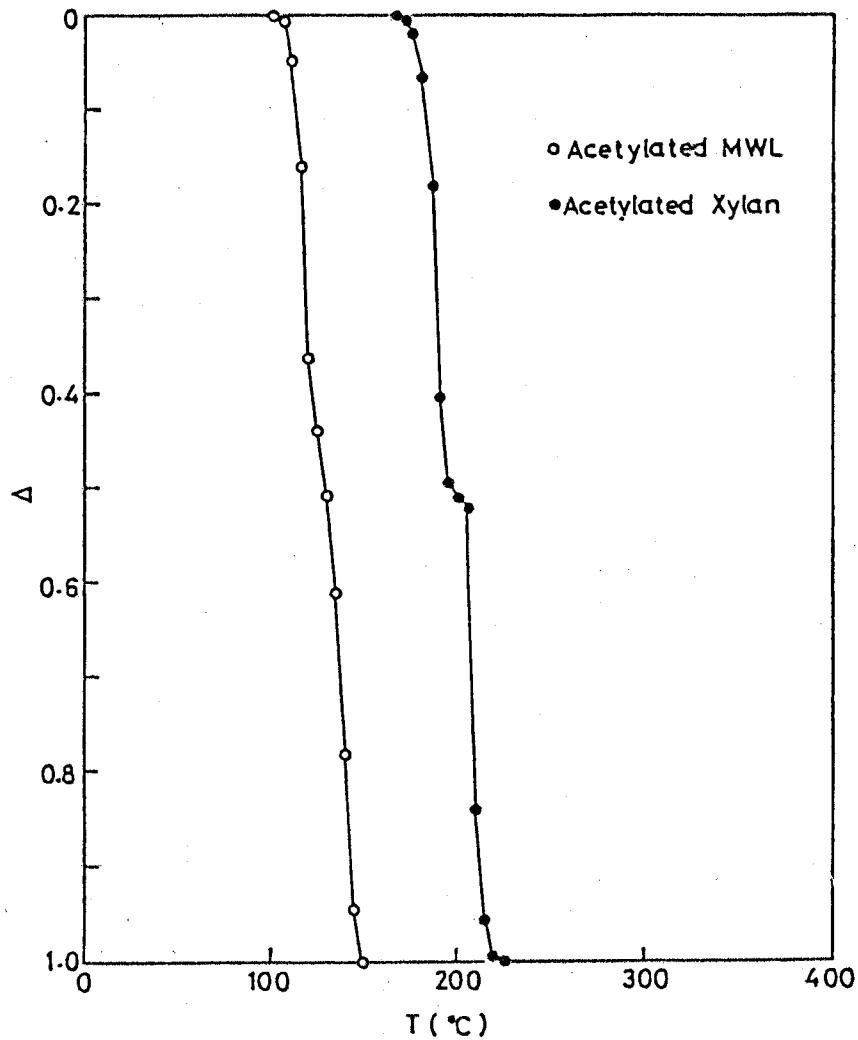


Fig. 2-7. Thermograms of acetylated milled wood lignin (MWL) and xylan.

Notes: Acetylation of MWL and xylan was carried out by a conventional method using excess of acetic anhydride - pyridine (1:1 (mole)) mixture as an acetylation reagent for 48 h at 25  $^{\circ}\text{C}$ .

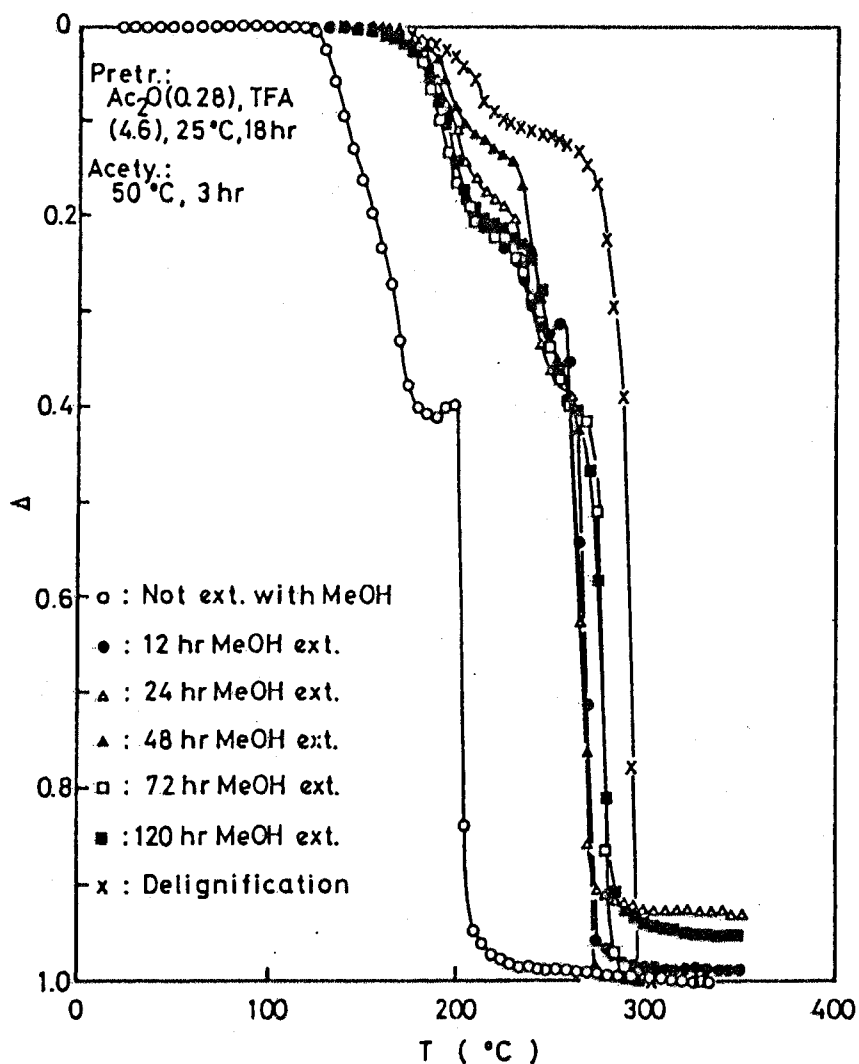


Fig. 2-8. Effect of extraction with methanol or delignification on the thermal softening and flow behavior of acetylated wood prepared after pretreatment with TFA - acetic anhydride mixture at 25°C for 18 h.

Notes: Pretreatment : TFA ( 4.6 ml/g wood ) - acetic anhydride ( 0.28 ml/g wood ), 25°C, 18 h; Acetylation : 50°C, 3 h; ○: control ( before methanol extraction ).

On the other hand, when acetylated wood prepared after a conventional pretreatment was similarly extracted with methanol for 120 h at room temperature, the extracted amount was found to be 17%. This is considerably less, about one half compared to that of the former case.

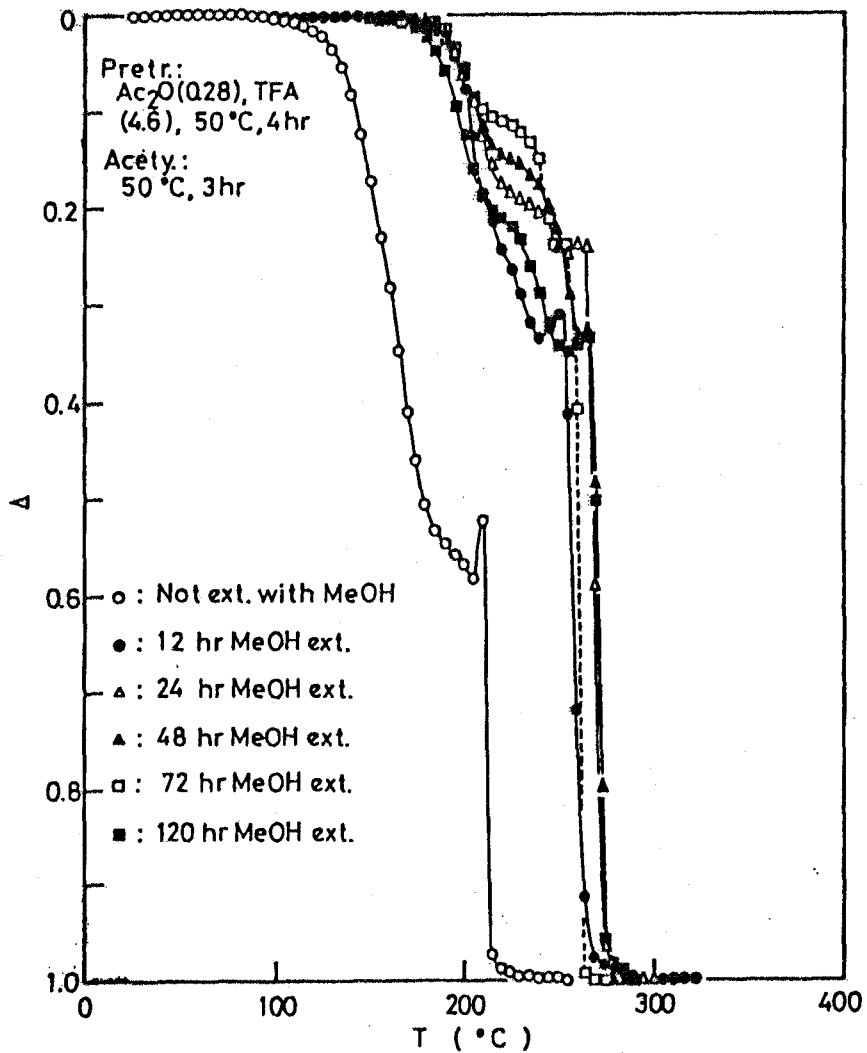


Fig. 2-9. Effect of extraction with methanol on the thermal softening and flow behavior of acetylated wood prepared after pretreatment with TFA - acetic anhydride mixture at 50 °C for 4 h.

Notes: Pretreatment : TFA ( 4.6 ml/g wood ) - acetic anhydride ( 0.28 ml/g wood ), 50°C, 4 h ; Acetylation : 50°C, 3 h ; ○ : control (before methanol extraction).

These findings reveal a lowering of the molecular weight of lignin during the acetylation after pretreatment with TFA. Actually, TFA is known to cleave the benzyl aryl ether bonds in addition to the ester bond, when applied at room temperature for several hours.<sup>17)</sup>

Lignin is known to contain very few ester and a certain amount of benzyl aryl ether bonds. The ester bonds include a part of the bonds between lignin and hemicellulose, and this comprises the lignin - carbohydrate complex. The benzyl aryl ether bonds in lignin, important from the point of view of the thermoplasticization of wood, is an acyclic  $\alpha$ -o-4 bond which exists in 6% quantity based on an intramolecular unit bonds in lignin.<sup>18)</sup> The scission of these bonds in lignin should certainly result in a lowering of the molecular weight and in an enhancement of the mobility and thermoplasticity of lignin.

On the other hand, the results in Figs. 2-8 and 2-9 can also explain why the acetylated wood prepared by the TFAA method showed an apparent melting temperature of 320°C,<sup>5, 10)</sup> which was already cited above. This is because, in the case of the TFAA method, the acetylated wood samples were washed with methanol, whereas the present products acetylated after pretreatment with TFA with perchloric acid catalyst method were washed with water.

Table 2-1. Methanol extraction of acetylated wood prepared after pretreatment with TFA ( 4.6 ml /g wood ) - acetic anhydride ( 0.28 ml/g wood ) mixture at 25 °C for 18 h and at 50 °C for 4 h.

MeOH extraction time (hrs)	Amount of MeOH extract (%)	
	Pretreatment 25°C, 18hrs	Pretreatment 50°C, 4hrs
12	29.5	29.6
24	30.8	31.5
48	30.9	31.2
72	30.5	31.0
120	31.2	32.1

Next, these methanol extracts were characterized by IR spectroscopy. Fig. 2-10 shows, from the top to the bottom, the IR spectrum of acetylated wood after pretreatment with a mixture of acetic anhydride - TFA at 50°C for 4 h; that of the same acetylated wood after extraction with methanol at room temperature for 12 h; that of an extract from the acetylated wood with methanol for 12 h and that of the extract with methanol for 24 h.

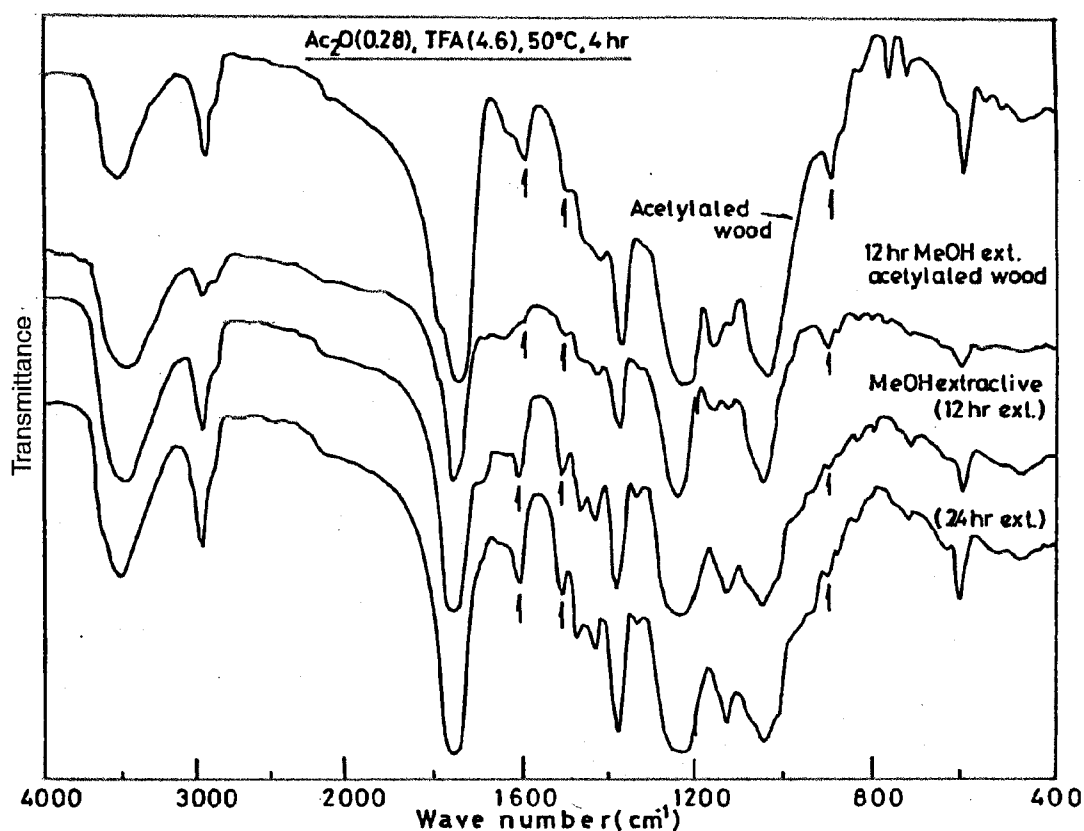


Fig. 2-10. IR absorption spectra of acetylated wood, acetylated wood extracted with methanol, and methanol extractives.

Notes: From the top to the bottom : acetylated wood ( pretreatment: TFA (4.6 ml/g wood) - acetic anhydride (0.28 ml/g wood), 50°C, 4 h; acetylation : 50°C, 3 h), acetylated wood extracted with methanol for 12 h, methanol extractives obtained by 12 h extraction and 24 h extraction at room temperature, respectively.

A certain amount of hydroxyl groups found to remain in the spectrum of the acetylated wood indicates hydrolysis, during the washing stage, of trifluoroacetic acid ester introduced during acetylation,<sup>18)</sup> but the amount is fairly small. When the spectrum of the acetylated wood is compared with that of the acetylated wood extracted with methanol for 12 h, it is found that peaks at around 1500 and 1600  $\text{cm}^{-1}$  decrease markedly by the extraction, showing that the acetylated lignin part is selectively extracted, whereas the peak at 897  $\text{cm}^{-1}$  does not change significantly. The peak at 897  $\text{cm}^{-1}$  is attributed to the  $\text{C}_1$ -group frequency or ring frequency and is related to the configuration at the  $\text{C}_1$  of the glucopyranose ring.<sup>16)</sup> The intensity of this peak is associated inversely with the degree of crystalline order. It is known that this absorption band appears a mere ripple in the spectrum of cellulose, whereas it becomes a relatively sharp and intense peak in that of xylan.<sup>20)</sup>

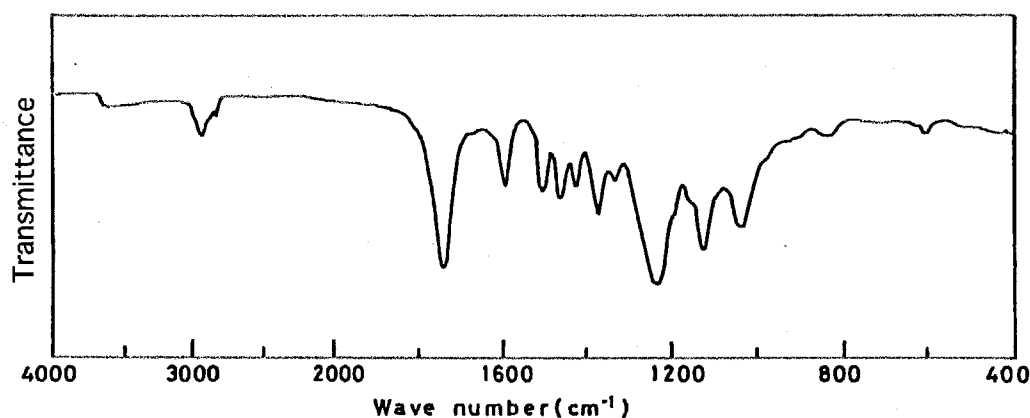


Fig. 2-11. IR spectrum of acetylated MWL.

Thus, it can be remarked that acetylated lignin is separated from the acetylated wood during extraction with methanol. This is further confirmed by the spectra of two extract samples in Fig. 2-10. That is, the spectra do not reveal a peak but show only a faint ripple at 897  $\text{cm}^{-1}$  implying that acetylated hemicellulose is not included in the extract. Furthermore, the spectra of the extracts agree well in their peak positions with a spectrum of acetylated MWL, shown in Fig. 2-11, with the exception of a band attributed to the OH stretching.

From the above findings and discussions it can be concluded that acetylated wood, which was prepared after TFA pretreatment, flows at a considerably lower temperature than the untreated control, and this is caused by the plasticization of cellulose acetate by acetylated lignin in the acetylated wood.

## 2-4 Summary

Acetylation by the conventional method (acetic anhydride) does not confer thermofluidity to wood. However, wood acetylated in a medium of trifluoroacetic anhydride-acetic acid (TFAA method) shows an apparent melting behavior at around 300°C. In this case, the action of trifluoroacetic acid (TFA) as a reagent for effectively cleaving some of the lignin's intramolecular bonding, can be postulated. Based on this finding, a simulation of the TFAA method has been proposed. That is, in order to confer thermoplasticity to acetylated wood, acetic acid used in the conventional pretreatment has been replaced by TFA. By using TFA as pretreatment reagent and employing other appropriate conditions for pretreatment, acetylated wood with thermofluidity has been obtained. This acetylation method is basically identical to the conventional one, except for the pretreatment. It is more interesting that the acetylated wood thus obtained shows an apparent melting temperature of about 210°C; that is, about 90°C below the apparent melting temperature (flow temperature) of cellulose acetate. The low flow temperature of the wood acetylated following the pretreatment with TFA can be attributed to the plasticization of cellulose acetate by acetylated lignin in the acetylated wood.

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## Chapter 3

# **Thermoplasticization of wood and its application : Blending of benzylated wood with polycaprolactone, and its bio- and photo- degradabilities<sup>1-8)</sup>**

### **3-1 Introduction**

Since lignocellulosics, including wood, are not thermally flowable materials; the methods for processing them are limited. If appropriate thermoplastic properties could be imparted to the lignocellulosics, they would become more useful materials.

Several years ago, it was found that wood could be converted into a plastic material by chemical modification, such as that by esterification and etherification.<sup>9)</sup> Chemical modification does not necessarily require special techniques ; conventional and simple methods work satisfactorily for this purpose.<sup>10, 11)</sup>

The phenomenon of thermal flow can be explained in terms of internal plasticization of wood. The introduction of large non-polar substituent groups into wood can result in a chemically modified material with high thermoplasticity. When small substituent groups and/or polar groups are introduced, such thermal fluidity cannot be achieved, therefore, the latter modification alone cannot produce plastic properties. However, this lack of plasticity can be solved by external plasticization.

All of these arguments reveal that chemically modified wood derivatives can be considered as novel biobased plastic materials, and experimental studies have targeted the development of composites with enhanced physical properties.

On the other hand, the development of synthetic polymers has resulted in their wide-spread usage, however, their stability under diverse environmental

conditions have caused considerable environmental problems. The low cost of synthetic polymers has encouraged inadequate disposal practices for many years. Their lack of biodegradability has led to their accumulation in the environment. As one of the potential solutions to this problem, degradable plastics, including photodegradable, chemidegradable, environmentally degradable and biodegradable ones, have attracted development efforts.

In this chapter, benzylated wood (BzW) is chosen as a thermoplastic among chemically modified wood derivatives developed by the author's group. Its plasticity was further enhanced by blending with polycaprolactone (PCL). The biodegradability and photodegradability of BzW and its blends with PCL were also studied.

## **3-2 Experiment**

### **3-2-1 Materials**

Wood meal from the sapwood portion of Mankanba (birch : *Betula maximowiczii* Regel) was used for benzylation after cold water extraction.

All the chemicals and solvents were of "extra-pure" or "guaranteed reagent" grade, and they were used without further purification.

PCL, PLACCEL H-4 ( $\overline{M}_n = 40,000$ ), Polypropylene (PP), J700G ( $MI = 7$ ) and styrene-maleic anhydride copolymer (SMA), Dylark 232 were supplied by Daicel Chemical Industries, Ltd., Idemitsu Petrochemical Co. Ltd. and Arco Chemical Co. Ltd., respectively.

### **3-2-2 Benzylation of wood meal**

BzW was prepared by the conventional method for the preparation of benzyl cellulose: after mercerization, wood meals was reacted with benzyl chloride at 110°C for 2.5 h. The products were thoroughly washed with methanol and water, and then dried *in vacuo*.

### **3-2-3 Blending of BzW with synthetic polymers**

Within 5 min, predetermined amounts of BzW and PCL, or BzW, PCL and SMA were charged into a Toyo-Seiki Labo-Plastmill (LPM 18-125) and they were kneaded at 180 - 190°C at a rate of 30 rpm for 15 min.

### **3-2-4 Molded sheets**

BzW or the kneaded blends were placed between a pair of polyethylene terephthalate (PET) sheets to be molded into sheets with a thickness of 0.4 mm by hot-pressing with a Toyo-Seiki 10T bench hot-press.

### **3-2-5 Tensile test**

Sample strips with a dimension of  $80 \times 5 \times 0.4$  (mm) were cut from the molded samples. Tensile tests were carried out on these specimens with a Shimadzu Autograph DSC R-500, using a span length of 40 mm and a crosshead speed of 5 mm/min, at 20°C and 60 % RH.

### **3-2-6 Melt fluidity**

Melt fluidity of BzW and its blends with PCL, with or without SMA, was measured with a Shimadzu flow tester CFT-500A and with a Toyo-Seiki Capirograph (Capillary rheometer).

## **3-3 Results and Discussion**

### **3-3-1 Mechanical and melt-flow properties of BzW**

As pointed out in the introduction, there are various types of thermoplasticized wood derivatives. Among them, BzW is known as a moldable material giving excellent mechanical properties.

Indeed, a sample of BzW showed a tensile strength of 42.7 MPa, which is fairly high when compared, for example, with that of Styron 666 (polystyrene (PS); a product of Asahi Chemical Industry Co. Ltd.); the tensile strength of Styron is 29.4 MPa under the same conditions. Differential scanning calorimetric measurements have revealed that both polymers are amorphous. Thus, the thermal softening behavior is similar, qualitatively, when measured with a thermo-mechanical analyzer.

Quantitatively, there are some differences. Experimental observations with a flow tester revealed that PS undergoes flow at 153°C, while BzW starts to flow at 175°C. Almost identical results are found when BzW is compared with PP which is also widely used as a thermoplastic polymer.

However, even though the flow temperature of BzW is higher than that of PS or PP, the temperature difference can be reduced to almost zero by blending PCL

in an amount of 20% with BzW.

Fig. 3-1 shows the dependence of melt viscosity ( $\mu$ ) and shear stress ( $\tau_w$ ) on the shear rate ( $\gamma$ ) of BzW and PP, measured with a Capirograph. It is seen that both the viscosity and the shear stress of BzW reveal similar shear rate dependences as those for PP. However, the values for BzW are one order larger than those for PP. This means that there exists a greater resistance to thermal processing for BzW.

In order to reduce this resistance, blends of BzW with PCL were studied since the latter has considerably greater thermoplasticity. Since PCL itself has a low melting point (ca. 60°C) and low tensile strength (19 MPa) at room temperature, its compounding with BzW would be of great significance. Results obtained are shown in Fig. 3-2. As BzW content increases, both the viscosity and shear stress are seen to decrease.

At a BzW content of 30%, the characteristic melt flow values converge with those for PP which are shown as dotted lines. Thus, the blended composite consisting of 70% BzW and 30% PCL has practically the same fluidity as PP.

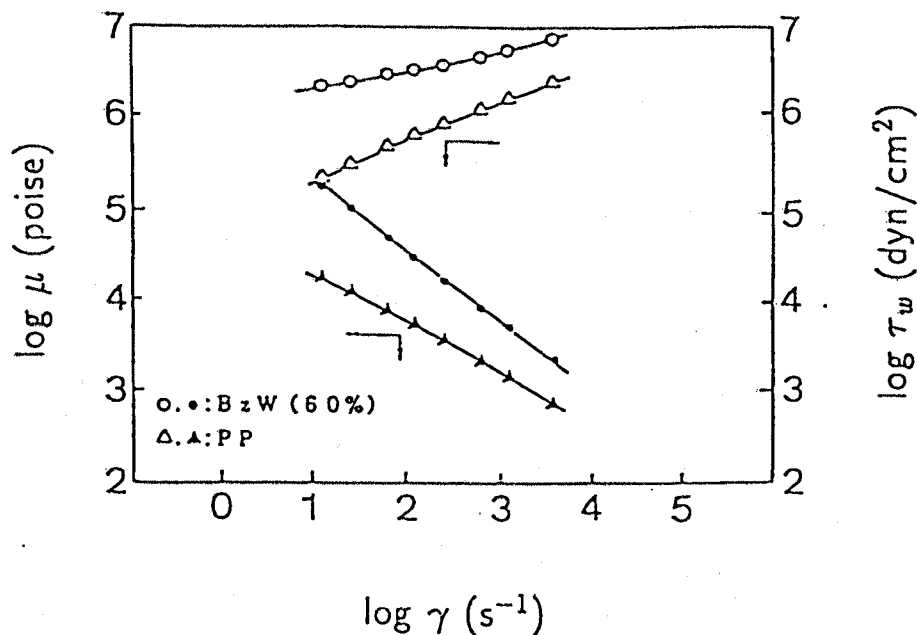


Fig. 3-1. Viscosity and shear stress vs. shear rate for BzW and PP.

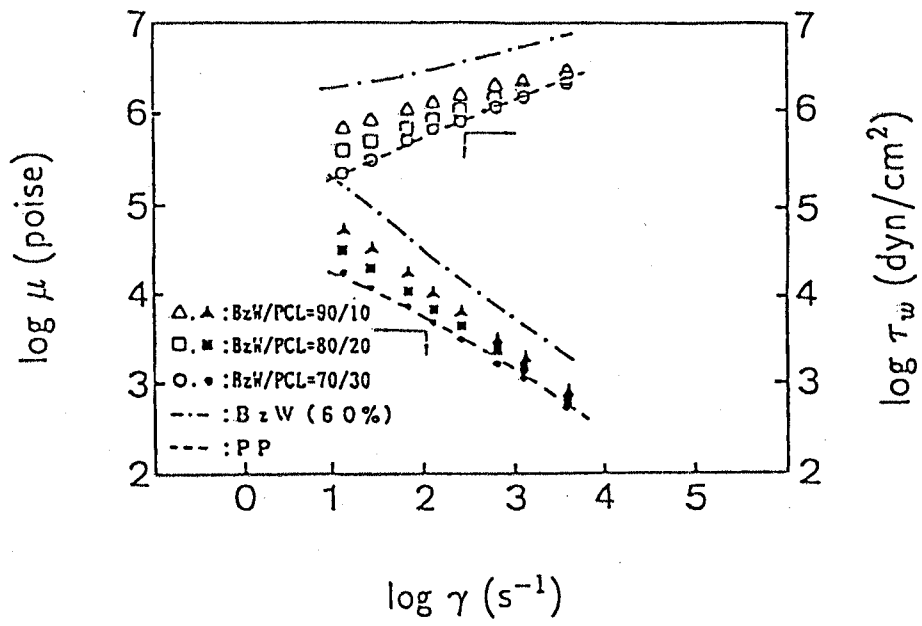


Fig. 3-2. Viscosity and shear stress vs. shear rate for the blends of BzW and PCL.

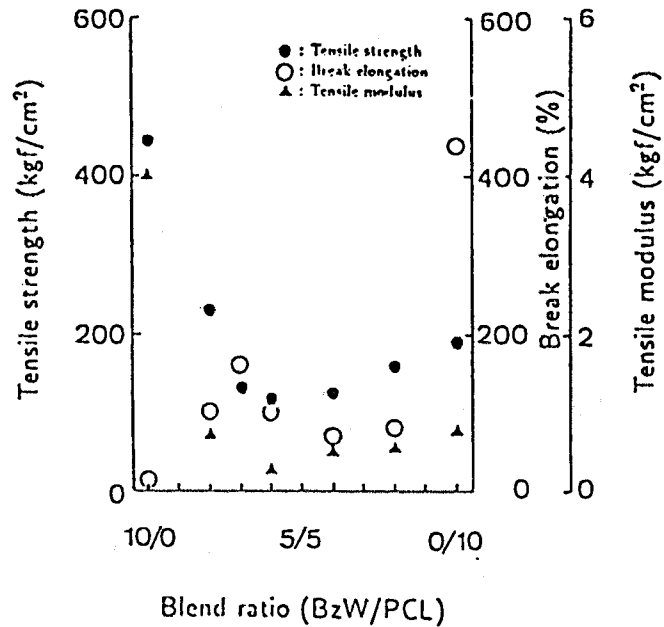
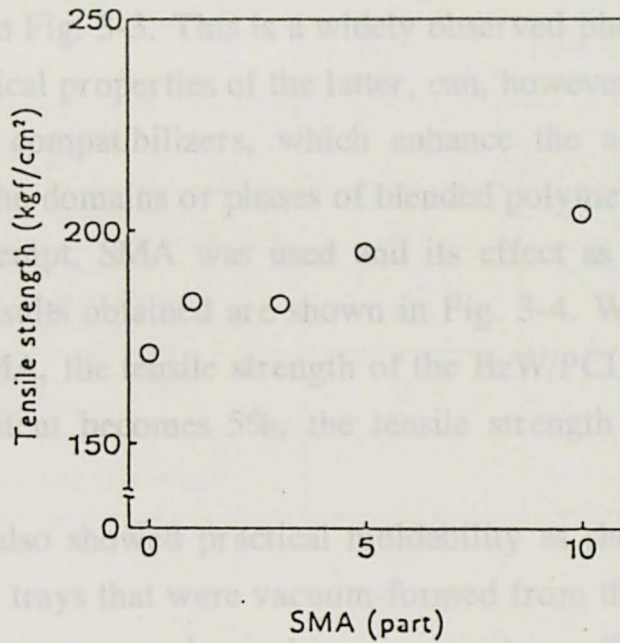


Fig. 3-3. Relationship between mechanical properties of the BzW sheets and PCL content.

However, the mechanical properties of the blends were reduced by this blending as shown in Fig. 3-4. This is a widely observed phenomenon in polymer blends. The mechanical properties of the latter, can, however, be improved by the use of appropriate compatibilizers, which enhance the adhesion of interfaces between or among the domains or phases of blended polymer.

As one such attempt, SMA was used and its effect as a compatibilizer was investigated. The results obtained are shown in Fig. 3-4. With an increase in the amount of added SMA, the tensile strength of the BzW/PCL sheet recovered, and when the SMA content becomes 5%, the tensile strength rises to 200 kgf/cm<sup>2</sup> (19.6 MPa).



The composite also showed a practical moldability as shown in Fig. 3-5. The photograph displays trays that were vacuum formed from the sheets of the blends. This kind of trays are commonly used in grocery stores. These trays possess not only reasonable strength but they also have functional properties as biodegradability and photodegradability, as shown later.

Fig. 3-4. Relationship between tensile strength of BzW/PCL [7/3 (w/w)] sheets and SMA content.

Novel thermoplastic materials, which have been developed by the chemical modification of wood, have been described in 3-3-1. Although they are of biological origin, an evaluation of the biodegradability and photodegradability characteristics of these thermoplasticized wood derivatives is indispensable.

Thus, the degradability of BzW was compared with that of synthetic polymers including PP, PS, polycarbonate and others. The results reveal that, while the sheets of synthetic polymers do not lose any strength after 30 days of immersion in aerobically active water, the sheets of BzW exhibited continuous deterioration with a significant reduction in strength. The results are shown in Table 3-1.

The results also show that BzW is more sensitive to sunlight than PP is said to be photodegradable. Although PP is said to be photodegradable, it did not show any change in its external appearance or its strength, whereas BzW became very brittle and was destroyed after 30 days of exposure to sunlight.



Fig.3-5. Trays from BzW/PCL blended composites.



However, the mechanical properties of the blends were reduced by this blending as shown in Fig. 3-3. This is a widely observed phenomenon in polymer blends. The mechanical properties of the latter, can, however, be improved by the use of appropriate compatibilizers, which enhance the adhesion of interfaces between or among the domains or phases of blended polymers.

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The composite also showed practical moldability as shown in Fig. 3-5. The photograph displays trays that were vacuum-formed from the sheets of the blends. This kind of trays are commonly used in grocery stores. These trays possess not only reasonable strength but they also have functional properties as biodegradability and photodegradability, as shown later.

### **3-3-2 Bio- and Photo- degradabilities of BzW and BzW/PCL composites**

Novel thermoplastic materials, which have been developed by the chemical modification of wood, have been described in 3-3-1. Although they are of biological origin, an evaluation of the biodegradability and photodegradability characteristics of these thermoplasticized wood derivatives is indispensable.

Thus, the degradability of BzW was compared with that of synthetic polymers including PP, PS, polycarbonate and others. The results reveal that, while the sheets of synthetic polymers did not lose any strength at all even after 80 days of immersion in aerobic and anaerobic activated sludge, sheets of BzW exhibited continuous deterioration and strength reduction. The results for BzW are shown in Table 3-1.

The results were most impressive in so far as, although PP is said to be photodegradable to a certain extent, it did not reveal any change in its external appearance or its strength, whereas BzW became very brittle and was destroyed after 80 days of exposure to sunlight.

Table 3-1. Biodegradability and photodegradability of BzW.

	Tensile strength (MPa)	Tensile breaking elongation (%)
Control (BzW)	42.7	9.8
Dipping in aerobic activated sludge for 80 days	37.7	4.1
Dipping in anaerobic activated sludge for 80 days	37.9	4.8
Dipping in sea water for 80 days	39.8	6.1
Exposing to sunlight	-	-

Furthermore, the BzW/PCL sheets were found to undergo to faster biodegradation than those of each individual sheet component as revealed by tests carried out under the same conditions (not shown). This fact is remarkable in as much as PCL is well-known for its high biodegradability.

### 3-4 Summary

In Chapter 2, it was reported that wood can be converted into a plastic material by chemical modification. Among the thermoplasticized wood derivatives, benzylated wood (BzW) has been characterized as a material with excellent mechanical properties, and with higher apparent melting point and higher melt viscosity compared with most commercial thermoplastic polymers. The melt properties could be further modified by blending with polycaprolactone (PCL), a common biodegradable synthetic polymer. Measurements by capillary rheometry (Capirograph) revealed that the addition of 20 to 30% of PCL converts BzW to a polypropylene-like plastic. BzW was also found to have biodegradability and considerable photodegradability. Blends of BzW and PCL resulted in higher biodegradability when compared to each individual component.

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## Chapter 4

# Plasticization of cellulose acetates by reaction with dibasic acid anhydrides and monoepoxides during melt-processing<sup>1-9)</sup>

### 4-1 Introduction

Synthetic polymers are now used widely in our daily life. The use of these polymers, however, has caused environmental pollution problems. For this reason, the development of biodegradable polymers is being actively pursued. These biodegradable polymers must not only be cost effective; but they must also have performance characteristics that are comparable to common synthetic polymers and, at the same time, they must be degradable in the environment. These requirements, however, are often mutually exclusive, and practical biodegradable polymers have not been realized yet.

It is known that the biodegradable chemical intermonomer bonds include glycosides, peptides, and aliphatic esters.<sup>10)</sup> Thus, some of the most attractive materials with greatest potential in terms of cost, material applications, and environmental compatibility include cellulose derivatives, especially cellulose esters. Among the cellulose esters, cellulose acetate (CA) has been produced industrially in large amounts. Thus, the greatest interest has recently focussed on the potential biodegradability of CAs. Buchanan et al.<sup>11)</sup> and Komarek et al.<sup>12)</sup> have demonstrated that CA with a degree of substitution (DS) of up to 2.5 can be degraded microbially. Sakai et al.<sup>13)</sup> have searched for fungi that decompose CAs; they demonstrated that *Neisseria sicca* can degrade CA with a DS of up to 2.3. It also has been suggested that CA would undergo an enzymatic splitting by acetyl esterase at the first stage, down to a DS of 1.0, before the degradation started by the action of cellulase enzymes.<sup>12-14)</sup>

Since cellulose diacetate (CDA) has been recognized as a biodegradable

polymer, various trials have been undertaken to impart sufficient thermoplasticity to CAs to render them melt-processable. This is because CDA, which has the greatest thermoplasticity among all CAs, fails to show adequate melting behavior without decomposition or discoloring. Thus, reducing the flow temperature of CAs is important and it requires the addition of plasticizers and flow promoters.

Traditional plasticization of CAs has been accomplished using conventional plasticizers with low-molecular weights, such as phthalates, glycerol derivatives, phosphates, etc. At present, phthalates and phosphates are used industrially in procedures that are often very time-consuming (i.e., 4-5 h per batch). These plasticizers are not suitable for the preparation of biodegradable polymers because of the harmful nature of their decomposition products. In this connection, there have been several attempts trying to utilize aliphatic polyesters as plasticizers for CAs.<sup>15)</sup>

In view of this situation, we have been attempting in the past 5 years to find novel plasticizers and plasticizing procedures by which biodegradable thermoplastic polymers can be obtained from CAs. Attempts have been made to introduce oligoester chains into CA molecules by reacting CA with dibasic acid anhydrides such as maleic anhydride (MA) and succinic anhydride (SA) together with monoepoxides such as phenyl glycidyl ether (PGE), styrene oxide (SO), and allyl glycidyl ether (AGE). The oligoesterifications of CAs have been carried out by the use of a compounding machine at high temperatures with constant kneading speed. The results of these attempts are described in this chapter.

## **4-2 Experiment**

### **4-2-1 Materials**

Cellulose acetates with different DSs, LL-10 and L-40, were supplied by Daicel Chemical Industries Co. Ltd. The DS of LL-10, monoacetate (CMA) (not utilized as thermoplastic), was 1.7-1.8, and that of L-40, diacetate (CDA) (commonly utilized as thermoplastic), was 2.4-2.5. Their degrees of polymerizations were 100-200, and 160, respectively. SA, MA, PGE, SO, and AGE, used as reactive plasticizing agents, and acetone for Soxhlet extractions were either extra pure or guaranteed grade.

## **4-2-2 Pretreatment**

Weighed amounts of CA (LL-10 or L-40), succinic anhydride (SA), and phenyl glycidyl ether (PGE), were mixed in a mortar by using a pestle. The mixtures were allowed to stand for 0 to 20 h under dry conditions at room temperature.

## **4-2-3 Reaction of CAs with plasticizers during melt processing**

Weighed amounts of CAs (LL-10 or L-40), dibasic acid anhydride (SA or MA) and monoepoxide (PGE, SO, or AGE) were preliminarily mixed in a beaker. The mixture was then charged into a kneader (Labo Plastomill LPM 18-125, Toyo-Seiki Co. Ltd.) that had been preheated at 70-180 °C while operating at 30 rpm for 5 min. The total amount of the mixture was 24 g, which corresponds to the void volume of the mixing chamber of the kneader and causes torque while blending and reacting. After charging the mixture into the chamber, the rate of rotation was increased to 90 rpm, and the kneading reaction was performed within 15-20 min to obtain a plasticized sample.

## **4-2-4 Preparation of molded sheets**

The kneaded samples were molded into sheets by hot pressing using a Toyo-Seiki 10 T bench hot press. The samples (about 3 g) were placed between polyethylene terephthalate (PET) sheets with a 0.4 mm thick spacer. The temperature of the heated press was 180-200 °C. For molding, a gage pressure of < 5 MPa was applied slowly, during 3-5 min in order to allow air bubbles to dissipate. The pressure was subsequently raised to 15 MPa and maintained for 30-45 s. The samples were cooled for 10-15 min to room temperature by cold pressing at 15 MPa.

## **4-2-5 Tensile tests**

Strips of samples, 80 × 5 × 0.4 (mm), were cut from the molded sheets, and these were allowed to stand for more than 48 h at 20 °C and 60% relative humidity. The tensile tests were then performed using these conditioned samples and a Shimadzu Autograph DCS-R-500 under the same atmospheric conditions. The measurements were made using a span length of 40 mm and a cross-head speed of 0.5 mm/min. Average values were obtained from eight repeated

measurements for the tensile strength, the breaking elongation, and Young's modulus.

#### 4-2-6 Solvent extraction of samples

The samples prepared as described in Sections 4-2-2-2 and 4-2-2-3 were dried and accurately weighed. These samples were extracted with acetone using Soxhlet extractors for 34 h. Then the extracted samples were dried and weighed again to obtain the weight decrease. The weight loss represents unreacted dibasic acid anhydride, monoepoxide, and free oligomers.

#### 4-2-7 Infrared spectroscopic measurements

A fourier-transform infrared spectrophotometer (Shimadzu FTIR-4000) was used for infrared (IR) spectroscopic measurements. The technique used KBr disks for the measurements.

#### 4-2-8 Flow tests

The thermal softening and flow behavior of the plasticized samples were observed using a flow tester (Shimadzu CFT-500A). The diameter and the length of the die used were 1 and 2 mm, respectively. The measurements were made at a heating rate of 10 °C/min under a constant load of 1 or 2 MPa.

#### 4-2-9 Viscosity measurements

The flow tester described above was used for measuring the melt-viscosity of the plasticized samples. The measurements were made at 200 °C under a constant compressive load of 1 MPa.

### 4-3 Results and discussion

#### 4-3-1 Plasticization of CAs by Reaction with SA and PGE

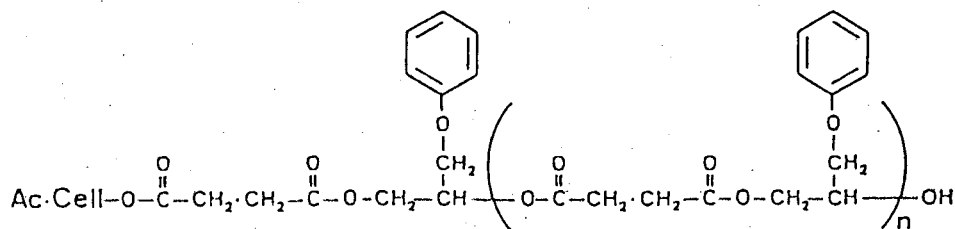


Fig. 4-1. Schematic chemical structure of CA oligoesterified with SA and PGE.



Oligoesterified CA, prepared by reacting CA with SA and PGE at temperatures ranging between 70 and 180 °C, has the hypothetical structure shown in Fig. 4-1. Similar oligoesterifications of wood have been studied extensively by Matsuda and others.<sup>17)</sup>

This kind of introduction of oligoester side chains into CA molecules enhances the thermoplasticity of the CA (internal plasticization). At the same time, homo-oligomers of the oligoester are produced, and these may act as external plasticizer.

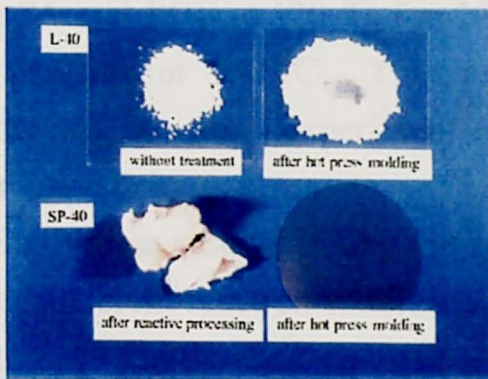


Fig.4-2. Effects of oligoesterification on L-40.

Notes: Upper left : untreated L-40 ; upper right : L-40 hot pressed at 190°C under 15 MPa for 30 s; lower left : L-40/SA/PGE (100/11.0/33.8) just after being kneaded at 120°C for 20 min without pretreatment ; lower right : a sheet from the kneaded sample (lower left) prepared by hot pressing at 190°C under 15 MPa for 30 s.

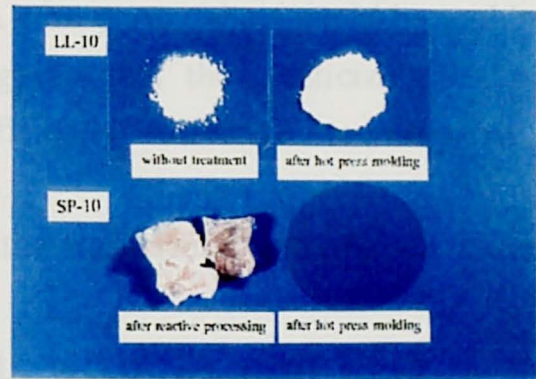


Fig.4-3. Effects of oligoesterification on LL-10.

Notes: Upper left : untreated LL-10 ; upper right : LL-10 hot pressed at 190°C under 15 MPa for 30 s ; lower left : LL-10/SA/PGE (100/11.0/33.8) just after being kneaded at 120°C for 20 min without pretreatment ; lower right : a sheet from the kneaded sample (lower left) prepared by hot pressing at 190°C under 15 MPa for 30 s.

The effect of the plasticization treatment can be seen in Fig. 4-2. The CDA sample, L-40, is shown in the upper left part in the figure, and a molded sheet prepared from the L-40 powder is shown in the upper right. Although CDA is known to have the greatest thermoplasticity among cellulose acetates, its thermal

fluidity is insufficient to form a uniformly transparent sheet, when hot pressed at 190 °C. Only the small central area of the sheet reveals a certain transparency. However, when the L-40 powder was reacted with SA and PGE at 120 °C for 20 min under kneading conditions, it was converted easily into a thermoplastic material, as shown in the lower part of Fig. 4-2.

The corresponding situation is illustrated for cellulose monoacetate (CMA), LL-10, in Fig. 4-3. Even though LL-10 was hot pressed at 190 °C, only a powderous briquette could be formed, revealing much less thermoplasticity than L-40 (CDA).

However, the thermoplasticity could be enhanced drastically by kneading it with SA and PGE at 120 °C for 20 min. A transparent sheet could be molded by hot pressing at 190 °C. This result suggests that the plasticizing technique attempted in this experiment is sufficiently effective to improve the thermoplasticity.

Since these results are very promising, the plasticization of CAs was examined under different reaction conditions.

### 4-3-1-1 Effect of pretreatments with SA and PGE

Table 4-1. Tensile properties of various polymers.

Polymers	Tensile strengths (MPa)	Young's moduli (MPa)	Elongations at break (%)
PS	30	860	4
PE	26	340	800
PCL	21	160	480
ACETYLOID <sup>a)</sup>	20-46	—	32-53
SP-10 <sup>b)</sup>	32-43	1000-1177	22-40
SP-40 <sup>c)</sup>	26-29	837-900	30-44

<sup>a)</sup> Cellulose acetate plastic commercialized by DAICEL CRAFT LTD., Japan; <sup>b)</sup> LL-10/SA/PGE=100/11.0/33.8; <sup>c)</sup> L-40/SA/PGE=100/11.0/33.8; <sup>b,c)</sup> kneading: 120°C, 30 rpm (5 min)-90 rpm (20 min); hot pressing: 190°C, 15 MPa, 30 S.

In Fig. 4-4, the results of CMA (LL-10) pretreatments with SA and PGE are shown. The mixtures had been allowed to stand for 0 to 20 h under dry and sealed conditions before they were reacted at 120 °C in the kneader operating at 90 rpm. They were then molded into sheets, and evaluated for tensile properties. It should be noted that CMA was found to be more resistant to plasticization than CDA. The results suggest that this kind of pretreatment is unnecessary for the plasticization. Actually, transparent sheets could already be obtained without any pretreatment,

and their tensile properties were found to be almost identical to those of the oligoesterified sheets prepared using pretreatment. The tensile properties were comparable to those of many synthetic polymers as well as conventional plasticized cellulose acetate, "ACETYLOID" (Table 4-1).

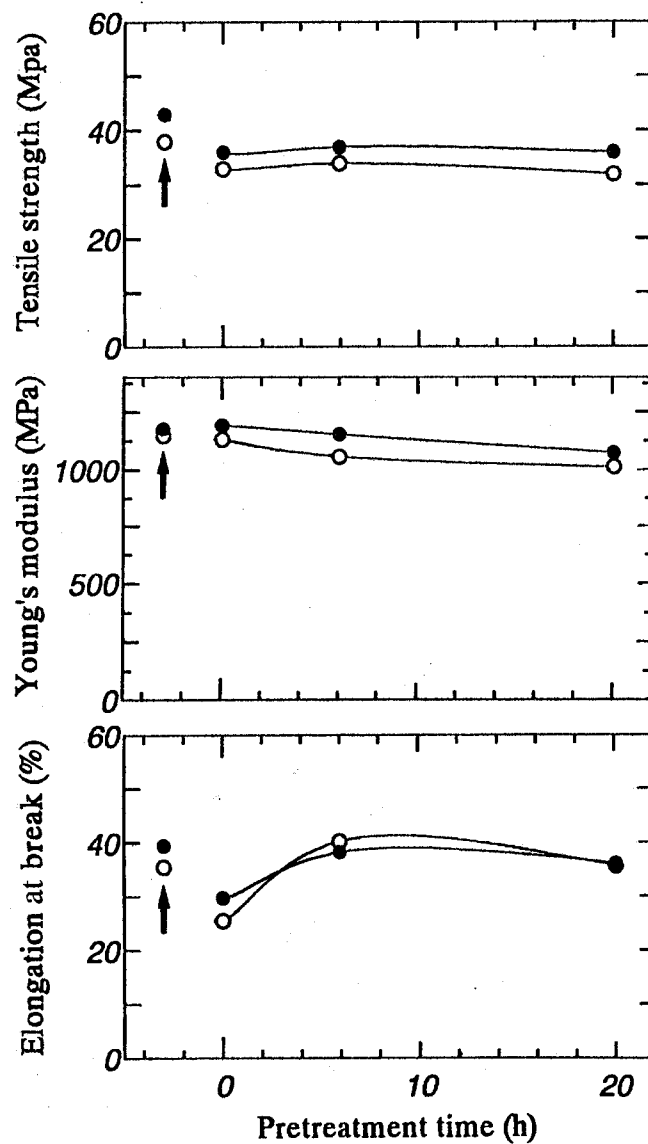


Fig. 4-4. Effect of pretreatments on the tensile properties of plasticized LL-10.

Notes : LL-10/SA/PGE=100/11.0/33.8 ; kneading: 120°C, 30 rpm (5 min) -90 rpm (20 min) ; hot pressing:○: 180°C, 15 MPa, 30s; ●: 190°C, 15 MPa, 30 s; the data with an arrow were obtained from plasticized LL-10 without pretreatment.

### 4-3-1-2 Effect of plasticizer addition

In the experiments of Section 4-3-1-1 , the amount of the plasticizer were kept constant at 30.9% (that is, CA:SA:PGE = 100:11.0:33.8 by wt.). In order to investigate the effect of the amount of plasticizer added, the amount was varied in the range from 8.7 to 47.3% (that is, CA:SA:PGE = 100:2.3:7.2 to 100:22.0:67.6). In this case, the molar ratio of SA to PGE was kept constant at 1:2, corresponding to the functionality. Using these amounts, the plasticization reaction in the kneader was accomplished at 120 °C without pretreatment, at a rotation speed of 90 rpm for 20 min, and the kneaded products were molded into sheets. The resulting sheets from LL-10 are shown in Fig. 4-5. The results indicate (a) that the thermal fluidity decreases less with lower amounts of plasticizer; and (b) that below certain amounts (about 18.3% for LL-10, as shown in Fig. 5, and about 8.7% for L-40, not shown), molding by hot pressing becomes impossible. The fact that LL-10 requires larger amounts of plasticizer compared with L-40 can be explained by the lower thermoplasticity of the former. Additionally, as less plasticizer is added, LL-10 (with the greater content of free hydroxyl groups) can be expected to crosslink more easily. Greater amounts of plasticizer would therefore be required for LL-10 to gain thermal fluidity. In Fig. 4-5, the samples with larger amounts of plasticizer more than 26.4% had enough thermal fluidity to be called thermoplastics.

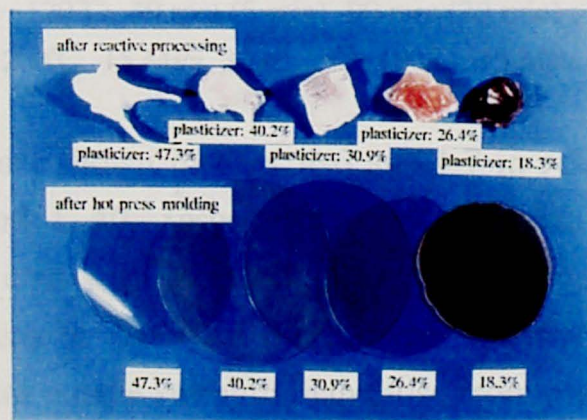


Fig. 4-5. Effect of plasticizer content on LL-10.

Notes: Reactive plasticizers used: SA and PGE ; plasticizer content : 18.3 - 47.3% ; prepared without pretreatment ; kneading : 120°C, 30 rpm (5 min) -90 rpm (20 min) ; hot pressing ; 190°C, 15 MPa, 30 s.

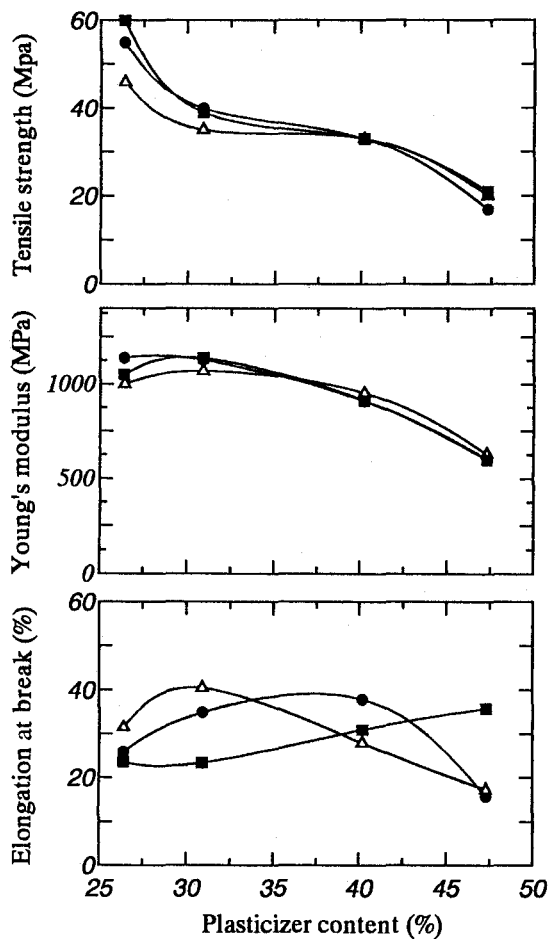


Fig. 4-6. Effect of plasticizer content on the tensile properties of plasticized LL-10.

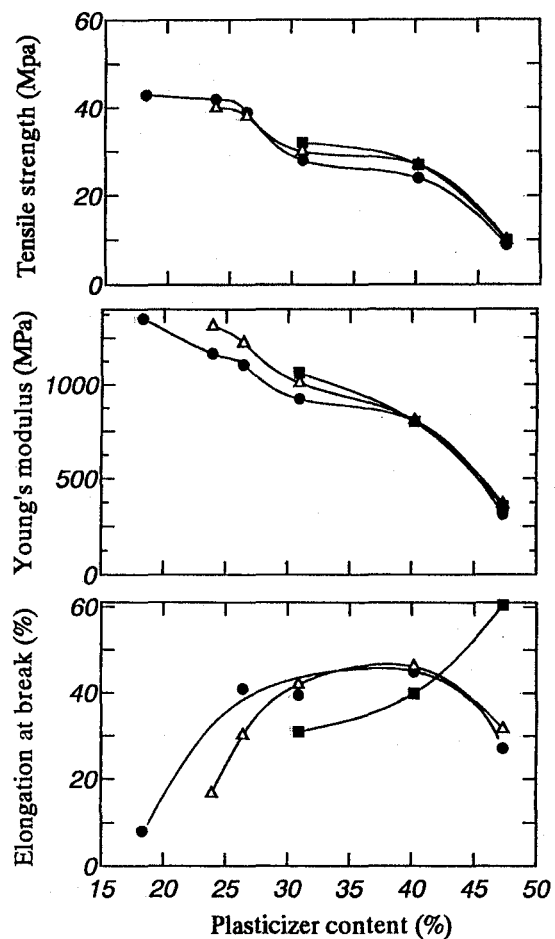


Fig. 4-7. Effect of plasticizer content on the tensile properties of plasticized L-40.

Notes for Figs. 4-6 and 4-7 : Reactive plasticizers used: SA and PGE ; prepared without pretreatment ; kneading : 120°C, 30 rpm (5 min) -90 rpm (20 min) ; hot pressing : ●: 190 °C, 15 MPa, 30 s ; △ :200°C, 15 MPa, 30 s ; ■: 190°C, 15 MPa, 300 s.

Tensile properties are shown in Figs. 4-6 and 4-7 in relation to the plasticizer content for LL-10 and L-40, respectively. As expected, tensile strength and Young's modulus decrease with increasing plasticizer content. By comparison of Figs. 4-6 and 4-7, it can be seen that the molded sheets from plasticized LL-10 have a somewhat greater tensile strength than those from plasticized L-40.

### 4-3-1-3 Effect of kneading temperature

The kneading temperature of the plasticization reaction was raised from 70 to 180 °C, with the plasticizer content and kneading time remaining constant at

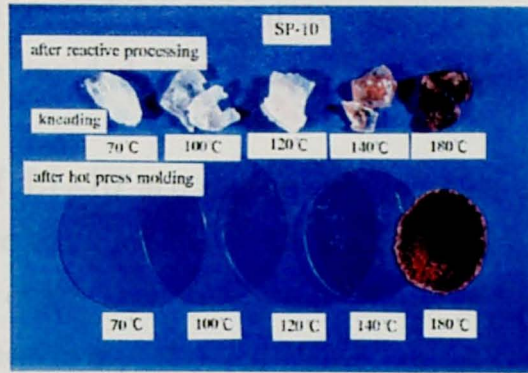


Fig. 4-8. Effect of kneading temperature on LL-10.

Notes : LL- 10/SA/PGE=100/11.0/33.8 ; prepared without pretreatment ; kneading: 70-180°C, 30 rpm (5 min) -90 rpm (20 min) ; hot pressing : 190°C, 15 MPa, 30 s.

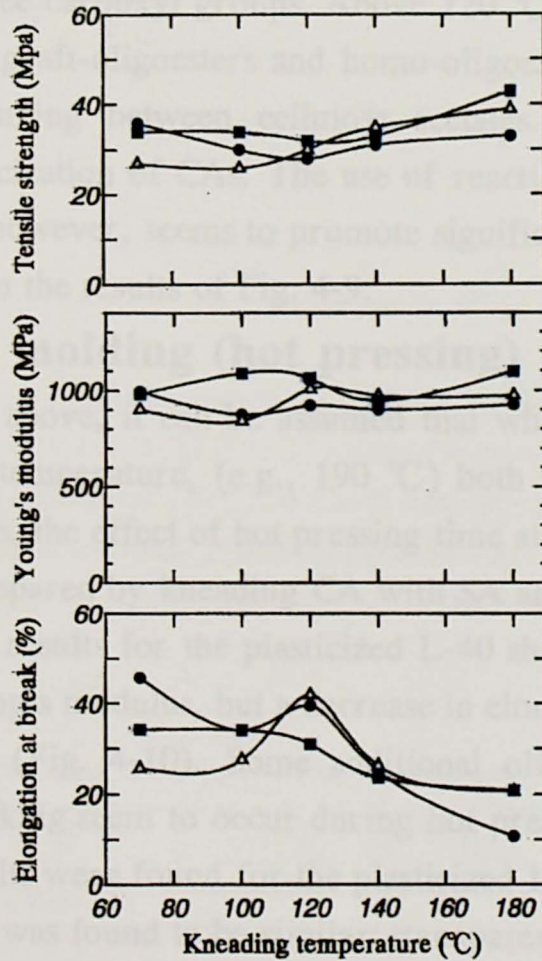


Fig.4-9 Effect of kneading temperature on the tensile properties of plasticized L-40.

Notes : L-40/SA/PGE=100/11.0/33.8 ; prepared without pretreatment ; kneading condition: 70-180°C, 30 rpm (5 min) -90 rpm (20 min) ; hot pressing condition: ●: 190 °C, 15 MPa, 30 s ; △: 200°C, 15 MPa, 30 s ; ■: 190°C, 15 MPa, 300 s.

30.9% (CA:SA:PGE = 100:11.0:33.8) and 20 min, respectively. The plasticized CAs thus obtained were molded into sheets, and their tensile properties were evaluated.

The molded sheets of LL-10 are shown in Fig. 4-8. With an increase in the kneading temperature, the color of the sheet becomes darker, and thermal fluidity decreases. The tensile strength and Young's modulus of the corresponding sheets obtained from L-40, however, showed little variation, but the values for elongation at break were found to decrease significantly (Fig. 4-9). Almost identical results were obtained for plasticized sheets of LL-10.

It has been pointed out<sup>7)</sup> that below 120 °C (the optimum reaction temperature in the kneader), the hydroxyl groups of cellulose react with acid anhydrides and epoxides but not with free carboxyl groups. Above 120 °C, they react even with carboxyl groups. Thus, graft-oligoesters and homo-oligoesters are thought to be formed without crosslinking between cellulose acetates. These are favorable conditions for the plasticization of CAs. The use of reaction temperatures above 120 °C in the kneader, however, seems to promote significantly the formation of crosslinks as judged from the results of Fig. 4-9.

#### **4-3-1-4 Effect of molding (hot pressing) time**

From the discussion above, it can be assumed that when oligoesterified CAs are hot pressed at high temperature, (e.g., 190 °C) both oligoesterification and crosslinking occurs. Thus, the effect of hot pressing time at 190 °C was examined. The sample used was prepared by kneading CA with SA and PGE at 120 °C, for 20 min, at 90 rpm. The results for the plasticized L-40 show a small increase in tensile strength and Young's modulus, but a decrease in elongation at break, as hot pressing time increased (Fig. 4-10). Some additional oligoesterification and a small amount of crosslinking seem to occur during hot pressing. Almost identical but less pronounced results were found for the plasticized LL-10. The appearance of all the sheets obtained was found to be similar: transparent and colorless.

The thermal fluidity of plasticized CA and the corresponding molded samples were measured and the data obtained are listed in Table 4-2. In the case of both LL-10 and L-40, the flow temperatures were found to have risen as the hot pressing time increased.

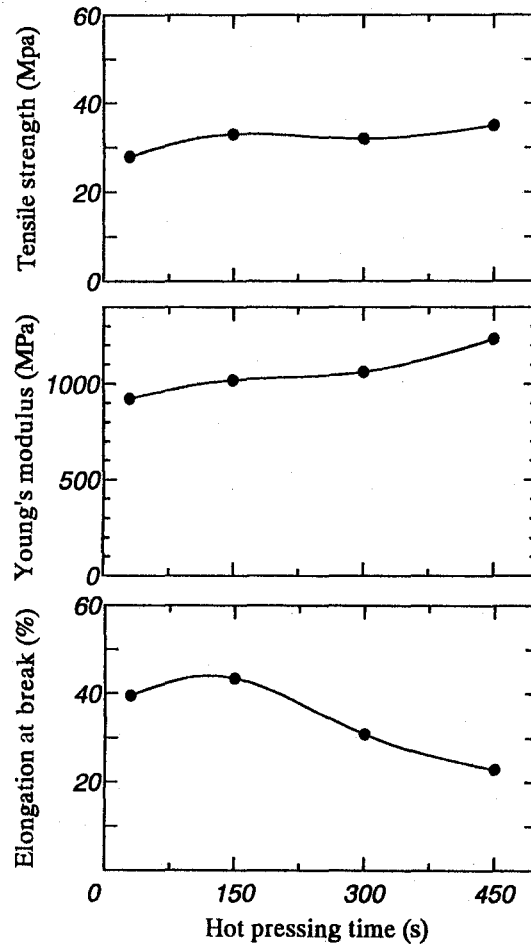


Fig. 4-10. Effect of hot pressing time on the tensile properties of plasticized L-40.  
 Notes : L-40/SA/PGE=100/11.0/33.8 ; prepared without pretreatment ;  
 kneading condition: 120°C, 30 rpm (5 min) -90 rpm (20 min) ;  
 hot pressing condition: 190°C, 15 MPa, 30-450 s.

Table 4-2. Effect of hot pressing on thermal flow properties.

Samples	Compositions (w/w)	Hot pressing times <sup>a)</sup> (s)	Flow temperatures <sup>b)</sup> (°C)
LL-10	—	—	259.9
SP-10	LL-10/SA/PGE=100/11.0/33.8	0	200.0
	LL-10/SA/PGE=100/11.0/33.8	300	234.8
L-40	—	—	249.8
SP-40	L-40/SA/PGE=100/11.0/33.8	0	169.9
	L-40/SA/PGE=100/11.0/33.8	300	199.9
	L-40/SA/PGE=100/11.0/33.8	2400	289.8

<sup>a)</sup> 190°C, 15 MPa ; <sup>b)</sup> flow test : die diameter : 1 mm, length : 2 mm ; plunger : 1 cm<sup>2</sup> ; heating rate : 10°C/min ; load : 10 kgf.



### 4-3-1-5 Mechanical and thermal properties of oligoesterified CAs with SA and PGE

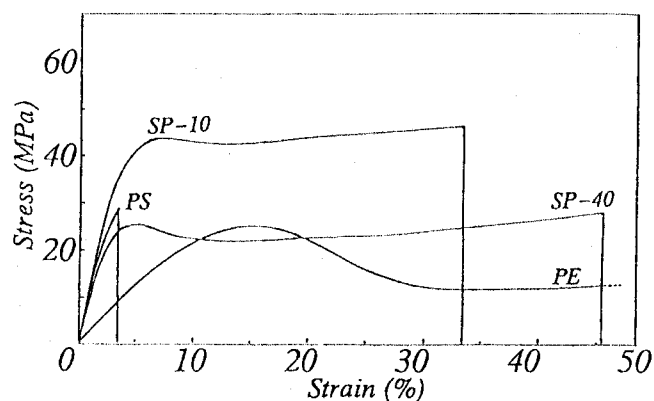


Fig. 4-11. Stress-strain curves of representative CAs plasticized with SA and PGE.

Notes: SP-10 (40) : LL-10 (L-40) / SA / PGE=100 / 11.0 / 33.8 ; prepared without pretreatment ; kneading condition : 120°C, 30 rpm (5 min) -90 rpm (20 min) ; hot pressing condition: 190°C, 15 MPa, 30 s ; tensile test : span: 40 mm ; crosshead speed : 5 mm /min.

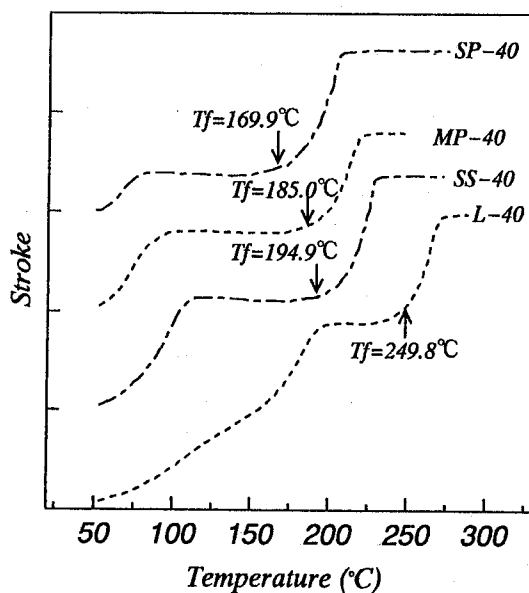


Fig. 4-12. Thermal softening curves for L-40 and its plasticized materials.

Legend: L-40: untreated, SP-40: L-40 / SA / PGE=100 / 11.0 / 33.8, MP-40: L-40 / MA /PGE= 100 / 10.8 / 33.8, SS-40: L40 / SA / SO=100 / 11.0 / 27.0.

Notes: Prepared without pretreatment ; kneading condition : 120 °C, 30 rpm (5 min)-90 rpm (20 min) ; flow test condition : load: 10 kgf; heating rate : 10°C / min ; Tf : flow temperature.

Representative stress-strain curves for L-40 and LL-10 oligoesterified with SA and PGE, termed SP-40 and SP-10, respectively, are shown comparatively in Fig. 4-11 along with those for PS and PE. From this figure, both SP-10 and SP-40 appear to have attractive mechanical properties. They are tougher than PS and stronger than PE.

Thermal softening curves for L-40 and its plasticized materials are shown in Fig. 4-12. Among the latter, SS-40 (oligoesterified L-40 reacted with SA and SO) is included as well. This belongs to the plasticized CAs discussed in the following section. From the figure, it can be seen that when L-40 was oligoesterified with SA and PGE in an amount of 30.9 wt% by the use of a reaction at 120 °C for 20 min in the kneader, the flow temperature dropped by about 80 °C (from 250 to 170 °C).

The same thermal flow properties were examined also for LL-10 and its plasticized samples. The flow temperature of LL-10 was found to be 259.9 °C, and this could be reduced to 200 °C by plasticization with 30.9 wt% of SA and PGE in the kneader. That is about a 60 °C-drop in the flow temperature.

### 4-3-2 Plasticization of CA by reactive melt-processing using various combinations of dibasic acid anhydride and monoepoxide

Table 4-3. Thermal flow properties of various samples.

Samples	Compositions (w/w)	Flow temperatures <sup>o)</sup> (°C)	Melt viscosities <sup>d)</sup> (poise)
LL-10	—	259.9	—
SP-10	LL-10/SA/PGE=100/11.0/33.8	200.0	38040
MP-10	LL-10/MA/PGE=100/10.8/33.8	214.9	59300
L-40	—	249.8	—
SP-40	L-40/SA/PGE=100/11.0/33.8	169.9	8615
MP-40	L-40/MA/PGE=100/10.8/33.8	185.0	11940
SS-40	L-40/SA/SO=100/11.0/27.0	194.9	83850
PP <sup>a)</sup> (MI <sup>b)</sup> =9)	PP/Antioxidant=100/3	194.6	8248
PP <sup>a)</sup> (MI=35)	„	180.9	3610

<sup>a)</sup> Produced by Ube Industries Ltd. J-109G; <sup>b)</sup> MI=Melt Index.; <sup>c)</sup> flow test: die diameter: 1 mm, length: 2 mm, plunger: 1 cm<sup>2</sup>, heating rate: 10°C/min; load: 10 kgf; <sup>d)</sup> flow test: die diameter: 1 mm, length: 2 mm, plunger: 1 cm<sup>2</sup>, set temperature: 200°C, load: 10 kgf.

Various combinations of dibasic acid anhydride and monoepoxide, SA-SO, MA-PGE, SA-AGE, and MA-AGE were adopted as reactive plasticizers for L-40

and LL-10. The use of MA resulted in plasticized CAs having higher flow temperatures than those obtained with SA. This is revealed in the curves for SP-40 and MP-40 in Fig. 4-12. They also have larger melt viscosities (Table 4-3) as well as molded sheet strengths and Young's moduli compared with those using SA. Also, in the case of combinations of MA-AGE and SA-AGE, the reactive melt-processing temperature was found to be reduced to 80 °C, because there occurred a large increase in sample temperature during kneading at 120 °C. This resulted in hardened materials that failed to undergo melt-flow. It was found that, especially in the case of the combination of MA-AGE, the reactive plasticizer content needed to be increased. For instance, the use of 26.8% reactive plasticizer of (that is, CA:MA:AGE = 100:10.8:25.9) resulted in an unmoldable kneaded product whereas the use of twice as much (53.6%) gave satisfactory transparent sheets.

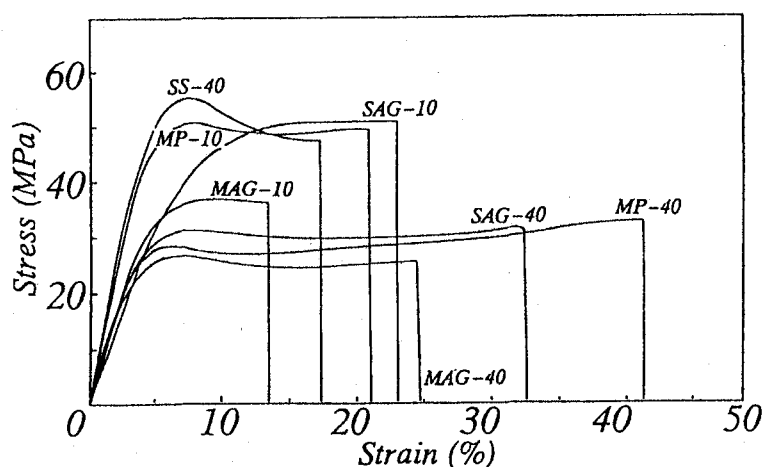


Fig. 4-13. Stress-strain curves of various plasticized CAs.

Notes : SS - 40 : L - 40 / SA / SO = 100 / 11.0 / 27.0 ; pretreatment: 12 h ; kneading : 120 °C, 30 rpm (5 min) -90 rpm (20 min) ; hot pressing: 190°C, 15 MPa, 30 s ;  
 MP-10 (40) : LL-10 (L-40) / MA / PGE=100 / 10.8 / 33.8 ; without pretreatment ;  
 kneading: 120°C, 30 rpm (5 min) -90 rpm (20 min) ; hot pressing: 190°C, 15  
 MPa, 30 s ; SAG-10 (40) : LL-10 (L-40) / SA / AGE = 100 / 11.0 / 25.9 ;  
 without pretreatment; kneading: 80 °C, 30 rpm (5 min) -90 rpm (15 min) ; hot  
 pressing: 190°C, 15 MPa, 30 s ; MAG-10 : LL-10 / MA / AGE = 100 / 21.5 /  
 51.8 ; without pretreatment ; kneading: 80°C, 30 rpm (5min) - 90 rpm (15 min) ;  
 hot pressing: 190°C, 15 MPa, 30 s ; MAG-40 : L- 40 / MA / AGE = 100 / 16.5 /  
 50.7 ; without pretreatment ; kneading : 80°C, 30 rpm (5 min) -90 rpm (15 min) ;  
 hot pressing. 200°C, 15 MPa, 30 s ; tensile test for all samples: span : 40 mm ;  
 crosshead speed: 5mm/min.

Stress-strain curves of various oligoesterified CAs are shown in Fig. 4-13. Thermal flow properties of several types of plasticized CAs are tabulated in Table 4-3. For comparison, the results of PP are also included. It is known that some of the plasticized CAs possess thermal flow properties comparable to those of PP.

### 4-3-3 Plasticizer migration ("bleeding")

The occasional appearance of white powders on the surface of molded sheets of plasticized CAs has been attributed to the bleeding-out of plasticizers. This is caused by fugitive plasticizers which are chiefly homo-oligomers, and by a small portion of unreacted acid anhydrides and monoepoxides. Since the acid anhydrides and the monoepoxides are highly reactive under the reaction conditions in the kneader, the amount of unreacted plasticizer must be small.

The occurrence of plasticizer bleeding was found to be much more pronounced for plasticized L-40 than for LL-10 (Fig. 4-14). This difference is presumably thought to be caused by a lack of miscibility, that is, a lack of affinity between the CAs and the oligoesters. To make two immiscible polymers (A and B, or polymer A and oligomer B) miscible or compatible, a compatibilizer is

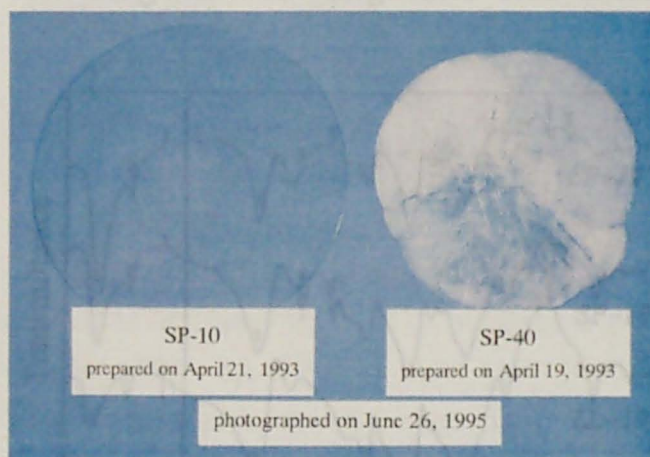


Fig. 4-14. Bleeding of plasticizer from sheets of plasticized L-40 and LL-10.

Note: SP-10 : LL-10 / SA / PGE = 100 / 11.0 / 33.8 ; prepared on April 21, 1993 ; SP-40 : L-40 / SA / PGE = 100 / 11.0 / 33.8 ; prepared on April 19, 1993 ; kneading condition: 120°C, 30 rpm (5 min) - 90 rpm (20 min) ; hot pressing condition: 190°C, 15 MPa, 30 s ; photographed on June 26, 1995.

required. Among compatibilizers, block or graft copolymers are most effective. Applying this knowledge to the above mentioned difference between the plasticized L-40 and LL-10, the loss of plasticizer can be attributed to the degree of occurrence of oligoester side chains along the CA main chain.

The introduction of oligoester side chains into the CA molecules can be expected to result in an enhanced affinity between the modified CAs and homo-oligoester, preventing the migration from inside to the surface of plasticizer. LL-10 has about three times as many hydroxyl groups as L-40 and thus three times greater probability of introducing oligoester substituents into the backbone. Actually, during the reaction in the kneader, a temperature rise of about 24 °C was observed for LL-10, whereas that of L-40 was only about 12 °C.

The grafting is also confirmed by the IR spectra obtained from LL-10 and oligoesterified LL-10 before and after acetone extraction, as in Fig. 4-15. In these spectra, absorptions appearing at 2943 and 1731  $\text{cm}^{-1}$  are attributed to methylene and carbonyl, respectively; those at 1600, 1500, 750, and 700  $\text{cm}^{-1}$  are all attributed to in-plane skeletal vibration of benzen ring or out-of-plane deformation vibration of CH belonging to benzene ring. It is apparent that even after acetone extraction, the absorptions at 1600, 1500, 750, and 700  $\text{cm}^{-1}$  are clearly observable, revealing that the oligoester side chains formed by the

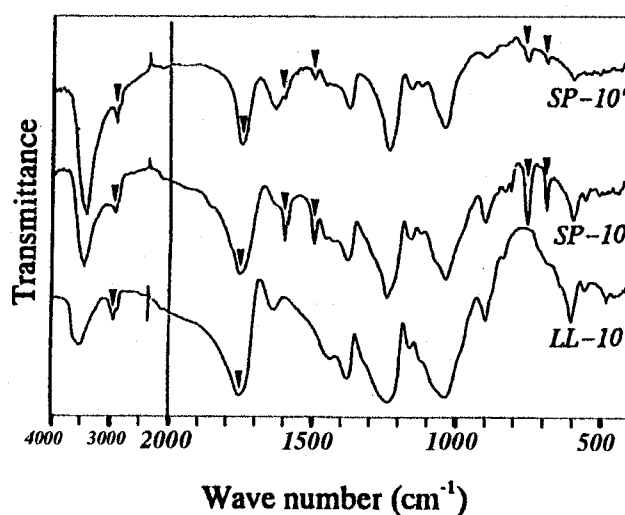


Fig. 4-15. IR spectra of CA and plasticized CA with and without acetone extraction.

Note: LL-10 : untreated CA ; SP-10 : LL-10 /SA /PGE = 100 / 11.0 / 33.8 ;  
 kneading condition : 120°C, 30 rpm (5 min)-90 rpm (20 min) ; SP-10' :  
 acetone extraction residue from SP-10.

reaction of SA and PGE substantially are introduced into LL-10. The degree of appearance of these key bands for oligoesterified L-40 is comparatively small.

In this connection, it is noteworthy that, when the same oligoesterification reaction was performed with cellulose triacetate (CTA), it did not result in a similar plasticization effect. In this experiment, a sample named MTR was used as CTA. Fig. 4-16 shows, that even though the CTA sample was treated under conditions normally effective for plasticizing CA, the resulting plasticized CTA did not reveal sufficient thermal fluidity for forming compression molded sheets.

These experimental results reveal that the chemical introduction of oligoester side chains into CA molecules is essential for CAs to gain significant thermoplasticity.

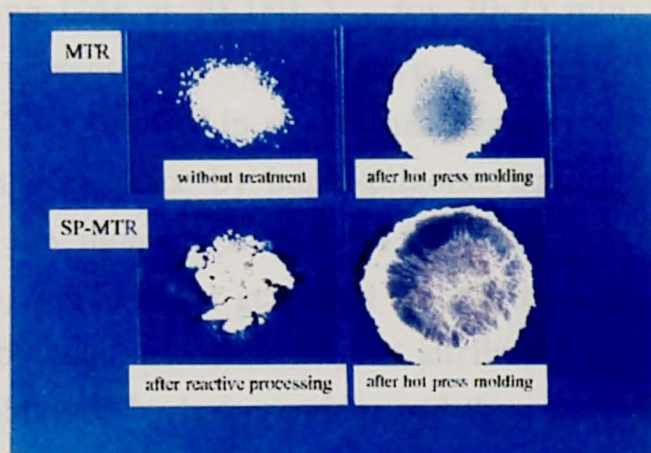


Fig. 4-16. Effect of plasticization on CTA.

Note : Upper left : untreated MTR ; upper right : MTR hot pressed at 190°C under 15 MPa for 30 s ; lower left : MTR / SA / PGE = 100 / 11.0 / 33.8 just after kneading at 120°C for 20 min without pretreatment ; lower right : a sheet from the kneaded sample (lower left) prepared by hot pressing at 190°C under 15 MPa for 30 s.

In another experiment, oligoesterification was performed in advance, followed by the preparation of a mixture with CDA and exposure to the reaction conditions in the kneader. The results indicated that a less effective plasticization of CA was

obtained. This also confirms the role of dibasic acid anhydride in order to modify the residual hydroxyl groups of CDA. When dibasic acid anhydride is reacted with monoepoxide without the presence of CDA, the acid anhydride groups will easily be consumed, and the probability of reaction with cellulosic hydroxyl groups diminishes.

#### 4-4 Summary

A plasticization method for cellulose acetates (CAs) that is based on the reaction with dibasic acid anhydrides and monoepoxides during melt processing was developed. This reactive melt-processing method allowed the preparation of biodegradable cellulosic plastics using practical process conditions. Some of the physical properties of the plasticized products were examined. The reactions were performed by kneading CAs at 70-180 °C, for 20-25 min, during which the hydroxyl groups present in CAs were subjected to esterification (oligoesterification). This resulted in an internal plasticization effect. In addition, external plasticization took place by homo-oligomerization between the dibasic acid anhydrides and the monoepoxides. Not only cellulose diacetate, but also cellulose monoacetate, which is not generally utilized as a plastic material, could be easily plasticized by this method. This was attributed to the low crystallinity of CA. Sheets were obtained by hot pressing, and they were transparent. Melting properties and melt processability of these plasticized products could be improved by selecting (a) the degree of substitution of CA used; (b) the species and the relative amounts of plasticizing reactive reagents; and (c) plasticization reaction conditions. Some of the resulting materials exhibited plasticizer loss by "bleeding"

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## Chapter 5

# Development of cellulose acetate plastics free from plasticizers bleeding and their biodegradabilities<sup>1-7)</sup>

### 5-1 Introduction

In the previous chapter, it was shown that cellulose acetates (CAs) can be effectively plasticized by reactive melt-processing. To achieve effective plasticization, CA must be graft copolymerized with oligomers (i.e., internal plasticization). Cellulose triacetate, which does not have any residual hydroxyl groups and which has no possibility to be grafted, can not be plasticized by this reactive melt-processing method.<sup>8)</sup>

It was also shown in the previous chapter that it often occurs a problem of (external) plasticizer bleeding. In this case, homo-oligomers prepared during melt-processing are not stable in the moldings and tend to migrate from the inside to the surface. In this regard, it was suggested that grafting can effectively suppress or prevent the bleeding of non-grafted homo-oligoesters that are formed during grafting. Cellulose monoacetate (CMA) more easily generates products with reduced bleeding compared to cellulose diacetate (CDA), supposedly because the grafting proceeds to a higher level in the former case.<sup>8)</sup>

In this chapter, the effect of oligomer grafting on reducing the bleeding of homo-oligomers was further enhanced by increasing the grafting efficiency. The biodegradability of the resulting oligoester-grafted CAs was also examined.

## **5-2 Experiment**

### **5-2-1 Materials**

Cellulose acetates with different degrees of substitution (DSs), LL-10 and L-40, were supplied by Daicel Chemical Industries Co. Ltd. The DS of LL-10, monoacetate (CMA) (not utilized as thermoplastic), was 1.7-1.8, and that of L-40, diacetate (CDA) (commonly utilized as thermoplastic), was 2.4-2.5. Their degrees of polymerizations were 100-200, and 160, respectively. Succinic anhydride (SA), maleic anhydride (MA), phenyl glycidyl ether (PGE), allyl glycidyl ether (AGE), and glycidyl methacrylate (GMA) were used as reactive plasticizing agents; sodium carbonate was used as esterification catalyst; dimethylformamide (DMF) and methanol were used as the solvent and the non-solvent, respectively, for the purification of plasticized CAs. These reagents were "extra pure" or "guaranteed grade" and were used as received.

### **5-2-2 Reaction of CAs with plasticizers during melt-processing**

Weighed amounts of CAs (LL-10 or L-40), dibasic acid anhydride (SA or MA) and monoepoxide (AGE, PGE, or GMA) were preliminarily mixed in a beaker. The mixture was then charged into a kneader (Labo Plastomill LPM 18-125 ; Toyo-Seiki Co. Ltd.) that had been preheated to 80-120 °C while operating at 30 rpm (revolutions per minute) for 5min. The total amount of the mixture was 24 g, which corresponds to the void volume of the mixing chamber of the kneader and causes torque while blending and reacting. After charging the mixture into the chamber, the rate of rotation was increased to 90 rpm, and the reaction in the kneader was performed within 10-40 min to obtain a plasticized sample.

### **5-2-3 Preparation of molded sheets**

The kneaded samples were molded into sheets by hot pressing using a Toyo-Seiki 10 T bench hot press. The samples (about 3 g) were placed between polyethylene terephthalate (PET) sheets with a 0.4 mm thick spacer. The temperature of the heated press was 180-200 °C. For molding, a gauge pressure of < 5 MPa was applied slowly, taking 3-5 min to allow air bubbles to dissipate. The pressure was subsequently raised to 15 MPa and maintained for 30-45 s. The

samples were cooled for 10-15 min to room temperature by cold pressing under the same pressure (15 MPa).

#### **5-2-4 Tensile tests**

Strips of samples,  $80 \times 5 \times 0.4$  (mm), were cut from the molded sheets, and these were allowed to stand for more than 48 h at 20 °C and 60% relative humidity. The tensile tests were then performed using these conditioned samples and a Shimadzu Autograph DCS-R-500 under the same atmospheric conditions. The measurements were made using a span length of 40 mm and a cross-head speed of 0.5 mm/min. Average values were obtained from eight repeated measurements for the tensile strength, the breaking elongation, and Young's modulus.

#### **5-2-5 Purification of the plasticized CAs by the dissolution and reprecipitation technique**

The sample prepared as described in Section 5-2-2 was dried and accurately weighed : A (g). The sample was dissolved in DMF (ca. 5 wt%) and reprecipitated in excess amount of methanol (ca. 40 times of DMF solution of the sample). Then, the reprecipitated product was stirred in methanol overnight. After that, it was collected by filtration and the precipitate was washed with water, and dried to constant weight : B (g). The weight gain of CA (%) was calculated based on the following equation.

$$\text{Weight gain of CA (\%)} = \frac{\text{B (g)} - \text{Calculated weight of CA in A (g)}}{\text{Calculated weight of CA in A (g)}} \times 100$$

#### **5-2-6 Gel permeation chromatography (GPC)**

The molecular weight distribution of the samples prepared as described in Section 5-2-2, their purification products and the corresponding methanol-solubles, were determined in a TOSOH HLC-8020 gel permeation chromatograph equipped with a refractive index (RI) detector using two TSK-GEL GMH<sub>HR</sub> columns connected in series. Measurements were conducted using tetrahydrofuran (THF) as mobile phase at a flow rate of 1.0 mL/min. The concentration of test samples was 0.5 % in THF and the injected amount was 100

$\mu$ l. The system was calibrated by monodisperse polystyrene standards.

### **5-2-7 Infrared spectroscopic measurements**

A Fourier-transform infrared spectrophotometer (Shimadzu FTIR-4000) was used for infrared (IR) spectroscopic measurements. The technique used KBr disks for the measurements.

### **5-2-8 Flow tests**

The thermal softening and flow behavior of the plasticized samples was analyzed in a flow tester (Shimadzu CFT-500A). The diameter and the length of the die used was 1 and 2 mm, respectively. The measurements were made at a constant heating rate of 10 °C/min under a constant load of 5 MPa.

### **5-2-9 Viscosity measurements**

The flow tester described above was used for measuring the melt-viscosity of the plasticized samples. The measurements were made at 200 °C under a constant compressive load of 1MPa.

### **5-2-10 Biodegradability tests**

#### ***soil burial test :***

Plasticized CA samples were buried in a standard soil composed of eight parts (by volume) of culture soil, one part of humus soil and one part of vermiculite. The sample was buried in soil located in a conditioning room (30°C, 80%RH), and the water content of the soil was adjusted to the original value (about 45 %) by repeated watering. Strips of samples, 80 × 5 × 0.4 (mm), were cut from the molded sheets and used for this test. The soil burial test periods were 1, 3, 6 and 12 months. After each soil burial test, the samples were washed and dried to their constant weights in a vacuum oven at 60 °C . Then, they were conditioned under the same conditions as those for test pieces for the above-mentioned tensile test, and evaluated with regard to their external appearance, weight loss and mechanical properties. High density polyethylene (HDPE), cellulose triacetate (CTA), Japanese cedar and polycaprolactone (PCL) were used as control samples in strip shapes.

#### ***Determination of oxygen consumption in a closed activated sludge suspension :***

Pulverized, plasticized CA samples were suspended in activated sludge, and oxygen consumption was measured by use of a coulometer, installed at Daicel Chemical Industries Co. Ltd. The activated sludge was obtained from the Himeji municipal sewage treatment plant.

## 5-3 Results and discussion

### 5-3-1 Role of grafting in preventing bleeding of the external plasticizer

In the previous chapter, it was suggested that the larger the amount of grafting onto CA is, the lower is the extent of bleeding of monomers and homo-oligomers toward the surface of plasticized CA moldings.<sup>8)</sup> The experimental data presented needs additional evidence for unequivocal proof.

#### 5-3-1-1 Grafting and its role on bleeding

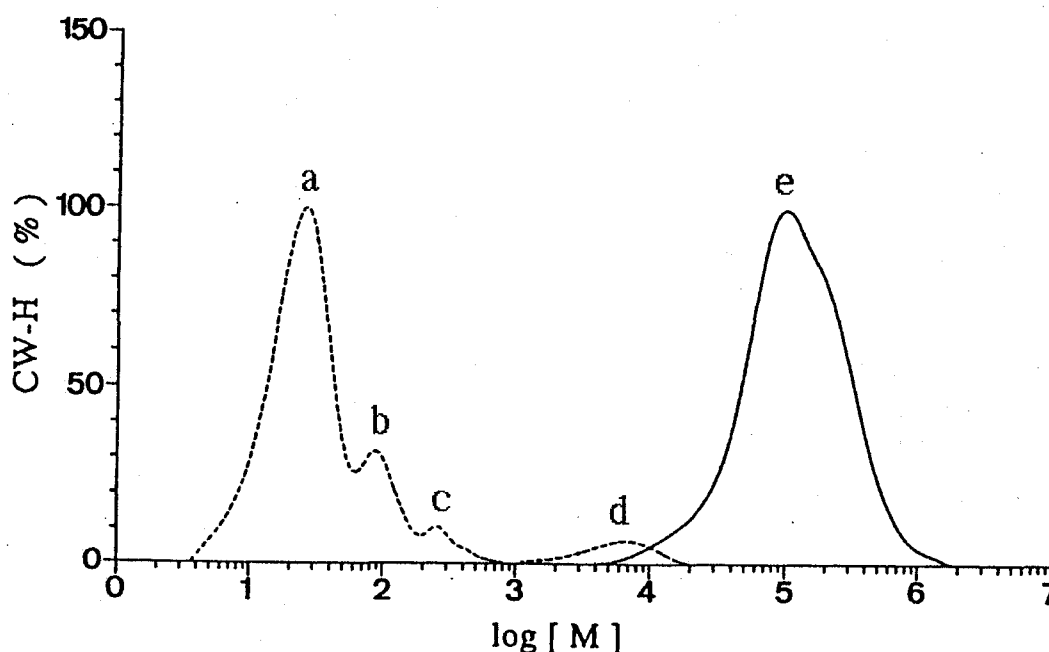


Fig. 5-1. GPC chromatogram of precipitated SP-40 and MeOH-soluble material of SP-40.

Legend: ——— : precipitated SP-40 ; - - - - - : MeOH-soluble material.

Notes: SP-40: L-40/SA/PGE=100/17.3/25.9 ; Kneading: 120°C, 90 rpm, 25 min.

In order to confirm the occurrence of oligoester grafting, crude products obtained by reactive melt-processing of CAs with dibasic acid anhydride and monoepoxides were first purified by the procedure described in Section 5-2-2-4. That is, DMF solutions of the crude products were poured into excess amounts of methanol. Both the precipitate and the filtrate were analyzed after washing and drying or after complete evaporation of methanol, respectively. An example of the results is shown in Fig. 5-1.

In the case presented in Fig. 5-1, 100 parts by wt. of CDA, L-40, was kneaded with 17.3 parts by wt. of SA and 25.9 parts by wt. of PGE at 120 °C, for 25 min. The solid line represents the reprecipitated material, and this is found to cover only the high molecular weight region, "e". On the other hand, the dotted line represents the methanol-soluble materials, and this is found to cover the low molecular weight region, "a" ~ "d". Thus, this provides clear evidence that the reprecipitated part contains only CA-related polymer and does not contain SA and PGE monomers and homo-oligomers; and the filtrate can be said to be composed of the monomers and homo-oligomers and no high molecular weight matter (not including acetic acid). Identical results were found in all other cases of this reactive melt-processing products, and this implies that the selection of solvent and non-solvent is appropriate, and that pure, grafted CAs can be obtained by this reprecipitation technique.

In the following, an attempt was made to determine semi-quantitatively the extent of graftings of oligoesters onto CAs. FT-IR spectroscopic measurements were used for these determinations. An example of the results is shown in Fig. 5-2.

In this figure, IR spectra of reprecipitated copolymers obtained after melt-processing CMA or CDA with MA and PGE at 120 °C for 15 min are compared with that of CMA, one of the starting CAs. In this case, the spectra **a**, **b** and **c** correspond to CMA (LL-10), oligoesterified CMA with MA and PGE (MP-10), and oligoesterified CDA with MA and PGE (MP-40), respectively. As is demonstrated by the results, a large number of absorption peaks, not existing in the spectrum **a**, are found in the spectra **b** and **c**. These include adsorption peaks at 700 and 750  $\text{cm}^{-1}$  being attributable to CH out-of-plane deformation vibrations of benzene rings with one substituent; peaks at 1500 and 1600  $\text{cm}^{-1}$  attributable to in-plane skeletal vibrations of benzene rings; peaks at 825  $\text{cm}^{-1}$  attributable to CH

out-of-plane deformation vibrations of olefine having a side chain in its double bond portion; peaks at  $1660\text{ cm}^{-1}$  attributable to the stretching vibrations between C=C of the cis form double bond; and so forth. These absorption peaks stem from MA and PGE and the corresponding grafting products.

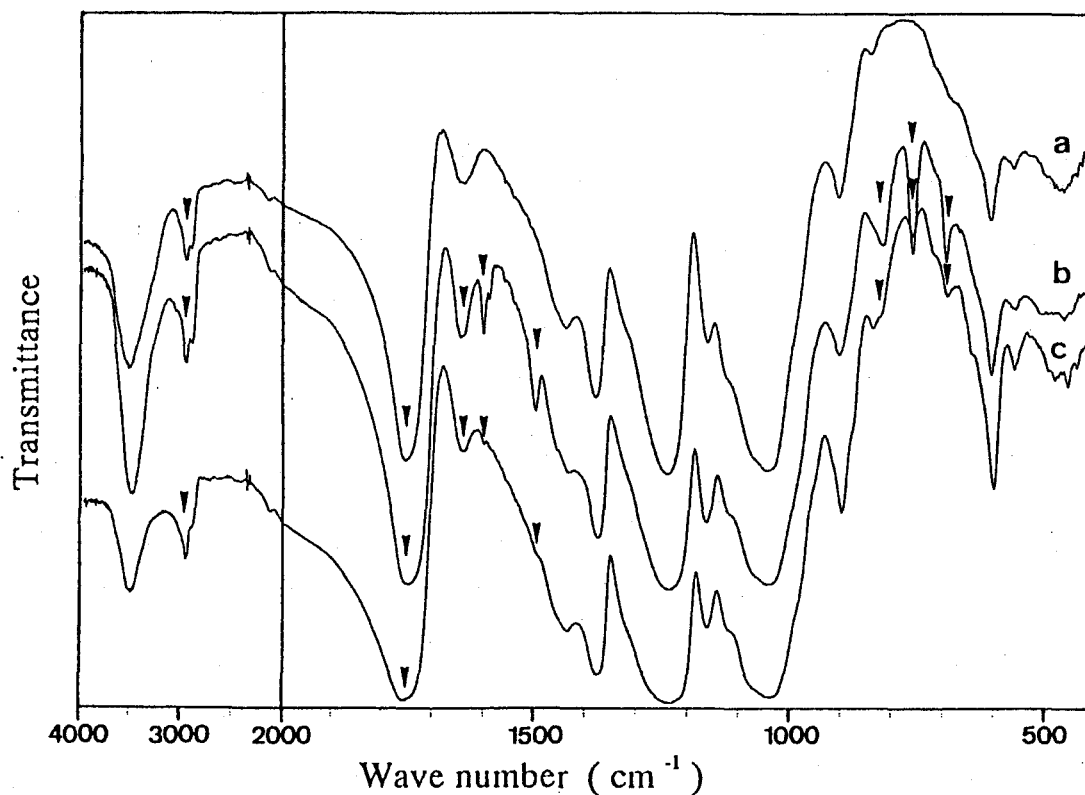


Fig. 5-2. IR spectra of precipitated MP-10 and MP-40.

Legend: a: untreated LL-10; b: precipitated MP-10; c: precipitated MP-40.

Notes: MP-10: LL-10/MA/PGE=100/21.3/32.6; MP-40:L-40/MA/PGE =100/21.3/32.6; Kneading:  $120^{\circ}\text{C}$ , 90 rpm, 15 min.

In Fig. 5-2, it is also possible to compare the amounts grafted for LL-10 and L-40. The characteristic absorption peaks attributable to the grafted oligoesters appear more markedly for the oligoesterified LL-10 (curve b in Fig. 2) than for the oligoesterified L-40 (curve c). Thus, the supposition made in the previous chapter that more oligomers can be introduced into LL-10 than into L-40<sup>8)</sup> finds further evidence. This observation also demonstrates that the copolymerization



capacity with homo-oligoester substituents is higher in the former case than in the latter.

### 5-3-1-2 Method for enhancing the grafting efficiency

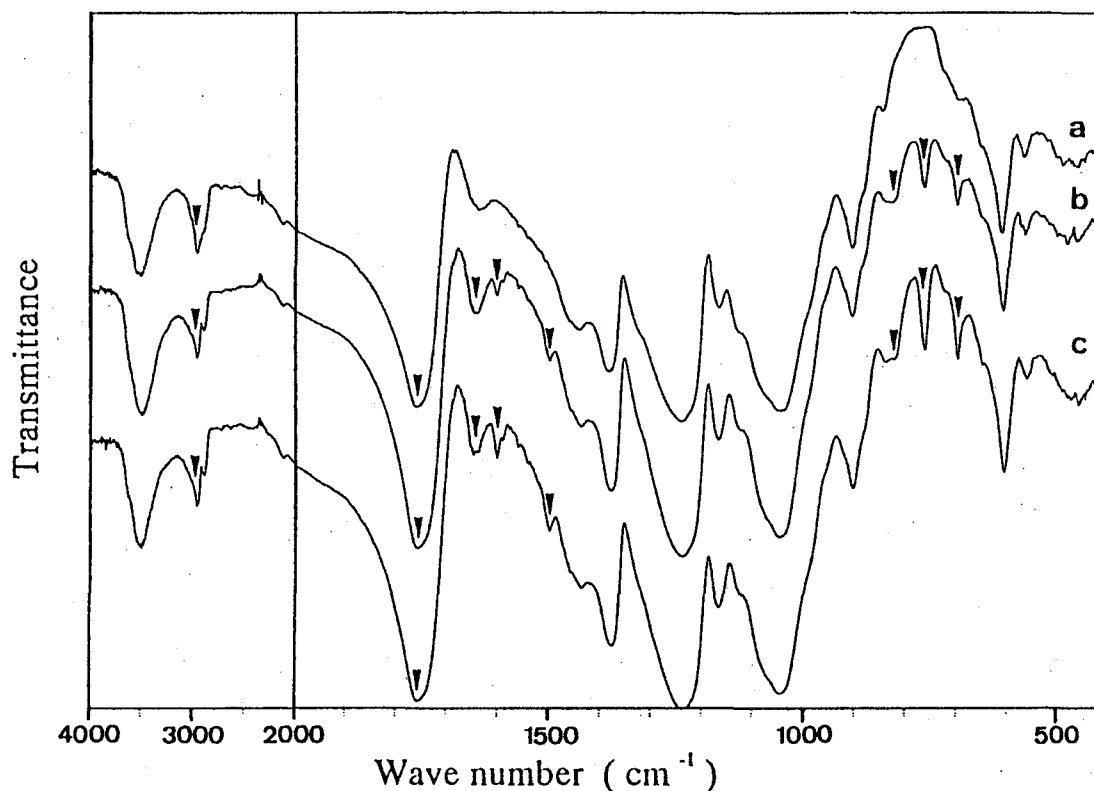


Fig. 5-3. IR spectra of untreated L-40 and MP-40.

Legend: **a**: untreated L-40; **b**: reprecipitated MP-40 (kneading: 20 min);  
**c**: reprecipitated MP-40 (kneading: 30 min).

Notes: MP-40: L-40/MA/PGE=100/16.9/25.9; Kneading: 120 °C , 90 rpm, 20 or 30 min.

In chapter 4, we concluded that it is the degree of grafting that controls the bleeding of homo-oligomers within the grafted CAs. Now, it became of interest to study the possibility whether the amount of grafting onto L-40 (CDA) could be increased by changing the conditions of reactive melt-processing.

In the first place, the reaction time was prolonged. Results obtained by FT-IR spectroscopy are shown in Fig. 5-3.

The IR spectrum of purified MP-40 (L-40/MA/PGE=100/16.9/25.9 by weight;

120 °C) prepared by kneading for 20 min (curve b) is compared with that prepared by kneading for 30 min (curve c). The IR spectrum of untreated L-40 (curve a) is also shown. It is clear from the analysis of the data that an increased amount of oligoester can be introduced into L-40 by increasing the kneading reaction time.

The determination of the actual grafting amount was pursued by measuring the weight increase of oligoesterified L-40 after purification.

The results are shown in Figs. 5-4 ~ 5-6 for MP-40, SP-40 (oligoesterified CDA with SA and PGE) and SG-40 (oligoesterified CDA with SA and GMA), respectively. In the figures, weight gains of L-40 after purification (amount of grafting), as well as flow temperatures of the corresponding grafted products are shown as a function of the kneading time.

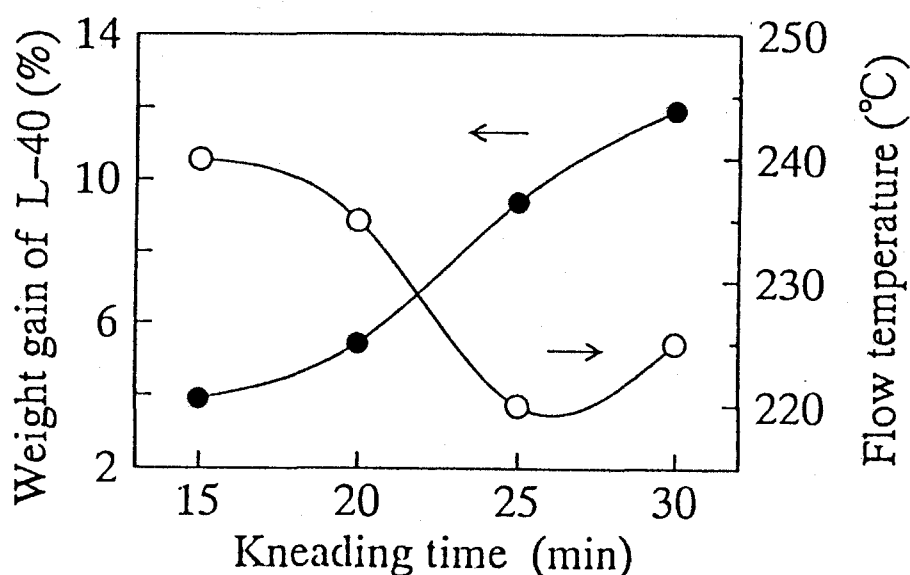


Fig. 5-4. Effect of kneading time with MA and PGE at 120°C on weight gain of L-40 and flow temperature of the grafted L-40.

Notes: Notes: L-40/MA/PGE=100/16.9/25.9; Kneading: 120 °C, 90 rpm; Flow test: Die: diameter: 1 mm, length: 2 mm; Plunger: 1 cm<sup>2</sup>; Load: 5 MPa; Heating rate: 10°C/min.

Legend: ●: Weight gain of L-40; ○: Flow temperature.

The weight gain and the flow temperature were found to depend on the reaction time in the kneader when all other conditions were kept constant. The data clearly illustrate that the amount of grafting (black circles in the figure) increases with increasing kneading time for all reactive plasticizers used. The increasing rate is especially significant in the case in which MA and PGE are used as plasticizers; in that case, the weight gain was found to be almost linear, reaching 12% after 30 min of reaction. In contrast, when SA and PGE, or SA and GMA, were used for grafting, less weight gain was observed. A certain dependence on the species of reactive plasticizer is observed. However, even in the case of SA/GMA, in which the grafting amount up to 30 min was very low, the amount could be drastically increased when the reaction time was extended to 40 min.

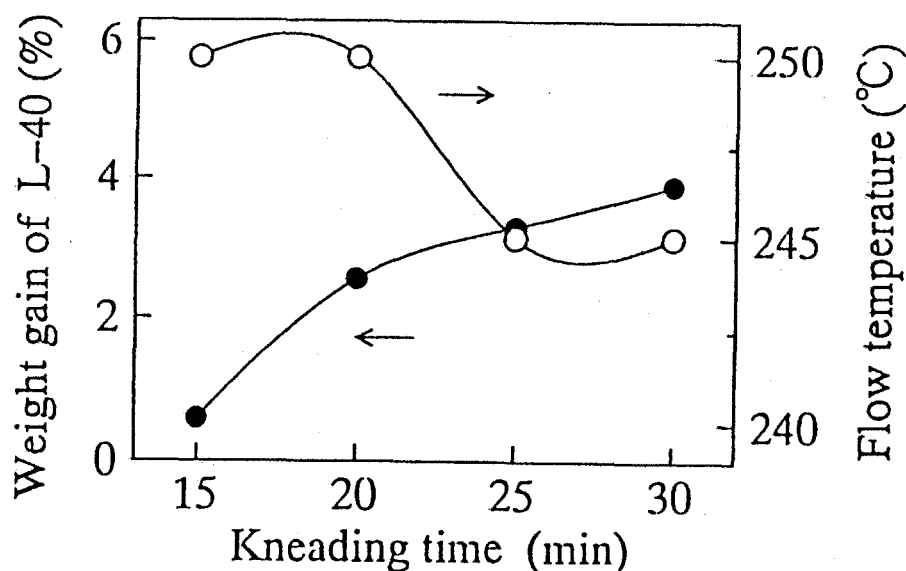


Fig. 5-5. Effect of kneading time with SA and PGE at 120°C on weight gain of L-40 and flow temperature of the grafted L-40.

Notes: L-40/SA/PGE=100/17.3/25.9; Kneading: 120°C, 90 rpm; Flow test: Die: diameter: 1 mm, length: 2 mm; Plunger: 1 cm<sup>2</sup>; Load: 5 MPa; Heating rate: 10 °C/min.

Legend: ●: Weight gain of L-40; ○: Flow temperature.

These results can be attributed to the difference in the reactivities among the plasticizers, that is, MA is a more reactive dibasic acid anhydride than SA, and PGE is more reactive than GMA as monoepoxide.

In accordance with the increase in the amount of grafting, the flow temperature decreases in every reaction system, confirming the effect of internal plasticization by grafting.

The effect is especially significant when MA/PGE is used as the reactive plasticizer; the flow temperature was found to decrease by as much as 20°C upon 25 min of kneading time. However, in the same reaction system, a small increase in the flow temperature is recorded between 25 to 30 min of reaction time regardless of the steady increase in the amount of grafting. This might be explained in terms of the occurrence of a small degree of crosslinking, or with the formation or enhancement of side-chain interactions in the grafted CDA.

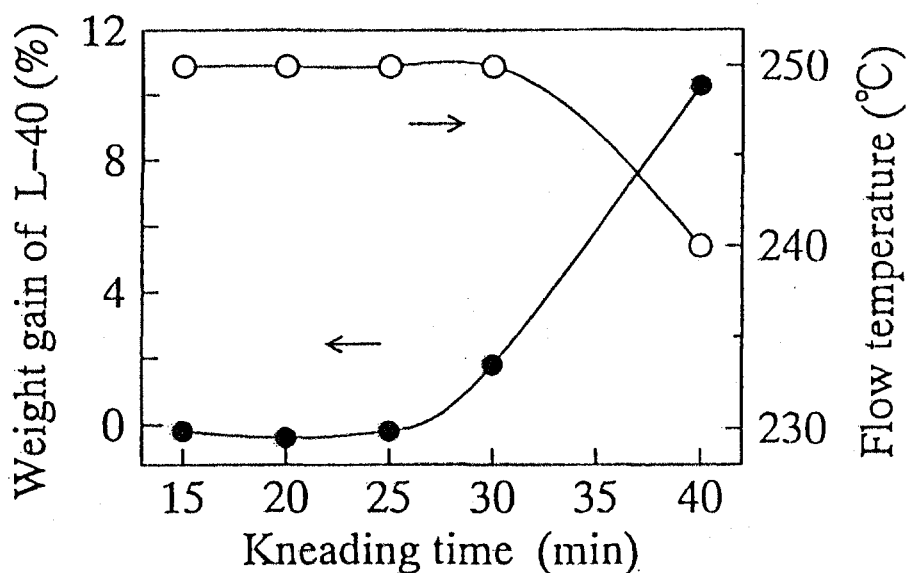


Fig. 5-6. Effect of kneading time with SA and GMA at 120°C on weight gain of L-40 and flow temperature of the grafted L-40.

Notes: Notes: L-40/SA/GMA=100/17.7/25.1; Kneading: 120°C, 90 rpm; Flow test: Die: diameter: 1 mm, length: 2 mm; Plunger: 1 cm<sup>2</sup>; Load: 5 MPa; Heating rate: 10°C/min.

Legend: ●: Weight gain of L-40; ○: Flow temperature.

A second attempt to raise the grafting efficiency focused on the addition of  $\text{Na}_2\text{CO}_3$  as catalyst. The experiment attempted to accelerate the esterification between the hydroxyl groups of CDA and the acid anhydride. The results are shown in Figs. 5-7 and 5-8.

As is apparent from these figures, the observed increase in grafting (i.e., the weight gain of CA) as well as the reduction in thermal flow temperature of the purified samples can be attributed to the addition of  $\text{Na}_2\text{CO}_3$  in every plasticizer system used.

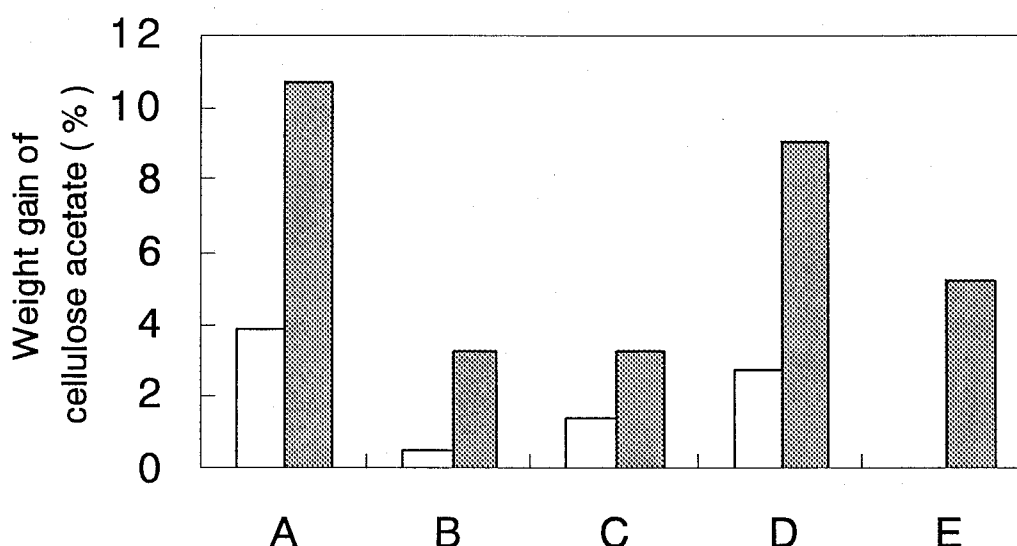


Fig. 5-7. Effect of catalyst ( $\text{Na}_2\text{CO}_3$ ) on weight gain of cellulose acetate.

Notes: Kneading :  $120\text{ }^\circ\text{C}$  , 90 rpm, 15 min ; Flow test : Die : diameter : 1 mm, length : 2mm ; Plunger :  $1\text{ cm}^2$  ; Load : 5 MPa ; Heating rate :  $10\text{ }^\circ\text{C}/\text{min}$ .

Legend: A: L-40/MA/PGE = 100/16.9/25.9 ( 30 % )  
 B: L-40/SA/PGE = 100/17.3/25.9 ( 30 % )  
 C: L-40/SA/PGE = 100/21.7/32.6 ( 35 % )  
 D: LL-10/SA/PGE = 100/21.7/32.6 ( 35 % )  
 E: L-40/SA/GMA = 100/17.7/25.1 ( 30 % )

\*Each value in parentheses shows reactive plasticizers content (wt%) in the starting material.

□ : without catalyst ( $\text{Na}_2\text{CO}_3$ ); ■ : with catalyst ( $\text{Na}_2\text{CO}_3$ )

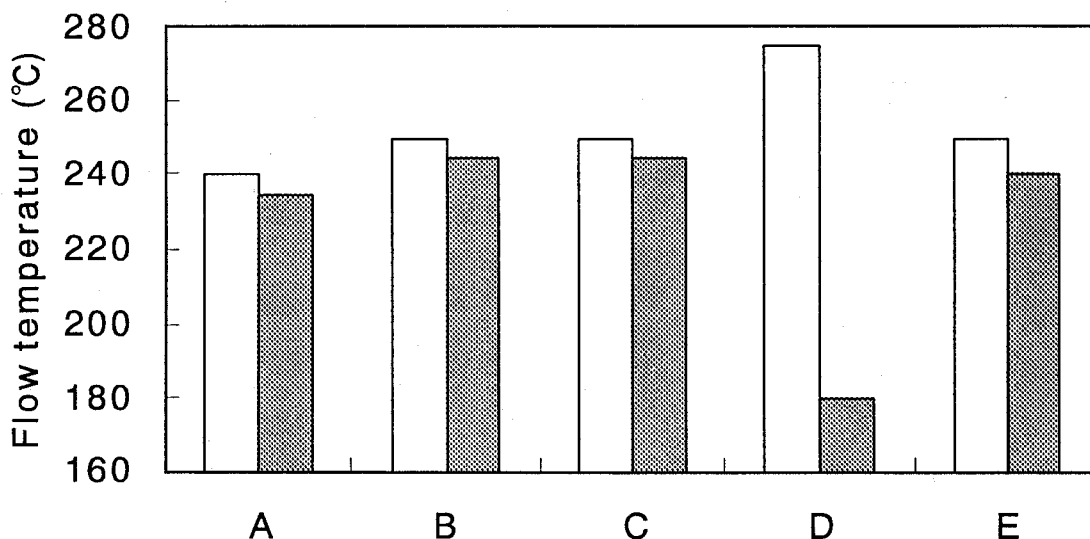


Fig. 5-8. Effect of catalyst ( $\text{Na}_2\text{CO}_3$ ) on melt processability of the purified products.

Notes: Kneading : 120 °C, 90 rpm, 15 min ; Flow test : Die : diameter : 1 mm, length : 2mm ; Plunger : 1 cm<sup>2</sup> ; Load : 5 MPa ; Heating rate : 10 °C/min.

Legend: A: L-40/MA/PGE = 100/16.9/25.9 ( 30 % )  
 B: L-40/SA/PGE = 100/17.3/25.9 ( 30 % )  
 C: L-40/SA/PGE = 100/21.7/32.6 ( 35 % )  
 D: LL-10/SA/PGE = 100/21.7/32.6 ( 35 % )  
 E: L-40/SA/GMA = 100/17.7/25.1 ( 30 % )

\*Each value in parentheses shows reactive plasticizers content (wt%) in the starting material.

□ : without catalyst ( $\text{Na}_2\text{CO}_3$ )

▨ : with catalyst ( $\text{Na}_2\text{CO}_3$ )

However, the catalyst effect varies depending on the composition of the reaction mixture. That is, when the reactive MA/PGE system was used as plasticizer in combination with LL-10 (the sample which has a higher residual hydroxyl content than L-40,) a greater grafting effect could be observed.

In addition, the catalytic effect of  $\text{Na}_2\text{CO}_3$  on the physical properties of the melt-processed and molded products was also studied. The results are shown in

Table 5-1. In all cases, the tensile strength and the Young's modulus of the molded sheet increased, and the breaking elongation decreased when catalyst was used. At the same time, both the melt viscosity and the apparent melt temperature of the melt-processed products increased. All these phenomena are interpreted in terms of the enhancement of grafting, as well as the increasing in homo-oligomer molecular weights. Bleeding of monomers and homo-oligomers was no longer observed, and it was completely prevented in sheets prepared from the L-40/MA/PGE and the LL-10/SA/PGE melt-processed products shown in Figs. 5-7, 5-8 and Table 5-1.

Table 5-1. Effect of catalyst (  $\text{Na}_2\text{CO}_3$  ) on physical and melt properties of the melt-processed products.

$\text{Na}_2\text{CO}_3$ Catalyst	Tensile strength ( MPa )	Elongation at break ( % )	Young's modulus ( MPa )	Melt viscosity ( poise )	Flow temp. ( $^\circ\text{C}$ )
L-40/MA/PGE=100/16.9/25.9					
without	37.2	23.9	1160	6110	165
with	49.9	10.8	1340	41570	185
L-40/SA/GMA=100/17.7/25.1					
without	34.4	30.8	1120	2400	145
with	50.8	11.5	1400	29820	165
L-40/SA/PGE=100/17.3/25.9					
without	29.9	25.5	1040	1580	165
with	31.3	15.9	1140	4500	170
L-40/SA/PGE=100/21.7/32.6					
with	25.6	26.6	840	480	135
LL-10/SA/PGE=100/21.7/32.6					
without	39.3	29.6	1110	16500	140
with	43.1	23.5	1250	73090	165

Notes : Kneading : 120  $^\circ\text{C}$ , 90 rpm, 15 min ; Hot pressing : 190  $^\circ\text{C}$ , 15 MPa, 5 min ;  
Flow test : Die : diameter : 1 mm, length : 2 mm ; Plunger : 1  $\text{cm}^2$  ; Load : 5 MPa;  
Set temperature : 200  $^\circ\text{C}$ ; Heating rate : 10  $^\circ\text{C}/\text{min}$ .

### 5-3-2 Biodegradability of CA plasticized by the oligoesterification

The plasticized CAs described above have been prepared by the use of reactive plasticizers which can be considered as biodegradable. Their preparation has also been based on the finding that CAs with a DS of up to 2.5 are biodegradable.<sup>9-13)</sup> The biodegradability of modified CAs, however, should be demonstrated experimentally.

The results of various soil burial tests in terms of changes in external appearance and changes in physical properties are summarized in Table 5-2 and Figs. 5-9 and 5-10. The figures are examples of the results obtained.

Although the high-density-polyethylene (HDPE) and cellulose triacetate (CTA) samples did not show biodegradability (Fig. 5-9), plasticized CAs prepared in this study, as well as Japanese cedar and polycaprolactone (PCL), revealed distinct degradability (Table 5-2, Fig. 5-10). In the case of plasticized CAs, the samples were degraded within relatively short periods of time (i.e., 3 to 6 months). Plasticized CAs from CMA (LL-10) were damaged more easily than those from CDA (L-40). Actually, the former were completely degraded within 3 to 12 months; and before their disappearance, the samples became cloudy and yellow, and their volume and weight increased. These changes can be explained by swelling, by the invasion of mycelia, and by the formation of internal voids. As degradation proceeds, swelling progresses and there is an increased mycelial invasion and accumulation, which prompts accelerated degradation. After 12 months, PCL was markedly degraded, leaving only several slivers; and plasticized CMA and CDA were either degraded completely or became cloudy. They yellowed, lost mass, and became brittle.

Overall, biodegradability was found to be affected by both amount and type of reactive plasticizer used. As might have been expected from their chemical structures, the results indicated that among the dibasic acid anhydrides SA, lacking unsaturation and having no possibility of forming cross linking structure, was more degradable as compared to MA; and that among the monoepoxides AGE, being free of aromaticity was easier to degrade than PGE. This means that by using glycerine in place of monoepoxide, a more degradable oligoesterified CA can be achieved.



Table 5-2. Changes of sample properties during soil burial test in incubator.

	loss(%)			Tensile strength		Young's modulus		Elongation at break	
	thickness	width	weight	(MPa)	loss(%)	(MPa)	loss(%)	(%)	loss(%)
<b>SP-10</b>									
0month	-	-	-	28	-	856	-	34.0	-
1month	-29.6	-3.7	-40.6	6	79	72	92	47.7	-40.3
3months	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
6months	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.
<b>SA-10</b>									
0month	-	-	-	31	-	996	-	22.6	-
1month	-47.5	-2.7	-136.3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
3months	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.
<b>MP-40</b>									
0month	-	-	-	45	-	1332	-	12.3	-
1month	-2.6	3.7	8.7	46	-2	1879	-41	3.6	70.7
3months	-0.8	6.2	12.8	57	-27	1927	-45	4.2	65.9
6months	-7.2	7.6	17.4	63	-40	2140	-61	4.2	65.9
12months	-0.3	7.1	18.5	53	-18	2125	-60	4.0	67.5
<b>MG-40</b>									
0month	-	-	-	36	-	1181	-	33.8	-
1month	-10.9	6.9	10.9	27	25	972	18	22.6	33.1
3months	-26.1	11.4	22.2	47	-31	1419	-20	5.4	84.0
6months	-16.7	13.4	29.2	25	31	1458	-23	2.5	92.6
12months	N.D.	N.D.	49.0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
<b>HDPE</b>									
0month	-	-	-	19	-	701	-	>50	-
1month	-0.9	0.6	-0.1	20	-5	733	4	>50	0
3months	0.6	0.9	0.0	19	0	618	13	>50	0
6months	4.9	1.8	0.1	22	-16	695	12	>50	0
12months	0.3	1.0	0.1	21	-11	753	-7	>50	0
<b>PCL</b>									
0month	-	-	-	18	-	462	-	6.9	-
1month	-2.8	1.2	1.4	17	6	555	-20	4.9	29.0
3months	-7.3	2.3	3.2	15	17	579	-25	3.8	44.9
6months	-	-	25.2	-	-	-	-	-	-
12months	-	-	79.7	-	-	-	-	-	-
<b>Japanese cedar</b>									
1month	-0.8	2.5	9.8	-	-	-	-	-	-
3months	-0.6	1.7	8.9	-	-	-	-	-	-
6months	-0.3	2.3	11.5	-	-	-	-	-	-
12months	N.D.	N.D.	81.8	-	-	-	-	-	-

Notes: SP-10: LL-10/SA/PGE=100/21.5/32.3 (w/w), Kneading: 120°C, 90 rpm, 20 min;  
 SA-10: LL-10/SA/AGE=100/25.1/28.7, Kneading: 80°C, 90 rpm, 15 min;  
 MP-40: L-40/MA/PGE=100/21.3/32.5, Kneading: 120°C, 90 rpm, 15 min;  
 MG-40: L-40/MA/Gly=100/16.7/16.7, Kneading: 120°C, 90 rpm, 20 min.  
 PCL: Daicel Chemical Industries, Co. Ltd. "PLACCEL H4"  
 HDPE: Mitsui sekiryu kagaku Co. "Hizex million 2100GP", N.D.: Couldn't be determined because samples were so deteriorated; S.D.: Sample's disappeared.

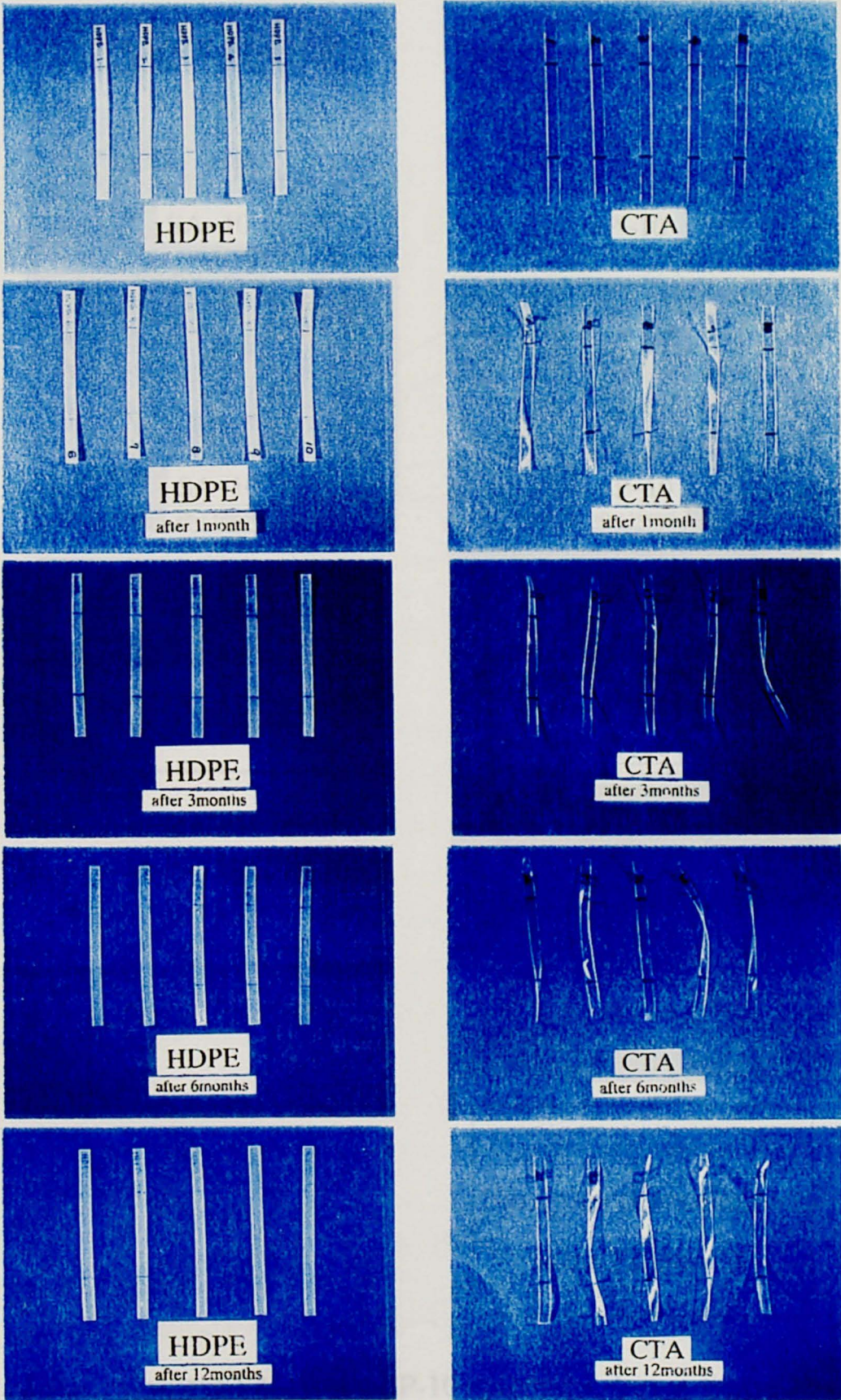


Fig. 5-9. Changes of HDPE and CTA specimens during the soil burial test in incubator.

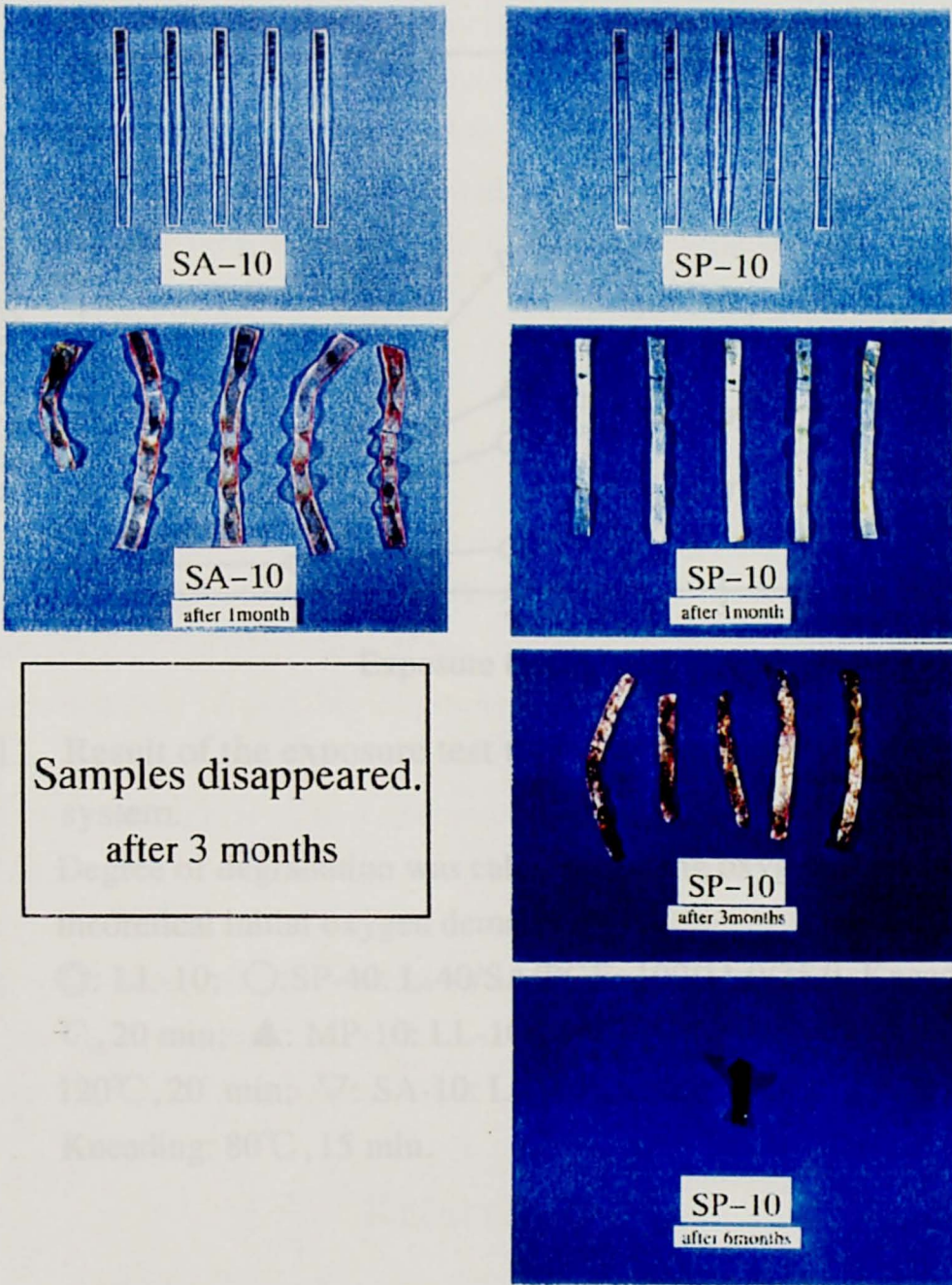


Fig. 5-10. Changes SA-10 and SP-10 specimens during the soil burial test in incubator.

Note: Composition and preparation conditions of the samples are shown in Notes of Table 5-2.

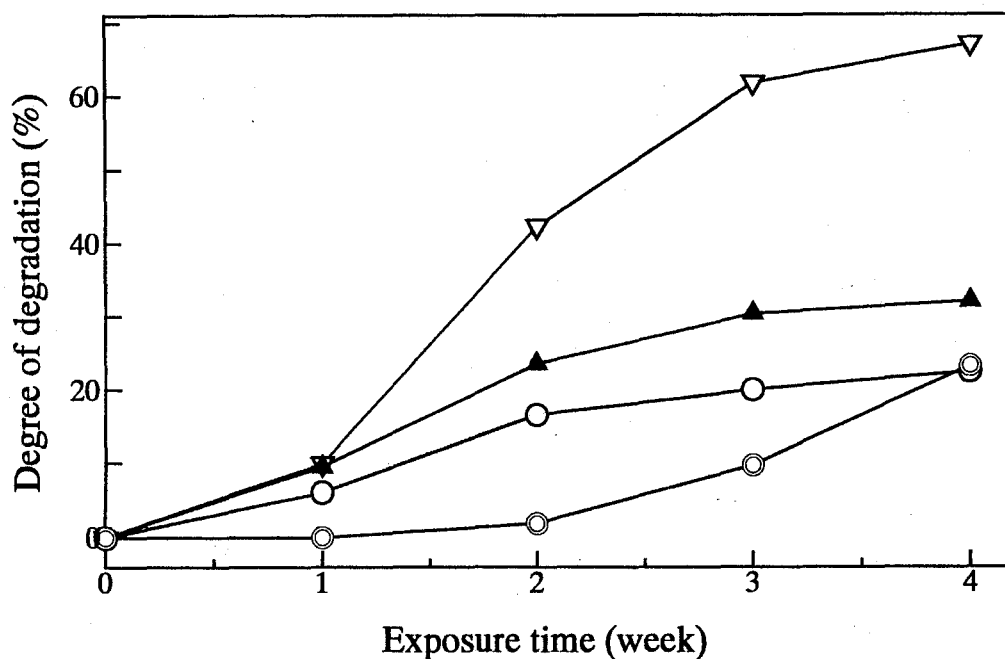


Fig. 5-11. Result of the exposure test to the closed activated sludge system.

Notes: Degree of degradation was calculated using oxygen consumption and theoretical initial oxygen demand.

Legend: ◎: LL-10; ○: SP-40: L-40/SA/PGE=100/11.0/25.9, Kneading: 120 °C, 20 min; ▲: MP-10: LL-10/MA/PGE=100/11.0/33.1, Kneading: 120 °C, 20 min; ▽: SA-10: LL-10/SA/AGE= 100/11.0/25.9, Kneading: 80 °C, 15 min.

The biodegradability of powdered, oligoesterified CMA (LL-10) was also measured by determining the oxygen consumption within a closed activated sludge suspension. The results are shown in Fig. 5-11. It is apparent that all samples are subject to significant biodegradation. The CMA control sample, LL-10, with a DS of 1.8 was degraded more slowly than any of the oligoesterified samples. The SA-10 sample, which had shown the most pronounced degradation in the soil burial test (Fig. 5-10), also revealed the most rapid degradation by the oxygen-consumption test, reaching a value of 67% after about 4 weeks. This is higher than the value of 60% required for official acceptance of a novel chemical compound in Japan.

Although this regulation is normally applied only to low molecular weight compounds, and in the case of polymers less stringent requirements are prescribed, the SA-10 sample was found to satisfy this requirement.

The degree of degradation was found to decrease in the order of SA-10, MP-10, SP-40 and control (CMA). This is consistent with the results of the soil burial test mentioned above.

## 5-4 Summary

A plasticization method for cellulose acetates (CAs) based on the reaction with dibasic acid anhydrides and monoepoxides during melt processing was developed. As a continuation of the discussion of the previous chapter<sup>1)</sup>, additional evidence is presented for the role of grafting oligoesters onto cellulose acetates in preventing the bleeding of homo-oligoesters from the inside of molded articles to their surface. Based on these results, a method for enhancing the amount of grafting has been pursued by varying the combination of dibasic acid anhydrides and monoepoxides. These resulting reactive melt-processing method allows for the preparation of biodegradable cellulosic plastics using practical process conditions.

Higher biodegradabilities have been found for the oligoester-grafted CAs compared to the unmodified parent CAs.

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## Chapter 6

# Thermoplasticization of cellulose acetates by grafting with cyclic esters<sup>1-3)</sup>

### 6-1 Introduction

At present, the development of biodegradable polymers is being actively pursued. As one of these trials, we have been trying to manufacture cellulose acetate (CA)-based biodegradable plastics, prepared by reaction with dibasic acid anhydrides and monoepoxides by a melt processing method.

In Chapter 4, it has been shown that cellulose acetates (CAs), especially cellulose diacetate (CDA) can be effectively plasticized by this method.<sup>4)</sup> To achieve effective plasticization, CA must be sufficiently graft copolymerized with oligomers (i.e. internal plasticization). It was also shown that it often occurred a problem of external plasticizer's bleeding. That is, homo-oligomers, formed during melt-processing, are not stable in the moldings, tending to migrate from the inside to the surface. Concerning this, it was remarked in Chapter 5 that direct evidence for the role of oligomer grafting onto CAs in preventing monomer and homo-oligomer bleeding was obtained experimentally. The amount of grafting was intended to increase, by which the bleeding of monomers and homo-oligomers that had been formed during grafting could be effectively suppressed.<sup>5)</sup>

From these findings, it appears the statement that the more effective grafting is attained, the more ideal plasticization of CA can be effectuated. With this idea in mind, we have come to a grafting work, in which cyclic esters are reacted with CA using Tin(II)-2-ethylhexanoate ( $\text{SnEht}_2$ ) as catalyst. This is based on the following information found in the relatively recent publications.

It is often said that little is known about the polymerization mechanism of cyclic esters in the presence of  $\text{SnEht}_2$ . Ikada described the same in his review article<sup>6)</sup> on "Polylactic acid" but introduced a mechanism that homopolymers are

produced predominantly, even though the ring-opening polymerization of cyclic esters is conducted in the presence of CDA.<sup>6, 7)</sup> On the contrary, Kricheldorf and his co-workers studied the polymerization of L-lactide catalyzed with SnEht<sub>2</sub> in the presence or absence of benzyl alcohol.<sup>8)</sup> When SnEht<sub>2</sub> and benzyl alcohol are used as catalyst and coinitiator, respectively, NMR spectroscopic examination of all polylactides obtained by the ring-opening polymerization revealed the presence of benzyloxy end-groups but the absence of 2-ethylhexanoate end groups.<sup>8)</sup> Based on this finding, he confirmedly insisted that the activation energy of initiation involving alcohols is much lower than that of initiation by neat SnEht<sub>2</sub>. This result also means that the hydroxyl group of alcohols plays an essential and direct role in initiating the ring-opening polymerization of cyclic esters. Thus, graft polymerization can be expected to occur selectively when the cyclic esters are polymerized in the presence of CA and SnEht<sub>2</sub>. This mechanism, being considerable to give high graft efficiency, was further discussed by Int'veld et al.<sup>9)</sup>

In this chapter, the co-grafting of  $\epsilon$ -caprolactone (CL) and L-lactide (LACD) onto CDA using SnEht<sub>2</sub> as catalyst was studied mainly by usual bench experiments using flask reactors. Part of these experiments was developed to reactive processings using a twin-screw extruder.

## **6-2 Experiment**

### **6-2-1 Materials**

Cellulose diacetate (CDA), L-40, was supplied by Daicel Chemical Industries Co. Ltd. The DS of the L-40 was 2.4-2.5 (combined acetic acid = 55 %) and its degree of polymerization was 160.

CL was also from Daicel Chemical Industries and used after vacuum distillation. LACD was supplied by Shimadzu Co. Ltd. and used without purification.

SnEht<sub>2</sub>, acetone, ethanol and methanol were purchased from Nacalai Tesque Co. Ltd. These reagents were extra pure or guaranteed grade to be used as received.

### **6-2-2 Graft polymerization with cyclic esters onto CDA in a flask reactor**



Weighed amounts of CDA (L-40), CL, and LACD were charged into a 100 ml flask. The standard charging amounts were 4 g for CDA, 10.6g for CL, 13.4g for LACD. After charging, the flask was placed in a 140 °C oil bath. CDA and LACD were dissolved in CL under stirring. After dissolution, 0.6 g of SnEht<sub>2</sub> was added to the homogeneous reaction mixture and then the reaction was continued for 1 to 60 min. All the operations were carried out in an atmosphere of dry nitrogen. The amounts of the reagents including the catalyst, the reaction temperature and other reaction conditions were changed depending on the present studies' demands.

After the prescribed reaction time, temperature was lowered below 50°C and 100 ml of acetone were added to the reaction mixture. The dissolution of the product into acetone was allowed to proceed with stirring. The resulting homogeneous solution was added dropwise into a vigorously-stirred large excess of methanol containing 1% amount of 1N-HCl. The obtained suspension was allowed to stand overnight with mild stirring. Then, the precipitate was collected by filtration using 0.5 μm PTFE membrane filter, redissolved in acetone, reprecipitated in a large excess of pure methanol, allowed to stand with stirring and collected by filtration. After repeating once this purification step, the collected cellulose derivative was dried using a forced convection oven and a vacuum oven, both at 60 °C.

### **6-2-3 Graft polymerization with cyclic esters onto CDA in a twin-screw extruder**

A Polylabo system PTW25 extruder (HAAKE, Karlsruhe, Germany) with co-rotating screws was used to graft-copolymerize CL and LACD onto CDA. The length of the extruder part was 36D (900 mm ; D: diameter = 25 mm). The extruder parameters were set and monitored by an IBM computer. For 100 weight parts of CDA, the total amount of CL and LACD was 200-600 weight parts, in which CL/LACD molar ratio was fixed to 5.0/2.0. The added amounts of SnEht<sub>2</sub> catalyst were changed in the range of 6-12 weight parts. The CDA sample was quantitatively fed by use of a powder feeder and the mixed solution of CL, LACD and SnEht<sub>2</sub> was fed by a metering pump (ProMinent Dosiertchnik GmbH, Heidelberg, Germany). The residence time was approximately 30 min and reaction temperature was 140 °C. When changed the reaction conditions, the

reactive extrusion was allowed to proceed at least for 40 min before collecting the corresponding reaction product.

The product was purified by the same dissolution and precipitation technique described in the above section.

#### **6-2-4 Gel permeation chromatography (GPC) analysis**

The molecular weight distribution of the samples prepared as described in the above sections, their purification products as well as the corresponding methanol-solubles, were determined on a TOSOH HLC-8020 gel permeation chromatograph equipped with a refractive index (RI) detector using two TSK-GEL GMH<sub>HR</sub> columns connected in series. Measurements were conducted using tetrahydrofuran (THF) as mobile phase at a flow rate of 1.0 ml/min. The concentration of test samples was 0.5 % in THF and the injected amount was 100  $\mu$ l. The system was calibrated by monodisperse polystyrene standards.

#### **6-2-5 Nuclear magnetic resonance (NMR) spectroscopic measurement**

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of purified grafted CDA samples were measured by using a Bruker ARX 300 NMR apparatus. The measuring conditions were as follows: the solvent was CDCl<sub>3</sub>; the concentration of samples was 30 mg/ml; the internal standard was TMS; the measuring temperature was 300 K ; the pulse delay was 2 seconds.

#### **6-2-6 Flow tests**

The thermal softening and flow behavior of the plasticized samples were observed using a flow tester (Shimadzu CFT-500A). The diameter and the length of the die used were 1 and 2 mm, respectively. The measurements were made at a heating rate of 10 °C/min under a constant load of 5 MPa.

#### **6-2-7 Preparation of molded sheets**

The kneaded samples were molded into sheets by hot pressing using a Toyo-Seiki 10 T bench hot press. The samples (about 3 g) were placed between polyethylene terephthalate (PET) sheets with a 0.4 mm thick spacer. The temperature of the heated press was 130-200 °C. For molding, a gauge pressure of  $\leq$ 5 MPa was applied slowly, taking 3-5 min to allow air bubbles to dissipate. The pressure was subsequently raised to 15 MPa and maintained for 30 s. The

samples were cooled for 10-15 min to room temperature by cold pressing under the same pressure.

### 6-2-8 Tensile tests

Strips of samples,  $80 \times 5 \times 0.4$  (mm), were cut from the molded sheets, and these were allowed to stand for more than 48 h at  $20\text{ }^{\circ}\text{C}$  and 60% relative humidity. The tensile tests were then performed using a Shimadzu Autograph DCS-R-500 under the same atmospheric conditions. The measurements were made using a span length of 40 mm and a cross-head speed of 5 mm/min. Average values were obtained from eight repeated measurements for the tensile strength, the breaking elongation, and Young's modulus.

## 6-3 Results and Discussion

### 6-3-1 Batch co-grafting with CL and LACD onto CDA in a flask reactor

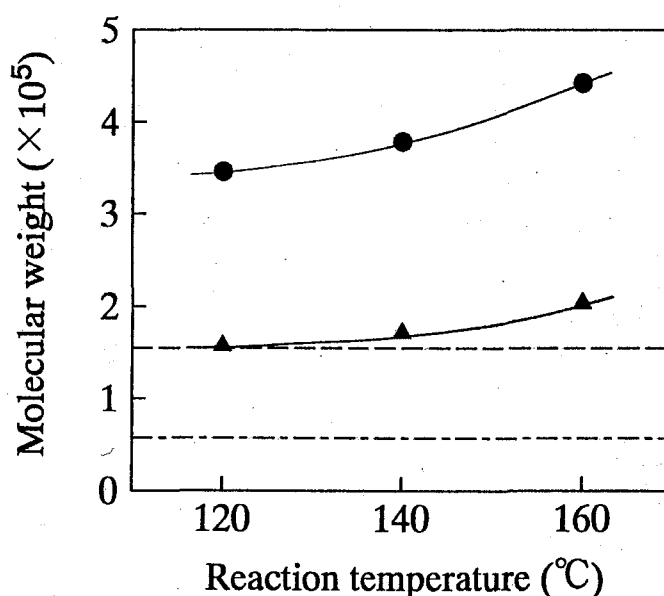


Fig. 6-1. Effects of the reaction temperature on the molecular weight of the grafted products.

Notes: Reaction time : 5 min ;

L-40/(LACD+CL)/catalyst : 100/600/15 (by weight) ;

LACD/CL : 1.0/1.0 (by mole).

Legend: ●:  $\overline{M}_w$  ; ▲:  $\overline{M}_n$ .

----- :  $\overline{M}_w$  of untreated L-40 , - - - - :  $\overline{M}_n$  of untreated L-40 .

Co-grafting with CL and LACD onto CDA using SnEht<sub>2</sub> as catalyst was conducted by usual bench experiments using a closed system. Contamination by moisture was carefully avoided. This is considered to be important from the view point of the related reaction mechanism described above.<sup>8,9)</sup>

First, the effect of reaction temperature on the progress of grafting was studied keeping other conditions constant, that is, the liquid ratio [(CL+LACD)/CDA] was 6.0; the molar ratio of CL to LACD was 1.0; the amount of SnEht<sub>2</sub> catalyst was 2.10 wt % based on the total amount; and the reaction period was 5 min. The results are shown in Figs. 6-1 to 6-3 and in Table 6-1.

Table 6-1. Effects of reaction temperature on tensile properties of poroducts.

Experiment	Reaction temperature (°C)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
F-1	120	n.d.	1.1	1279.8
F-2	140	24.9	39.7	667.8
F-3	160	18.8	73.9	207.7

Notes: Reaction time: 5 min; L-40/LACD/CL/catalyst=100/600/15 (by weight); LACD/CL=1.0/1.0 (by mole).

The molecular weights of the grafted products increased with the reaction temperature (Fig. 6-1). In this case, although the reaction period was only 5 min,  $\overline{M}_n$  and  $\overline{M}_w$  values exceeded by two times those of the starting CDA (Fig. 6-1).

This result is sensitively reflected to the significant decrease in the flow temperature of the grafted products (Fig. 6-2) and their tensile properties (Table 6-1). The flow temperature decreased to 135 °C even in the case where the lowest grafting temperature was applied. With the progress of the reaction, the grafted products changed from a rigid and brittle polymer to an elastomer. This point will be discussed later based on the corresponding data.

These results indicate that the grafting is easily proceedable with high rates and, at the same time, effective in providing thermoplasticity to CDA and in modifying its physical properties.

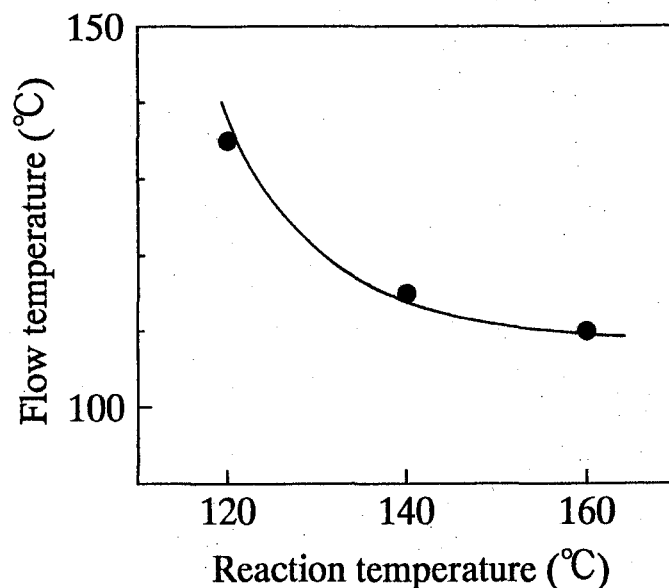


Fig. 6-2. Effects of the reaction temperature on the flow temperature of the grafted products.

Notes: Reaction time : 5 min ; L-40/(LACD+CL)/catalyst : 100/600/15 (by weight) ; LACD/CL : 1.0/1.0 (by mole).

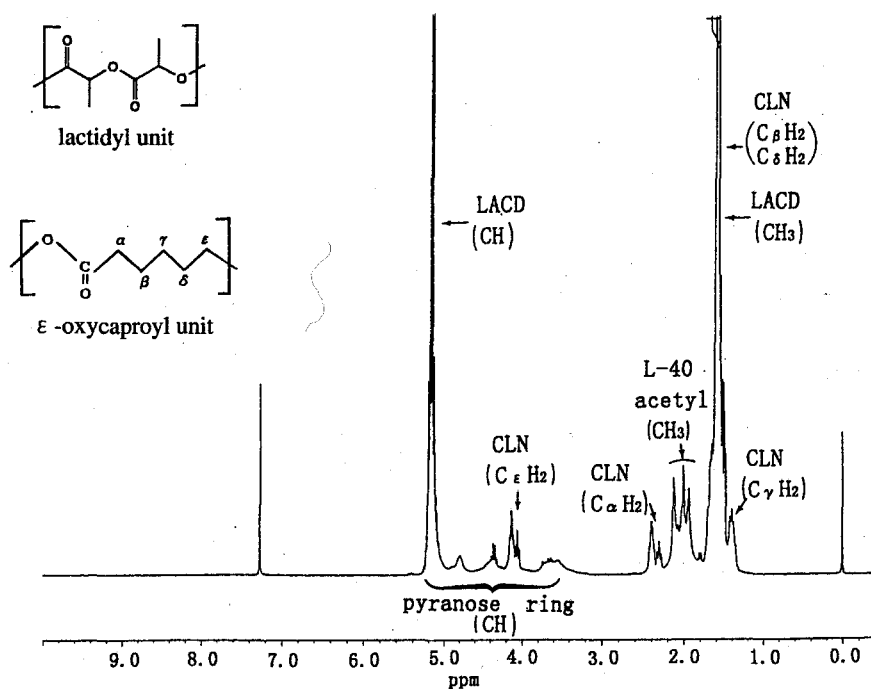


Fig. 6-3-1. <sup>1</sup>H-NMR spectrum of (CL-co-LACD) grafted CDA.

Notes: Reaction time : 5 min ; Reaction temperature : 120°C  
L-40/(LACD+CL)/catalyst : 100/600/15 (by weight) ;  
LACD/CL : 1.0/1.0 (by mole).

The molar substitution values of LACD and CL onto the residual hydroxyl groups of CDA, determined by  $^1\text{H-NMR}$  (calculated based on the integrated areas of the peaks, ranging from 1.8 to 2.2 ppm, ascribed to the acetyl methyl groups in the CDA with the degree of substitution of 2.5; the peaks, ranging from 2.3-2.5 ppm, ascribed to  $-\text{C}_\alpha\text{H}_2-$  in CL molecule, and the peaks, ranging from 1.3-1.7 ppm, ascribed to the methyl group in LACD molecule; cf. Fig. 6-3-1), as a function of the reaction temperature are shown in Fig. 6-3-2. (In this case, the molar substitution value was not based on a unit glucoside but on a unit residual hydroxyl group in CDA.)

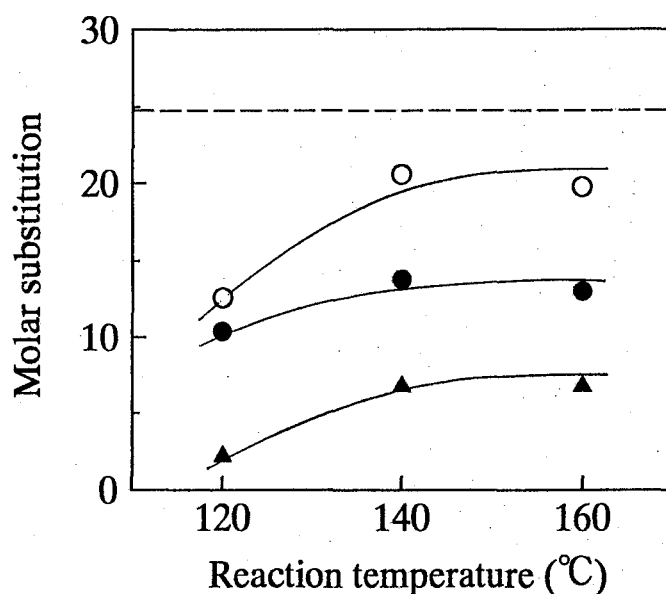


Fig. 6-3-2. Effects of the reaction temperature on the molar substitution of LACD and CL.

Notes: Reaction time : 5 min ;  
 L-40/(LACD+CL)/catalyst : 100/600/15 (by weight) ;  
 LACD/CL : 1.0/1.0 (by mole).

Legend: ●: LACD ; ▲: CL ; ○: LACD+CL ;  
 --- : Theoretical maximum value of (LACD+CL).

It is clear that the molar substitution values increased with the grafting temperature, but it is worthier of note that LACD was always introduced in an amount more than two times larger than CL, irrespective of the grafting temperature. The molar substitution values increased drastically with the reaction

temperature of up to 140 °C but slightly from 140 to 160 °C, and the total values were significantly high, that is, about 20 (Fig. 6-3-2).

The large increase in the molar substitution between 120 and 140 °C was mainly caused by an increase in the CL addition. About 90 % of the theoretical maximum value for molar substitution of LACD could be attained even at 120 °C.

Therefore, the drastic and slight increases in the CL grafting in the reaction temperature region ranging from 120 to 140 °C and that ranging from 140 to 160 °C, respectively, account for the tensile properties' changes of the molded sheets of grafted CDAs (Table 6-1).

In the second series of experiments, the reaction temperature was kept constant at 140 °C and the reaction time was changed from 0 to 60 min. The other reaction conditions remained unchanged as described in the experimental section. The results are shown in Figs. 6-4~6-8 and in Table 6-2.

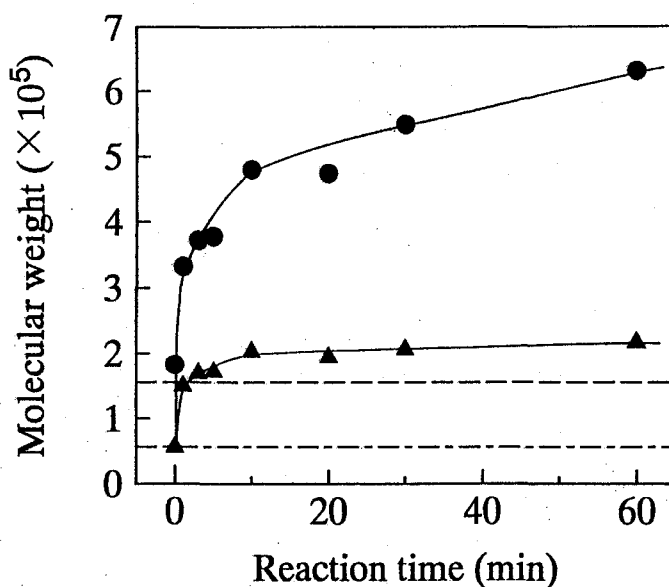


Fig. 6-4. Effects of the reaction time on the molecular weight of the grafted and purified CDA.

Notes: Reaction temperature : 140°C;  
L-40/(LACD+CL)/catalyst : 100/600/15 (by weight) ;  
LACD/CL : 1.0/1.0 (by mole)

Legend: ● :  $\overline{M}_w$  , ▲ :  $\overline{M}_n$ .  
--- :  $\overline{M}_w$  of untreated L-40, --- :  $\overline{M}_n$  of untreated L-40.

The reaction time of 0 min means that the mixture was stirred for 30 min at 140 °C for the dissolution of CDA and LACD in CL, and then, without addition of the catalyst, the CDA was directly recovered by precipitation using a large excess of methanol as non-solvent. Even with this treatment, a small amount of grafting was detected, as shown in Figs. 6-4~6-7.

Even though the reaction period was as short as 1 min, there occurred surprisingly big changes; the molecular weights,  $\overline{M}_n$  and  $\overline{M}_w$ , increase almost two fold (Fig. 6-4), the yield value showed 3 fold increase (Fig. 6-5), the flow temperature decreased to about the half of that of CDA (Fig. 6-6), films or sheets were moldable without using any plasticizer, the molar substitution of LACD became a value close to the theoretical maximum value while that of CL was small, that is, about 1/4 of its maximum value (Fig. 6-7).

Further increase in the reaction time caused progressive but small changes when compared with those occurred during the first minute. All of the measured parameters tended to reach a plateau after about 10 min of reaction.

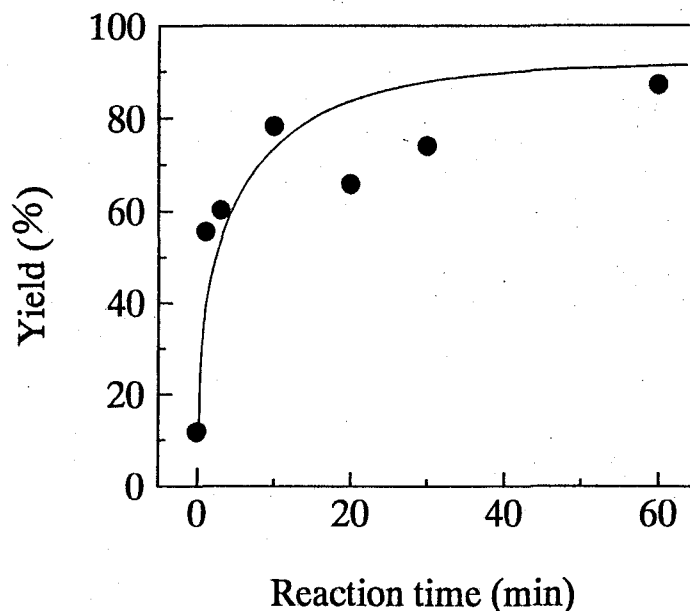


Fig. 6-5. Effects of the reaction time on the yield.

Notes: Reaction temperature : 140°C ;  
 L-40/(LACD+CL)/catalyst : 100/600/15 (by weight) ; LACD/CL : 1.0/1.0 (by mole) .



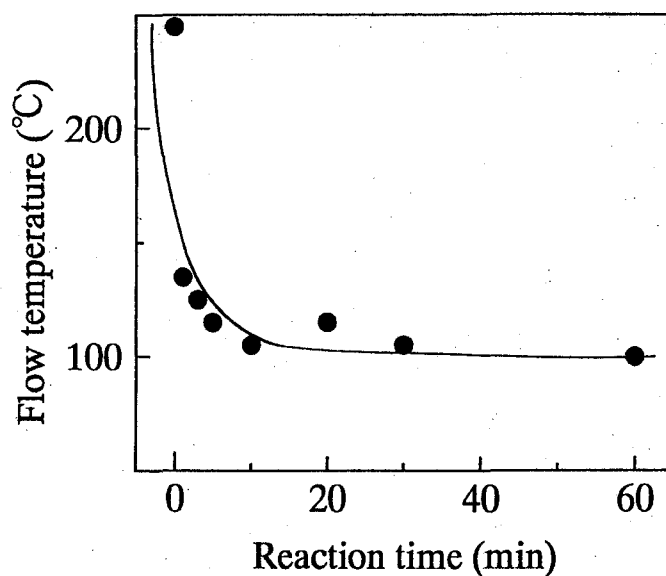


Fig. 6-6. Effects of the reaction time on the flow temperature.

Notes: Reaction temperature : 140°C ;  
 L-40/(LACD+CL)/catalyst : 100/600/15 (by weight) ;  
 LACD/CL : 1.0/1.0 (by mole) .

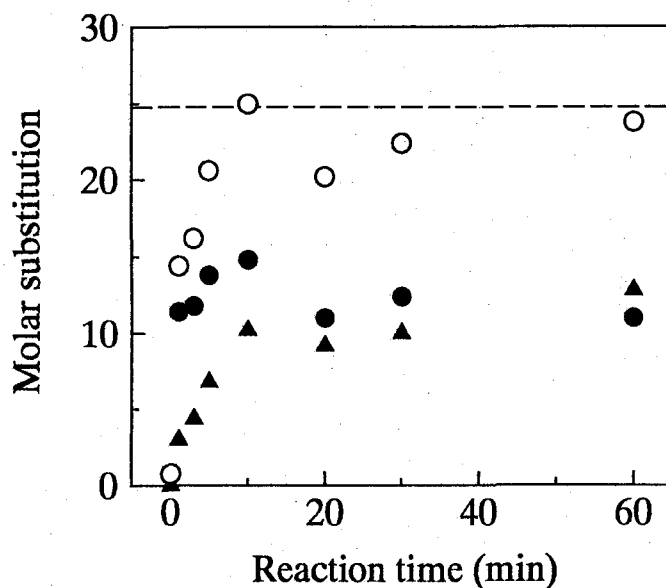


Fig. 6-7. Effects of the reaction time on the molar substitution.

Notes: Reaction temperature : 140°C ;  
 L-40/(LACD+CL)/catalyst : 100/600/15 (by weight) ;  
 LACD/CL : 1.0/1.0 (by mole).

Legend: ● : LACD ; ▲ : CL ; ○ : LACD+CL ;  
 ---- : Theoretical maximum value of (LACD+CL).

Table 6-2. Effects of reaction time on tensile properties of products.

Experiment	Reaction time (min)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
F-4	1	n.d.	1.6	n.d.
F-5	3	37.0	3.1	1599.6
F-2	5	24.9	39.7	667.8
F-6	10	13.8	116.1	79.8
F-7	20	16.8	120.9	80.3
F-8	30	9.1	147.0	21.7
F-9	60	6.8	215.0	5.9

Notes: Reaction temperature: 140 °C ; L-40/LACD/CL/catalyst=100/600/15 (by weight);  
LACD/CL=1.0/1.0 (by mole).

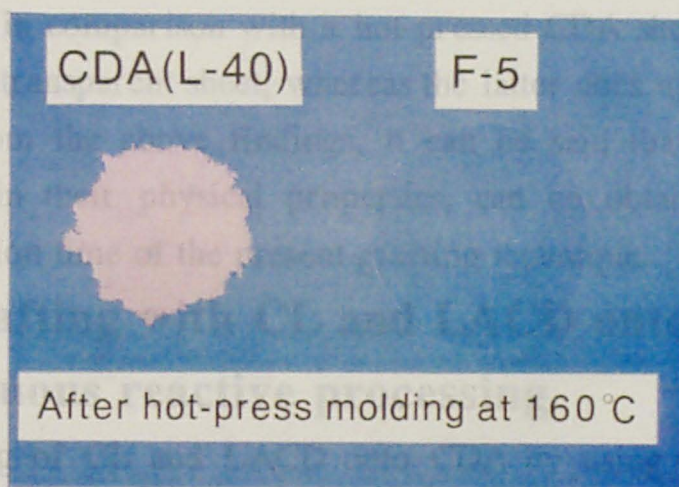


Fig. 6-8. Hot-press molded sheet of F-5 product.

Notes: Left : L-40 after hot pressed at 160°C ;

Right : F-5 product after hot pressing at 160°C.

Moreover, from Fig. 6-7, it can be said that the total molar substitution reached its theoretical maximum value after 10 min of grafting. This result showed that the graft reaction proceeded with a high rate and that the selective grafting was achieved completely without significant production of homocopolymers or homo-co-oligomers. This is the complete support for the reaction mechanism proposed by Kricheldorf *et al.* and Int'veld *et al.*<sup>8,9)</sup>

The above result satisfied also author's intention which has been so far pursued.<sup>5)</sup> That is, plasticizer's bleeding from inside of the plasticized CDA molding to the surface is considered to be completely prevented by this development of sophisticated grafting method.

Fig. 6-7 also revealed that although the graft reaction of LACD could proceed in a high rate from the beginning of the reaction, that of CL reacted with a slower rate, increasing linearly through the reaction period of 0 to 10 min. This grafting characteristics are directly reflected in the physical properties of the grafted CDA. After short times (up to around 3 min) of grafting, brittle polystyrene-type polymers could be obtained. With increasing the reaction time, the elastic properties of the resulted products gradually increased and showed elastomers' features (Table 6-2). The latter phenomenon can be thus attributed to the increase in the amount of grafting CL.

In Fig. 6-8, a sheet prepared from the 3 min grafted CDA by the hot-press molding is shown in comparison with a hot-pressed CDA sheet. The former is a homogeneous and transparent sheet, whereas the latter does not necessarily reveal thermal flow. From the above findings, it can be said that various polymers, widely differing in their physical properties, can be obtained from CDA by adjusting the reaction time of the present grafting technique.

### **6-3-2 Co-grafting with CL and LACD onto CDA by continuous reactive processing**

The co-grafting of CL and LACD onto CDA by using conventional flasks, described in the previous section, was tried by using a twin-screw extruder.

As described in the experimental section, the reaction temperature was fixed to 140 °C and the liquid ratio (cyclic esters/CDA weight ratio) was varied. In this case, LACD was dissolved into CL before feeding into the extruder. However, CL/LACD molar ratios higher than 5.0/2.0 could not be obtained because of insufficient dissolution. This creates irregularities in the feeding of the reactants. A CL/LACD molar ratio of 5.0/2.0 was therefore chosen for the continuous processing.

The results obtained by using the continuous reactive processing are shown in Table 6-3. From the table, it can be pointed out first that, in all the cases, the number and the weight average molecular weights of the grafted products became

much higher than those of the original CDA. Concerning this, related GPC curves can be used as visual confirmation of the molecular weight increase as well as confirmation of the effect of purification of the products after grafting.

A typical example is shown in Fig. 6-9. From this figure, it is also found that, by this reactive processing, significant amounts of homo-co-oligomers or homo-copolymers originating from LACD and CL could be formed, which was not apparently found in the batch reaction. This was thus initiated by moisture contamination during the graft polymerization. This phenomenon would be able to be avoided by the appropriate usage of apparatus and optional devices.

The table also shows that the flow temperatures of the grafted products became much lower than that of the original CDA, revealing that thermoplasticity of CDA could be enhanced also by this reactive processing.

It can be seen from the table that the grafting resulted in products having considerably large breaking elongations and moderate tensile strengths and Young's modulus. In other words, elastomers are readily obtainable from CDA by this simple and rapid grafting method.

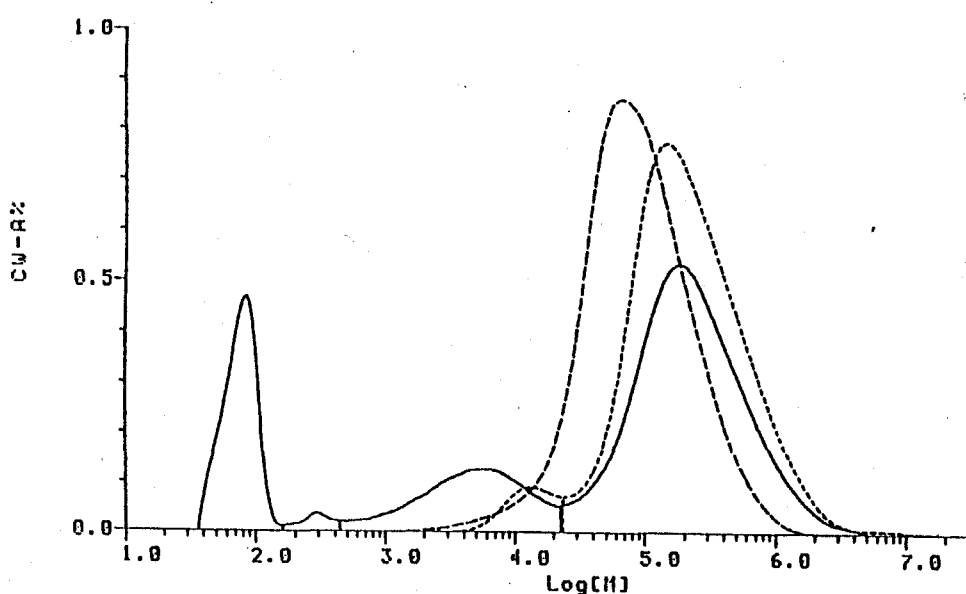


Fig. 6-9. GPC chromatograms of (CL-co-LACD) grafted CDA, H-7.

Legend: ——— : Unpurified H-7  
 - - - - - : Three times purified H-7  
 - · - · - : Untreated L-40

Data in Table 6-3 reveals several other important facts.

It is possible to study the effect of catalyst amounts on this grafting among the experiments H-4, 5, 7 and 8, keeping constant the liquid ratio (6), the molar set ratio of LACD and CL (2.0/5.0), the reaction temperature (140 °C) and the reaction time (ca.30 min). The range of the SnEht<sub>2</sub> catalyst concentration, based on the total weight amounts of the reaction system is not so wide, that is, ranging from 0.85 to 1.7 wt %.

With increasing the SnEht<sub>2</sub> catalyst amount, even within such a narrow range, the molecular weights of grafted CDA increased slightly, in which their lowest values became roughly two times larger than those of CDA; the flow temperature decreased from 145 to 120 °C, which is a satisfactory lowered range of temperatures; and the molded sheets showed enhanced elastomeric properties.

The last reveals that an increase in the SnEht<sub>2</sub> catalyst amount can promote the reaction of less reactive CL, whose introduction into the graft chains results in a decrease of the flow temperature and in elastomeric property enhancement.

Table 6-3. Reaction conditions and characterization of the graft products prepared by reactive processing.

Experiment	Liquid ratio	Catalyst (%)	Molecular weight		Flow temperature (°C)	Molar substitution		Tensile properties		
			Mn (×10 <sup>5</sup> )	Mw (×10 <sup>5</sup> )		LACD	CL	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
H-1	2	3.2	1.5	3.7	135	3.3	6.4	13.4	159	35.1
H-2	4	1.2	1.3	3.1	160	-	-	17.9	169	122
H-3	4	2.3	1.8	5.0	125	-	-	8.3	173	5.7
H-4	6	0.85	1.3	3.7	145	3.4	5.6	21.8	119	243
H-5	6	1.1	1.3	3.5	140	-	-	18.4	143	102
H-6	6	1.1	1.5	3.6	135	-	-	13.7	164	27.2
H-7	6	1.4	1.5	3.7	120	5.2	7.8	10.6	138	18.4
H-8	6	1.7	1.7	4.6	125	-	-	9.1	218	6.9
CDA			0.57	1.6	255					

Notes: Reaction temperature: 140°C; Reaction time: H-1~5,7,8: 30 min, H-6: 70 min; LACD/CL=2.0/5.0 (by mole).

The increase in CL grafting with the increase in  $\text{SnEht}_2$  catalyst amount was experimentally confirmed by measuring the chemically binding amounts of each monomer with  $^1\text{H-NMR}$  analyses. From the NMR data, the rates of monomers combined within grafted chains were calculated to be 70% for LACD and 40 % for CL in the case of the grafting in the presence of 1.4 wt % of catalyst, whereas these values were 45 % for LACD and 30 % for CL in the case of the catalyst amount of 0.85 wt %.

In Table 6-3, the experiment H-1 dealt with the case in which the liquid ratio was 2. Under this very small liquid ratio, dissolution was difficult and the viscosity of the solution became extraordinary high. Such conditions cannot be tested in a flask-reactor. The fact that the grafting can be achieved with a liquid ratio as low as 2 is one of the big benefits of using a twin-screw extruder as reactor for the grafting. Actually, as shown in Table 6-3, the product prepared under such conditions showed satisfying large molecular weights with large molar substitution values, a low flow temperature and satisfactory mechanical properties. If the amount of catalyst is calculated based on the weight of CDA, the experiment H-7 is considered to have the same experimental conditions except that the liquid ratio is three times larger than experiment H-1. Even though this difference, both of the grafted products revealed quite comparable characteristics in grafting results and tensile properties, demonstrating that grafting with such a low liquid ratio of 2 can effectively proceed in a twin-screw extruder. Furthermore, about 90 % of provided LACD and CL monomers participated in the formation of the side chain in the case of liquid ratio = 2, whereas only 40 % of the monomers were grafted in the case of liquid ratio = 6. From the latter, about 70 % of the set amounts of LACD were chemically introduced into the graft-chains.

### **6-3-3 Microstructure determination of (LACD-co-CL) graft side chains**

As it was demonstrated in the previous section, LACD is more reactive than CL. Then, how the structure of (LACD-co-CL) graft side chain was constructed during the grafting became an interesting topic. In that sense, an analysis of the structure was performed by means of high resolution  $^{13}\text{C-NMR}$  spectroscopy.

In Fig. 6-10,  $^{13}\text{C-NMR}$  spectrum of one of the (LACD-co-CL) grafted CDA

(H-1) (from twin-screw extruder) is shown. The assignment of peaks in the spectrum is detailed in Table 6-4.

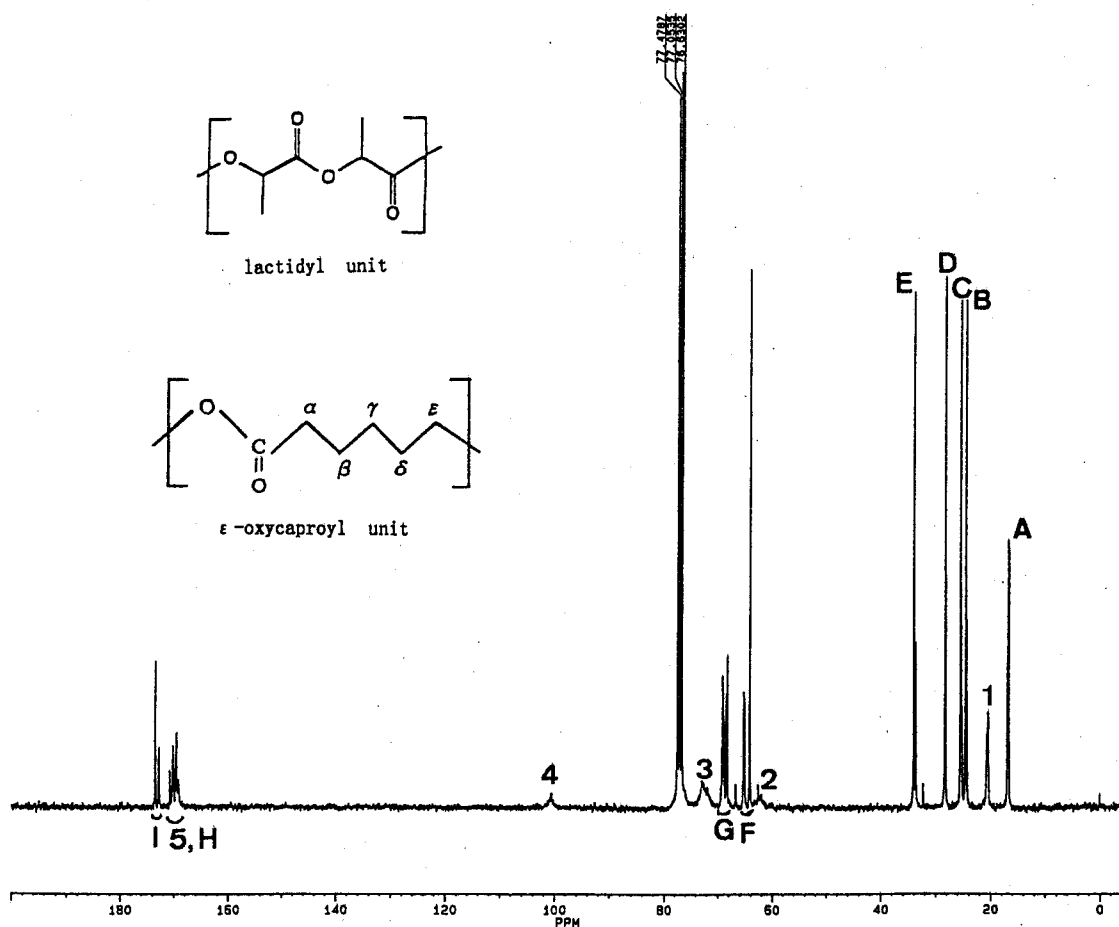


Fig. 6-10.  $^{13}\text{C}$ -NMR spectrum of (CL-co-LACD) grafted CDA, H-1.

It is recognizable that in addition to peaks ascribed to CDA, those due to LACD and CL appeared, confirming again the grafting of these cyclic esters onto CDA. Because of the occurrence of the high yield of grafting, the magnitude of the peaks caused from CDA became small.

On the basis of carbon signals present in the  $^{13}\text{C}$ -NMR spectra, the structure of oligo or poly (LACD-co-CL) introduced into CDA as the graft side chain was analyzed. In Fig. 6-11, the region of carbonyl carbon atoms in the  $^{13}\text{C}$ -NMR spectrum of the H-1 product prepared by the reactive processing method is shown under magnification. Two groups of splitting signals are found in the figure

which are ascribable to carbonyl carbon peaks of  $\epsilon$ -oxycaproyl and lactidyl units. Carbonyl carbon peaks ascribed to CDA are partly seen in the lactidyl carbonyl carbon region.

It can be seen that the carbonyl carbon signal of  $\epsilon$ -oxycaproyl units splits into four lines in the chemical shift region ranging from 172 to 174 ppm, which suggests triad sensitivity in the distribution of  $\epsilon$ -oxycaproyl units and lactidyl unit.

The same splitting is seen for the carbonyl carbon signal of lactidyl unit in the chemical shift ranging from 169 to 171 ppm but these signals are overlapping with relatively weak carbonyl carbon signals caused from CDA.

When the  $\epsilon$ -oxycaproyl unit is denoted by C and lactidyl unit by LL, each of the splitting spectral lines for carbonyl carbon of  $\epsilon$ -oxycaproyl unit can be assigned as shown in the figure by reference to the Kasperczyk and Bero's work.<sup>10)</sup>

Table 6-4. Chemical shifts for  $^{13}\text{C}$ -NMR spectrum of grafted CDA.

Peak	Chemical shift (ppm)	Assignment
A	16-17	$\text{CH}_3$ carbon of graft chain
1	20-21	$\text{CH}_3$ carbon of CDA
B	24	$\text{C}_\gamma$ of graft chain
C	25	$\text{C}_\beta$ of graft chain
D	28	$\text{C}_\delta$ of graft chain
E	34	$\text{C}_\alpha$ of graft chain
2	62-63	C-6 carbon of CDA
F	64-66	$\text{C}_\epsilon$ of graft chain
G	68-70	CH carbon of graft chain
3	71-73	C-2, 3, 4, 5 carbons of CDA
4	100	C-1 carbon of CDA
5	169-171	C=O carbon of CDA
H	169-171	C=O carbon of graft chain (LACD)
I	172-174	C=O carbon of graft chain (CL)



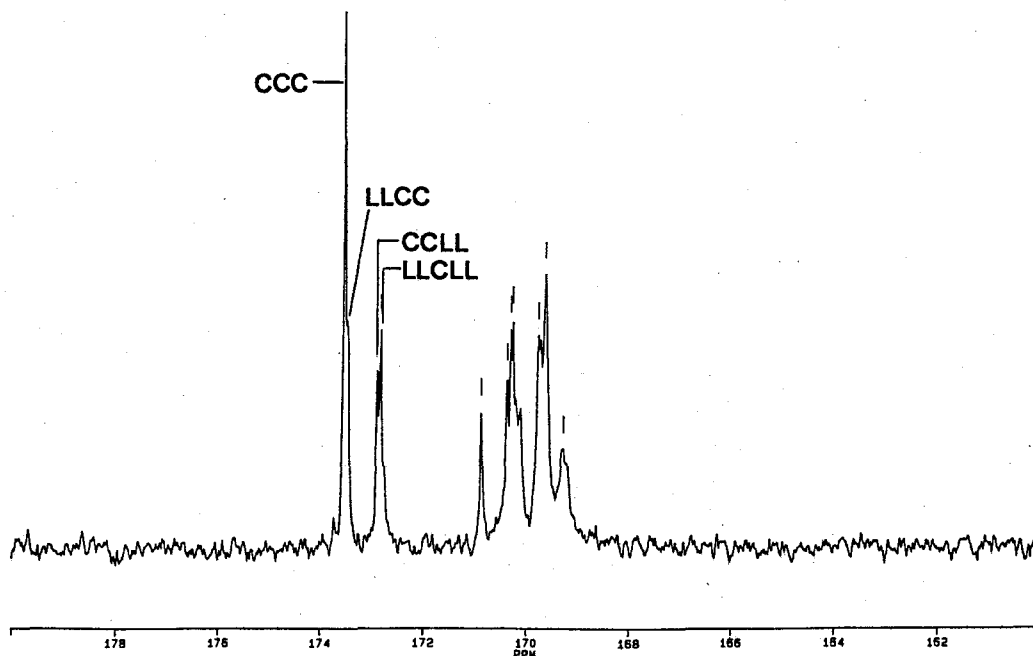


Fig. 6-11.  $^{13}\text{C}$ -NMR spectrum of (CL-co-LACD) grafted CDA, H-1.

Note: Region of carbonyl carbon atoms of  $\epsilon$ -oxycaproyl units, lactidyl unit and CDA.

The results of Fig. 6-11 mean that even for the grafted CDA product prepared by using liquid ratio of 2, introduced (LACD-co-CL) side chains are long enough to reveal triad sensitivity and confirm the above-mentioned molecular weight and the molar substitution data for H-1 in Table 6-3. The set molar ratio of LACD/CL was 2.0/5.0 for experiment H-1; the rate of CL was much larger than LACD. By this reasoning, the signals for the graft polymerized products due to CCC and CLLC (170.2-170.3 ppm) sequences appear in relatively large quantities and those due to LLCLL and LLLLLL (169.5-169.6 ppm) triads are relatively small. Existence of LLCC, CCLL and LLCLL sequences and the fact that the total amount of the signal strengths of these sequences are comparable or more than that due to the CCC sequence show meaningful occurrence of randomly polymerized parts of CL and LACD within the graft side chains. This fact confers irregularity and it is considered to be related with the appearance of the high thermoplasticity and high elasticity found and discussed above in relation with the H-1 data shown in Table 6-3.

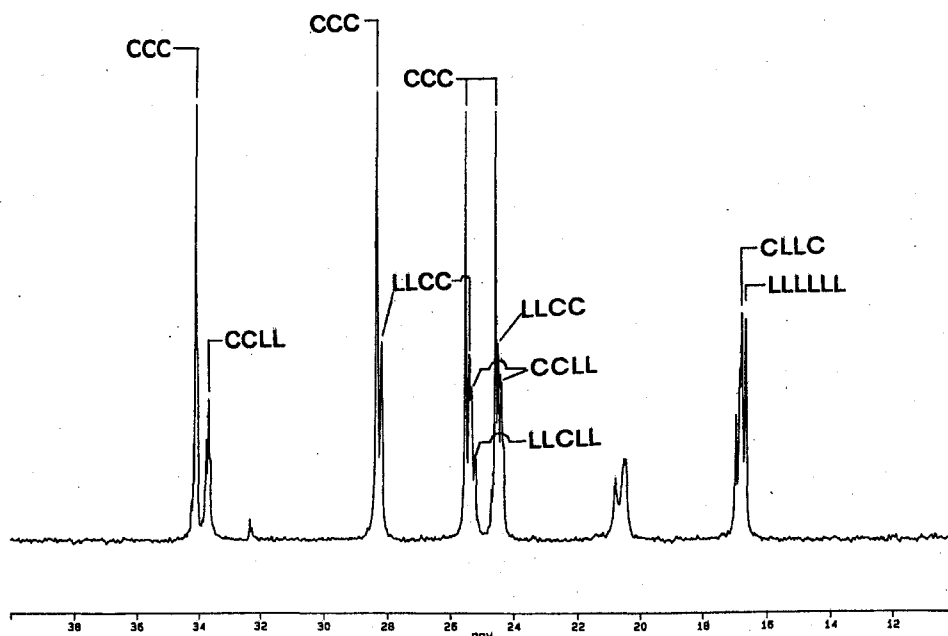


Fig. 6-12.  $^{13}\text{C}$ -NMR spectrum of (CL-co-LACD) grafted CDA, H-1.

Note: Region of  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ -methylene carbon atoms of  $\epsilon$ -oxycaproyl units, methyl carbon atoms of lactidyl unit and acetyl methyl carbon atoms of CDA.

The present discussion can be supported by the spectrum data shown in Fig. 6-12 where  $^{13}\text{C}$ -NMR spectrum of  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ -methylene carbon of  $\epsilon$ -oxycaproyl units and methyl carbon of lactidyl unit in the H-1 product and the assignments of the spectral lines to appropriate sequences are shown.

In Fig. 6-13,  $^{13}\text{C}$ -NMR spectrum of (LACD-co-CL) grafted CDA, F-6 (from batch reactor), is shown. The assignment of peaks in the spectrum is the same as shown in Table 6-4. It is recognizable that peaks ascribed to CDA become less pronounced and those due to LACD and CL are more enlarged compared with the cases for the former H-1, showing that the grafting proceeded in higher extent. Because of the occurrence of the high yield of grafting, the importance of the peaks caused from CDA became small and negligible.

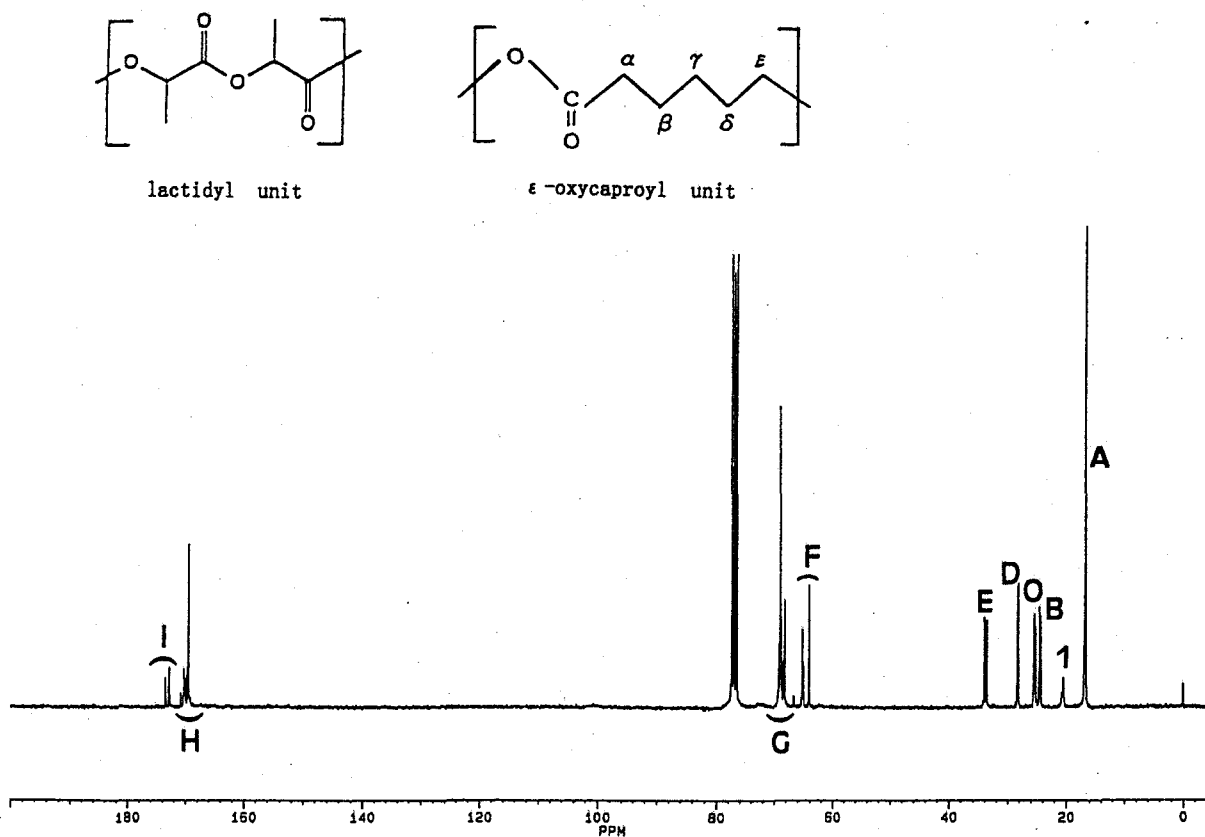


Fig. 6-13.  $^{13}\text{C}$ -NMR spectrum of (CL-co-LACD) grafted CDA, F-6.

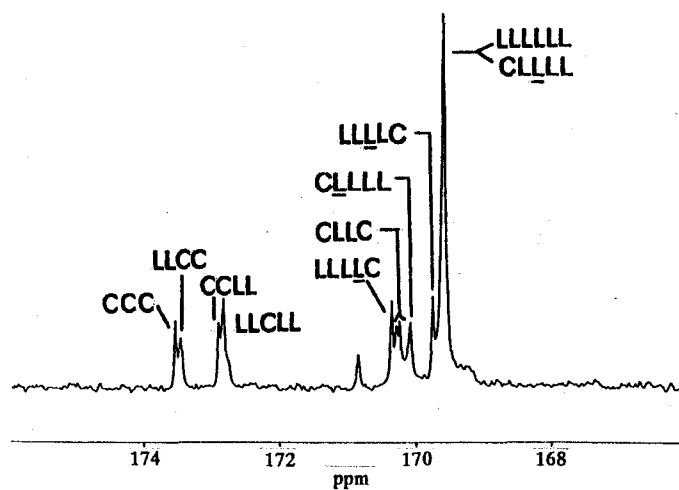


Fig. 6-14.  $^{13}\text{C}$ -NMR spectrum of (CL-co-LACD) grafted CDA, F-6.  
 Note: Region of carbonyl carbon atoms of  $\epsilon$ -oxycaproyl units, lactidyl unit and CDA.

For the preparation of F-6, the liquid ratio used was 6, three times larger than for H-1, the molar ratio of LACD/CL was 1/1, two times more LACD rate than for H-1, the catalyst concentration, based on the total reactant amount, was 2.1 % ( 3.2 % for H-1), reaction temperature was 140 °C and reaction period was 10 min, which gave an almost level off yield. All of these reaction conditions, especially the large liquid ratio and the high composition of LACD, allowed to obtain a larger yield of grafting than in the H-1 case.

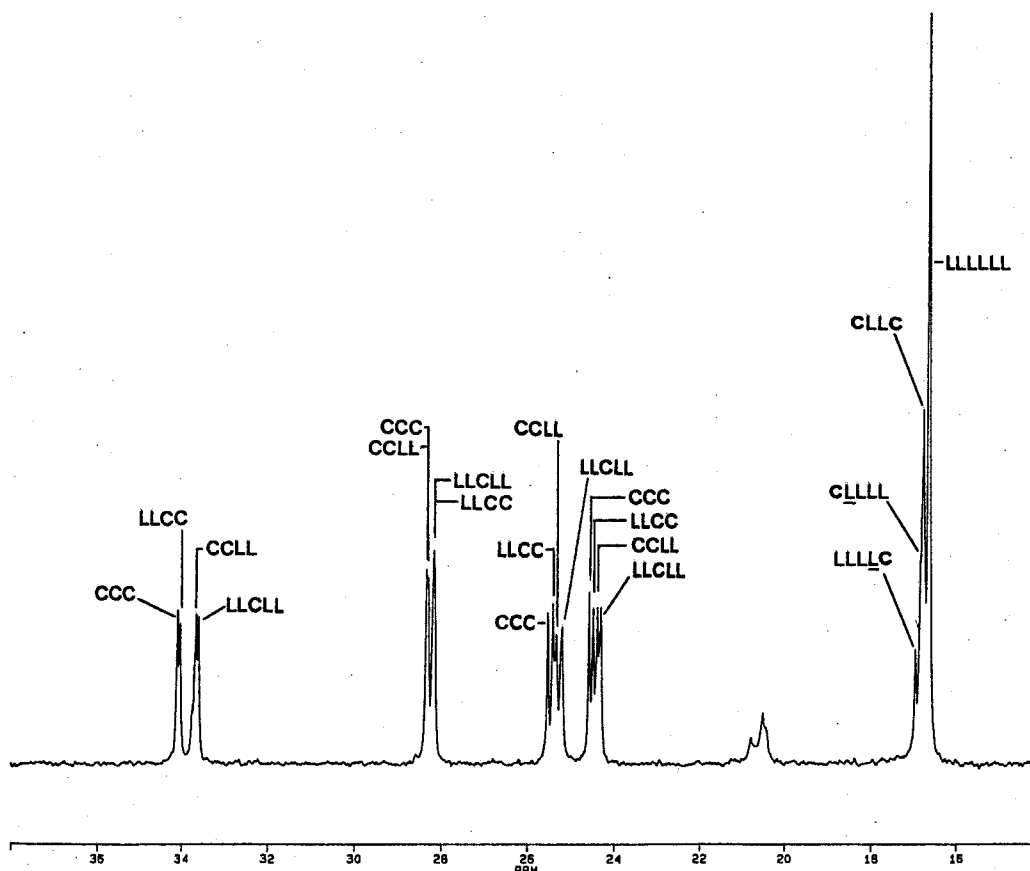


Fig. 6-15.  $^{13}\text{C}$ -NMR spectrum of (CL-co-LACD) grafted CDA, F-6.

Note: Region of  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ -methylene carbon atoms of  $\epsilon$ -oxycaproyl units, methyl carbon atoms of lactidyl unit and acetyl methyl carbon atoms of CDA.

In Figs. 6-14 and 6-15, the regions of carbonyl carbon atoms and of  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ -methylene carbon of  $\epsilon$ -oxycaproyl units as well as methyl carbon of lactidyl unit, respectively, in the  $^{13}\text{C}$ -NMR spectrum of the F-6 is shown under magnification. The assignments of the spectral lines to appropriate sequences are shown on the figure.

The most important point is that since LACD was used in a higher ratio, that is, equimolar to CL, the largest sequence found in these figures are LLLLLL.

However, other mixed sequences were also found in meaningful occurrence.

Thus, the grafted product can be said to be rich in lactidyl block polymer portions, coexisting with a large proportion of randomly polymerized sequences. Hence, as shown in Table 6-3, a product with a low enough flow temperature as well as a molded sheet with elastomer-like properties was obtained.

## 6-4 Summary

A plasticization method for cellulose acetates (CAs) based on the selective grafting of  $\epsilon$ -caprolactone (CL) and lactide (LACD) has been developed. The selective-grafted products could be prepared by ring opening polymerization in the melt state at  $140\text{ }^\circ\text{C}$  using  $\text{Sn}(\text{II})$ -2-ethylhexanoate ( $\text{SnEht}_2$ ) as catalyst, where CAs with remaining hydroxyl groups worked as initiator.

Plasticization of CAs by this selective grafting can solve the problem encountered in Chapters 4 and 5 that the bleeding of unreacted monomers and homo-oligomers from the inside of molded articles to their surface was often found.

By using adequate reaction conditions, the grafting reaction proceeded rapidly and could be completed within 10 to 30 min. LACD is grafted more rapidly than CL onto CAs, producing relatively rigid and brittle products in the earlier stages and elastomer-like ones in the later stages. Transparent amorphous molded articles were obtainable depending on the reaction conditions.

The analysis of the structure of the grafted side chains by means of high resolution NMR spectroscopy showed that, although the grafted side chains are composed of large amounts of  $\epsilon$ -oxycaproyl or lactidyl block polymer portions depending on the reaction conditions, a large amount of randomly polymerized

parts coexist in the grafted chains, which confer high thermoplasticity, elasticity and amorphous nature to the grafted products obtained.

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## CONCLUSION

In this dissertation, Chapter 1 describes first the background of this study. It also shows the aim and outline of this investigation.

In Chapter 2, it was reported that acetylated wood pretreated with trifluoroacetic acid, shows a extraordinarily high thermoplasticity. This was proved to occur by the presence of acetylated lignin, but this acetylated lignin is considered to break its  $\alpha$ -O-4 bond which exists in up to 20% amount within the chemical linkage of lignin unit (C<sub>9</sub> unit). The scission of the  $\alpha$ -O-4 bond will increase the lignin molecular motion. Nevertheless, this lignin is still a high molecular weight polymer as it was shown in the stepwise extraction and in the appearance of IR peaks (Fig. 2-10). Thus, it occurred a polymer blending between cellulose acetate and acetylated lignin. Therefore, it can be pointed out that by the TFA pretreatment, thermoplasticization of cellulose acetate can be proceeded by polymer to polymer interaction, which is usually considered to occur in very rare cases. This is, in this sense, an interesting finding.

Thermoplasticization of wood by benzylation and polycaprolactone blending, and the bio- and photo-degradabilities of the thermoplasticized product were shown and discussed in Chapter 3. Among the thermoplasticized wood derivatives, benzylated wood (BzW) has been characterized as a material with excellent mechanical properties, and with higher apparent melting point and higher melt viscosity compared with most commercial thermoplastic polymers. The melt properties could be further modified by blending with polycaprolactone (PCL), a common biodegradable synthetic polymer. Measurements by capillary rheometry (Capirograph) revealed that the addition of 20 to 30% of PCL converts BzW to a polypropylene-like plastic. BzW was also found to have biodegradability and considerable photodegradability. Blends of BzW and PCL resulted in higher biodegradability when compared to each individual component.

Although these facts are extremely fascinating as a subject for academic studies, the benzylation is considered to be impractical, at least at present, because the reagent for benzylation, benzyl chloride, is a serious poison, and it is explosive. Benzyl cellulose is therefore not industrially produced in western or



advanced countries.

It appears that an extensive development effort is required before a practical production technology can be defined. From this point of view, the author decided to focus further attention on wood acetylation. In order to simplify the problem and to take advantage of published information, the author decided to concentrate on advancing the conversion of cellulose acetates (CAs) into effective and genuine plastics. This decision was also motivated by the fact that CAs have been the most widely produced industrial cellulose derivatives, and that CAs having degrees of substitution of  $\leq 2.5$  have been demonstrated to be biodegradable. In this regard, it should be noted that CAs are processed chiefly through dissolution in certain solvents, that is, dry molding processes are not so often adopted in the industry. This is caused by the fact that present plasticization technologies for CA are still unsatisfactory.

In that sense, plasticization studies on CAs have been conducted in the author's group and the parts of the obtained results are described in Chapters 4-6.

In Chapter 4, the methodology concerning the plasticization of CAs by reaction with dibasic acid anhydrides and monoepoxides during melt-processing was reported. The formation of oligoesters chains as grafted branches of CAs, together with homo-oligomers enhances the thermoplasticity of the products, it causes "bleeding", especially when the amount of grafting is insufficient.

This kind of plasticizer loss is considered to be caused by a lack of miscibility. To make two immiscible polymers, A and B (or polymer A and oligomer B), miscible, a compatibilizer is often added. As one type of compatibilizer, A-B block or graft copolymers have been found to be effective. Therefore, a large amount of oligoester side chains attached to CA molecules can be expected to enhance the affinity between the modified CAs and the homo-oligomer. The results concerning this aspect are discussed in Chapter 5.

The biodegradability of representative samples obtained was examined by a soil burial test in a controlled environment (30°C, 80%RH) as well as by the measurement of oxygen consumption in a closed system where test samples were exposed to standard activated sludge. The latter test method is adopted from methodology advocated by JIS. The results of these trials are presented and discussed in Chapter 5.

In order to prevent the bleeding of homo-polymer, more effective grafting methods have been studied. "Effective grafting" thereby includes all those reactions that produce more grafting and enhanced grafting efficiency within a short reaction period. It was a requirement that the grafted products, (that is, grafted CDA,) were biodegradable.

The accomplishments of this study are summarized in Chapter 6. This describes methods based on plasticizing CDA by graft copolymerization using  $\epsilon$ -caprolactone (CLN) and/or lactide (LA).

The selective-grafted products could be prepared by ring opening polymerization in the melt state at 140 °C using Tin(II)2-ethylhexanoate ( $\text{SnEht}_2$ ) as catalyst, where CAs with remaining hydroxyl groups worked as initiator. Plasticization of CAs by this selective grafting can solve the problem encountered in Chapters 4 and 5 that the bleeding of unreacted monomers and homo-oligomers from the inside of molded articles to their surface was often found. By using adequate reaction conditions, the grafting reaction proceeded rapidly and could be completed within 10 to 30 min. LACD is grafted more rapidly than CL onto CAs, producing relatively rigid and brittle products in the earlier stages and elastomer-like ones in the later stages. Transparent amorphous molded articles were obtainable depending on the reaction conditions. The analysis of the structure of the grafted side chains by means of high resolution NMR spectroscopy showed that, although the grafted side chains are composed of large amounts of  $\epsilon$ -oxycaproyl or lactidyl block polymer portions depending on the reaction conditions, a large amount of randomly polymerized parts coexist in the grafting chains, which confer high thermoplasticity, elasticity and amorphous nature to the grafted products obtained.

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