

# Cellulosic Nanocomposites. I. Thermally Deformable Cellulose Hexanoates from Heterogeneous Reaction

HIROYUKI MATSUMURA,<sup>1\*</sup> JUNJI SUGIYAMA,<sup>2</sup> WOLFGANG G. GLASSER<sup>1</sup>

<sup>1</sup> Biobased Materials/Recycling Center, Department of Wood Science & Forest Products, Virginia Tech, Blacksburg, Virginia 24061

<sup>2</sup> Division of Wood Bioscience, Wood Research Institute, Kyoto University, Kyoto, Japan

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**ABSTRACT:** Partially derivatized cellulose esters were prepared from dissolving-grade wood pulp fibers by reaction with a mixed *p*-toluene sulfonic/hexanoic anhydride system in a nonswelling (cyclohexane-based) reaction medium. The partially derivatized pulp fibers, which failed to undergo a significant change in shape or appearance during the modification, proved to be resistant to swelling (in water), were thermally deformable, and retained their biodegradability. Because X-ray diffractometry provided evidence for the presence of unsubstituted, ordered cellulose with cellulose I morphology, the thermally reshaped and consolidated sheets were found to consist of commingled mixtures of cellulose esters and cellulose I. The transparent or semitransparent consolidated sheets (depending on the degree of substitution) were found to represent composites in which cellulose I serves as a discontinuous inclusion that reinforces a continuous, partially ordered cellulose ester matrix. The composites, which revealed cohesive or adhesive failure at rupture, depending on the degree of substitution, had modulus values and tensile strengths as high as 1.3 GPa and 25 MPa, respectively. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2242–2253, 2000

**Key words:** cellulose esters; modification; biodegradation; thermoplastic composites; microfibrils; X-ray diffraction; pulp

## INTRODUCTION

Cellulose is nature's most abundant polymer. It is generated for a variety of purposes and plant functions in worldwide amounts measured in gigatons.<sup>1</sup> Cellulose serves plants as cell and fiber walls and as reinforcement for all plant materials. The structure of cellulose, which is a linear polymer of anhydroglucose (AHG), is well understood. Its order involves crystallinity and micro-

fibrillar orientation that is the subject of extensive reviews.<sup>2–4</sup> Cellulose is isolated by the pulp and paper industry in amounts exceeding 100 million tons per year, and this industry rivals the size of the chemical industry worldwide.

The chemical modification of dissolving-grade wood pulp fibers with a variety of acids and anhydrides represents longstanding industrial practice.<sup>5</sup> Cellulose ethers and cellulose esters are used for a wide variety of products in the food, household products, health care, textile, and many other industries.<sup>5,6</sup> Esters with short alkyl chains (acetate or propionate) form solvent-soluble, spinnable fibers; esters with bulky substituents (butyrate, hexanoate, and higher) are progressively more thermally deformable under

Correspondence to: W. G. Glasser.

\*On leave from Daicel Chemical Industries, Ltd., Himeji, Japan.

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pressure. The commercial practice of generating cellulose esters with a degree of substitution (DS) of 2.2–2.5 involves a heterogeneous phase reaction of cellulose in pulp fibers to an initial DS of 3 in the more accessible AHG units while leaving the less accessible (crystalline) portion unreacted. Therefore, this practice necessitates the acid-catalyzed deacylation of very highly substituted cellulose ester derivatives (DS  $\approx$  3.0). This process is basically undesirable from the economic and resources conservation standpoints.<sup>7</sup> Recent research involving titanium isopropoxide as a catalyst and dimethylacetamide (DMAc) as a cellulose-swelling medium showed that apparently uniform cellulose esters with a DS of 2.2–2.8 can also be prepared in a single reaction that begins heterogeneously and ends homogeneously.<sup>7,8</sup> This development allows the synthesis of partially acylated cellulose esters in a single reaction without the need for deacylation of highly substituted ester derivatives. When this reaction is carried out in the presence of alkanolic anhydrides having alkyl substituents in excess of five, highly melt deformable, thermoplastic derivatives emerge that have attractive melt-rheological properties.<sup>8</sup>

Thermoplastization of cellulose recently experienced renewed interest because new catalysts and reaction methodologies<sup>7–15</sup> were explored and because cellulosic plastics are recognized as renewable and biodegradable plastics.<sup>16–18</sup> We focused on the transitional stages between a multimorphological, insoluble, infusible solid and a melt-flowable thermoplastic.

Although Shiraishi et al. reported extensively on thermally deformable materials from wood and pulp fibers derivatized with aliphatic acids and other substituents, no detailed information is available on the required overall degree or uniformity of substitution for moldability to be achieved.<sup>19–23</sup>

It is a long-held view that cellulose esterification starts from the disordered (or amorphous) region before proceeding to the ordered (or crystalline) region.<sup>24,25</sup> An alternative view was presented by Shimamoto et al. who found that esterification proceeds from the surface of each pulp fiber to the interior, thereby producing a skin-core structure.<sup>26</sup> Another possible scenario is that esterification starts at the surface of microfibrils, which have a diameter of 10–50 nm, and progresses to the interior. Although there is little consequence of the precise sequence of events if a cellulose derivative with constant and uniform DS is desired, this progression can be expected to

have a significant impact on the properties of partially modified pulp fibers. If it is the amorphous cellulose component alone that is affected by an incipient modification, no changes in bulk behavior can be expected. A skin-core morphology on the scale of pulp fibers (with dimensions in the 10's of microns) can be expected to form materials that progressively gain solubility from the surface. If esterification proceeds from the surface of the microfibril to its core (on a scale of 10's of nanometers), a two-phase morphology can be expected that reflects both cellulose and cellulose ester characteristics on the nanoscale.

The crystalline order of cellulose was the subject of extensive research over many generations. Cellulose crystallites are recognized for their strength and size, and they are organized into microfibrils whose orientation in pulp fibers is genetically controlled.<sup>3,27</sup> By virtue of their strength and shape, cellulose crystallites have qualifications for polymer reinforcement. Cellulosic crystallites isolated as “whiskers” from tunicate or other raw materials by mineral acid treatment were recently explored as reinforcements for nanocomposites in a variety of manmade thermoplastics.<sup>28–33</sup> These studies demonstrated that cellulose whiskers can contribute significant stiffness to cellulose-containing (i.e., <20%) composites, especially with elastomers, and even at very low fiber contents.

In this study we explore the effect of incipient modification on pulp fiber properties. A wood pulp partially esterified in a nonswelling (and/or poor) solvent for both cellulose and the resulting cellulose ester is prepared with a method that preserves most of the original ultrastructure. The objectives of the study focus on the consequence of the incipient cellulose esterification with hexanoyl groups on thermal properties. The apparently heterogeneous distribution of ester groups in the derivatives containing unmodified cellulose regions is expected to lead to unique properties.

## EXPERIMENTAL

### Materials

Commercial dissolving-grade wood pulp (made from hardwood) was disintegrated in water with a household blender, washed with acetone on a Buchner funnel, and then dried under a vacuum at 50°C. The obtained fluffy pulp fibers were kept

in a desiccator and used as starting material for the heterogeneous hexanoylation.

Homogeneous cellulose hexanoates with varying DSs were prepared from cellulose powder (Whatman CF-11) dissolved in DMAc/LiCl following the protocol reported previously.<sup>11</sup>

All reagents were obtained from Aldrich Chemical Company (Milwaukee, WI) and were used as received.

## Methods

### Modification Reaction

*Mixed p-Toluenesulfonic/Hexanoic Acid Anhydride System (Ts System).* Pyridine (6 eq/OH), cyclohexane, hexanoic acid (2 eq/OH), and *p*-toluenesulfonyl chloride (2 eq/OH) were mixed in this order at 70°C under dry nitrogen. Pulp fibers were then added to start the hexanoylation reaction. After keeping the reaction mixture under steady agitation, the heterogeneous suspension was poured into excess methanol. The undissolved solids (fibers) were filtered and washed repeatedly with methanol before being dried under a vacuum at 50°C. Their DS was determined by FTIR spectroscopy.

*Titanium(IV) Isopropoxide Catalyzed System (Ti System).* Pulp fibers were activated by soaking them in DMAc at 100°C for 1 h under dry nitrogen. The mixture was heated at 110°C for 45 min following the addition of 1 part xylenes per 1 part of DMAc before hexanoic anhydride (2 eq/OH) was added and the temperature raised to 140°C. Titanium(IV) isopropoxide (6 wt % based on pulp fibers) was then added to start the hexanoylation reaction. After keeping the reaction mixture under steady agitation, the heterogeneous suspension was poured into excess methanol. The undissolved solids (fibers) were filtered and washed repeatedly with methanol before being dried under a vacuum at 50°C. Their DS was determined by FTIR spectroscopy.

### Compression Molding

Modified pulp fibers (and control) were dispersed in methanol or water to form a uniform fiber slurry. The fiber suspension was filtered using a Buchner funnel to prepare a uniform fiber mat. This mat was removed from the funnel, dried under a vacuum, and pressed for 4 min at 155–170°C (or at room temperature) under 310 kg/cm<sup>2</sup> of pressure in a Carver hot press. The basis

weight of the resulting sheets was approximately 250 g/m<sup>2</sup>.

### Determination of Mechanical Properties

Small rectangular samples (5 × 20 mm) were cut from the compression-molded sheets using a razor blade. The mechanical properties of these samples were determined using a Minimat (Polymer Laboratories, Loughborough, U.K.) material tester in tensile mode. The data reported are averages of at least four samples per data point. The stress relaxation curves were obtained with the same tester. About 13 MPa of stress (initial stress *I*) was applied to the samples (5 × 20 mm) in tensile mode. The change in stress (residual stress *R*) was recorded over a 2-h test period. The ratio of the residual stress (*R*) to the initial stress (*I*) was used as the relaxation index.

### Sorption and Swelling Tests (Water Resistance Test)

Compression-molded sheet samples (ca. 0.3-mm thickness) were evaluated for water sorption and swelling (water resistance) using modified Tappi standard T491 om-95. In brief, rectangular samples of approximately 7 × 20 mm were first dried under a vacuum and accurately weighed. The samples were then immersed in deionized water at a depth of 8 cm with wire screens to prevent floating to the surface. After a designated time period at room temperature, the samples were removed, pressed with a roller between filter papers to remove excess water, and then accurately reweighed. The weight gain (WG) was calculated from

$$\text{WG}(\%) = (b - a) \cdot a^{-1} \cdot 100$$

where *a* represents the weight of the dry sample and *b* is the sample weight after sorption.

### Solubility Tests

About 0.5 g of dried and weighed heterogeneously hexanoylated pulp fibers were stirred in 49.5 g of solvent (chloroform or DMSO) at room temperature for 18 h. The mixture was filtered using a Buchner funnel with a sintered glass disk (ASTM 30). The insoluble substances were washed repeatedly with the solvent, dried under a vacuum, and weighed. The insoluble mass (IM) was calculated from

$$IM(\%) = B/A \times 100$$

where  $A$  represents the original sample weight and  $B$  is the sample weight after the solubility test.

### Biodegradability

To eliminate the differences in physical properties, samples (heterogeneously hexanoylated pulp fibers, unmodified pulp fibers, and homogeneous cellulose hexanoates) were pretreated as follows. The samples (ca. 250 mg) were soaked in DMAc (4 mL) for 7 days, followed by the addition of 23 mL of DMAc/LiCl (ca. 9% LiCl content). The mixture was stirred at 80°C for 1 h before being cooled to room temperature with agitation for another 2 h. This experimental protocol (i.e., heating and cooling with stirring) was repeated 3 times. The samples were highly swollen or dissolved in DMAc/LiCl solution by this treatment. The samples so pretreated were then regenerated and the solvent exchanged using methanol/H<sub>2</sub>O (50/50 wt %), washed first repeatedly with deionized water and then with acetate buffer (pH 4.9), and dispersed in 25 mL of acetate buffer. Excess cellulase enzyme preparation (100 μL, Cytolase 123, Genencor Inc., San Francisco, CA) was added to start the hydrolysis in accordance with Glasser et al.<sup>17</sup> The suspension was agitated at 50°C. A small amount of supernatant was removed from the suspension after 2 days of incubation and filtered with a small amount of glass wool in a disposable pipette to determine the concentration of the reducing glucose (*o*-toluidine assay of Sigma Diagnostics<sup>34</sup>) produced during the enzymatic hydrolysis. After the incubation, residual samples were recovered by filtration with a Buchner funnel with a sintered disk (ASTM 10-15), washed repeatedly with deionized water, and dried under a vacuum at 50°C. The results were interpreted using a homogeneity index (HI) defined as

$$HI(\text{wt}\%) = B - A = (a - b - c) \cdot a^{-1} \cdot 100$$

where  $A = c/a \times 100$  (wt %),  $B = (a - b)/a \times 100$  (wt %),  $a$  is the initial weight of a sample used for incubation,  $b$  is the glucose weight produced from the sample by incubation, and  $c$  is the residual weight of the sample recovered by filtration after the 7 days of incubation.

### X-Ray Diffractometry

Compression-molded (cold and hot) samples were analyzed by X-ray diffractometry operated in re-

flection mode with CuK $\alpha$  radiation ( $\lambda = 0.15406$  nm) generated at 35 kV and 200 mA. Interplanar spacing (IS) was calculated using Bragg's formula

$$IS = n\lambda / (2 \sin \theta)$$

where  $n = 1$ ,  $\lambda$  is the wavelength of the X-ray radiation used (0.15406 nm), and  $\theta$  is Bragg's diffraction angle (°).

The size (width) of the cellulose crystallites was estimated from the width of the peak at  $2\theta = 22.8^\circ$  at half-height after removal of the background noise using the formula by Scherrer

$$\text{crystal size} = \kappa\lambda / (\beta \cos \theta)$$

where  $\kappa = 0.9$ ,  $\lambda$  is the wavelength of the X-ray radiation used (0.15406 nm),  $\beta$  is the peak width at half-height (rad), and  $\theta$  is Bragg's diffraction angle (°). In this study the  $\beta$  was determined by deconvoluting the overlapping peaks in the usual manner.

### Scanning Electron Microscopy (SEM)

The SEM of fractured surfaces of compression-molded sheets was conducted on an Amray 180 D instrument using a cold-sputtering technique. The microscope was operated at 15 kV.

## RESULTS AND DISCUSSION

### Modification Reaction

The chemical modification of cellulose leading to solvent-soluble or thermoplastic cellulose esters usually involves heterogeneous reaction conditions. Dissolving-grade pulp fibers are usually suspended in cellulose-swelling and cellulose ester dissolving solvents while being reacted with a suitable anhydride. By selecting a nonswelling (and/or poor) solvent as the suspending agent for the pulp fibers and target cellulose ester, the derivatization of inaccessible cellulose morphologies was expected to be retarded or prevented. These morphologies can be expected to have a high modulus (130 GPa from Cavaille et al.<sup>28-33</sup> and 90–140 GPa from Sugiyama et al.<sup>27</sup>) and high aspect ratio. Cyclohexane and xylenes both qualify as nonswelling (and/or poor) suspending agents for the hexanoylation of pulp fibers as was revealed by the solubility characteristics of homogeneously prepared cellulose hexanoates (Table I). Cyclo-

**Table I Solubility of Homogeneous Cellulose Hexanoate in Solvents in Relation to DS**

Solvent	DS = 0.5	DS = 1.0	DS = 1.6	DS = 2.1	DS = 2.5
Cyclohexane	IS	IS	IS	IS	IS
Xylenes	IS	IS	IS	PS or S	S
Acetone	IS	IS	S	S	S
DMAc	S	S	S	S	S
DMSO	S	S	S	S	S

S, Soluble; PS, partially soluble; IS, insoluble.

hexane and xylenes were therefore employed for the modification of cellulose with a mixed *p*-toluenesulfonic/hexanoic acid anhydride system (Ts system) and a Ti(IV) isopropoxide catalyzed system (Ti system), respectively. Cyclohexane, whose boiling point is 80.7°C, is ineffective in the Ti system, which requires higher temperatures. In the Ti-based reaction system, hexanoylation was found to produce significant derivatization only when pulp fibers had been activated with DMAc and the reaction was performed at high temperature (140°C).

Pulp fibers modified by both systems were not visually significantly different from the starting material until the DS reached 2.3 for the Ts system and 1.3 for the Ti system (Fig. 1). However, when the pulp fibers were subjected to compression molding at elevated temperatures (155–170°C), transparent or semitransparent sheets were formed by apparent thermoplasticity and molecular consolidation (Fig. 2).

The DS of heterogeneously hexanoylated pulp fibers was determined by FTIR using the absorption ratio between 1750 and 1060  $\text{cm}^{-1}$ . The calibration curve was obtained using homogeneously prepared cellulose hexanoates having DS values previously established using NMR spectroscopy and/or aminolysis<sup>35</sup> (Fig. 3, inset). Using this method of calibration, heterogeneously hexanoylated pulp fibers were revealed to have DS values that increased with reaction time (Fig. 3). There was no noticeable difference between the Ts and the Ti systems.

#### Thermal Consolidation and Composite Properties

The heterogeneously hexanoylated pulp fibers were found to be reshapeable at both room and elevated temperatures. Deformation by compression molding produced self-adhering sheets that were at least semitransparent. (Samples compression-molded at

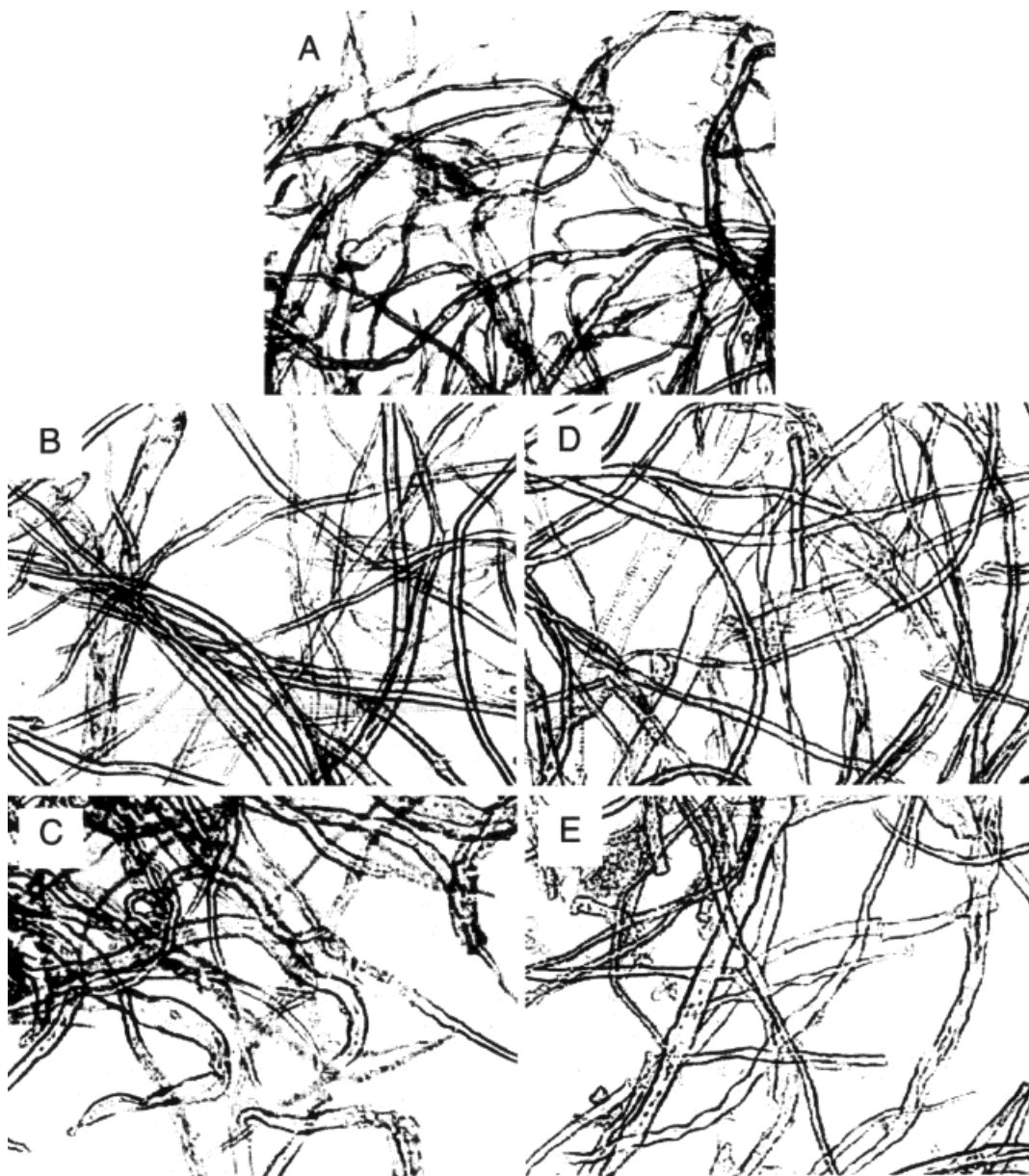
room temperature as opposed to elevated temperature had similar X-ray diffraction patterns, but they were different in other properties.) Heterogeneously hexanoylated pulp fibers consolidated by compression molding at 155–170°C produced sheets that had mechanical properties that varied dramatically with the DS (Fig. 4). The tensile strength increased from 3 to about 25 MPa as the DS rose to 1.0. The modulus increased sevenfold when the DS rose from 0 to 0.5; it had a maximum of 1.3 GPa, and it declined at higher DS levels. Remarkably, elongation increased with the DS, even as tensile strength and modulus increased. This is unusual because most biphasic composites lose extensibility when strength and modulus rise. There was no significant difference in mechanical properties between the Ts and Ti reaction systems.

The SEM of the fractured surfaces of the compression-molded sheets revealed the fibrous nature of the composites (Fig. 5). Remarkably, the lower DS fibers appeared to fracture cohesively during failure while the higher DS samples exhibited significant fiber pull-out, suggesting an adhesive failure mode.

The viscoelastic properties of the compression-molded (biphasic) sheets were tested using a stress relaxation experiment at  $22 \pm 2^\circ\text{C}$ . All sheets were found to relax when stressed to constant strain, regardless of the DS [Fig. 6(a)]. The degree of stress relaxation, however, was clearly related to the DS [Fig. 6(b)].

#### Water Sorption and Swelling (Water Resistance)

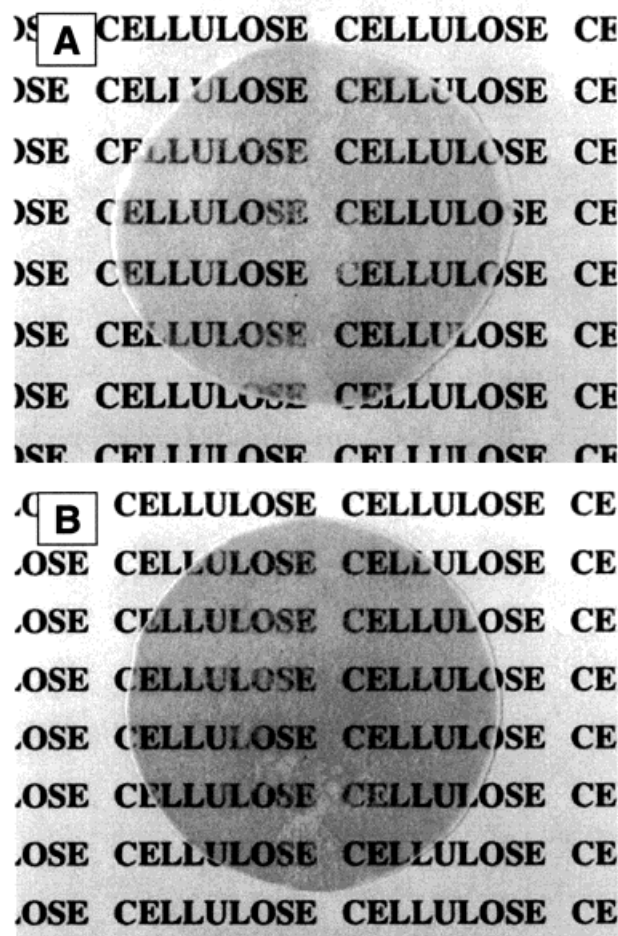
The gradual and progressive removal of accessible hydroxyl groups of pulp fibers by esterification can be expected to have a dramatic effect on moisture pickup and swelling. Using a (modified) standard test designed for paperboard (Tappi Standard T491 om-95), moisture pickup by swelling was recorded as the weight gained with immer-



**Figure 1** Optical light micrographs of heterogeneously hexanoylated pulp fibers with the degree of substitution (DS) rising from 0 to 2.3 in (A) control (DS = 0), (B) Ts (DS = 1.0), (C) Ts (DS = 2.3), (D) Ti (DS = 0.9), and (E) Ti (DS = 1.3). Note the virtual absence of any change in the visual appearance.

sion time in water. The results indicated that swellability (or weight gain) declined dramatically with the DS. The weight gain of a sheet of unmodified control pulp was approximately 100%, while even the least modified pulps (DS = 0.5 of Ti system) exhibited a weight gain of <4%, even after 1 week of water immersion (Fig. 7). This is in agreement with the well-known dimensional stabilization effect of (surface-) acetylated wood.<sup>36</sup> Only very modest differences were

determined for the heterogeneously hexanoylated pulps in relation to the DS. The weight gain of a sheet of fibers having the highest DS (1.7, Ts system) remained at <1% throughout the duration of the test (1 week). These results strongly suggest that hexanoylation in a nonswelling medium effectively removes accessible hydroxyl groups and/or the surfaces of fibers or sheets are covered with cellulose hexanoate with a DS greater than required for melt flow.



**Figure 2** Compression-molded sheets of heterogeneously hexanoylated pulp fibers of the (A) Ts system (DS = 1.0) and (B) Ti system (DS = 1.3). Note the transparency of both sheets.

A close examination of the weight gain profile versus the DS for heterogeneously hexanoylated pulps using the Ts system rather than the Ti system revealed minor differences between the two systems (Fig. 8). The Ts-based reaction product lost water swellability more rapidly as the DS rose than the corresponding Ti-based product. This can be interpreted with a more selective modification, resulting in higher DS levels in the accessible regions for the Ts system as compared to the Ti-based reaction product.

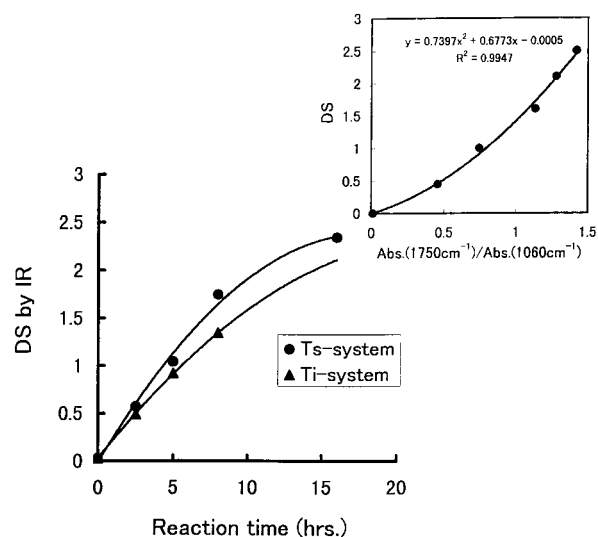
A partially esterified pulp fiber conceptually represents a mixture of an unsubstituted cellulose and a cellulose ester. The dimensional parameters of this mixture can be described with any of the following three models: it could represent a surface-esterified pulp fiber in accordance with Shimamoto et al.,<sup>26</sup> it could consist of micro-

fibrils that have unsubstituted cores and cellulose ester surface layers, or it could consist of a mixture of esterified AHG units in disordered regions and unsubstituted AHG units in ordered regions. The first model (i.e., a surface-core architecture at the fiber level) would likely render the highly substituted surface layer soluble in a suitable solvent (like acetone, methyl ethyl ketone, DMSO, or chloroform) whereas the third model would produce an insoluble two-phase material because of molecular networking via crystalline regions. In the second model, however, the commingling of unsubstituted (crystalline) and esterified cellulose molecules would be on the intrafibrillar and intramolecular level that prevents all intermolecularly distinctive motion by solvents.

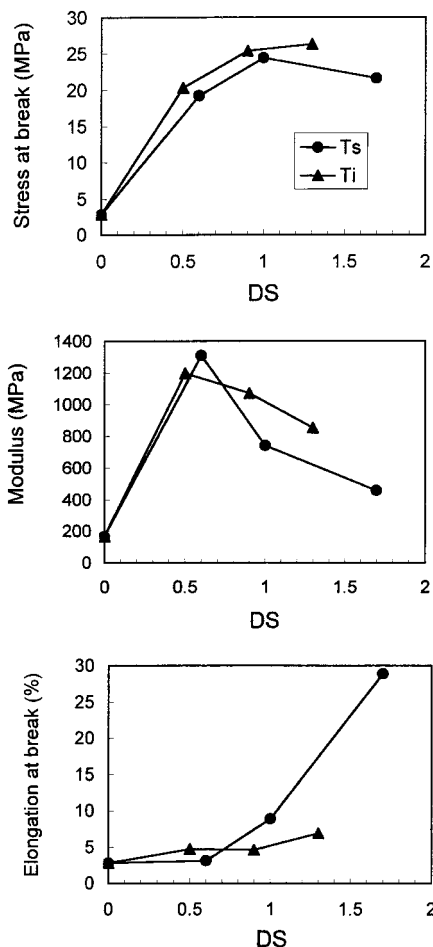
Subjecting heterogeneously hexanoylated pulps to dissolution tests using DMSO and chloroform as a solvent revealed that the modified pulp fibers remained virtually insoluble (<10% of solids dissolved) in both solvents up to a DS of 1.7 (Fig. 9). At DS values of >2.0, approximately 50% of the cellulose hexanoate became soluble in chloroform. This is consistent with the second and third hypothetical cases, which stipulate that esterified cellulose regions and unsubstituted cellulose morphologies are present on a nanometer scale.

### Biodegradability Tests

The biodegradability of cellulose derivatives with variable DSs was the subject of extensive prior



**Figure 3** The relationship between the DS and reaction time for heterogeneously hexanoylated pulps using the Ts and Ti systems. The calibration curve used to determine the DS of hexanoylated cellulose by FTIR is shown in the inset.



**Figure 4** The mechanical properties of compression-molded sheets of heterogeneously hexanoylated pulp fibers in relation to the DS of the (●) Ts system and (▲) Ti system.

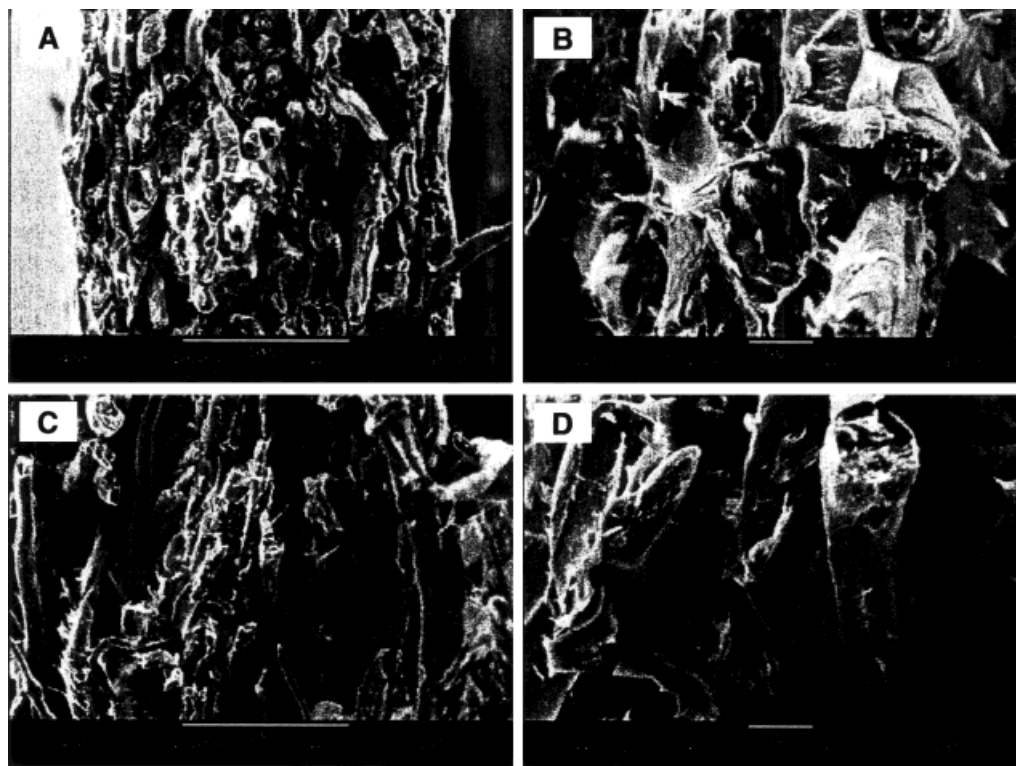
work.<sup>16–18,37–40</sup> Using isolated cellulolytic enzyme mixtures, cellulose ethers were found to be undegradable when each AHG unit possessed one substituent.<sup>39</sup> In addition, cellulose ethers of low DS were found to undergo chain cleavage (initially at a faster rate) along contiguous unsubstituted AHG units, followed by degradation at a slower rate involving unsubstituted AHG units adjacent to AHG derivatives.<sup>40</sup> Similar results were obtained with cellulose esters that were found to be degradable in relation to both the DS and substituent size. Degradability progressively declined even at a DS of <1.0 when the substituent size rose beyond 3 (propionate).<sup>17</sup>

Adoption of an enzymatic biodegradability assay based on commercially available cellulases was therefore expected to produce indications of the level of uniformity in the distribution of sub-

stituents in cellulose derivatives. Whereas the initial results using modified pulp fibers without any pretreatment revealed no difference from homogeneously prepared cellulose esters of the same DS (data not shown), samples subjected to prolonged swelling in DMAc/LiCl solution prior to testing revealed significant differences in degradability between homogeneously and heterogeneously hexanoylated cellulose (Fig. 10). Although homogeneously hexanoylated cellulose with a DS of 0.5 produced about 20% glucose with cellulase enzymes, it was nearly 50% for the corresponding heterogeneously hexanoylated pulp. No glucose was formed from homogeneous cellulose hexanoate at a DS of 1.0, but heterogeneously hexanoylated pulp still produced nearly 25% of its weight as glucose following 2 days of incubation with cellulase enzymes. These results clearly indicate the presence of significant amounts of unsubstituted AHG units in heterogeneously hexanoylated pulp fibers, even at a DS of 1.7. These results demonstrate that heterogeneously esterified pulp has biodegradability characteristics that are different from cellulose esters with a uniform distribution of substituents.

Using a “homogeneity index” representing the difference between the mass fraction that is enzymatically converted to glucose and the mass fraction recovered by filtration after biodegradation, differences between the Ts and Ti mediated cellulose ester products were revealed (Fig. 11). If all of the enzymatically degraded portions were converted into glucose, the homogeneity index ( $B - A$ ) should be zero. On the other hand, if some of the degraded portions produced cellulosic oligomers with some hexanoyl groups that do not produce glucose but generate unrecoverable filtrate, the homogeneity index ( $B - A$ ) should be much greater than zero. This result, as well as the result of the water resistance test, suggests that there is a difference in the distribution of hexanoyl groups (that means a difference in homogeneity) between the Ts and Ti reaction products. Figure 12 is a conceptual model for the difference in structure (or uniformity of substituent distribution) between Ts and Ti reaction products. Both systems have an apparent blocky structure that alternates between regions with a high DS ( $X$  and  $X'$ ) and a low DS ( $Y$  and  $Y'$ ). The results obtained with the Ts system are representative of the  $X$  and  $Y$  case whereas the Ti system reflects the  $X'$  and  $Y'$  model. The lower maximum DS of the substituted regions of the Ti system contributes to a higher water pickup (Fig. 8) and the forma-





**Figure 5** SEM photomicrographs of the fracture surfaces of compression-molded sheets from heterogeneously hexanoylated pulp (Ts system) with (A) DS = 1.0 (low magnification), (B) DS = 1.0 (high magnification), (C) DS = 1.7 (low magnification), and (D) DS = 1.7 (high magnification). Note the virtual absence of interfacial adhesive failure for samples with DS = 0.6 and 1.0 and the pronounced adhesive failure for the sample with DS = 1.7.

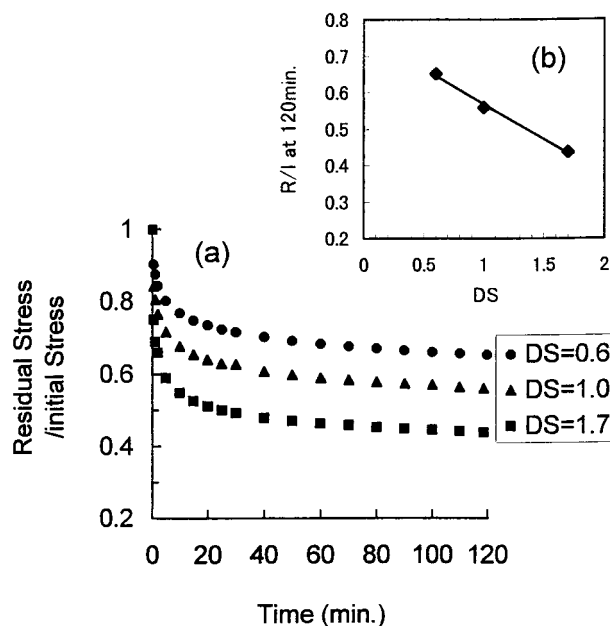
tion of cellulosic oligomer fractions by cellulase hydrolysis. All attempts to characterize the molecular sizes of the undegradable fractions by GPC failed because of insolubility in THF. Neither deacylation/percarbanilation nor peracylation were successful in increasing THF solubility.

#### X-Ray Diffractometry

The X-ray diffraction patterns of compression-molded sheets of hexanoylated pulp fibers revealed the typical crystallographic pattern of cellulose I for all samples [Fig. 13(a)]. (Samples compression molded at room temperature had virtually identical diffraction patterns; data not shown.) The four peaks at  $2\theta = 14.6^\circ$ ,  $16.4^\circ$ ,  $22.8^\circ$ , and  $34.7^\circ$ , which are characteristic of crystalline cellulose I, are most apparent in the sample with a DS of zero. As the DS with hexanoyl groups rises, the intensity of the four cellulose I peaks declines while the intensity of the peaks around  $2\theta = 4.9^\circ$  (sharp) and  $19.5^\circ$  (broad) gradually in-

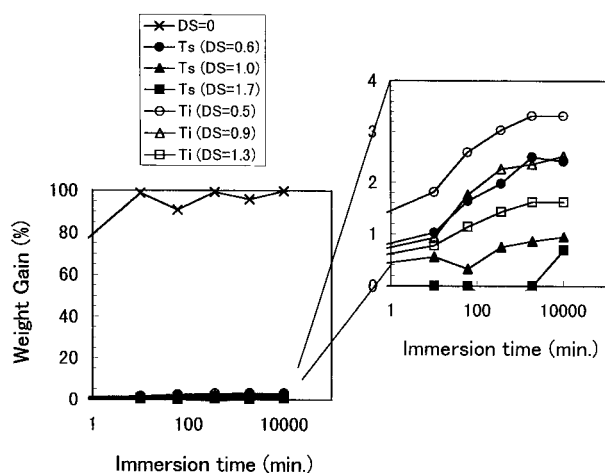
creases. The interplanar spacing for the peak at  $2\theta = 4.9^\circ$  is 1.79 nm, and this is assumed to be the distance between two neighboring cellulose hexanoate chains based on the X-ray study of a series of aliphatic cellulose esters reported previously by Okamura et al.<sup>41</sup> It is therefore concluded that the heterogeneously hexanoylated pulp fibers contained unsubstituted cellulose with a crystalline cellulose I morphology, as well as ordered cellulose hexanoate. This suggests that regions X and Y (and X' and Y') of the molecular scheme of Figure 12 are both (at least partially) ordered (or crystalline) in the consolidated composite. Variations in the X-ray patterns of Figure 13(a) with the DS suggest that the cellulose I regions decline and the cellulose ester component increases as the DS rises.

The crystal size (width) of residual cellulose I in heterogeneously hexanoylated pulp was estimated using Scherrer's equation from the peak at  $22.8^\circ$  [Fig. 13(b)]. The crystal size gradually de-

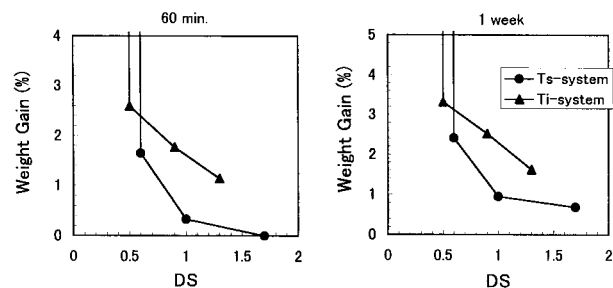


**Figure 6** (a) Stress relaxation curves of compression-molded sheets of heterogeneously hexanoylated pulp fibers (Ts system) with (●) DS = 0.6, (▲) DS = 1.0, and (■) DS = 1.7. (b) The relationship between the ratio of residual stress after 120 min to the initial stress and DS obtained (a).

creased with increasing DS. If heterogeneously hexanoylated pulp has a complete surface–core architecture at a single fiber level (first hypothesis above), the crystal size of the residual cellulose I should not change, at least during the early



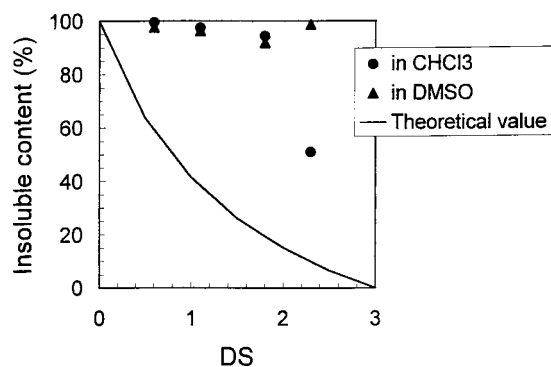
**Figure 7** The swelling behavior (or weight gain) of compression-molded sheets of heterogeneously hexanoylated pulp fibers in relation to water immersion time. The inset is the expanded ordinate.



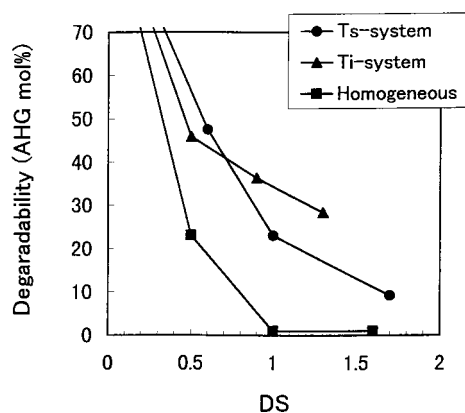
**Figure 8** The difference in the swelling behavior (or weight gain) of compression-molded sheets between Ts and Ti systems in relation to the DS. Note the greater apparent weight gain for the Ti system compared to the corresponding Ts system. This suggests minor differences in the distribution of substituents.

stages of hexanoylation. Therefore, this result again rejects the first hypothesis and supports the third hypothesis. However, the observation that the modified pulp fibers can be consolidated by compression molding suggests the existence of fusible cellulose hexanoate molecules, even if their total DSs are low; this supports the second hypothesis.

It is therefore suggested that hexanoylation starts from the surface of individual microfibrils (second hypothesis) and the disordered regions (third hypothesis) before proceeding to the interior of the microfibrils and the ordered regions, thereby producing well-oriented cellulose hexanoates under nonswelling reaction conditions.



**Figure 9** The solubility of heterogeneously hexanoylated pulp fibers (Ts system) in (●) chloroform and (▲) DMSO in relation to the DS. The theoretical curve is obtained by assuming that the hexanoate groups are distributed between cellulose hexanoate (DS = 3.0) and cellulose (DS = 0); only cellulose hexanoate is solvent soluble.

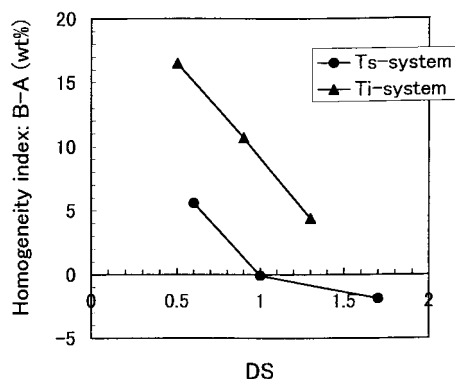


**Figure 10** The cellulolytic biodegradability of heterogeneously (Ts system and Ti system) and homogeneously hexanoylated cellulose after pretreatment (see text) in relation to the DS.

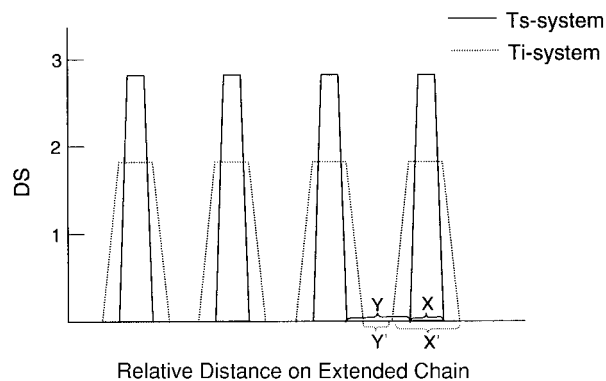
## CONCLUSIONS

The reaction of dissolving-grade wood pulp fibers with a mixed *p*-toluenesulfonic/hexanoic acid anhydride system (Ts system) and a titanium(IV) isopropoxide catalyzed system (Ti system) under nonswelling reaction conditions produces fibers that represent biphasic (blocky) cellulose derivatives.

Transparent or semitransparent composite sheets can be formed in which the thermoplastic cellulose hexanoate phase is consolidated into a continuous matrix reinforced with discontinuous cellulose I domains.



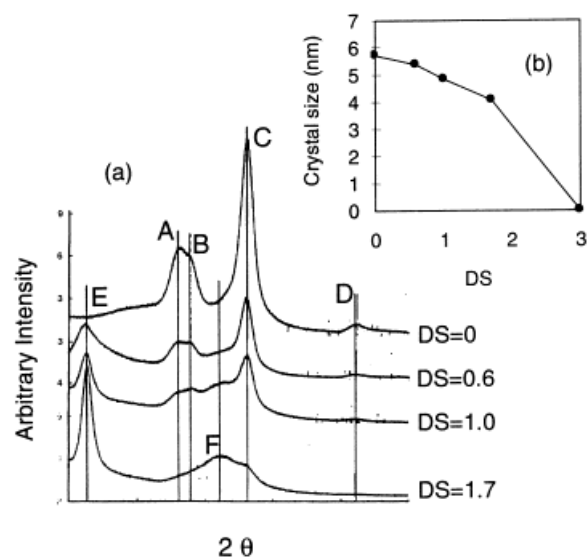
**Figure 11** A comparison of the homogeneity index ( $B - A$ ) representing the substituent distribution on the molecular level between the Ts and Ti systems;  $A =$  recovered sample weight by filtration after biodegradation/initial weight  $\times 100$ ;  $B =$  [(initial weight - glucose yield)/initial weight]  $\times 100$ .



**Figure 12** A schematic illustration of the blocky nature of heterogeneously hexanoylated pulp fibers. A material with the  $X - Y$  type structure would be different than a  $X' - Y'$  type morphology in terms of swelling and glucose generation (with cellulolytic enzymes).

The compression moldable, thermoplastic cellulose ester component varies with the extent of modification; it provides for thermal deformability.

The cellulose I component also varies with the extent of modification, and it provides for biodegradability and reinforcement (i.e., high modulus). The biodegradability of heterogeneously hex-



**Figure 13** (a) X-ray diffractograms of compression-molded partially hexanoylated pulp samples (Ts system) in relation to the DS:  $2\theta = 14.6^\circ$  (peak A),  $16.4^\circ$  (peak B),  $22.8^\circ$  (peak C),  $34.7^\circ$  (peak D),  $4.9^\circ$  (peak E), and  $19.5^\circ$  (peak F). (b) The size (width) of the cellulose I crystalline morphology in the compression-molded sheets in relation to the DS.

anoylated pulp is much different than the corresponding homogeneous cellulose hexanoate.

Although no precise dimensions can be determined for the respective phase domains, the low solubility of the products and the decrease in the crystal size of cellulose I suggest that they are on the nanometer scale.

There are differences in some properties based on the difference in the distribution of substituents between the materials generated by the Ts and the Ti systems.

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