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Mariko Yoshioka [a] & Nobuo Shiraishi [a]

[a] Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University, Kyoto, 606-8502, Japan

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Biodegradable Plastics from Cellulose

MARIKO YOSHIOKA and NOBUO SHIRAISHI

Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University, Kyoto, 606–8502, Japan

Brief history of the attempts trying to develop biodegradable plastics from cellulose acetates were reviewed in the first part. Then, two kinds of authors' trials were introduced. One of them is a plasticization trial for cellulose acetates (CAs) that is based on the reaction with dibasic acid anhydrides and monoepoxides during melt processing under practical process conditions. This reactive melt-processing method allowed the preparation of biodegradable cellulosic plastics with enough thermoplasticity and moldability. The biggest problem was the occurrence of external plasticizer's bleeding, which was found to be prevented by effective yield of grafting. Higher biodegradabilities have been found for the grafted CAs compared to the unmodified CAs. From the above trial, the amounts of grafting and the graft efficiency were intended to increase. As one of its extensions, a plasticization method for CA based on selective grafting of ε -caprolactone (CL) and lactide (LACD) has been developed. The selective-grafted products could be prepared by ring-opening polymerization in the melt state. By using adequate reaction conditions, the grafting reaction proceeded and completed rapidly (within 10–30 min). Transparent amorphous molding were obtainable. The fact that the formed graft side-chains contain a large amount of randomly polymerized parts explains the high thermoplasicity and amorphous nature of the grafted products.

BACKGROUND

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,[1] as well as efforts to identify excellent plasticizers for cellulose acetate (CA),[2,3] 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 disemphasized 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 with gradually growing demands for the circulatory materials which desirably originated from biomass. One of the works of the authors' group must be includable, in which wood could be converted into thermally flowable materials by chemical modification, such as esterification and etherification.[4-7] That is, 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, wood plasticization can be considered as one of the attempts for pursuing recycling technology.

The second motivation resulted 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 and synthetic polymers are more actively and extensively pursued compared to the case of polymers from natural origin. In the other side, 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 pointed out that it will take five to ten more years before the development of biodegradable polymers reaches a practical level.[8]

It is known that the biodegradable chemical intermonomer bonds include glycosides, peptides, and aliphatic esters.[9] 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.

Until end of the 1960s, it was accepted as axiomatic that cellulose acetates having DS$\geqq$ 1.0 are resistant to hydrolysis by enzyme.[10] In 1969, however, Cantor and Mechalas[11] found that even cellulose diacetates (CDAs) having the degree of substitution up to 2.5 could be degraded by the microbial attack. Their investigation was carried out with the objective of relating losses in semipermeability of cellulose acetate (DS 2.5) reverse-osmosis membranes to microbiological degradation. They were discussing about durability of cellulose diacetate

used for the reverse osmosis membranes. That is, they did not have any interst with biodegradable plastics.

In that sense it can be said that the first person to find the microbiological degradation of CDA in relation with biodegradable polymers were the research groups of Eastman Chemical Company and University of Massachusetts.

Buchanan *et al.*[12] and Komarek *et al.*[13] demonstrated that CA with a degree of substitution (DS) up to 2.5 can be degraded microbially. Gu *et al.*[14] studied the cellulose acetate biodegradation upon exposure to simulated aerobic composting and anaerobic bioreactor environments. Sakai *et al.*[15] have searched for fungi that decompose CAs; they demonstrated that *Neisseria sicca* can degrade CA with a DS up to 2.3. It also has been suggested that CA would undergo an enzymatic splitting by acetyl esterase in a first stage, down to a DS of 1.0, before the degradation would continue by the action of cellulase enzymes.[13-15]

Since cellulose diacetate (CDA) was recognized as a biodegradable polymer, various trials have been undertaken to impart sufficient thermoplasticity to CAs in order to render them melt-processable. This is because CDA, which has the greatest thermoplasticity among all kinds of 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 by 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 natures of their decomposition products. In this connection, there have been several attempts trying to utilize aliphatic polyesters of bacterial origins as well as synthetic ones as plasticizers for CAs.[16-21]

In these experimental studies, thermodynamic miscibilities could be found between bacterial poly(3-hydroxybutylate) and cellulose acetate butylate (CAB) or cellulose acetate propionates (CAP), and amorphous optically clear miscible blends could be formed also between CAB and poly(hydroxybutylate-co-valerate). It can be pointed out that novel thermoplastic materials being moldable to give transparent homogeneous sheets could be prepared by these blendings. The problems of these are the main uses of cellulose esters such as CAB, the biodegradabilities of which have not been studied to an enough level, and higher cost performance of CAB compared with that of CA.

At any rate, these studies have been proceeded with intentions to enhance the biodegradabilities of the materials obtained and furthermore to increase their themoplasticities by blending the polymeric materials with high biodegradabilities.

On the other hand, the addition of low molecular weight plasticizers has been taken as

the second type of plasticization of cellulose acetates. Buchanan *et al.*[22] reported that CA can effectively plasticized by thermal compounding with triethyl citrate. The compounded resins were converted to compression-molded film and injection molded bars. Their biodegradabilities were evaluated and confirmed by composting.

Concerning this plasticization of CA with low molecular weight plasticizers, there appeared, in newspapers, several announcements of commercialization of biodegradable plasticized CA. One was an announcement from Planet Polymer Technologies, Inc. (California, U.S.A.) that CA plasticized with triacetine was going into Japanese market with trade name of Lunare. The other was from Daicel Chemical Industries, LTD using polycaprolactone oligomer having molecular weight of 500 as plasticizer for CA.

As the methods for plasticization of CA, in addition to two kinds of external plasticizations which were mentioned above and are usually adopted, it is possible to make use of the internal plasticization, that is, the chemical modification or the grafting methods.

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. In the early stage, attempts have been made to introduce oligoester side chains into CA molecules by the reactions of CA with dicarboxylic 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 shown later.

With the advancement of this study, it became clear that CA must be sufficiently graft copolymerized in order to prevent the bleeding of co-produced homo-oligomers or homo-polymers. From these findings, it came to the understanding that the more effective grafting is attained, the more ideal plasticization of CA can be effected. With this idea in mind, authors have come to a grafting work, in which CAs are plasticized by cyclic esters' grafting using Tin(II)2-ethylhexanoate ($SnEht_2$) as catalyst.

Plasticization of cellulose acetate by reaction with dibasic acid anhydrides and monoepoxides during melt-processing

Authors tried to develop the methodology concerning the plasticization of CAs by reaction with dibasic acid anhydrides and monoepoxide during melt-processing.[23] In this case, oligoesterified CA, prepared by the reaction of CA with SA and PGE, for example, at temperature between 70 and 180℃, has the hypothetical structure shown in Fig. 1.

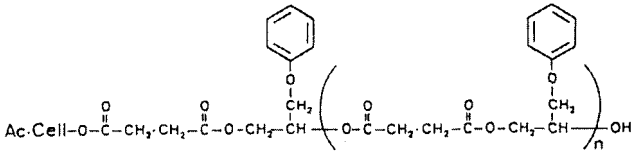

Fig. 1 Schematic chemical structure of CA oligoesterified with SA and PGE.

This kind of introduction of the oligoester side chain into CA molecule would enhance the thermoplasticity of CA (internal plasticization). At the same time, homo-oligomers of the oligoester would be produced and these would be able to act as external plasticizers. The effect of the plasticization treatment can be seen in Fig. 2. From the figure, it is known that CDA, though it has the greatest thermoplasticity among cellulose acetates, still lacks melt-processability, whereas when it was reacted with SA and PGE at 120℃ for 20 min under kneading conditions, it was converted easily into a thermoplastic material. Thus, the above supposition, that the formation of oligoester chains as grafted branches of CAs together with homo-oligomers enhances the thermoplasticity of the products, was confirmed.

Since these results are very promising, the plasticization of CAs was examined under different conditions, including amounts of these reactive plasticizers added, kneading reaction temperature, molding (hot pressing) time and so forth.

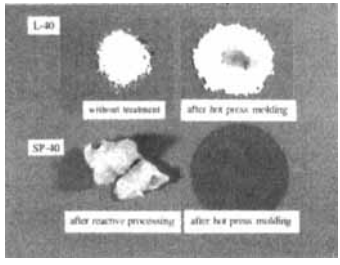

Fig. 2 Effets of oligoerification on L-40.

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

Thus, moldable plasticized products having various mechanical and thermal properties could be obtained. Representative stress-strain curves of CDA and cellulose monoacetate (CMA) oligoesterfied are shown comparatively in Fig. 3 along with those for polystyrene (PS) and polyethyrene (PE). From this figure, it appears that both SP-10 and SP-40 have attractive mechanical properties. They are tougher than PS and stronger than PE.

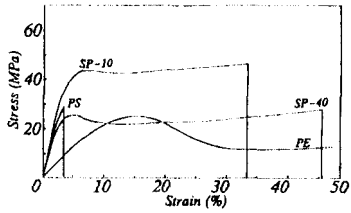

Fig. 3 Stress-strain curves of representative CAs plasticized with SA and PGE.

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

Thermal softening curves of L-40 and its plasticized materials are shown in Fig. 4. Among the latter, SS-40 (oligoesterified L-40 reacted with SA and SO) is included as well. From the figure, it can be seen that when CDA was oligoesteified by the reaction with SA and PGE, for example, in an amount of 30.9 wt% at 120℃ for 20 min in the kneader, the flow temperature dropped to 170℃ from 250℃. Considerable decrease in the flow temperature of CDA can be attained by this oligoesterification grafting.

Although these results concerning thermoplasiticization of CDA and the mechanical properties of the products were extremely fascinating, there often occured a plasticizer migration (bleeding) problem. This was caused by fugitive plasticizers which are mostly homo-oligomers.

The occurrence of plasticizer bleeding was found to be much more pronounced for plasticized CDA than for plasticized CMA (Fig. 5). In the latter, almost no bleeding was found. This difference is thought to be caused by a lack of miscibility, that is, a lack of affinity between the CAs and the oligoesters. To make immiscible polymers (or polymer A and oligomer B) miscible or compatible, 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 chain attached to CA molecule can be expected to enhance the

affinity between the modified CAs and the homo-oligomer. That is, grafting can effectively suppress or prevent the bleeding of non-grafting homo-oligomers. CMA can be proceeded grafting to a higher level compared with the case for CDA.

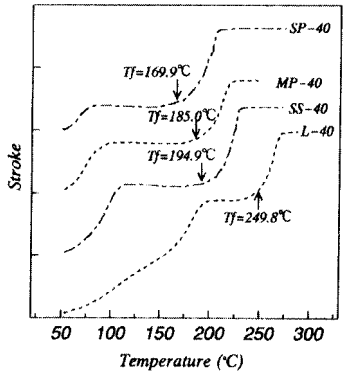

Fig. 4 Thermal softening curves for L-40 and its plasticized materials.

Legend: L-40: untreated CDA, 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 ℃, 30 rpm (5 min)-90 rpm (20 min) ; flow test condition : load: 10 kgf; heating rate : 10℃/ min ; Tf : flow temperature.

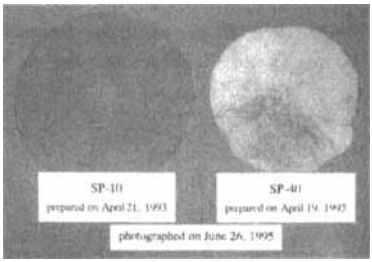

Fig. 5 Bleeding of plasticizer from sheets of plasticized L-40 and LL-10.

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℃, 30 rpm (5 min) - 90 rpm (20 min) ; hot pressing condition: 190℃, 15 MPa, 30 s; photographed on June 26, 1995.

Based on these consideration, methods for enhancing the amount of grafting were pursued by varying the combination of dibasic acid anhydride and monoepoxide, by extending the kneading reaction period, by using grafting catalyst (Fig. 6) and so forth.[24] By these trials, the grafting could be enhanced, which actually resulted in the suppression of the plasticizer bleeding.

The biodegradabilities of the representative samples obtained were examined by a soil burial test in a controlled environment (30℃, 80%RH) and by the measurement of oxygen consumption in a closed system where test samples were exposed to standard activated sludge.[24]

Concerning the former, it was found as a few examples in Fig. 7 that the plasicized CA samples were degraded and disappeared within relatively short periods (i. e., within 3 to 12 months).

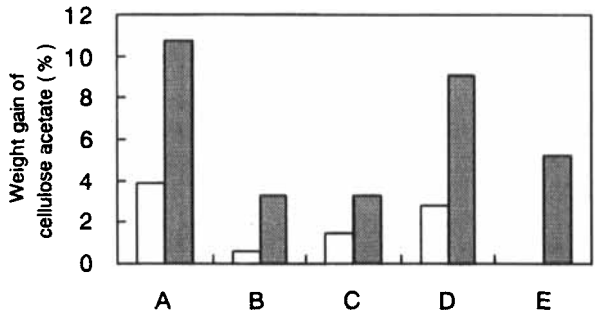

Fig. 6 Effect of catalyst (Na_2CO_3) on weight gain of cellulose acetate.

Notes: Kneading : 120℃, 90 rpm, 15 min ; Flow test : Die : diameter : 1 mm, length : 2mm ; Plunger : 1 cm^2 ; Load : 5 MPa ; Heating rate : 10 ℃/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 (Na_2CO_3)
■ : with catalyst (Na_2CO_3)

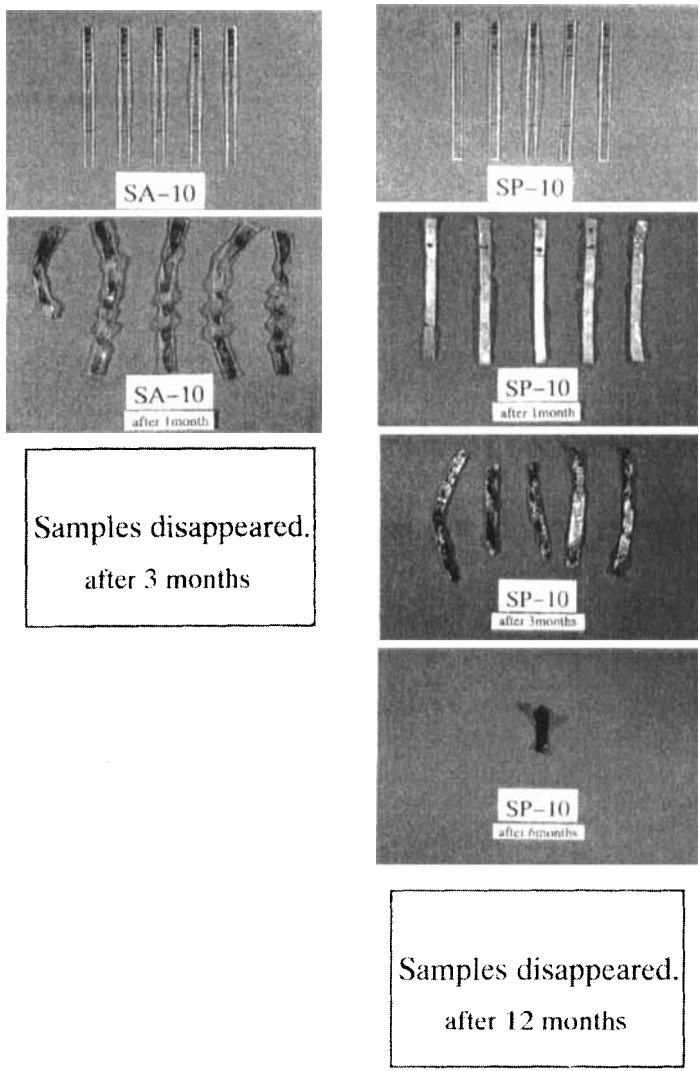

Fig. 7 Changes SA-10 and SP-10 specimens during the soil burial test in incubator.

Results of the biodegradation test measured by means of the oxygen consumption within a closed activated sludge suspension are shown in Fig. 8. It is apparent that all samples are subjected to significant biodegradation. The CMA control sample, of which biodegradaion had been literarily confirmed, was degraded more slowly than any of the oligoesterified samples.

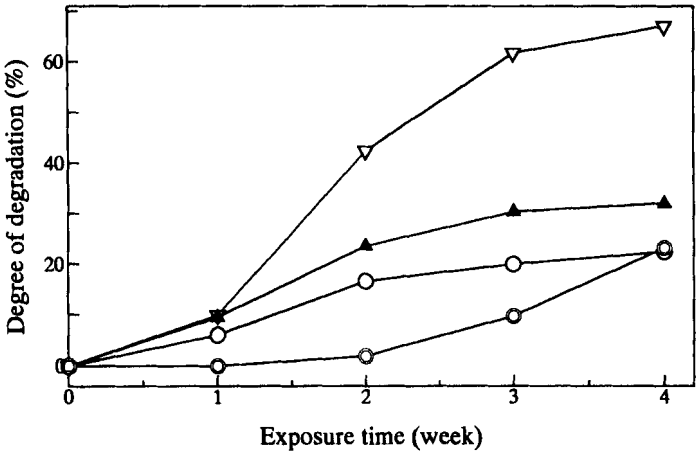

Fig. 8 Results of the exposure test to the closed activated sludge system.

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℃, 20 min; ▲: MP-10: LL-10/MA/PGE=100/11.0/33.1, Kneading : 120℃, 20 min; ▽: SA-10: LL-10/SA/AGE= 100/11.0/25.9, Kneading: 80℃,15 min.

Thermoplasticization of CA by grafting with cyclic esters[25-27]

In the previous section, it was shown that CA must be sufficiently graft polymerized in order to achieve effective plasticization and to prevent the bleeding of homo-oligomers. Thus, the amounts of grafting and the graft efficiency were intended to increase. As an extension of the efforts, authors have come to a grafting work, in which cyclic esters are reacted with CA

using $SnEht_2$ as a 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 $SnEht_2$.[28,29] Ikada described the same in his review article[28] on "Polylactic acid", but introduced a mechanism by which homo-polymers are produced predominantly, even though the ring-opening polymerization of cyclic esters is conducted in the presence of CDA. On the contrary, Kricheldorf and his co-workers studied the polymerization of L-lactide catalyzed with $SnEht_2$ in the presence or absence of benzyl alcohol.[30] When $SnEht_2$ and benzyl alcohol are used as a catalyst and a co-initiator, respectively, NMR spectroscopic examination of all polylactides obtained by the ring-opening polymerization revealed the presence of benzyl ester end-group but the absence of 2-ethylhexanoate end groups.[30] This result means that hydroxyl group of alcohols plays an essential and direct role in initiating the ring-opening polymerization of cyclic esters. In this sense, graft polymerization can be expected to occur selectively when the cyclic esters are polymerized in the presence of CA and $SnEht_2$.

Thus, authors started co-grafting study of ε -caprolactone (CL) and L-lactide (LACD) onto CDA using $SnEht_2$ as a catalyst in order to realize grafting with considerably high graft efficiency. In these cases, the reaction temperature was kept constant at 140℃ and the reaction time was changed from 0 to 60 min. The other reaction conditions are known from the foot notes of the relating figures (Figs. 9-12).

One of the characteristics of this grafting is that the grafting reaction can proceed rapidly and can be completed within 10 to 30 min (Fig. 9), and in the correspondence with this, the flow temperature decreased to about the half of that of CDA (Fig. 10). The obtained products are moldable to films or sheets without using any plasticizer. Furthermore, it is known from Fig. 11 that LACD is grafted more rapidly than CL, producing relatively rigid and brittle products in the earlier stages and elastmer-like ones in the latter stages of the grafting. From Fig. 11, it can be also said that the total molar substitution reached its theoretical maximum value after 10 min of the grafting. This result confirms that the graft reaction proceeds with a high rate and shows that the selective grafting is achieved completely without significant production of homo-polymers or homo-oligomers. This is a support for the reaction mechanism proposed by Kricheldorf *et al.*[30] Transparent sheets were obtained depending on the reaction conditions, showing their amorphous nature. In this concern, the triad structure of the grafted side chain was analyzed by means of high resolution NMR spectroscopy. An example of the NMR data is shown in Fig. 12, in which the ε -oxycaproyl unit is denoted by C and lactidyl unit by LL. Each of the splitting spectral lines for $\alpha, \beta, \gamma, \delta$ -methylene carbons of ε -oxycaproyl units and methyl carbon of lactidyl unit in a grafted product was assigned by reference to the Kasperczyk and Bero's work.[31] The spectrum of Fig. 12 means that even for a grafted CDA (H-1) prepared by using the liquid ratio of 2, LACD/CL=2/5

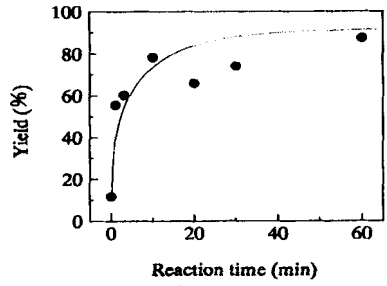

Fig. 9 Effects of the reaction time on the yield.

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

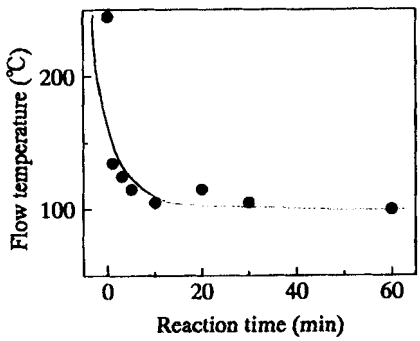

Fig. 10 Effects of the reaction time on the flow temperature.

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

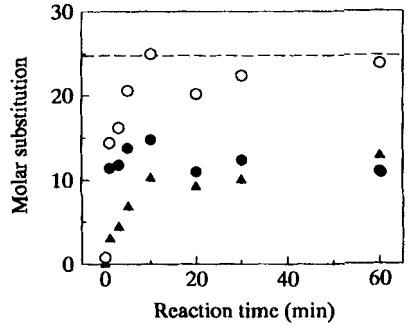

Fig. 11 Effects of the reaction time on the molar substitution.

Notes: Reaction temperature : 140 ℃ ; 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).

(by mole), reaction time of 30 min, and the reaction temperature of 140℃, the introduced graft side chains are long enough to reveal triad sensitivity.

Existences 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 occurrences of randomly polymerized parts of CL and LACD within the graft side chains. This fact confers irregularity in graft chains and it is considered to be related with the appearance of the high thermoplasticity and amorphous nature found and discussed above. In other words, it can be said that the analysis of the structure of the grafting side chain by means of NMR spectroscopy showed that, although the side chain are composed of a certain large amounts of ε -oxycaproyl or lactidyl block polymer portions, a considerable amounts of randomly polymerized parts coexist in the grafting chains, which confer high thermoplasticity and amorphous nature to the grafted product obtained.

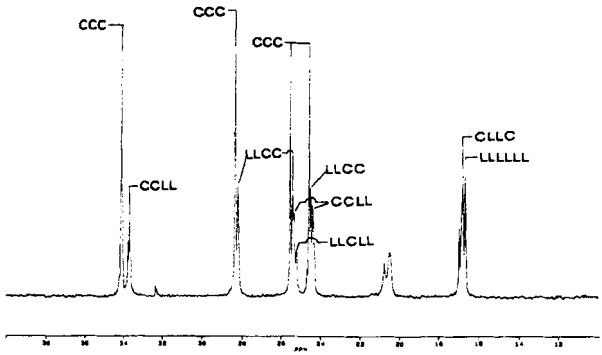

Fig. 12 ^{13}C-NMR spectrum of (CL-co-LACD) grafted CDA, H-1.
Region of $\alpha, \beta, \gamma, \delta$ -methylene carbon atoms of ε -oxycaproyl units, methyl carbon atom of lactidyl unit and acetyl methyl carbon atoms of CDA.

References

[1] Marusawa H., Uda K. : "Plastic Materials Series [17], Cellulosic Resins", Nikkan Kogyo Shinbun Ltd.,Tokyo (1970).
[2] Kita M. : "Handbook of Novel Wooden Materials", Haraguchi, T. *et al.*, eds., Gihodo Pub., Tokyo (1996), p. 594–604.
[3] Fordyce C. R., Meyer L. W. A.: *Ind. Eng. Chem.*, **32,** 1053–1060 (1940).
[4] Shiraishi N., Matsunaga T., Yokota T. : *J. Appl. Polymer Sci.*, **24,** 2361 (1979).
[5] Shiraishi N. : "Chemistry of Wood Utilization", Imamura H., Okamoto H., Goto T., Yasue Y., Yokota T. and Yoshimoto T. (eds.), Kyoritsu Publisher Inc., Tokyo, p.294 (1983).
[6] Shiraishi, N. : Plasticization of wood and its application, "Cellulose Utilization, Research and Rewards in Cellulosics", Inagaki H. and Phillips G. O. (Eds.), Elsevier Applied Science, London & New York, p. 97–309 (1989).
[7] Shiraishi, N. : Wood plasticization,"Wood and Cellulosic Chemistry", Hon D. N. S. and Shiraishi N. (Eds.), Marcel Dekker, Inc., New York & Basel, p. 861–965 (1991).
[8] Biodegradable Plastic Society, Japan: "Opening of New Plastic Era -- Report of the Committee for Developing Biodegradable Polymers to Practical Usage", March 1995, p.1.
[9] Sawada H. : Biodegradable plastics making use of cellulose and polycaprolactone. In "Practical Biodegradable Plastics", CMC Co. Ltd., Tokyo, 1992, p. 38.
[10] Reese, E. T. : *Ind.Eng. Chem.*, **49** (1), 89–93 (1957).
[11] Cantor, P. A., Mechalas, B. J. : *J. Polymer Sci.*, Part C, **28,** 225–241 (1969).
[12] Buchanan C. M., Gardner R. M., Komarek R. J. : *J. Appl. Polym. Sci.*, **47,** 1709–1719 (1993).
[13] Komarek R. J., Gardner R. M., Buchanan C. M., Gedon S. C. : *ibid.*, **50,** 1739–1746 (1993).
[14] Gu Ji-Dong, Eberiel, D. T., McCarthy, S. P. and Gross, R. A. : *J. Environ. Polymer Degradation,* **1** (2), 143–153 (1993).
[15] Sakai K., Yamauchi T., Nakatsu F., Ohe T. : Abst. of the 1994 National Meeting of Agric. Chem. of Japan, Tokyo, 1994, p. 511, 3FP5.
[16] Buchanan C. M., Gardner R. M., Wood M. D., White A.W., Gedon S.C., Barlow F. D. : U. S. Patent, 5292783 (1994).
[17] Scandola, M., Ceccorulli, G., Pizzoli, M. : *Macromolecules,* **25,** 6441–6446 (1992).

[18] Ceccorulli, G., Pizzoli, M., Scandola, M. : *ibid,* **26,** 6722–6726 (1993).
[19] Buchanan, C. M., Gedon, S. C., White, A. W., Wood, M. D. : *ebid,* **25,** 7373–7381 (1992).
[20] Buchanan, C. M., Gedon, S. C., White, A. W., Wood, M. D. : *ebid,* **26,** 2963–2967 (1993).
[21] Buchanan, C. M., Gedon, S. C., Pearcy, B. G., White, A. W., Wood, M. D. : *ebid,* **26,** 5704–5710 (1993).
[22] Buchanan, C. M., Dorschel, D. D., Gardoner, R. M., Komarek, R. J., White, A. W. : *J. M. S. -Pure Appl. Chem.,* **A32** (4), 683–697 (1995).
[23] Yoshioka M., Miyazaki T., Shiraishi N.: *Mokuzai Gakkaishi,* **42** (4), 406–416 (1996).
[24] Yoshioka, M., Okajima, K., Miyazaki, T., Shiraishi, N. : *J. Wood Sci.,* in press.
[25] Yoshioka, M. : *Preprints of 98–2 Regular Meeting of the Society for the Study of Eco-material,* Soc. Polymer Sci., Japan, p.1–6 (1998).
[26] Yoshioka, M., Mizumoto, H., Hagiwara, N., Shiraishi, N. : *Preprint of '98 Cellulose R&D,* 5th Annual Meeting of the Cellulose Soc., Japan, 26–27 (1998).
[27] Yoshioka, M., Hagiwara, N., Shiraishi, N. : *Cellulose,* accepted.
[28] Ikada, Y. : Polylactic acid, "Handbook of Biodegradable Plastics", Doi, Y. *et al.* (eds), N. T. S. Ltd., Tokyo, p.279–280 (1995).
[29] Kowalski, A., Duda, A., Penczek, S. : *Macromolecule Rapid Communication,* **19,** 567–572 (1998).
[30] Kricheldorf, H. R., Kreiser-Saunders, I., Boettcher, C. : *Polymer,* **36** (6), 1253–1259 (1995).
[31] Kasperczyk, J., Bero, M. : *Macromolecule Chemistry,* **192,** 1777–1787 (1991).