Cellulosic Nanocomposites. II. Studies by Atomic Force Microscopy

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ABSTRACT: Dissolving-grade wood pulp fibers were partially esterified by mixed *p*-toluene sulfonic/hexanoic acid anhydride in a nonswelling suspending agent. A biphasic morphology was revealed by atomic force microscopy (AFM) for the compression-molded, partially modified pulp fibers. The AFM phase images indicated distinct periodicity on the scale of several 10's of nanometers. Surface etching with cellulolytic enzymes of the modified pulp fibers produced height images that had virtually the same periodicity. These results indicate that the modified pulp fibers are nanocomposites comprising unmodified cellulose and cellulose hexanoate. Regenerated lyocell fibers (from N,MMNO solvent) subjected to the same esterification system as applied to pulp fibers, by contrast, exhibited AFM phase images that indicated a high level of surface (skin) versus core reactivity. Modified lyocell fibers with an average diameter of about 12 μm and having an overall DS of 0.6 had surface layers that were approximately 1 μm thick. The latter represented a transitional phase in which the chemical composition and the physical properties were intermediate between a highly substituted surface (skin) and an unsubstituted core. When a compression-molded sheet of the modified lyocell fibers was analyzed by microthermal analysis, the thermoplastic matrix on the lyocell fiber surface was revealed to have an apparent T_g of 75°C corresponding to cellulose hexanoate, whereas no significant thermal transition was determined for the (unmodified) fiber core. These results suggest that both partially modified lyocell fibers and partially modified pulp fibers are capable of producing composites with morphologies that have grossly different scales. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 2254–2261, 2000

Key words: cellulose esters; AFM; thermoplastic composites; pulp; lyocell fibers; microthermal analysis

INTRODUCTION

In an earlier study,[1] it was demonstrated that the chemical modification of dissolving-grade pulp in a solvent that fails to swell cellulose and does not dissolve the resulting cellulose ester produces

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partially modified fibers that consist of two distinctly different morphological regions. Unmodified cellulose I crystalline regions were found to be commingled with cellulose ester regions that are also partially ordered. While the cellulose I-component contributes high modulus, thermal stability, and biodegradability, among others, the cellulose ester component provides for thermoplastic deformability, resistance to swelling in water (dimensional stability), and resistance to biodegradation. Although this commingled polymer mixture was found to retain, at all DS levels,

the original pulp fiber appearance upon visual inspection, the fibers were capable of undergoing consolidation by compression molding, and they formed semitransparent sheets.

Having established the coexistence of two distinctive cellulose chemistries in two morphological phases, the question arises as to phase dimensions. What is the precise size of the included unmodified cellulose region in a composite based on a cellulose ester matrix? Since the attempt to establish dimensional parameters via enzymatic degradation and molecular weight analysis of the undegradable, undissolved portion failed, another approach needed to be found.[1] Whereas dimensional studies of cellulose crystallites have involved a vast number of different X-ray and transmission electron microscopic studies, the present study was to exploit the power of atomic force microscopy (AFM) in combination with various pretreatments as well as complementary analysis techniques.

AFM is a technique which can detect both the variation in height (or topography) of a sample surface (given as a height image) and the variation in composition, adhesion, friction, and viscoelasticity (given as a phase image).[2] Since AFM provides easy access to observations under native and near-native conditions (in contrast to SEM and TEM which are applicable only to biologically inactive, dehydrated samples and generally require extensive sample preparation, such as staining or metal coating[3]), AFM has often been applied to the study of cellulose fibers and crystals,[4–10] cellulose derivatives,[11–17] pulp and paper products,[18–22] and wood[19] under both dry and wet conditions. Gray et al. used AFM to study the local surface variations in pulp, such as the orientation of microfibrils and the aspect of fibrillation by beating[18–20] and such parameters as lamellation for wood.[19] Baker et al. studied the surface topography of Valonia cellulose I microcrystals under propanol and water and obtained images that revealed clear structural details consistent with the 0.54-nm repeat unit (glucose) along the cellulose chains. An intermolecular spacing of about 0.6 nm was also described.[4,5] AFM was also often used to evaluate the phase dimensions of cellulosic blends and composites.[11,12,14,23–26] Although most of these studies employed topographical imaging alone, there are also several studies which involved phase imaging. For example, the distribution of lignin on the surface of a wood pulp fiber could be visualized on the phase image while it did not appear in the height images.[21,22] This is because the properties of lignin and its functions, such as adhesion, friction, and viscoelasticity, are different from those of cellulose and hemicelluloses. These studies suggest that AFM phase imaging can distinguish between the unmodified cellulose regions and the cellulose ester regions in the modified pulp fibers.

It was therefore the objective of the current study to evaluate the phase dimensions of two-phasic thermoplastic composites from compression-molded, partially esterified cellulose pulp fibers by AFM. A parallel attempt involved partially modified lyocell fibers.

EXPERIMENTAL

Materials

The modified (heterogeneously partially hexanoylated) pulp fibers used were those described in the previous article.[1] Lyocell fibers were a commercial product of Acordis (Coventry, UK); they were used as received.

Methods

Modification Reaction

Dissolving-grade wood pulp fibers and lyocell fibers were partially hexanoylated by a mixed p-toluenesulfonic/hexanoic acid anhydride system (Ts system) in the presence of cyclohexane, which is a nonswelling solvent for cellulose and a poor solvent for the resulting cellulose hexanoate. Details of the preparation were given in the previous article.[1]

AFM

Heterogeneously partially hexanoylated cellulose samples (compression-molded sheets or fibers) were embedded in epoxy resin (EPO-FIX by Struers, Westlake, OH). The embedded samples were trimmed with a diamond knife mounted on an ultramicrotome to obtain smooth surfaces suitable for AFM analysis. A Dimension 3000 with a Nanoscope IIIa controller by Digital Instruments was used with TESP tips by Nanosensor in the tapping mode. For enzymatic etching, the embedded and trimmed samples were incubated in 25 mL of acetate buffer (pH 4.9) with 100 μm of cellulase preparation (Cytolase 123 by Genencor Inc.) at 50°C for 7 days. The etched samples were
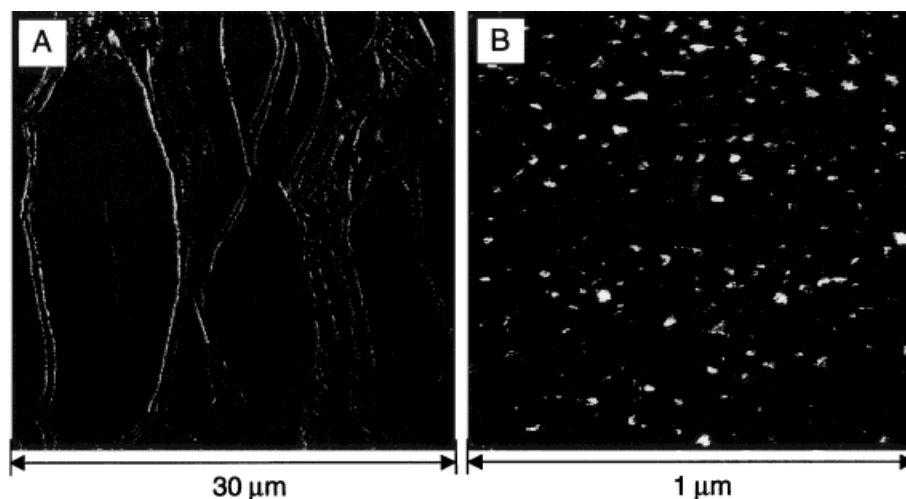
Figure 1 AFM phase images of a compression-molded sheet of heterogeneously hexanoylated pulp fibers with a DS of 0.6: (A) low magnification; (B) high magnification.

washed with deionized water, air-dried in a fume hood, and then subjected to AFM.

Microthermal Analysis (µTA)

Compression-molded sheets of modified lyocell fibers were analyzed with a 2990 Micro-Thermal Analyzer by TA Instruments. Thermal displacement was measured from 25 to 200°C at a heating rate of 100°C/min.

RESULTS AND DISCUSSION

AFM is capable of measuring phase as well as height differences on the surface of materials on the micro- and nanometer scale. When thermoplastically shaped (by compression molding), partially esterified (with hexanoic acid) dissolving-grade pulp fibers in sheet form (semitransparent) were examined by AFM, indications for a heterogeneous morphology were obtained (Figs. 1 and 2). The AFM phase images at low magnification [Figs. 1(A) and 2(A)] provide evidence for the retention of the pulp fiber structure with the approximate dimensions of 10–20 μm in diameter and 5–10 μm in cell wall thickness. The modified pulp fibers had collapsed lumina, and their cell boundaries were largely intact while the fibers were fused to each other via a thermoplastic cellulose hexanoate matrix. There was a consider-
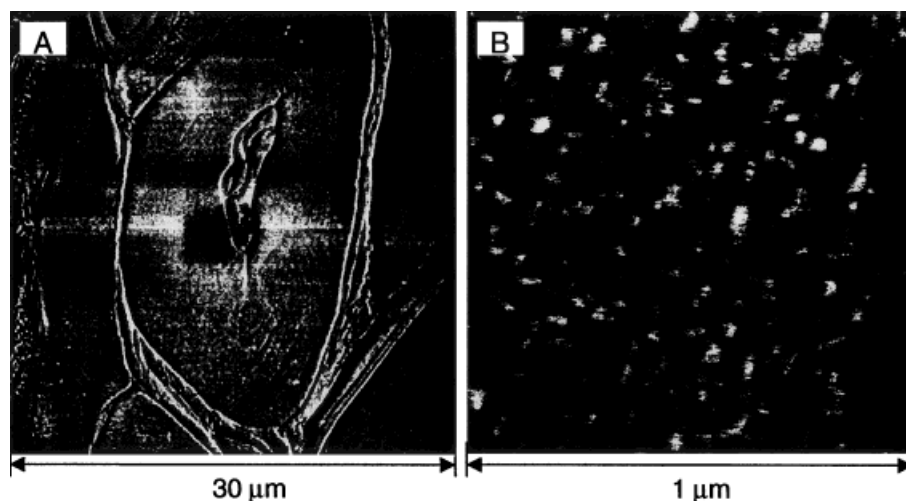
Figure 2 AFM phase images of a compression-molded sheet of heterogeneously hexanoylated pulp fibers with a DS of 1.0: (A) low magnification; (B) high magnification.
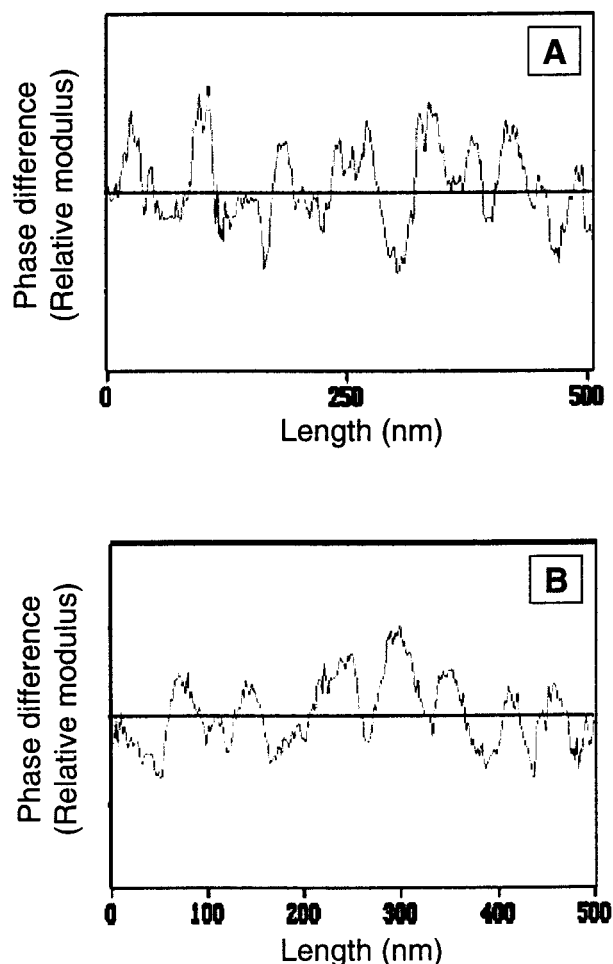
Figure 3 Phase difference versus distance (or length) in Figures 1(B) and 2(B) for samples with different DS: (A) DS = 0.6; (B) DS = 1.0.

able void fraction in the spaces between the fibers and in the lumina before compression molding. There were no signs indicating that the cell wall mass was chemically nonuniform.

The AFM phase images at high magnification revealed a series of dark and light spots for the pictures focusing on the cell wall mass [Figs. 1(B) and 2(B)]. Because AFM phase images can detect variations in composition, adhesion, friction, and viscoelasticity (stiffness, modulus),[2] this result indicates that there exist two phases in the cell wall mass with differences in those properties. Whether a stiffer region is expressed as a lighter or darker spot depends upon the tapping condition, namely, the ratio of the set-point amplitude to the driving oscillation amplitude. When the ratio is in the moderate range, a stiffer region is expressed as a lighter spot.[27] From studying the

partially modified lyocell fibers (shown later), it is suggested that the esterified (softer) region appears darker than does the unmodified cellulose (stiffer) region. It is therefore assumed that the tapping condition applied in this study was in the moderate range and that the light spots in Figures 1(B) and 2(B) correspond to cellulose regions while the dark spots represent regions rich in cellulose hexanoate.

In the previous study,[1] it was concluded that the cellulose regions in the modified pulp fibers were ordered cellulose with cellulose I morphology and the cellulose hexanoate regions are also ordered to some degree. A fairly uniform periodicity was more clearly revealed when relative property differences (e.g., modulus) in the phase image of AFM were shown on a dimensional scale (Fig. 3). Periodic relative property variations were on the scale of 30–40 nm for the modified pulp fibers having a total DS of 0.6, and they were 40–50 nm if the DS rose to 1.0. This can schematically be interpreted with periodic DS variations (giving rise to differences in such properties as modulus) versus the dimensions of a microfibril (Fig. 4). The microfibril (or, simply called, the fibril) is the smallest fibrous unit constituting a pulp fiber and has a diameter of 10–50 nm. The periodic change from a light to dark phase represents the change, for example, from a high- to a low-modulus phase as well as from low- to high-DS material. The volume fraction of the dark-phase material obviously increases with overall DS.

Recognizing that the (microtomed) surface of compression-molded sheets of the modified pulp fibers consist of a mixture of cellulose and cellulose hexanoate, a cellulolytic "etching" method
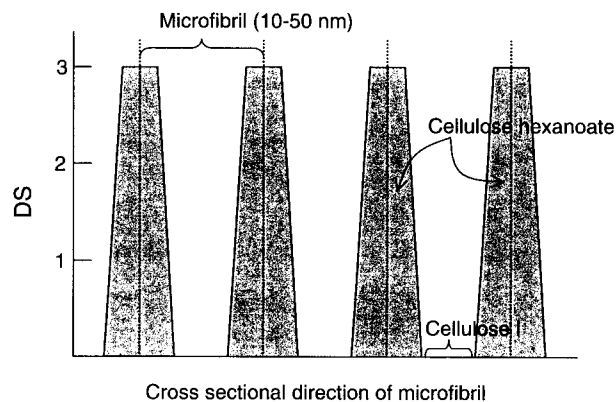
Figure 4 Schematic illustration of the core of a heterogeneously hexanoylated pulp fiber.
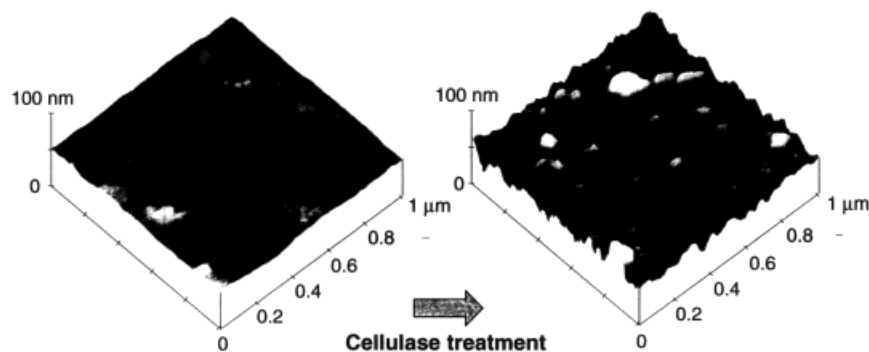
Figure 5 AFM height images of compression-molded sheets of heterogeneously hexanoylated pulp fibers with a DS of 1.0 (left) before and (right) after treatment with a mixture of isolated cellulase enzymes.

was adopted to highlight any differences in chemical composition at the surface (Fig. 5). The relatively featureless surface (by AFM height image, Fig. 5, left) of the untreated compression-molded sheet became distinctly featured following a surface treatment with a cellulase preparation (Fig. 5, right). Periodic peaks and valleys became apparent on the etched sheet surface that presumably represent highly substituted cellulose hexanoate portions (i.e., peaks) and unmodified cellulose regions (i.e., valleys). The valleys were supposed to be created by enzymatic degradation at the cellulose regions. This provides further support for the heterogeneous, two-phase nature of the composites on the scale of several 10's of nanometers.

Dissolving-grade pulp may be subject to dissolution in either the viscose rayon process or the novel lyocell technique.[28,29] Lyocell fibers represent regenerated cellulose following dissolution in N,MMNO and regeneration from a nonsolvent. Lyocell fibers are produced with a draw ratio that is responsible for the fibers' high order. Lyocell fibers were subjected to the same partial, heterogeneous hexanoylation in a nonswelling solvent as applied to dissolving-grade pulp fibers. The lyocell fibers failed to undergo significant change in shape following visual inspection, just as pulp fibers failed to change following the reaction. By embedding the original lyocell fibers and the partially modified lyocell fibers in an epoxy resin and preparing cross sections for examination, AFM revealed a distinctive surface-to-core reaction difference (Fig. 6). The approximately 12-μm-thick unmodified lyocell fibers produced a featureless AFM phase image [Fig. 6(A)]. On the other hand,
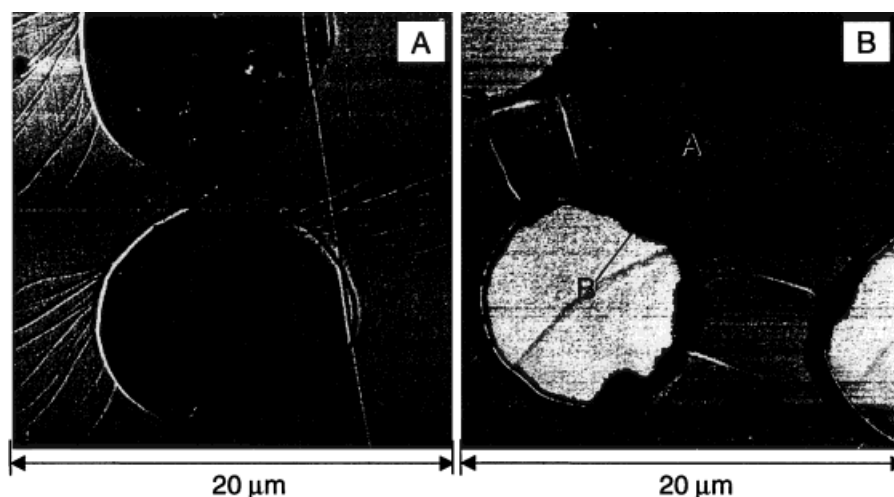
Figure 6 (A) AFM phase image of cross section of unmodified lyocell fibers and (B) phase image of heterogeneously hexanoylated lyocell fibers with a DS of 0.6.
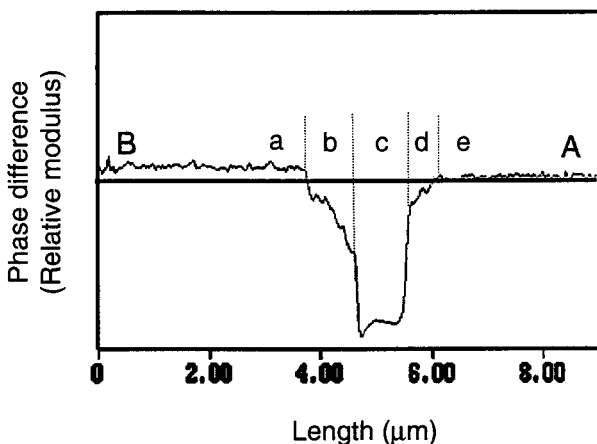
Figure 7 Image analysis of phase differences between point A and point B of Figure 6(B): (a) cellulose; (b) cellulose hexanoate (CH) with low DS; (c) CH with high DS; (d) mixture of CH and epoxy resin; (e) epoxy resin.

the partially modified lyocell fibers provided a highly distinctive phase image, which suggests significant core versus surface differences [Fig. 6(B)].

An examination of the phase changes that occur on the A → B trajectory of Figure 6(B) representing the transition from the epoxy resin matrix to the fiber core reveals distinctions which are reflective of differences in the degree of modification (Fig. 7). The changes along the A → B axis suggest a cross-sectional surface region (c) with a relatively low modulus extending to a distance of about 1 μm, with a gradual rise on both sides (b and d) of the surface to regions with a relatively high modulus that extends over a distance of several micrometers. The high-modulus regions can be assigned to the cellulose fiber core (a) and the epoxy matrix (e), respectively. The gradual transition from fiber core (a) to surface (b) can be interpreted as a gradual increase in the DS-level of the cellulose mass from inside to outside, and the gradual transition in the modulus from the fiber surface (d) to the epoxy resin (e) must be explained with partial miscibility of the (highly substituted) cellulose hexanoate mass on the surface of the fiber with epoxy resin prior to cure.

In comparing the transparency of compression-molded, partially thermoplastic, partially hexanoylated pulp fibers with those of the corresponding lyocell fibers, differences in clarity are observed (Fig. 8). Whereas a sheet from a partially hexanoylated pulp sample with an overall DS of 1.0 (A) is almost uniformly semi-transpar-

ent, a corresponding lyocell sheet with an overall DS of 0.6 (B) reveals a much greater degree of heterogeneity. Whereas clear zones can be visually discerned in the lyocell sample (B), there is ample evidence for the presence of nontransparent (fibrous) inclusions. By μTA, which is a combination of AFM with thermomechanical analysis (TMA) and FTIR, compositional differences can be detected that relate to thermal deformation (μTA) as well as to chemical composition (FTIR). The μTA picture of Figure 9(A) (thermal conductivity image) represents a fiber-reinforced thermoplastic composite in which fibers having a dimension of 10–15 μm are embedded in a featureless matrix. By probing the material located at point #2 representing the matrix, point #3 representing the fiber, and point #1 representing the transitional mass between matrix and fiber, three different thermograms are produced. These are represented in Figure 9(B). The materials located in positions #1 and #2 showed apparent thermal transitions at about 75°C, and this corresponds to a glass transition temperature (T_g) (or the melting point which is a little higher than T_g) of cellulose hexanoate with a high DS.[30] On the other hand, the material located in position #3 did not show a clear transition between 25 and 200°C, and this behavior mimics that of unmodified cellulose. Furthermore, FTIR spectroscopy of the
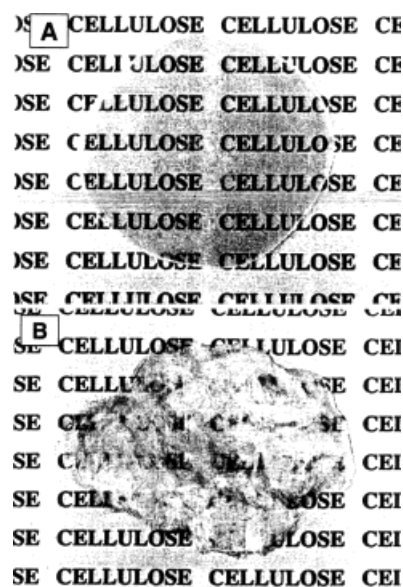
Figure 8 Optical photographs of compression-molded sheets prepared from (A) heterogeneously hexanoylated pulp fibers with DS = 1.0 and (B) lyocell fibers with DS = 0.6.
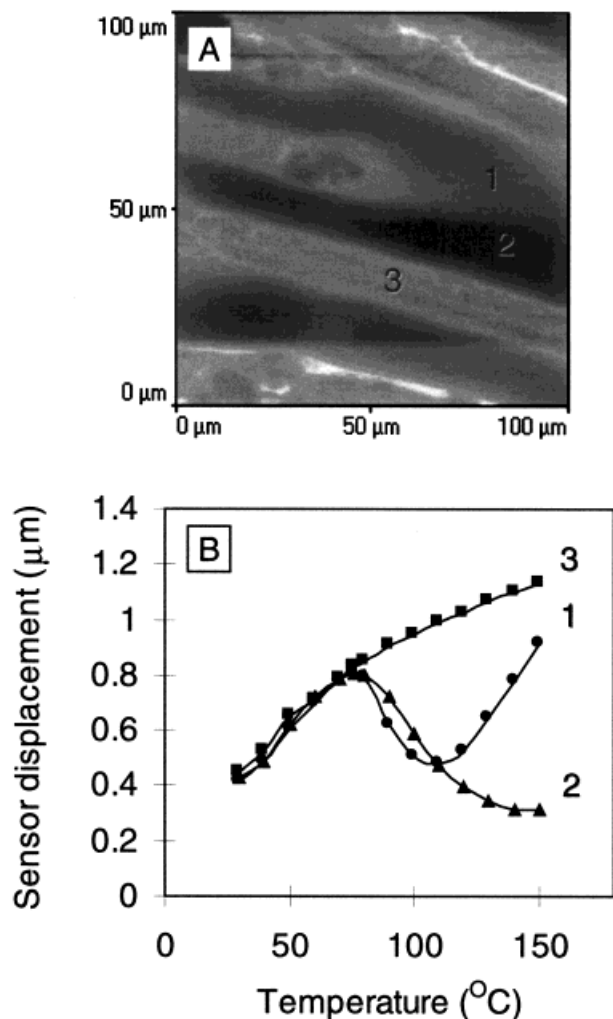
Figure 9 (A) AFM thermal conductivity image of compression-molded sheet of heterogeneously hexanoylated lyocell fibers. (B) μTMA thermogram for points 1–3 in (A).

mass located in position #2 indicated cellulose hexanoate with a DS of 2.1. From these results, it was concluded that a compression-molded sheet of partially modified lyocell fibers with an overall DS of 0.6 is composed of unesterified cellulose fiber and a cellulose hexanoate matrix with a high DS (e.g., DS = 2.1).

By considering all results, including the results of the previous article,[1] we can propose a schematic model for the progress of esterification in a nonswelling solvent (Fig. 10). The first image represents either a microfibril with a diameter of 10–50 nm in a pulp fiber or a lyocell fiber with a diameter of 10–15 μm. Esterification starts from the more accessible regions, namely, the surface and the amorphous components of the microfibril

or the lyocell fiber (second image, where gray areas represent esterified regions). Then, the esterification advances toward the inside of the microfibril or the lyocell fiber (third image). The esterified regions are retained on the surfaces of the microfibrils and lyocell fibers because the esterification was performed in a poor solvent for the cellulose ester produced. Because the esterified regions are thermoplastic, heterogeneously esterified microfibrils or lyocell fibers can adhere to each other by the formation of a continuous matrix following compression molding with heat. As a result, nanocomposites can be obtained from pulp fibers and microcomposites can be generated from lyocell fibers.

CONCLUSIONS

The evidence supports the generation of a two-phase composite structure from compression-molded, partially hexanoylated cellulose in which a high modulus, highly ordered cellulose phase is embedded in a thermoplastic matrix of cellulose hexanoate. The partial hexanoylation is achieved by the heterogeneous reaction of pulp or lyocell fibers in a nonswelling solvent.

Distinctive phase dimensions on the level of several 10's of nanometers are discerned in compression-molded, heterogeneously hexanoylated pulp fibers (nanocomposites). These dimensions are on the 10-μm scale for the corresponding heterogeneously hexanolyated lyocell fibers (microcomposites).
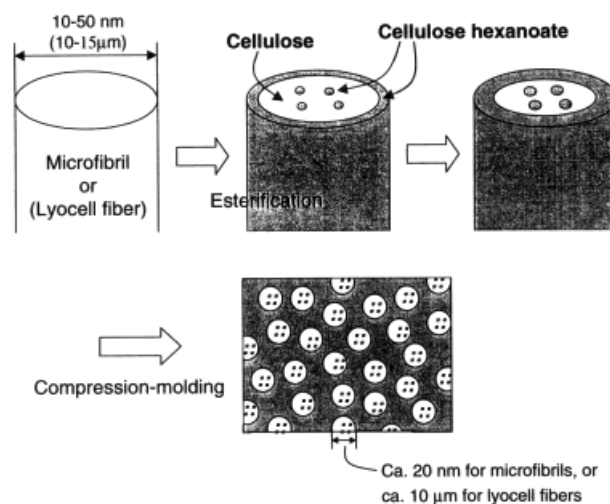
Figure 10 Schematic illustration of the process of heterogeneous hexanoylation of pulp fibers and lyocell fibers.

Whereas there are no indications for a surface-to-core heterogeneity in modified pulp fibers with an average diameter of 15 μm, there are clear indications in support of a highly distinctive surface structure in the case of modified lyocell fibers having an average diameter of 12 μm. It is proposed that the esterification starts from the surface of each microfibril with a diameter of 10's of nanometers for pulp fibers and the surface of each fiber filament for lyocell fibers and then proceeds to the interior.

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