Surface Acylation of Cellulose Whiskers by Drying Aqueous Emulsion

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A simple chemical modification route to confer high hydrophobicity to crystalline cellulose surface was demonstrated using tunicin whiskers as model material. An alkyenyl succinic anhydride (ASA) aqueous emulsion was mixed with cellulose suspension, freeze-dried, and heated to 105 °C. The bulk degree of substitution (DS) was evaluated by FT-IR spectrometry, elemental analysis, and weight gain. The surface DS was quantified by X-ray photoelectron spectroscopy. The surface-acylated whiskers retained their morphological and crystalline integrity, but due to their surface acylation, they are readily dispersible in solvents of low polarity such as 1,4-dioxane. These whiskers can also be well dispersed in polystyrene to form a nanocomposite.

Introduction

Research and development of polymer nanocomposites has been intensely pursued in the past decade for their potential usefulness based on an advantageous combination of properties.[1] Since the first report of using cellulose whiskers obtained by acid hydrolysis as the reinforcement in polymer matrix,[2] cellulose whiskers have been extensively used as model fillers in several kinds of polymeric matrices to discuss the possibility of their application in nanocomposites.[3−9]

One of the drawbacks of cellulose whiskers with polar surfaces is poor dispersibility/compatibility with nonpolar solvents or resins. Reducing its surface energy and improving the degree of dispersion in the matrix are a difficult task for cellulose nanocrystals. Thus, their incorporation as reinforcing materials for nanocomposites has so far been largely limited to aqueous or polar systems. To overcome this problem and broaden the type of possible polymer matrices, efforts of surface modification have been made in the past few years.[10−12] These attempts include surfactant coating,[10]graft copolymerization,[11] and silane treatment.[12] Among these methods, surfactant coating was the simplest method. However, this method was developed for improving dispersibility of whiskers in organic solvents and is not expected to be effective in composite applications because of the lack of covalent bonding between the whiskers' surface hydroxyls and surfactant's alkyl groups. On the other hand, the long-chain-alkyl acylation of the cellulose surface might be effective in enhancing dispersibility and adhesion with synthetic matrixes.

There are two reports employing alkenyl succinic anhydride (ASA) for acylating polysaccharide nanocrystals.[13,14] Both these works used organic solvents to avoid hydrolysis of the ASA. Gopalan Nair and Dufresne[13] achieved acylation of chitin whiskers in a dioxane system with 4-(dimethylamino)pyridine as the catalyst. The reaction was carried out for 1 week at 70 °C. A toluene suspension of the modified whiskers showed colloidal behavior when observed between crossed polars, indicating their good dispersibility. Angellier et al.[14] used the toluene/(dimethylamino)pyridine system to modify maize starch nanocrystals. The low polarity of the modified nanocrystal surface was demonstrated by their migration to the methylene chloride phase from the aqueous phase. However, no attempts have been reported about ASA modification of cellulose whiskers.

Meanwhile, ASA is widely used as a sizing agent in papermaking, where ASA is applied to pulp fibers in aqueous systems. In the present work, we attempted the use of a aqueous system in ASA application to cellulose whiskers, followed by complete drying and heating to effect acylation of hydroxyl groups of cellulose. The degree of esterification was evaluated by FT-IR spectrometry, elemental analysis, weight gain, and X-ray photoelectron spectroscopy (XPS). The hydrophobic nature of modified celulose whiskers was demonstrated by their dispersibility in organic solvents and compatibility with polystyrene.

Experimental Section

Reagents and Materials. ASA reagents used were *iso*-octadecenyl succnic anhydride (*iso*-ODSA) and *n*-tetradecenyl succinic anhydride (*n*-TDSA), obtained from Tokyo Kasei Kogyo Co. The former consisted of a mixture of oligomers with different sizes, centering on C-18 (M_n = 350 g/mol); the latter had a purity of 85%. They have the general structures shown in Figure 1. Polystyrene with the degree of polymerization (DP) of 2000 for dispersion test and other reagents were purchased from Wako Pure Chemical Industries and used without further purification.

Cellulose whiskers were prepared from the mantle of sea animal *Halocynthia roretzi* as described earlier.[3] Briefly, the mantle material was treated by 5% (w/w) NaOH and a mixture of 0.3% (w/w) $NaClO_2$ in 0.1 M acetate buffer (pH = 4.5) with a ratio of 50:50 (v/v) successively. Then the material was cut into pieces and disintegrated by a double-cylinder type homogenizer (Physcotron, Microtec Nichion,

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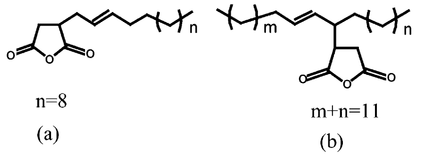

n=8

(a)

m+n=11

(b)

Figure 1. Structure formula of alkenyl succinic anhydrides used in experiment. (a) *n*-TDSA. (b) *iso*-ODSA.

Co., Tokyo) and treated with 50% H_2SO_4 at 70 °C for 8 h under strong stirring. A nonflocculating, flow-birefringent aqueous suspension of tunicate cellulose whiskers were obtained by thorough washing by centrifugation and dialysis.

Surface Acylation. 18.5∼185 mg *iso*-ODSA or 15.5∼155 mg n-TDSA was dispersed in 3.6 mL of distilled water by homogenizer to obtain white emulsions. Since these emulsions were essentially unstable in both the dispersion state and the chemical nature, they were prepared immediately before use every time. This emulsion was added to 1.0 mL of 1.5% (w/w) cellulose whisker suspension and mixed for 5 min and then filtered by a 0.45 μm membrane filter by suction. The quantity of ASA added was 2∼20 times molars to the surface hydroxyls of cellulose whiskers. (The proportion of surface hydroxyls was calculated according to Terech et al., who gave the typical crystallite size of tunicin microcrystals of 18.2 nm × 8.8 nm.[15]) The whiskers were then collected as a filter cake, freeze-dried, and then heated to 105 °C for 5, 15, 30, 60, 120, and 240 min, respectively. The dry sheet was dispersed in acetone by sonication, and the unreacted ASA and its hydrolyzed product, ASAcid, were completely removed by filtering the acetone dispersion solution repeatedly. Purified whiskers were collected by a membrane filter. The dried sheets were characterized by elemental analysis, X-ray diffraction, FT-IR, XPS analyses, and dispersion tests.

Fourier Transform Infrared Spectroscopy (FT-IR). A Fourier transform infrared spectrophotometer (JASCO FT-IR 615) was used to analyze the thin film specimens. The spectra were recorded in transmission mode in the range of 400−4000 cm^{-1}, with accumulation of 64 scans and a resolution of 4 cm^{-1}.

X-ray Photoelectron Spectrometry (XPS). X-ray photoelectron spectra of unmodified and modified cellulose microcrystals were recorded by using a Rigaku XPS-7000 spectrometer with an unmonochromated magnesium Kα source (1253.6 eV) operating at 25 mA and 10 kV under a pressure of 2×10^{-6} Pa. The takeoff angle was fixed at 45°. The binding energy scale was shifted to place the main hydrocarbon C_{1S} feature at 284.6 kV and the main oxygen O_{1S} feature at 532 kV. The sensitivity factors of each component S_i ($S_c = 1.046$, $S_o = 1.027$) were determined using the following equation (eq 1) cited from the handbook of the XPS-7000

$$S_i(E_i) = S_0 \exp(aE_i + bE_i^2 + cE_i^3) \tag{1}$$

where E_i is the kinetic energy of the component ($E_c = 969$ kV, $E_o = 721.6$ kV), $S_0 = 0.888$, $a = 3.40\times10^{-4}$, $b = -2.33\times10^{-7}$, and $c = 5.85\times10^{-11}$. The atomic ratio of oxygen to carbon (O/C) was calculated from their peak areas as the eq 2[16]

$$O/C = (I_o/I_c)(S_c/S_o) \tag{2}$$

where I_o and I_c are the areas of the peaks for oxygen and carbon and S_c and S_o are the sensitivity factors of carbon and oxygen.

Determination of the Degree of Substitution (DS). The bulk DS was evaluated by weight gain, elemental analysis results (Mitsui Chemical Analysis & Consulting Service), and FT-IR calibration method. The surface DS was estimated by using a XPS calibration method.

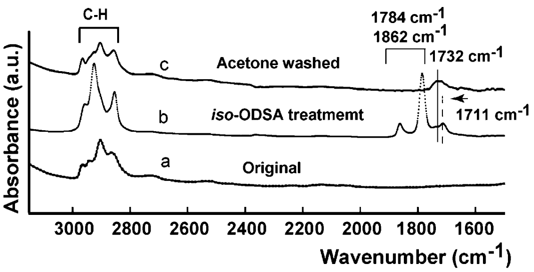

Figure 2. IR spectra of cellulose whiskers treated with *iso*-ODSA.

FT-IR and XPS Calibration Method. Cellulose alkenyl succinic esters having various DS were prepared using the homogeneous esterification method.[17] Briefly, 4 g of fibrous cellulose powder (Whatman CF11) was activated for 12 h in distilled water at room temperature. Subsequently, the cellulose was dehydrated in methanol and *N*, *N*-dimethyl acetamide (DMAc) for 12 h each and then vacuum-dried. In parallel, a solution of 8 g of LiCl in 100 mL of DMAc was prepared. The dried cellulose powder was then dissolved in the LiCl/DMAc solution, and a particle free, transparent cellulose solution with 4% (w/w) concentration was obtained after stirring the mixture for 24 h at room temperature. The desired amount of ASA was added to 20 g of the cellulose−LiCl/DMAc solution under continuous stirring at room temperature, followed by addition of 0.5 mL of 1-methylimidazole as a catalyst. This mixture was heated to 50 °C in an oil bath and stirred for 12 h. The reaction was stopped by pouring the reaction mixture into distilled water, and the precipitate was washed with acetone and then vacuum-dried at room temperature for 4 h. White, *N*, *N*-dimethyl sulfoxide (DMSO) soluble materials were obtained. By varying the addition amount of ASA from 0.3 to 0.8 mole ratio to one anhydroglucose unit, the DS of acylated cellulose were 0.19−0.50. Thin films for FT-IR and XPS analysis were cast from DMSO solutions and vacuum-dried at 60 °C overnight. Calibration graphs of DS vs the area ratio of C═O peak (1732 cm^{-1}) to OH peak (3400 cm^{-1}) in FT-IR spectra and DS vs the value of O/C in XPS analysis were then obtained.

Transmission Electron Microscopy (TEM). Drops of whisker suspension in water, in 1,4-dioxane, or in 2% polystyrene/toluene solution were mounted onto carbon coated grids and then allowed to dry. The whisker specimens in water or in 1,4-dioxane were negatively stained with aqueous uranyl acetate (2.0%). Observations were carried out with a JEOL 2000EX at an acceleration voltage of 120 kV.

X-ray Diffraction. X-ray diffraction diagrams of the original and modified whiskers were obtained with a rotating anode X-ray generator, RotaFlex RU-200BH (Rigaku), using nickel-filtered Cu K_α radiation ($\lambda = 0.15418$ nm) operated at 100 mA and 50 kV. The diffraction diagrams were recorded on imaging plates (FUJIX BAS300UR, Fuji Film) and were read with a RAXIS DS3 (Rigaku).

Results and Discussion

Surface Acylation. Acylation could be detected by the appearance of a carbonyl stretching band at 1732 cm^{-1} from esters in FT-IR spectra (Figure 2c). The carbonyl stretching of unreacted anhydride and the acid groups formed during hydrolysis appeared at 1784 cm^{-1}/1862 cm^{-1} and 1711 cm^{-1}, respectively (Figure 2b). These bands disappeared after the sample was washed by acetone, indicating that they arose from unreacted ASA and ASAcid molecules.

Unlike usual chemical modification of cellulose, the DS was nearly independent of the reagent−cellulose ratio; that is, nearly the same DSs were obtained when using 2∼20 times ASA addition to the surface hydroxyls of cellulose. The lowest level of ASA addition, i.e., two times moles to the surface hydroxyls corresponds, to 1.2 g of *iso*-ODSA or 1.0 g of *n*-TDSA for 1.0 g of dry cellulose. With ASA levels lower than this, obtained whiskers could not be dispersed in acetone though the esterification occurred to some degree. These results suggest that ASA acts not only as an acylation reagent for hydroxyls but also as

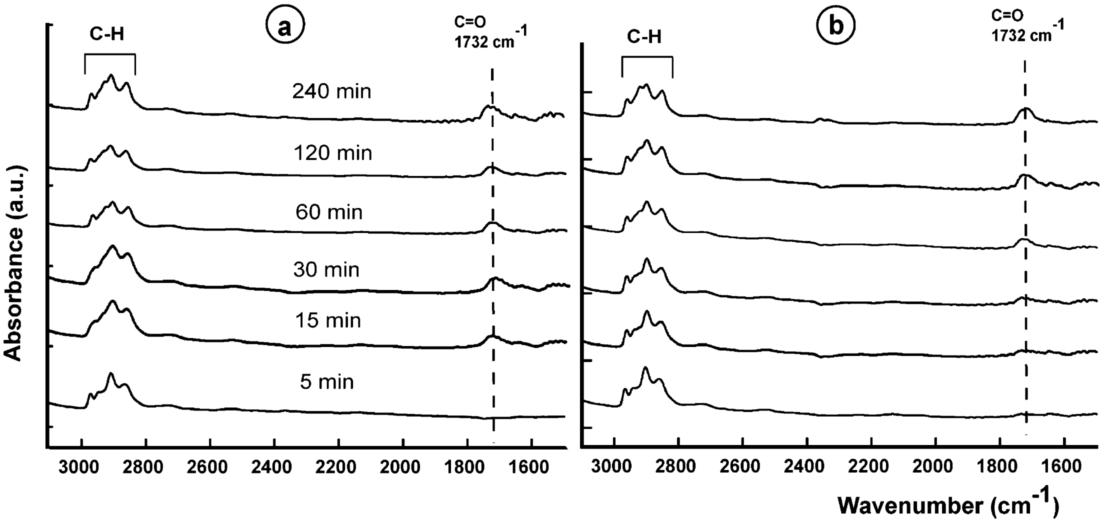

Figure 3. Effect of heating time (105 °C) on acylation. (a) *n*-TDSA modified whiskers. (b) *iso*-ODSA modified whiskers.

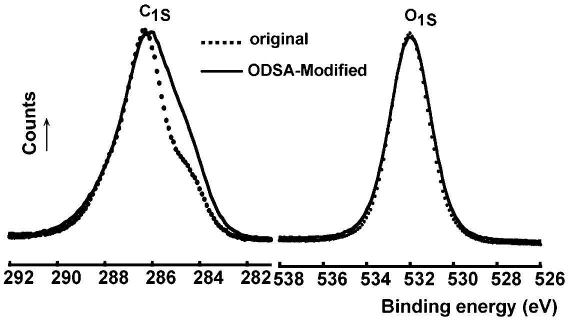

Figure 4. XPS spectra for C_{1S} and O_{1S} of original and *iso*-ODSA modified cellulose whiskers.

a spacer between whiskers, preventing hydrogen bond formation during drying and heating processes. In practice, ASA addition at above 2 times moles to the surface hydroxyls was infallible to obtain hydrophobic and dispersible whiskers in low-polar organic solvents. The samples described below were prepared by ASA/surface hydroxyl ratio of 5:1. One problem here is the whiskers' tendency to aggregate to form bundles, as seen in TEM micrographs (Figure 7); therefore, the number of surface hydroxyl groups based on the cross section reported by Terech et al.[15] is an overestimation for our sample, and the actual ASA-surface hydroxyl ratio was probably higher than the values described above.

Figure 3 shows a series of FT-IR spectra monitoring the influence of heating time on acylation reaction. For either ASA reagent, the heating time of 5 min seems too short to form esters. However, acylation proceeded rapidly afterward. In the case of using *n*-TDSA as the acylation reagent (Figure 3a), a significant absorbance peak at 1732 cm^{-1} ascribed to ester groups appeared when heated the dry sample for 15 min. The reaction then slowed and reached a plateau after 60 min. This sample showed the weight gain of 3.2%, corresponding to the DS of 0.0176. On the other hand, when using *iso*-ODSA as acylation reagent, 15-min heating gave a trace of C═O band. The band intensity increased with heating time and reached a maximum after 2 h (Figure 3b). This sample gave a weight gain of 3.5%, corresponding to the DS of 0.0162. For the two same samples, elemental analysis gave DS values of 0.0165 and 0.0158, respectively. By FT-IR calibration method, the values were 0.024 and 0.022, respectively. These results indicate that weight gain owing to modification is small, showing its advantage in application in nanocomposite.

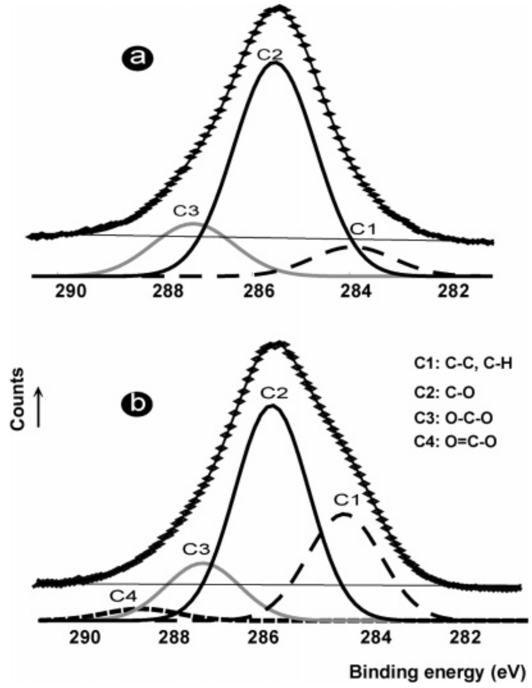

Figure 5. XPS intensity vs binding energy from deconvolved C_{1S} spectra of original (a) and *iso*-ODSA modified whiskers (b).

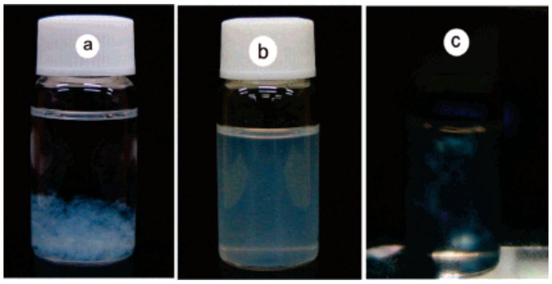

Figure 6. Dispersibility of cellulose whiskers in 1,4-dioxane. (a) Original whiskers. (b) *iso*-ODSA modified whiskers. (c) Suspension (b) viewed through crossed polars.

Figure 4 shows XPS spectra of carbon (1s) and oxygen (1s) for the sheet from the original and the *iso*-ODSA modified whiskers with a maximum DS. The carbon (1s) peak showed an increased shoulder on the right side (low binding energy) of the main peak for the modified whiskers, while the oxygen (1s)

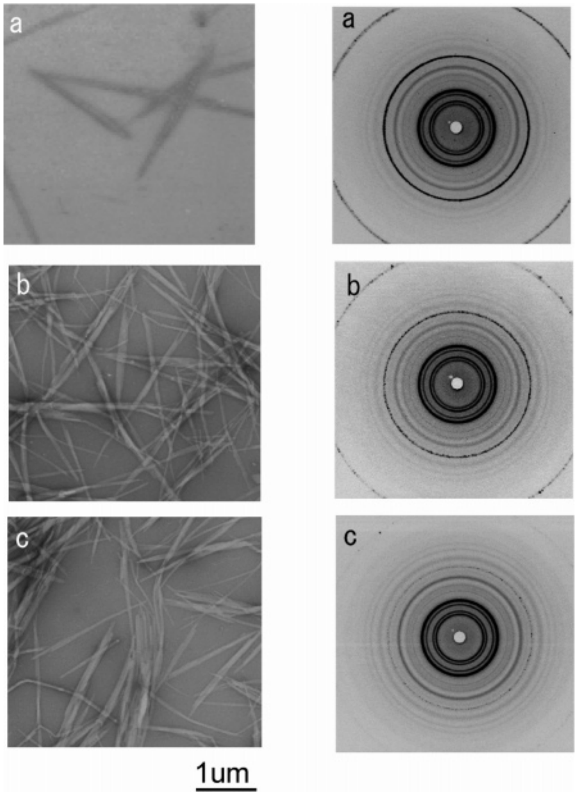

Figure 7. Electron micrographs and X-ray diffraction diagrams of original and ASA-modified whiskers. (a) Original whiskers dried from water. (b) *n*-TDSA-modified whiskers dried from 1,4-dioxane, DS $\sim$ 0.02. (c) *iso*-ODSA modified whiskers dried from 1,4-dioxane, DS $\sim$ 0.02.

peak nearly kept its shape and area. Therefore, the ratio of O/C decreased with 12.5% after modification, corresponding to the surface DS of 0.097. Results of curve-fitting for the C_{1S} region by using a Gaussian function are shown in Figure 5. For the modified samples, a low peak ascribed to esters (C4) could be separated, and the peak at 284.5 eV characteristic for C−C and C−H increased dramatically due to the introduced alkyl groups from *iso*-ODSA. Since the XPS analysis deepness is ca. 7 nm when the takeoff angle is 45°,[18] this value (against 0.0158 by elemental analysis) indicates the strong localization of ester groups on the surface of the nanocrystals.

Dispersion and Morphology Characteristics. Acylated whiskers obtained by varying the heating time show different dispersibilities. In the case of *n*-TDSA modification, both the whiskers obtained by 15 and 30 min heating time can be dispersed in a series of solvents ranging from DMSO ($\epsilon = 46.45$) to ethanol ($\epsilon = 24.55$). (The DS was around 0.01−0.015 by FT-IR calibration method). The whisker samples treated with *n*-TDSA by heating to 45 min could be dispersed in moderately polar solvents, i.e., DMSO to THF ($\epsilon = 7.58$). On the other hand, the *iso*-ODSA-treated whiskers heated for 15 min could not disperse in any solvent except for DMSO, but those heated in 30 or 45 min could be dispersed in DMAc ($\epsilon = 37.78$). Either for *n*-TDSA or *iso*-ODSA, heating over 1 h gave good dispersion in a wide range of solvents including 1,4-dioxane ($\epsilon = 2.209$). The high dispersibility is visually demonstrated in Figure 5, where the *iso*-ODSA acylated whiskers (120 min heating) shows flow birefringence in 1,4-dioxane. Table 1 summarizes the dispersibility of *iso*-ODSA treated whiskers in various solvents.

The TEM images of the acylated whiskers are presented in Figure 7, where panel a shows the original whiskers dried from water, and panles b and c show the acylated whiskers dried from 1,4-dioxane. The morphology of individual whiskers did not change after ASA modification, and there was no further aggregation. The X-ray diffraction pattern was identical for the original and the ASA-modified whiskers, indicating the modification did not alter the cellulose I crystallinity. In addition, TEM micrographs of whisker/polystyrene nanocomposites prepared via toluene suspension/solution casting (Figure 8) show the whiskers' good dispersion in polystyrene. In contrast, the original whiskers aggregated in the casting mixture and such observation was not possible.

Table 1. Dispersibility of Original and *iso*-ODSA Modified Cellulose Whiskers (DS $\sim$ 0.02) in Various Solvents

		dispersion	
solvent	relative permittivity (25 °C)	original	*iso*-ODSA modified
water	78.54	*a*	*c*
formic acid	58.5 (16 °C)	*a*	*c*
dimethyl sulfoxide	46.45	*a*	*b*
N,*N*-dimethylacetamide	37.78	*a*	*a*
methanol	32.66	*b*	*a*
ethanol	24.55	*c*	*a*
acetone	20.56	*c*	*a*
1-butanol	17.51	*d*	*a*
dichloroethane	10.37	*d*	*a*
dichloromathane	8.93	*d*	*a*
tetrahydrofuran	7.58	*d*	*a*
chloroform	4.806 (20 °C)	*d*	*a*
toluene	2.37	*d*	*a*
1,4-dioxane	2.209	*d*	*a*
cyclohexane	2.02	*d*	*b*
hexane	1.8799	*d*	*c*

[a] Good dispersion. [b] Incomplete dispersion. [c] No dispersion. [d] Not tested.

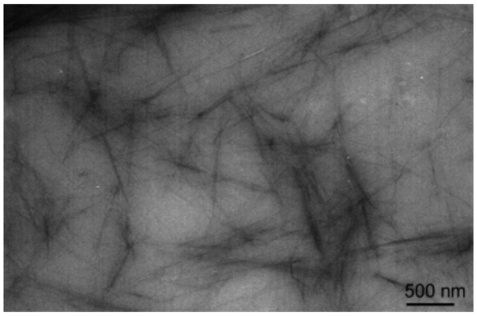

Figure 8. Transmission electron micrograph of ASA-modified cellulose whisker (DS $\approx$ 0.02) embedded in thin polystyrene film.

Conclusion

An environmental friendly chemical modification route to confer high hydrophobicity to crystalline cellulose was developed. With low reagent consumption and simple treatment procedures, highly hydrophobic whiskers can be obtained. The acylated whiskers could disperse in medium- to low-polarity solvents, i.e., DMSO ($\epsilon = 46.45$) to 1,4-dioxane ($\epsilon = 2.209$). By controlling the heating time, whiskers with different dispersibility could be obtained. Based on its organic-solvent dispersibility, the acylated whiskers are expected to be useful in direct mixing with synthetic resins to form nanocomposites with improved dispersion and adhesion with matrices.

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