Interface Adhesion Properties of Syndiotactic Polypropylene/Cellulose Group Composite: Relationship Between Chemical Structure of Coupling Agent and Reactivity for Cellulose Group

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ABSTRACT: Reinforcement of interfacial adhesion between syndiotactic polypropylene (SPP) and fibrous pure cellulose (FC) was performed by the FC silanizations with 3-aminopropyltrimethoxysilane (APTMS), with hexyltrimethoxysilane (HTMS) and by an addition of a SPP grafted with dimethyl itaconate (SPP-g-DMI: number-average molecular weight = 3.3×10^4, DMI cont. = 0.11 wt %), respectively. The adhesion and the morphology were improved by them, respectively. However, their behavior was considerably different. The hexyl group in the HTMS converted the FC surface into hydrophobicity, leading to the hindrance of the interhydrogen bonding in the FC. The silanized FC was embrittled with the increase of the degree of the silanization. In the case of the APTMS, the inter hydrogen bonding was kept because of the existence of the amino group. Whereas, the SPP-g-DMI was unable to penetrate into the cellulose because of its higher molecules, and the interhydrogen bonding was not hindered. The keeping the inter hydrogen bonding was important for the reinforcement of the tensile properties such as Young's modulus and tensile strength in the composite. Furthermore, the interfacial adhesion between the SPP and holocellulose (HC) was studied as well as the SPP/FC. Although the tensile properties were slightly improved by the APTMS silanization and by the addition of the SPP-g-DMI, respectively, the reactivity of the HC was much less than that of the FC. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2798–2806, 2011

Key words: additives; composites; poly(propylene) (PP); interfaces

INTRODUCTION

Cellulose has been one of the most popular polymeric materials in the world and has been used as raw materials of building materials and paper for a long time ago. Cellulose is low cost, high modulus, renewable, and biodegradable material. Recently cellulose has attracted much attention as composite material[1–10] since it has great potential for the preparation of composite materials having high modulus and renewability. As most popular composite based on cellulose, the composite with polyolefin such as isotactic polypropylene (IPP) has been extensively prepared. However, FC is hydrophilic and tends to aggregate, causing poor processability and inherent incompatibility with hydrophobic polyolefin. The improvements of these properties have been studied on the modifications of FC surface. Silane coupling agent is one of the adhesion promoter and is often employed in the FC composite.[11] Adequate silanization brings about a higher FC dispersion in the polyolefin matrix and an interface having a good adhesion strength. In our previous work,[12] the silanized FC with APTMS showed a good adhesion strength to syndiotactic PP (SPP) matrix. The APTMS silanization brought about an excellent improvement of SPP/FC tensile properties such as the Young's modulus, and the improvement degree increased with the increase of the APTMS content in the silanization.

The APTMS has two kinds of bifunctional group. As shown in Figure 1, one is methoxyl group and the other is amino one. The amino group has an ability to catalyze the reaction between silane molecules and silanol groups to form siloxane bond.[13,14] Therefore, aminoalkoxysilane is easily polymerized.[14] In addition, amino group has an ability to form hydrogen bonding with ROH[15] or SiOH[14] groups. These amino

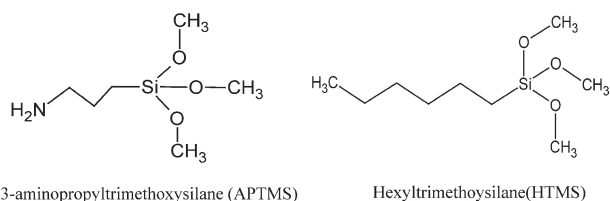3-aminopropyltrimethoxysilane (APTMS)   Hexyltrimethoysilane(HTMS)

Figure 1 Chemical structures of APTMS and HTMS.

group functionalities are believed to contribute to the excellent improvement of SPP/FC tensile properties.

The purpose of the present work is to clarify the effects of the APTMS silane coupling agent on the FC modification. The APTMS silanization certainly affects physical properties of the FC itself, leading to the improvement of the SPP/FC composite. To clarify the APTMS role, the FC silanization with hexyltrimethoxysilane (HTMS) having nonpolar hexyl group has been performed, and the morphology and the tensile properties of the SPP/silanized FC with the HTMS have been studied as compared with those of the SPP/silanized FC with the APTMS. The ATMS permeates the FC and would affect the hydrogen bonding among celluloses in it. The polarity difference between the APTMS and the HTMS would reveal a change of the hydrogen bonding among celluloses in the silanized FC. In addition, an additive effect of high molecular weight SPP-g-DMI on the morphology and the tensile properties of the SPP/FC also have been studied. The SPP-g-DMI is unable to penetrate into the FC because of its high molecular weight, and the reaction with the OH group in cellulose is confined on the FC surface. The differences between the APTMS silanization and the SPP-g-DMI would reveal the change of the FC itself by the silanization. Moreover, the SPP/silanized HC with the APTMS have prepared, and the morphology and the tensile properties have been also studied as compared with those obtained from the SPP/HC with the SPP-g-DMI additive agent.

EXPERIMENTAL

Materials

SPP was supplied by Sanwayuka Industry Co. The trade name is TOTAL 1751. The number-average molecular weight (M_n) and the polydispersity (M_w/M_n) were 3.5×10^4 and 3.0, respectively. FC (W-100GK) was donated by Nippon Paper Chemicals Co. Ltd. The FC was dried in desiccator for 7 days before preparation. The moisture of the FC was below 0.7 wt %. The FC dimensions are over 90 wt % pass 100 mesh (below 150 μm), the average length was ∼ 37μm; 3-aminopropyltrimethoxysilane (APTMS) and hexyltrimethoxysilane (HTMS) were purchased from Shinetsu Silicon Chemicals Co. The

chemical structures of APTMS and HTMS are shown in Figure 1. Methanol and dimethyl itaconate (DMI) were purchased from Wako Pure Chemical Industry, respectively. Dicumyl peroxide (DCP) was purchased from Sigma Aldrich. These were used without further purification.

Preparation of holocellulose (HC)

A dwarf bamboo (*Sasa kurilensis*) was treated by chlorite to remove lignin component,[16] was enough dried in desiccator and then was ground by a vibration mill pot. The average length of the sample was ∼ 75μm. The sample was used as "HC."

Silanization

Mixing of 30 mL methanol solution of the silane coupling agent (APTMS or HTMS) and the FC (1 g) were performed using a 0.1-L glass equipped with a stirrer at 23°C for 24 h. The methanol solvent was evaporated using a rotary evaporator. The samples obtained were dried at 60°C for 6 h at in a vacuum oven and were used as "silanized FC or HC."

Synthesis of SPP grafted with dimethyl itaconate (SPP-g-DMI)

The SPP was reprecipitated from a boiling xylene solution into methanol and dried at 60°C for 8 h and was used as the sample without antioxidant. The synthesis of SPP-g-DMI was carried out with an Imoto Seisakusyo IMC-1884 melting mixer. The SPP (2 g), DMI (0.2 g), and DCP radical initiator (0.016 g) were sequentially added, and their mixing was performed at 180°C at 100 rpm for 60 min. The sample obtained was first dissolved in xylene at its refluxing temperature under nitrogen atmosphere, and the solution was precipitated by pouring into methanol. The precipitate obtained was washed repeatedly with fresh methanol, was dried in a vacuum oven at 60°C for 7 h and was used as the SPP-g-DMI sample. The M_n and M_w/M_n were 3.3×10^4 and 2.3, respectively. The chemical structure[17] is shown in Figure 2. The grafting rate was measured by FTIR spectroscopy[17] and was 0.11 wt %.

X-ray photoelectron spectroscopy (XPS) measurement

In the case XPS measurement, the silanized FC and HC were purified by a Soxhlet-extraction with boiling acetone for 8 h to remove the silane, which was not chemically bonded to the FC and HC surfaces. The X-ray photoelectron spectra of the silanized samples were measured by an X-ray Photoelectron Spectrometer (Rigaku XPS-7000) with an
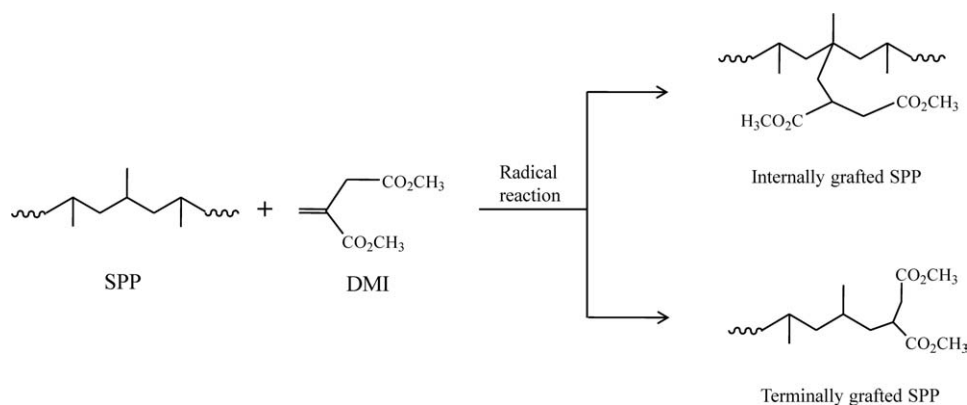
Figure 2 Chemical structure model of SPP-*g*-DMI.

unmonochromated magnesium K_α source (1253.6 eV). The magnesium K_α source was operated at 10 kV and 5 mA or at 10 kV and 30 mA. The samples were mounted onto a holder with double-sided adhesive tape and placed in a vacuum in the range 1.33×10^{-6} to 1.33×10^{-5} Pa. The analyzed sample area was $\sim$ 4 mm $\times$6 mm. The atomic percentages of the elements present were derived from spectra run of the corresponding region.

Preparation of composites

Composites are prepared by an Imoto Seisakusyo IMC-1884 melting mixer. All mixtures were carried by each weight ratio. After a small amount of phenolic antioxidant (Adekastab AO-60, $\sim$ 0.5%) was added, the mixing was performed at 150°C at 60 rpm for 5 min. The composites obtained were molded into the film (100 μm) by compression molding at 150°C under 4 MPa for 5 min.

Scanning electron microscope (SEM) observation

SEM observation was carried out with a JEOL JSM-5800 at 20 kV. The sample was fractured in liquid nitrogen, and then was sputter-coated with gold.

Tensile testing

Stress-strain behavior was observed using a SHIMADZU EZ-S at a cross-head speed of 3 mm/min. The sample specimens were cut with dimensions 30 × 5 × 0.1 mm shape in which the gauge length was 10 mm. We chose the specialized specimen (like ISO reed-shape) to adapt to the size of our tensile testing machine. All of tensile testing was performed at 20°C. The values of Young's modulus were obtained from the slope of the stress-strain curve (until about 1% of the strain value). All results obtained were the average values of ten measurements.

RESULTS AND DISCUSSION

Figure 3 shows the SEM micrographs of fractured surfaces of the SPP/FC and the SPP/silanized FC with the APTMS, with the HTMS and the SPP/SPP-*g*-DMI/FC, respectively. As shown in Figure 3(a), large voids exist between the FC and the SPP matrix, suggesting that the interfacial adhesion is very poor. Whereas, the size of the voids dramatically decreases by the two kinds of silanization and by the addition of the SPP-*g*-DMI graft-polymer, indicating that the interfacial adhesion is certainly improved. It seems, however, that there are some differences in the morphology of the interface. In the case of the SPP/silanized FC with the HTMS, it seems that the boundary between the FC and the matrix is much distinct than others. In addition, as shown in Figure 3(c), the cracked FCs can be observed, suggesting that the HTMS silanization brings about an embrittlement of the FC.

Figure 4 shows the changes of the Young's moduli of the SPP(70%)/silanized FC(30%) composites with various contents of the APTMS, the HTMS and of the SPP ((70 − x) wt %)/SPP-*g*-DMI(x wt %)/FC (30 wt %) composite, respectively. In the cases of the SPP/silanized FC with the APTMS and the SPP/SPP-*g*-DMI/FC, the Young's moduli linearly increase with the increases of these agent contents, suggesting that the adhesive strengths of these interfaces are reinforced by the APTMS and by the SPP-*g*-DMI, respectively. Whereas, in the case of the SPP/silanized FC with the HTMS, the Young's moduli reach the maximum at the 1 wt % HTMS content and then decrease with the HTMS content.

Figures 5 and 6 show the changes of the tensile strengths and the elongations at break of the SPP (70%)/silanized FC (30%) composites with various contents of the APTMS, the HTMS and of the SPP ((70 − x) wt %)/SPP-*g*-DMI (x wt %)/FC (30 wt %), respectively. In the case of the composite with the APTMS, the tensile strength reaches the maximum
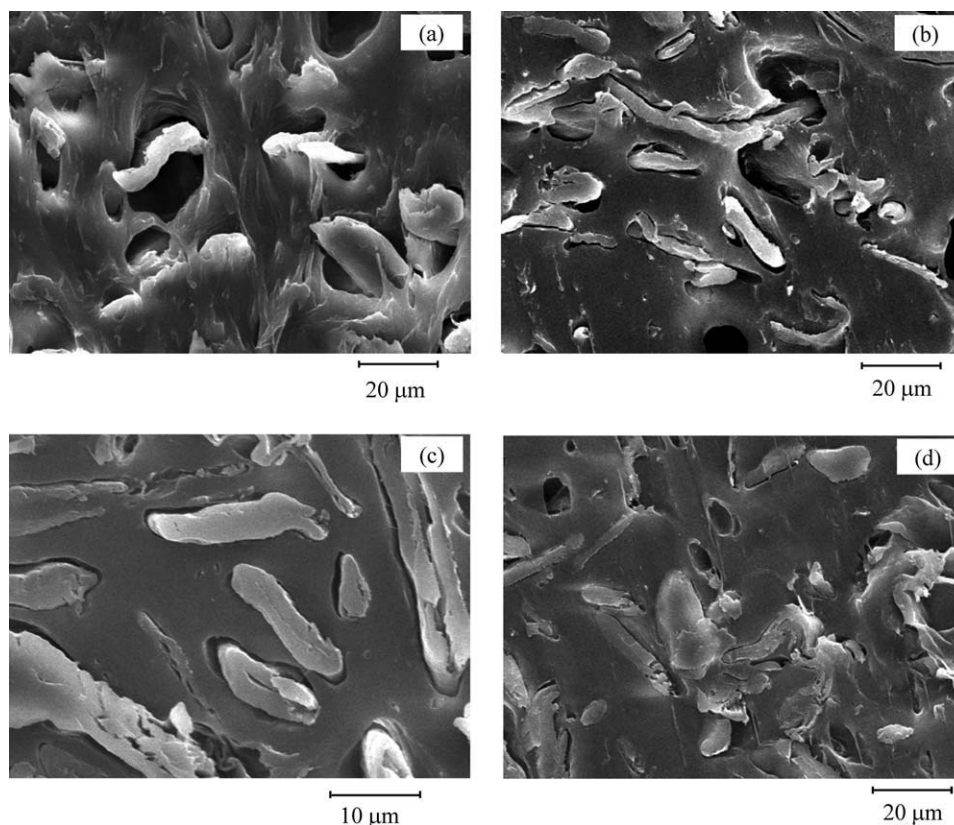
Figure 3 SEM microphotographs of the surfaces of the SPP/FC, of the SPP/silanized FC with APTMS or with HTMS, and of the SPP/SPP-*g*-DMI/FC. (a): SPP (70 wt %)/FC(30 wt %). (b): SPP (70 wt %)/silanized FC (30 wt %) with APTMS (2 wt %). (c): SPP (70 wt %)/silanized FC (30 wt %) with HTMS (2 wt %). (d): SPP (60 wt %)/SPP-*g*-DMI (10 wt %)/FC (30 wt %).

value at the 4 wt % APTMS content, and the elongation at break drops rapidly at the 5 wt % content. The embrittlement behavior is explainable in terms of the increase of the interface strength.[7] At the 5 wt %, the interface strength is believed to exceed the native strength of the FC itself. Therefore, the break

of the FC occurs under the tensile loading, leading to the crack initiation.[18] In the case of the SPP ((70 − x) wt %)/SPP-*g*-DMI (x wt %)/FC (30 wt %), the tensile strength linearly increases with the increase of the SPP-*g*-DMI amount, and the elongation at break linearly decreases with the increase of the one.
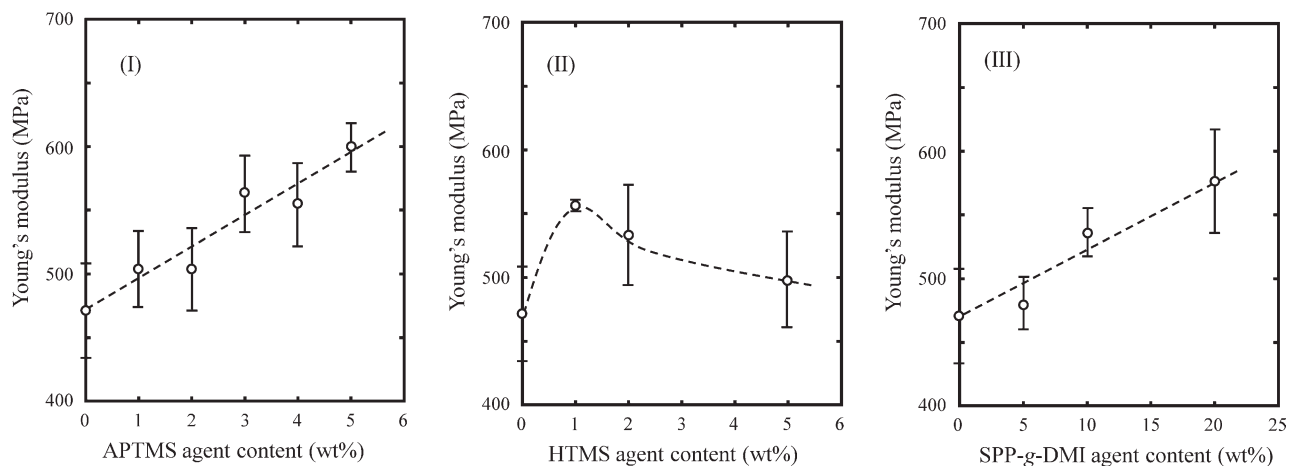

Figure 4 Young's moduli of the SPP/silanized FC with APTMS or with HTMS, and of the SPP/SPP-*g*-DMI/FC (I): SPP (70 wt %)/silanized FC (30 wt %) with various content of APTMS. (II): SPP (70 wt %)/silanized FC (30 wt %) with various content of HTMS. (III): SPP ((70 − x) wt %)/SPP-*g*-DMI (x wt %)/FC (30 wt %).
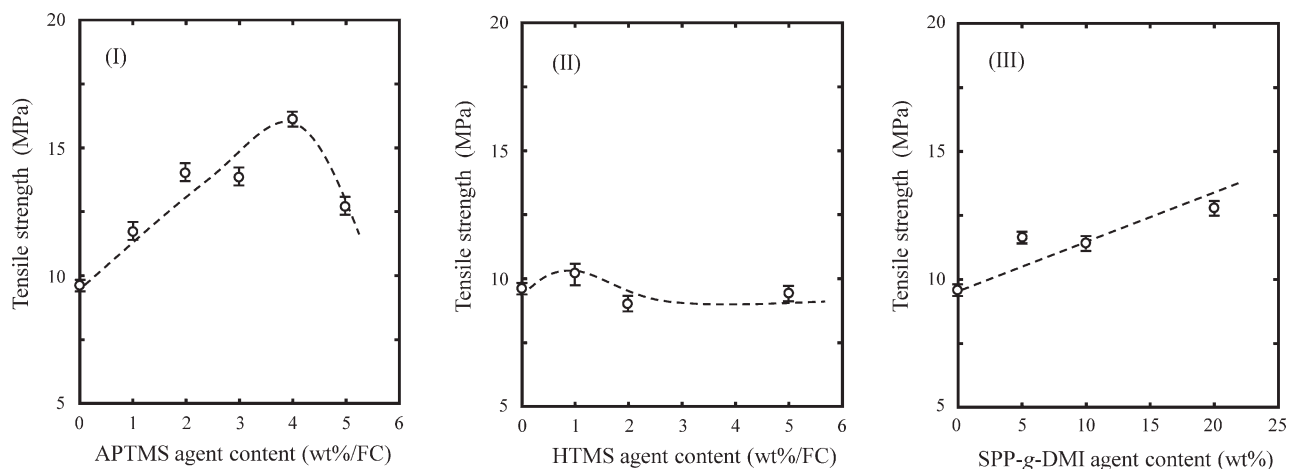
Figure 5 Tensile strengths of the SPP/silanized FC with APTMS or with HTMS, and of the SPP/SPP-*g*-DMI/FC (I): SPP (70 wt %)/silanized FC (30 wt %) with various content (wt %) of APTMS. (II): SPP (70 wt %)/silanized FC (30 wt %) with various content (wt %) of HTMS. (III): SPP ((70 − *x*) wt %)/SPP-*g*-DMI (*x* wt %)/FC (30 wt %).

The ester groups of the SPP-*g*-DMI can react with OH groups on the FC. The reaction is a kind of esterification reaction and produces the ester binding between them. The reactivity certainly depends on the SPP-*g*-DMI amount. The FC is gradually linked to the SPP-*g*-DMI with the increase of the additive amount, and the interface strength becomes stronger. Since the SPP-*g*-DMI has the high molecular weight, the degree of the entanglement between the SPP-*g*-DMI and the SPP chains must be considerably high. Therefore, the entanglement strength is believed to be higher than the FC strength itself. When a stress is applied to the composite, the FC must be preferentially fractured. In Figure 6(III), the embrittlement of the composite is likely due to the increase of the FC destructive deformation, by which formation of void in the SPP matrix is simultaneously caused.[19] Whereas, in the case of SPP (70%)/silanized FC

(30%) composites with various content of HTMS, the behavior of the tensile strength and the elongation at break as well as that of the Young's modulus is considerably strange. The tensile strengths reach the maximum at the 1 wt % HTMS content and then become constant with the higher content. The elongations at break reach the minimum at the 2 wt % HTMS content and then increase at the 5 wt %. The tensile behavior is considerably different as compared with other samples and would be due to the silanization with the HTMS. The FC is composed of cellulose aggregations. The cohesion force is originated from hydrogen bonding network among the celluloses. As shown in Figure 1, the HTMS has the nonpolar hexyl group in the chemical structure. The hexyl group is located at the one side chain end and converts the cellulose surface into hydrophobicity after the silanization. The HTMS silanization
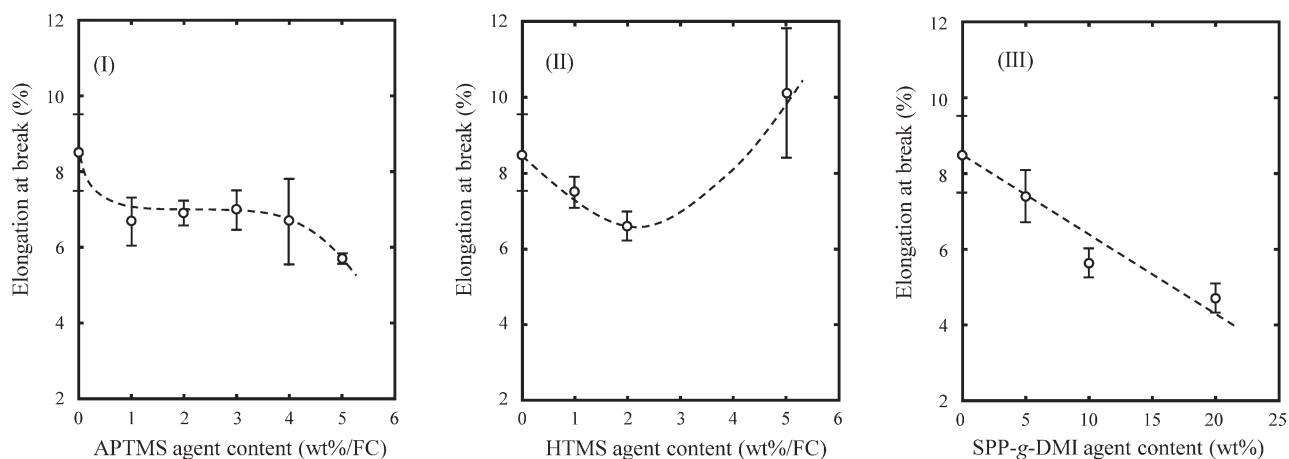

Figure 6 Elongations at break of the SPP/silanized FC with APTMS or with HTMS, and of the SPP/SPP-*g*-DMI/FC (I): SPP (70 wt %)/silanized FC (30 wt %) with various content (wt %) of APTMS. (II): SPP (70 wt %)/silanized FC (30 wt %) with various content (wt %) of HTMS. (III): SPP ((70 − *x*) wt %)/SPP-*g*-DMI (*x* wt %)/FC (30 wt %).

TABLE I
Elemental Compositions (mol %) of the FC and the Silanized FC Determined from XPS

Silanized FC	O/C	Si/O	Elemental composition (mol %)				Binding energy (eV)			
			O	C	Si	N	O	C	Si	N
FC	0.85	0.02	45.6	53.5	0.9	0.0	532.9	286.6	101.1	–
Silanization at 2 wt %										
APTMS	0.40	0.40	23.9	59.6	9.5	7.0	532.4	285.0	102.4	398.9
HTMS	0.76	0.05	42.2	55.7	2.1	0.0	533.1	286.8	102.3	–
Silanization at 5 wt %										
APTMS	0.43	0.42	25.0	57.5	10.5	7.0	532.8	285.6	102.8	399.3
HTMS	0.71	0.06	40.4	57.1	2.5	0.0	533.2	286.8	102.4	–

certainly disturbs the hydrogen bonding network among the celluloses. Therefore, the cohesion force among celluloses becomes weaker with the increase of the degree of the silanization, and the silanized FC must be embrittled. In fact, as mentioned above, the cracked FCs can be observed in Figure 3(c). The strange tensile behavior is due to the block of the inter hydrogen bonding formation by the HTMS silanization. When the tensile stress is applied, the weaker FC is preferentially deformed. Many cracks are preferentially generated in the FC, leading to the relaxation of strain constraint.[20] That is, the constant value of the tensile strength and the increase of the elongations at break at the higher HTMS content are due to the FC embrittlement. In addition, it seems that the SPP-g-DMI is unable to penetrate into the FC because of its higher molecules. Therefore, such tensile behavior would be not exhibited in the SPP/SPP-g-DMI/FC composite series.

The elemental compositions obtained from the XPS spectra of the FC and the silanized FCs with the APTMS and the HTMS coupling agents are summarized in Table I. The FC has the oxygen-to-carbon (O/C) atomic ratio of 0.85, and its rate means that the FC is composed of pure cellulose.[15,18] In the cases of the 2 wt % solutions, the O/C ratios for the silanized FCs with the APTMS and the HTMS are 0.40 and 0.76, respectively. The difference suggests that there exists a relationship between the chemical structure of silane coupling agent and the reactivity with the cellulose in the FC. These O/C ratios

slightly change against the higher silane coupling agent concentration (5 wt %). In addition, the silanizations with the 5 wt % solution of the silane agents bring about the slight (~ 10%) increases of the Si contents as compared with those with the 2 wt % solution. These silanizations with the higher concentration solution certainly raise the coverage on the cellulose. It is noted here that the Si content in the silanized FC with the APTMS is several times higher than that with the HTMS. The APTMS has the bifunctional nature[13,14] and is likely captured by OH groups on the cellulose because of a hydrogen bonding formation between the cellulose and the APTMS. The covalent bond (—Si—O—C—) formation between them proceeds through the condensation of the hydrogen bonded APTMS. The APTMS shows a higher reactivity against OH group on the cellulose since the amino group exists in the chemical structure. In addition, since the APTMS has the bifunctional nature, the hydrogen bonding between the silanized and the unsilanized celluloses would be kept. Therefore, unlike the HTMS, the APTMS silanization does not bring about the FC embrittlement.

The reactivity between silane agent and OH group on the cellulose and the keeping of the hydrogen bonding between the silanized and the unsilanized celluloses are certainly important for reinforcement of tensile properties in SPP/cellulose composite. It is noted here that the FC is composed of only pure

TABLE II
Analyses of High Resolution C_{1s} Peaks of the FC, HC, and the Silanized HC with APTMS

Silanized samples	Analysis of C1s peaks (%)			Binding energy (eV)		
	C1	C2	C3	C1	C2	C3
FC	24.5	55.9	19.6	285.0	286.6	288.0
HC	32.0	53.2	14.9	285.0	286.8	288.6
Silanization						
At 1 wt %	32.8	49.9	17.3	284.9	286.7	288.5
At 10 wt %	38.7	46.1	15.2	285.0	286.5	288.3
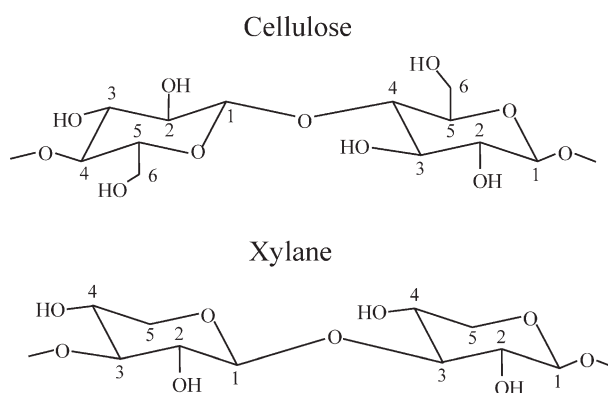
Figure 7 Chemical structures of cellulose and xylane.

Silanized FC	O/C	Si/O	Elemental composition (mol %)				Binding energy (eV)			
			O	C	Si	N	O	C	Si	N
HC	0.69	0.04	39.8	58.1	1.7	0.4	533.0	286.6	102.1	399.9
Silanization										
At 1 wt %	0.65	0.04	38.5	59.3	1.5	0.7	533.0	286.7	102.4	399.8
At 10 wt %	0.71	0.03	40.7	57.4	1.1	0.8	532.7	286.3	102.1	399.6

Determined by XPS.

cellulose. Practically cellulose materials such as wood flour are composed of not pure cellulose only but various impurities as well. Natural cellulose exists as a mixture of cellulose and hemicellulose. The mixture is called as holocellulose (HC). Since hemicellulose is composed of a group of complex carbohydrates, the reactivity between the silane agents and the OH groups on the HC must be considerably different from that on the FC (pure cellulose). To study the reactivity with HC, the SPP (70%)/silanized HC (30%) composites with various contents of the APTMS have been prepared and, the tensile behavior and the morphology have been studied. In addition, the tensile behavior and the morphology of the SPP $((70 - x)$ wt %)/SPP-g-DMI (x wt %)/HC (30 wt %) also have been studied to clarify the reactivity between the HC and the SPP-g-DMI.

The analyses of high resolution C_{1s} peaks of the FC, HC, and the silanized HC with APTMS are summarized in Table II. In the case of the C_{1s} spectrum of the FC, it consists of three peaks at $\sim$ 285, 287, and 288 eV, arising from C1 (carbon atoms to a carbon and/or hydrogen atoms (C—C/C—H)), C2 (carbon atoms bonded to a single oxygen atom, other than a carbonyl oxygen (C—OH)), and C3 (carbon atoms bonded to two noncarbonyl oxygen atoms or to a single carbonyl oxygen atom (O—C—O, C=O), respectively.[15] Since the C2 (corresponding to OH group) ratio of the HC is almost the same as that of the FC, the amount of the OH group in the HC must be close to that in the FC. However, in the case of holocellulose obtained from bamboo species such as the *Sasa kurilensis*, the holocellulose is commonly composed of $\sim$ 70% cellulose and $\sim$ 30% hemicellulose,[21,22] of which major component is xylan. As shown in Figure 7, unlike cellulose, xylan has no primary alcohol having a higher reactivity. If the HC has the same amount of the OH group as the FC, the reactivity with silane agent must be considerably less. In fact, as shown in Table III, the Si content of the silanized HC with the APTMS is around 1.5 mol % regardless of the APTMS concentration. The less dependence of the concentration on the Si content suggests that the reactivity of the OH group in the HC is much less than that in the FC.

Young's moduli, tensile strengths and elongations at break of the SPP (70 wt %)/silanized HC (30 wt %) with various content of APTMS are shown in Figure 8. In the cases of the Young's modulus and the tensile strength of the SPP/silanized HC with the 1 wt % content, these values increase $\sim$ 18% and
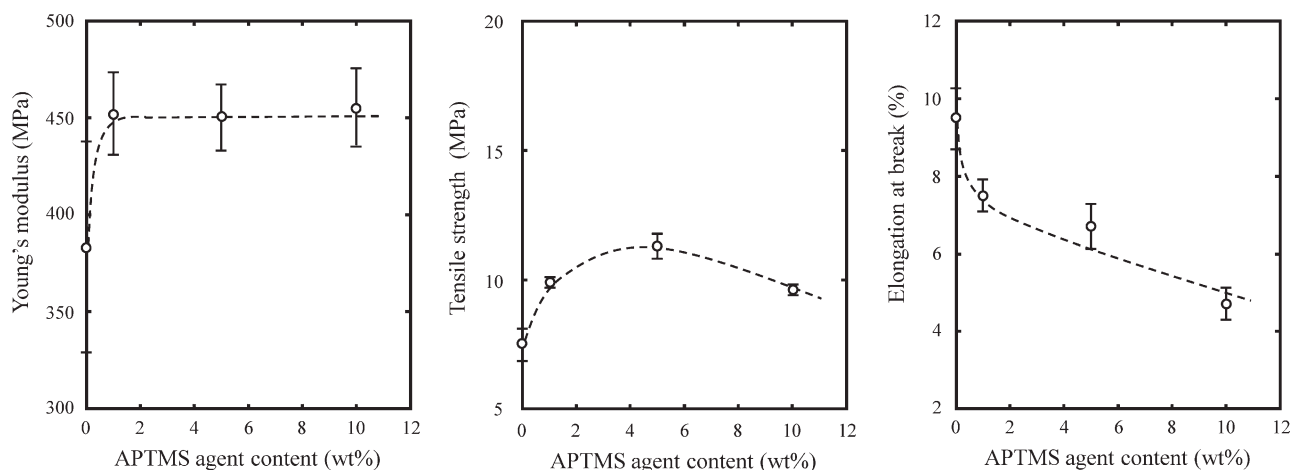

Figure 8 Young's moduli, tensile strengths, and elongations at break of the SPP (70 wt %)/silanized HC (30 wt %) with various content of APTMS.
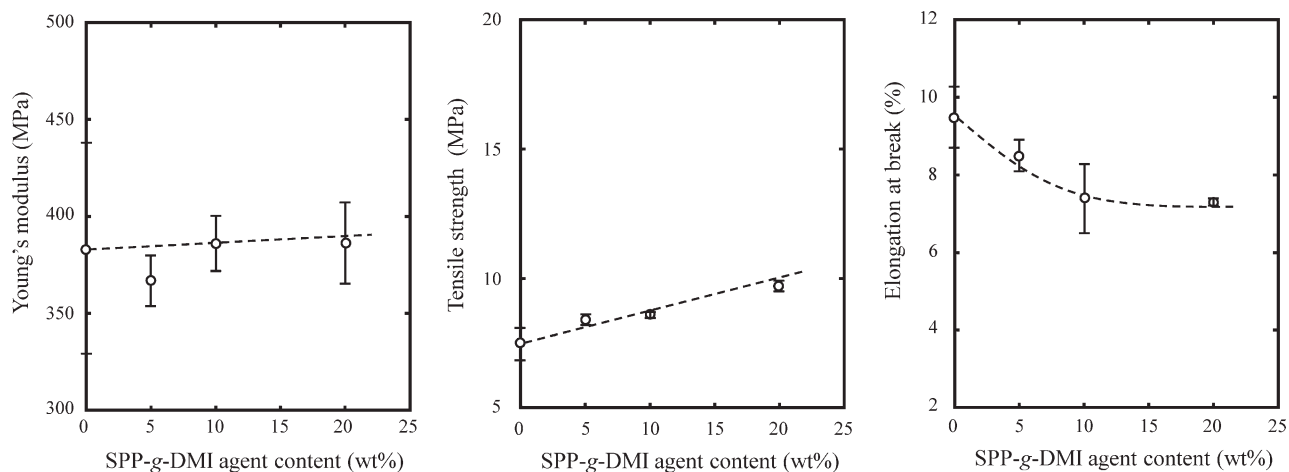
Figure 9 Young's moduli, tensile strengths, and elongations at break of the SPP ((70 − x) wt %)/SPP-g-DMI (x wt %)/ HC (30 wt %).

~ 30%, respectively, as compared with those of the SPP/HC. These behaviors suggest that the interface between the SPP and the HC is considerably reinforced even by the small formation of the covalent bond (—Si—O—C—). As shown in Figure 8, these values are almost constant up to the 10 wt % content,

suggesting that the amount of the covalent bond does not change with the increase of the APTMS content. It seems that most of an active OH group in the HC reacts with the APTMS at the 1wt %. The APTMS in excess of the 1 wt % hardly works as the coupling agent. Whereas, the elongations at break quickly
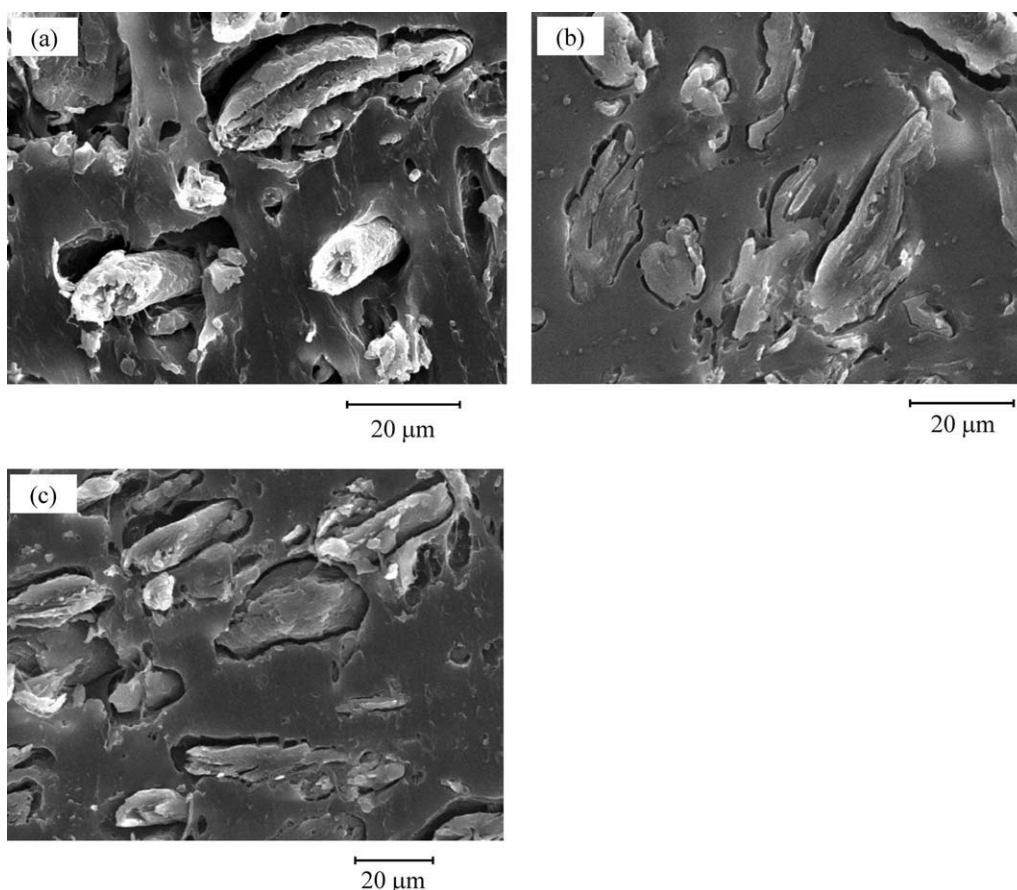

Figure 10 SEM microphotographs of the surfaces of the SPP/HC, of the SPP/silanized HC with APTMS, and of the SPP/SPP-g-DMI/HC. (a): SPP (70 wt %)/ HC (30 wt %). (b): SPP (70 wt %)/silanized FC (30 wt %) with APTMS (10 wt %). (c): SPP (60 wt %)/SPP-g-DMI (10 wt %)/HC(30 wt %).

decrease with the increase of the APTMS content (see Fig. 8), suggesting that the embrittlement of the SPP matrix is developed by the excess of the APTMS.

Young's moduli, tensile strengths and elongations at break of SPP $((70 - x)$ wt %)/SPP-g-DMI (x wt %)/HC (30 wt %) are shown in Figure 9. The Young's moduli and the tensile strengths gradually increase with the increase of the SPP-g-DMI content. Whereas, the elongations at break gradually decrease with the increase of the SPP-g-DMI content. These dependences are similar to those in SPP/SPP-g-DMI/FC and are, however, much lower. These results suggest that the reactivity with the OH group on the HC is considerably low as well as the APTMS.

Figure 10 shows the SEM microphotographs of the surfaces of the SPP/HC, the SPP/silanized HC with the APTMS, and the SPP/SPP-g-DMI/HC, respectively. As shown in Figure 10(a), large voids exist between the HC and the SPP matrix, suggesting that the interfacial adhesion is very poor as well as that of the SPP/FC. In the cases of the SPP/silanized HC with the APTMS and of the SPP/SPP-g-DMI/HC, the size of the voids dramatically decreases as well as those of these FC samples (see Fig. 3), indicating that the interfacial adhesions are certainly improved. However, these boundaries between the HC and the SPP matrix are considerably distinct, demonstrating that the interfacial adhesion is considerably weak.

CONCLUSIONS

The reinforcement of the interfacial adhesion between the SPP and the FC was performed by the FC silanizations with the APTMS and the HTMS and by the addition of the SPP-g-DMI graft-polymer, respectively. It was confirmed that the interfacial adhesion was certainly improved by them. However, the reinforcement behavior was considerably different among these methods. In particular, the FC silanization with the HTMS showed the specific tensile behavior. The existence of the hexyl group in the HTMS led to the block of the inter hydrogen bonding in the FC. Therefore, the cohesion force among the celluloses became weaker with the increase of the degree of the silanization, and the silanized FC was embrittled. In the case of the APTMS, the hydrogen bonding among the celluloses was kept because of the existence of the amino group. Whereas, the SPP-g-DMI was unable to penetrate into the celluloses because of its higher molecules, and the inter hydrogen bonding was not blocked. It was found that the keeping the inter hydrogen bonding among the celluloses was important for the reinforcement of the tensile properties such as Young's modulus and tensile strength in the SPP/FC composite.

In addition, to study the reactivity with HC which is the mixture of cellulose and hemicellulose, the SPP/silanized HC with the APTMS and the SPP/SPP-g-DMI/HC were prepared and, the tensile behavior and the morphology were studied. The Young's moduli and the tensile strengths were considerably improved by the APTMS silanization and by the addition of the SPP-g-DMI, respectively. Whereas, these improvements hardly showed dependency on the APTMS content and the SPP-g-DMI amount. The behavior suggested that the each of reactivities with the OH group in the HC were considerably low. In the SEM observations of the SPP/silanized HC with the APTMS and the SPP/SPP-g-DMI/HC, it was confirmed that these interfacial adhesion was certainly improved. However, these boundaries between the HC and the SPP matrix were considerably distinct, demonstrating that the interfacial adhesion was considerably weak. It was found that the reactivity of the HC was much less than that of the FC composing of pure cellulose.

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