Effect of Chemical Structure of Silane Coupling Agent on Interface Adhesion Properties of Syndiotactic Polypropylene/Cellulose Composite

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ABSTRACT: To improve interaction between syndiotactic polypropylene (SPP) and fibrous cellulose (FC), effects of chemical structure of silane coupling agent on the reactivity for the surface hydroxyl group on the FC were studied by X-ray photoelectron spectroscopy (XPS) measurement. Among the three kinds of the silane coupling agent, the 3-aminopropyltrimethoxysilane (APTMS) showed the highest reactivity with the surface hydroxyl group on the FC, and the linear silane compound with methoxyl group was found to be suitable for the reaction. Although the morphology of the SPP/FC composite is hardly affected by the difference in the kinds of the silane coupling agent, the tensile properties were considerably different. In particular, in the case of using higher silane coupling agent solution (over 3 wt %), the chemical structure of silane coupling agent certainly affected the tensile properties of the SPP/silanized FC composite. It was found that the tensile properties were distinctly affected by the reactivity between the surface hydroxyl group on FC and the silane coupling agent. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 1732–1741, 2011

Key words: composites; ESCA/XPS; polyolefins; syndiotactic; poly(propylene) (PP)

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. Recently, cellulose has attracted much attention as a 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 isotactic polypropylene (IPP) has been extensively prepared. This is due to the commercial importance of IPP as industrial products. In the case of the composite, fibrous cellulose (FC) has been generally used as the cellulose source since it has been expected instead of glass and carbon fibers. However, FC is hydrophilic and tends to aggregate, causing poor processability and inherent incompatibility with hydrophobic IPP. To obtain the applicable composite has been studied on the modifications of FC surface using a maleated IPP (MAPP),[1,6,11] a surfactant,[11]

corona discharge,[12–14] silane coupling agent,[15] and a novel mechanochemical method.[9,16]

As another type of PP semicrystalline polymer, there is syndiotactic PP (SPP).[17,18] SPP has excellent properties in the resistance against thermal oxidative degradation,[19–21] and recently its composites containing glass fillers and nano silicates have attracted considerable interest in the reinforced tensile properties.[22,23] In our previous work,[24] the effects of the FC surface modification with 3-Aminopropyltriethoxysilane (APTES) on the SPP/FC composite were studied in the morphology and the tensile properties. The surface modification brought about an increase of the Young's modulus of the SPP/FC composite, suggesting that the silane modification of FC surface is a useful method for the improvement of SPP/FC tensile properties.

Silane coupling agent is a most common adhesion promoter and is widely employed in polymeric composite involving glass or silicate substrate. Some investigators reported that silane coupling agent effectively worked in surface modification of FC as well as glass or silicate substrate, and the silanized FC brought about the tensile properties of the composites with polyethylene[3] or IPP[15] Raj et al. reported that silane A-172 [Vinyltri(2-methoxyethoxy) silane] efficiently worked as a silane coupling agent for aspen and commercial wood fibers, and the

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silanization brought about improvements of the tensile properties of the composites with polyethylene.[3] Adequate silanization brings about a higher wood fiber dispersion in the polymer matrix and a fair degree of adhesion at the interface. However, the effects of chemical structure of the silane coupling agent on the tensile properties have not been extensively studied.

The purpose of the present work is to clarify the effects of chemical structure of the silane coupling agent on the morphology and the tensile properties of the SPP/FC composite. The silanized FC samples have been prepared by three kinds of silane coupling agents having different chemical structure. The adhesion between the silane coupling agent and the FC was studied by XPS, and the interface between the SPP and the silanized FC was done by scanning electron microscope (SEM) observation and by tensile testing, respectively.

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. 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 ca. 37 μm, and the crystallinity was ca. 70%. 3-Aminopropyltrimethoxysilane (APTMS), 3-Aminopropyltriethoxysilane (APTES), isobutyltrimethoxysilane (IBTMS), and ethanol were purchased from Shinetsu Silicon Chemicals Co. and Wako Pure Chemical Industry, respectively. These were used without further purification.

Preparation of silanized FC

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

X-ray photoelectron spectroscopy (XPS) measurement

In the case XPS measurement, the silanized FC was purified by a Soxhlet-extraction with boiling acetone for 8 h to remove the silane, which was not chemically bonded to the FC surface. The X-ray photoelectron spectra of the silanized FC samples were measured by an X-ray Photoelectron Spectrometer (Rigaku XPS-7000) with an 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 FC samples were mounted onto a holder with double-sided adhesive tape and placed in a vacuum in the range $1.33 \times 10^{-6} - 1.33 \times 10^{-5}$ Pa. The analyzed sample area was ca. 4 mm × 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, ca. 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 mm × 5 mm × 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 were 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

The elemental compositions obtained from the XPS spectra of the FC and the silanized FCs with the 2 wt % and the 5 wt % solutions of APTMS, APTES, and IBTMS coupling agents are summarized in Table I. The FC has the oxygen-to-carbon (O/C) atomic ratio of 0.85. The rate is close to the O/C ratio (0.83) for pure cellulose, indicating that the FC is composed of pure cellulose.[25] In the case of the 2 wt % solution, the O/C ratios for the silanized FCs with APTMS, APTES, and IBTMS are 0.40, 0.70, and

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

Silanized FC	O/C	Si/O	Elemental compositions (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
APTES	0.70	0.08	38.8	55.5	3.2	2.5	532.7	286.1	102.3	399.1
IBTMS	0.84	0.02	45.1	53.8	1.1	0.0	533.0	286.6	102.1	–
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
APTES	0.72	0.11	39.4	55.1	4.4	1.1	532.9	286.3	102.3	399.3
IBTMS	0.82	0.06	43.8	53.7	2.5	0.0	533.3	287.1	102.4	–

0.84, respectively. The difference suggests that there exists a relationship between the kind of silane coupling agent and the reactivity with the FC surface. 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 increases in Si contents as compared with those with the 2 wt % solution. It seems that the silanization with the higher concentration solution raises the coverage on the FC surface.

Figure 1 shows the high resolution C_{1s} spectra of the FC and the silanized FCs. In the case of the C_{1s} spectrum of the FC, it consists of three peaks at 285.0, 286.6, and 288.0 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 non-carbonyl oxygen atoms or to a single carbonyl oxygen atom (O—C—O, C=O)], respectively.[25] These results are summarized in Table II. In the case of the silanized FCs with APTMS, the C1 and the C2, and the C3 fractions are 79.3%, 20.7%, and 0%, respectively. These ratios are considerably different as compared with those of the FC, indicating that APTMS can well cover the FC surface even by the 2 wt % solution. By contrast, the C1, C2, and C3 fractions of the
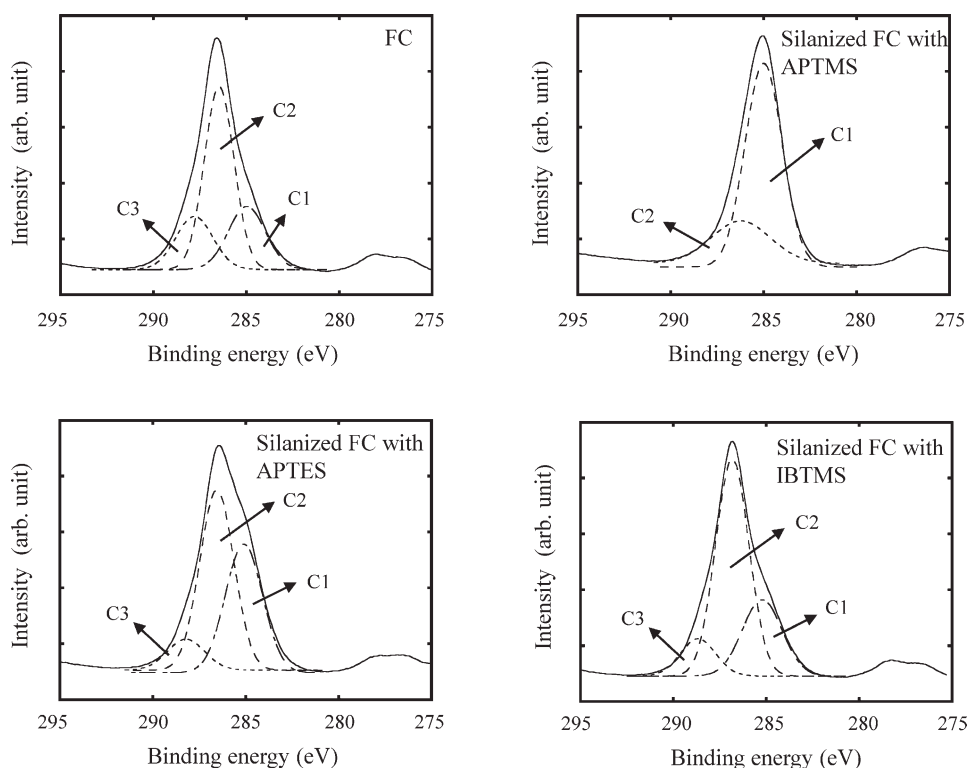

Figure 1 High resolution C_{1s} spectra of FC and silanized FCs (silanization at 2 wt % content).
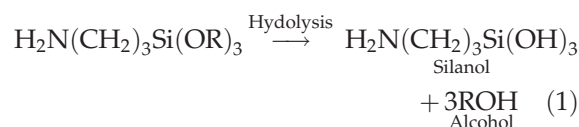
TABLE II
Analysis of High Resolution C_{1s} Peaks of the FC and the Silanized FC

Silanized FC	Analysis of C_{1s} peaks (%)			Binding energy (eV)		
	C1	C2	C3	C1	C2	C3
FC	24.5	55.9	19.6	285.0	286.6	288.0
Silanization at 2 wt %						
APTMS	79.3	20.7	0.0	285.0	286.3	–
APTES	43.0	48.8	8.2	285.0	286.6	288.2
IBTMS	27.7	63.6	8.7	285.0	286.8	288.7
Silanization at 5 wt %						
APTMS	86.2	13.8	0.0	285.6	287.2	–
APTES	44.8	36.3	18.9	285.0	286.7	287.8
IBTMS	21.2	71.1	7.7	285.0	287.1	289.0

silanized FC with IBTMS agree fairly well with those of the FC, indicating that the coverage on the FC surface is considerably low. Whereas, these ratios of the silanized FC with APTES show the values intermediate between the FC and the silanized FC with APTMS. It seems that APTES partially covers the FC surface. These results suggest that the coverage on the FC surface is affected by the difference in the chemical structure of silane coupling agent. As shown in Table II, in the cases of the silanized FCs with the 5 wt % solutions of APTMS and APTES, the C2 (C—OH) fractions become lower about 10% as compared with those with 2 wt % ones. These results suggest that the free surface hydroxyl group on the FC is decreasing. In contrast, in the case of the silanized FC with the 5 wt % IBTMS solution,

the C2 becomes higher about 10% as compared with that with 2 wt % one. This behavior seems to be strange. Since the amount of the linked IBTMS is considerably low even with the 5 wt % solution, the margin of error of the XPS data must be considerably large. The change of IBTMS coverage would be considerably small. The reactivity between the FC and IBTMS is considerably low, suggesting that the amount of the linked IBTMS is considerably small even with the 5 wt % solution. The effect of difference in IBTMS concentration on the coverage must be small. In addition, in the silanized FCs with the 5 wt % solutions of APTES, the C3 (O—C—O, C=O) fraction is much higher than that with 2 wt % one. This is believed to be due to impurities in APTES since there do not exist the corresponding chemical groups in APTES chemical structure.

Matuana et al. reported that there were two kinds of reaction step in the coupling reaction between a FC surface and an aminoalchoxysilane coupling agent such as APTES.[25] In the first step, the silane agent is smoothly hydrolyzed to silanol by the water on the FC surface as shown in eq. (1):

$$H_2N(CH_2)_3Si(OR)_3 \xrightarrow{\text{Hydolysis}} H_2N(CH_2)_3Si(OH)_3$$
$$\text{Silanol}$$
$$+ 3ROH \quad (1)$$
$$\text{Alcohol}$$

In the second step, the absorbed silanol partially reacts with the surface hydroxyl group on the FC to form ether bond. Some parts of the silanol condense
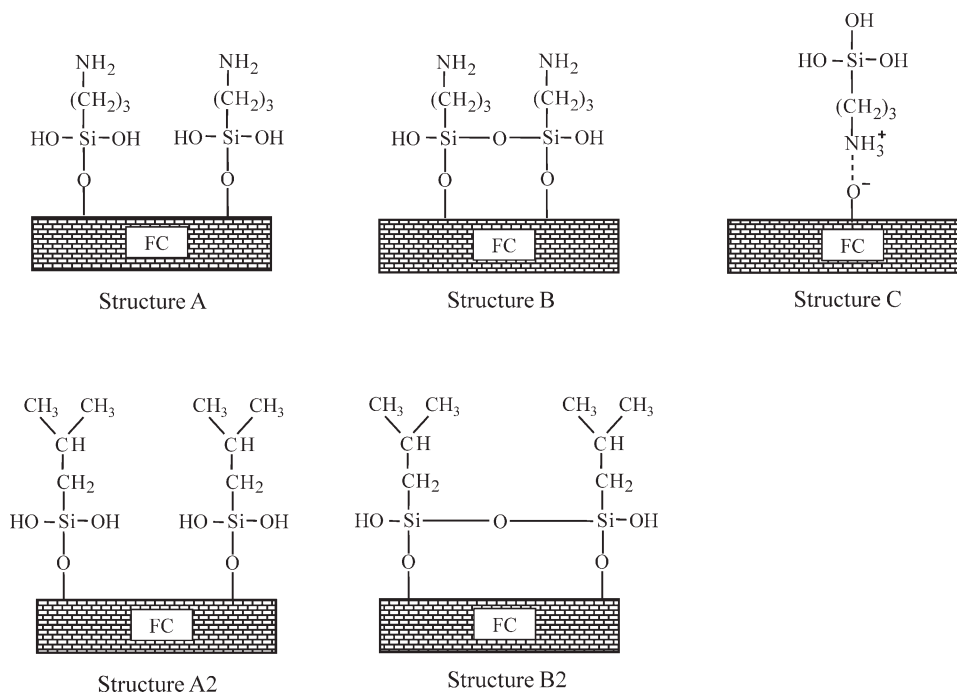

Figure 2 Structural model of aminoalkylsilanol bound to the surface of fibrous cellulose (FC). Structure A–C: APTMS and APTES structural model binding to the FC surface. Structure A2 and B2: IBTMS structural model binding to the FC surface.
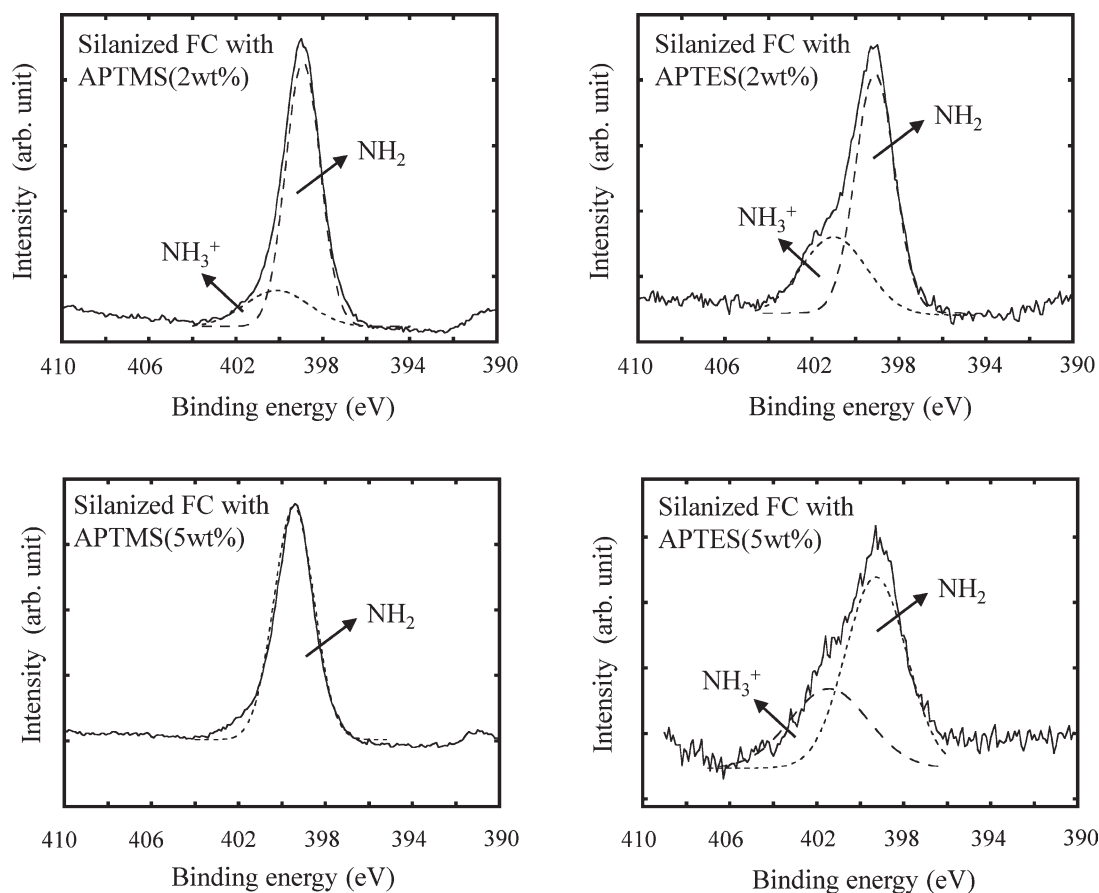
Figure 3 High resolution N_{1s} spectra of silanized FCs with APTMS and APTES.

among themselves and produce a polymeric silanol. Therefore, as shown in Figure 2, there exist the monomeric (Structure A and A2) and the polymeric (Structure B and B2) structures having the ether bond. In addition, the hydroxyl group on the FC can react with the amino group as well as the silanol. The protonated ammonium nitrogen ($-NH_3^+$) is produced and can also form a hydrogen bond with the hydroxyl group of the FC (Structure C).[25] In fact, as shown in Figure 3, the peak at the higher binding energy (at 400.1 or at 401.0 eV) assigned to the protonated ammonium nitrogen ($-NH_3^+$) can be separated in the N_{1s} spectra of the silanized FCs with APTMS and APTES, respectively. The protonated ammonium nitrogen ratio in the silanized FC with APTMS is considerably lower than that with APTES (see Table III). The formation of the ether linkage ($-O-Si-$) and of the hydrogen bond ($-O^--NH_3^+-$) would be a competing reaction. Naturally the hydrogen bond cannot be formed at the hydroxyl group used by the formation of the ether linkage. Thus, the amount of the hydrogen bond depends almost entirely on the amount of the residual hydroxyl group on the FC. The difference between APTMS and APTES silane coupling agents is due to the kind of alkoxy group. In fact, the rates

of the hydrolysis of alkoxy groups are related to their steric bulk[26]: MeO$-$ > EtO$-$ > t-BuO$-$. Thus, the formation of the ether linkage between the hydroxyl group and APTMS is easy, and the residual OH amount must be less. In the case of the silanized FCs with APTMS, the less fraction of the hydrogen bond is due to the higher hydrolysis reactivity. In addition, although IBTMS is composed of methoxy (MeO-) group, the reactivity between the

TABLE III
Analysis of High Resolution N_{1s} Peaks of the FC and the Silanized FC

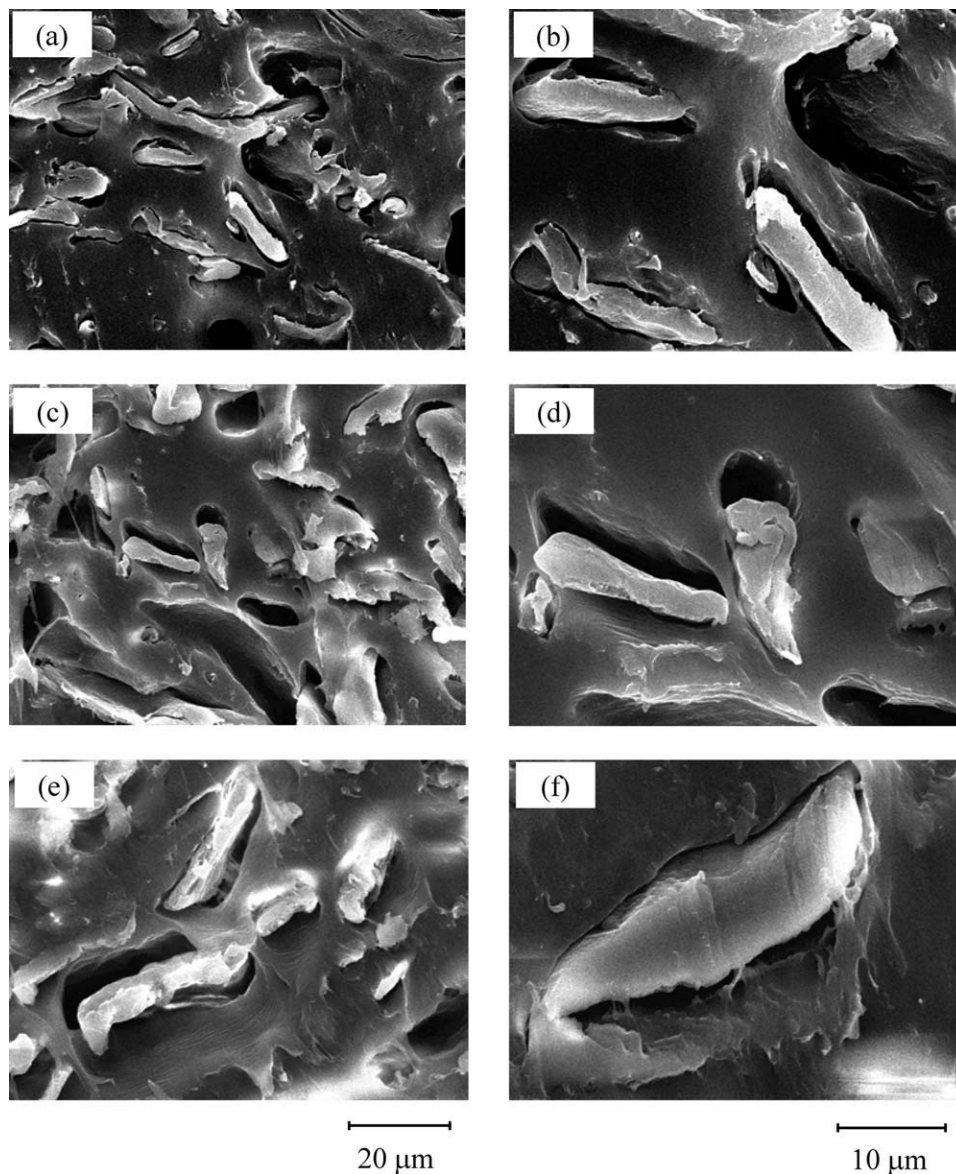| Silanized FC	Analysis of N_{1s} peaks (%)		Binding energy (eV)	
	NH_3^+	NH_2	NH_3^+	NH_2
FC	–	–	–	–
Silanization at 2 wt %				
APTMS	18.0	82.0	400.1	398.9
APTES	32.5	67.5	401.0	399.0
IBTMS	–	–	–	–
Silanization at 5 wt %				
APTMS	≈ 0	≈ 100	–	399.3
APTES	40.9	59.1	401.4	399.3
IBTMS	–	–	–	–

Figure 4 SEM microphotographs of the surface of the SPP (70 wt %)/silanized FC (30 wt %) with various silane coupling agents composites. With APTMS (2 wt %): (a) Low magnification. (b) High magnification. With APTES (2 wt %): (c) Low magnification. (d) High magnification. With IBTMS (2 wt %): (e) Low magnification. (f) High magnification.

FC and IBTMS is lowest among these silane coupling agents. The lowest reactivity is believed to be explainable by the hydrolysis inhibition due to the existence of the sterically bulky isobutyl group.

Figure 4 shows the SEM micrographs of fractured surfaces of the SPP/ silanized FC with the silane coupling agents (2 wt %), respectively. The FC in the SPP matrix shows good dispersibility in all the composites. It seems that the dispersibility is hardly affected by the coverage on the FC surface. In fact, as shown in Figure 5, the SEM micrographs of the SPP/silanized FC with the higher silane coupling agent contents (5 wt %) composites show good dispersibility of the FCs as well as that with the lower silane coupling agent contents (2 wt %). It seems, however, that there is a difference in the adhesive

strength of the interface. In the cases of the composites with the higher silane coupling agent contents (5 wt %), the voids are smaller, and the adhesive bondings between the FC and the SPP matrices can be partially observed. In addition, IBTMS seemed to have better compatibility due to the smaller voids between the phase interface. The better compatibility is likely due to the chain end (iso-Butyl) group having hydrophobicity. In the cases of APTMS and APTES, the chain end group is mainly the amine group having relatively weak hydrophilicity. Therefore, it seems that the silanized FC by IBTMS shows better compatibility in the hydrophobic SPP.

Figure 6 shows the changes of the Young's moduli of the SPP (70%)/silanized FC (30%) composites with various contents of APTMS, APTES,
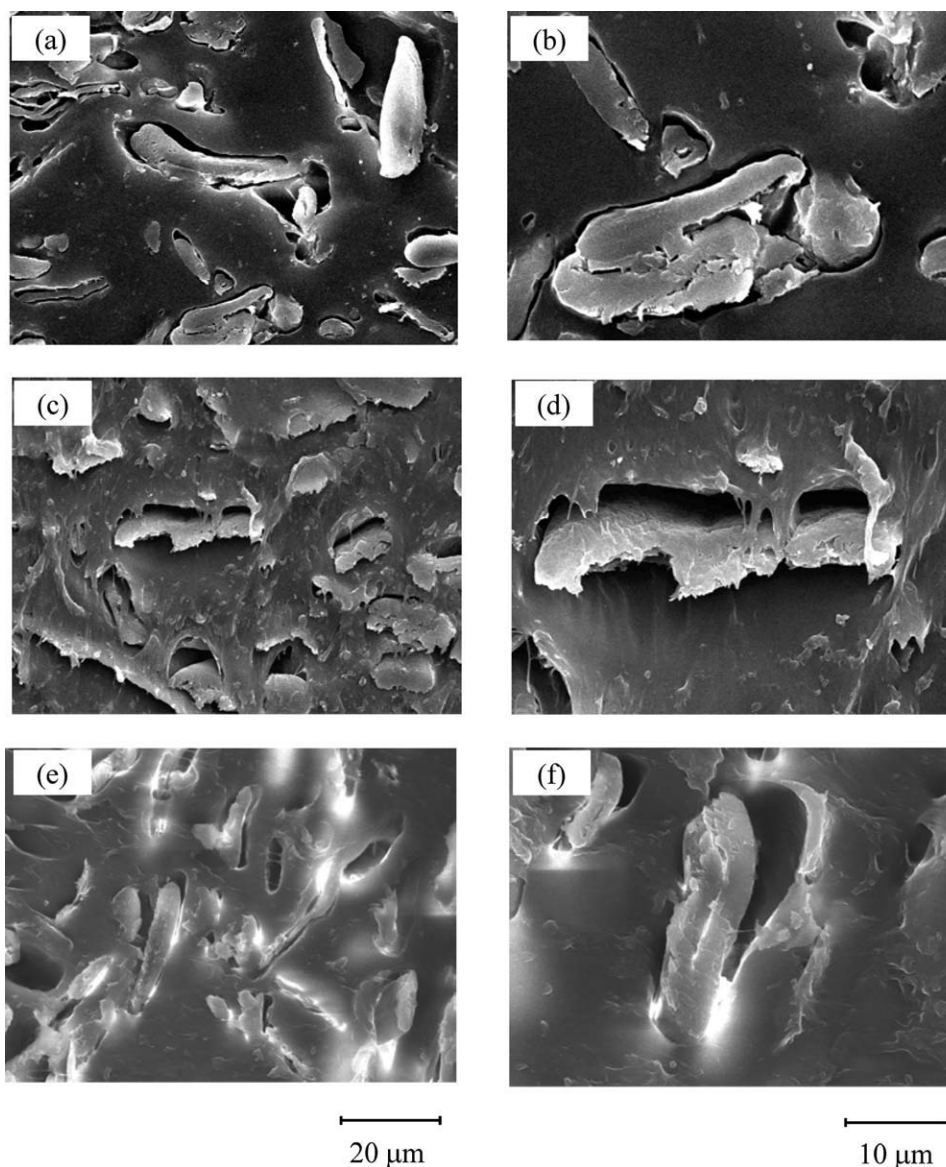
Figure 5   SEM microphotographs of the surface of the SPP (70 wt %)/silanized FC (30 wt %) with various silane coupling agents composites. With APTMS (5 wt %): (a) Low magnification. (b) High magnification. With APTES (5 wt %): (c) Low magnification. (d) High magnification. With IBTMS (5 wt %): (e) Low magnification. (f) High magnification.

and IBTMS silane agents, respectively. Interestingly, the composites with the 2 wt % solutions show almost the same Young's moduli (ca. 500MPa) regardless of the kind of the silane coupling agent. As mentioned above, APTMS coupling agent can well cover the FC surface even by the 2 wt % solution. However, as shown in Table III, the protonated ammonium nitrogen ratio in the silanized FC is 18%. The bonding strength of hydrogen bond is considerably weaker than that of covalent bond. Thus, the protonated ammonium nitrogen part serves as a starting point of internal defect during the tensile testing of the composite. The increase of APTMS content brings about the increase of Young's modulus. This behavior is due to the decrease of the protonated ammonium nitrogen part. In fact, as shown

in Figure 3 and Table III, the composite with the 5 wt % APTMS solution shows almost the 0% protonated ammonium nitrogen content. In the case of the composite with APTES, the Young's modulus approximately shows an upward trend up to the 3 wt % APTES content. This behavior is due to the increase of the ether linkages as well as that of APTMS. However, the Young's moduli reach the constant value over the 3 wt % APTES content. This behavior would be due to the lower reactivity of APTES. As mentioned above, the rate of the hydrolysis of the ethoxy group in APTES is slower than that of the methoxy group in APTMS. Thus, the formation of the ether linkage between the hydroxyl group and APTES is considerably slow, and the protonated ammonium nitrogen ($-NH_3^+$) easily forms
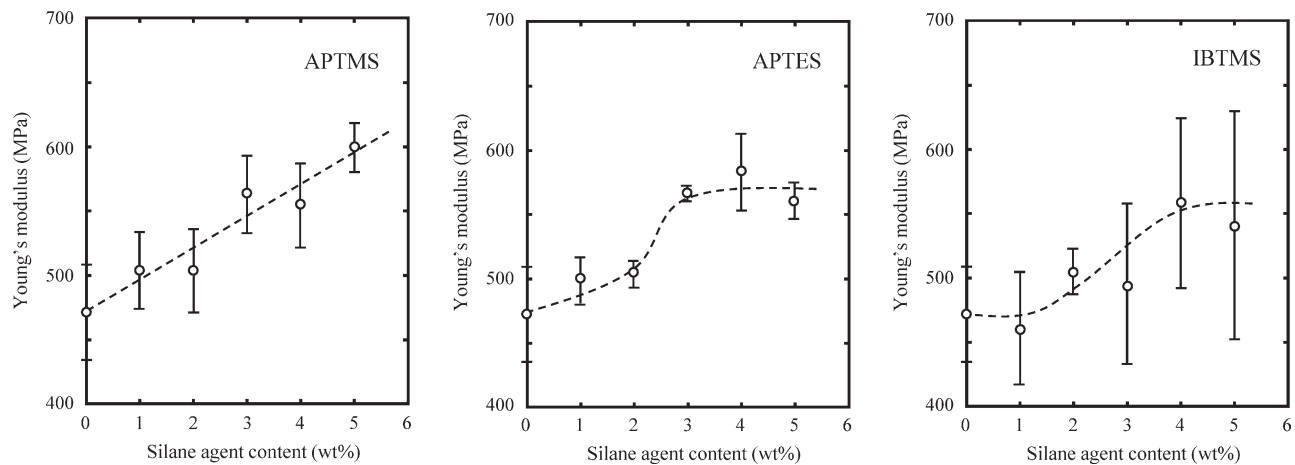
Figure 6 Young's moduli of SPP (70 wt %)/silanized FC (30 wt %) composites with various contents of APTMS, APTES, and IBTMS silane agents, respectively: SPP (100 wt %) = 341 ± 2 MPa.

the hydrogen bond with the hydroxyl group of the FC. The hydrogen bond is weaker than the ether one and becomes a defect on tensile properties. The lower reactivity of APTES would bring about the saturation behavior of the Young's modulus against APTES content. Figures 7 and 8 show the changes of the tensile strengths and the elongations at break of the SPP (70%)/silanized FC (30%) composites with various contents of APTMS, APTES, and IBTMS silane agents, respectively. In the case of the composite with APTMS, the tensile strength reaches the maximum value at the 4 wt % APTMS content. In addition, the elongation at break drops rapidly at the 5 wt % APTMS content. This embrittlement behavior is due to the increase in the interface strength. At the 5 wt % APTMS, the interface strength would exceed the native strength of the FC itself. Therefore, the break of the FC occurs under the tensile loading, leading to the crack initiation. In the case of the composite with APTES, the tensile strength and the

elongation at break reach the constant values over the 2 wt % and over the 3 wt % APTES contents, respectively. These behavior is similar to the Young's modulus one. The amount of the ether linkage between the hydroxyl group and APTES would be saturated around 3 wt % APTES content because of its lower reactivity.

In the case of using higher silane coupling agent solution (over 3 wt %), the difference in the chemical structure of silane coupling agent markedly affects the tensile properties of the SPP/silanized FC composite. In particular, IBTMS coupling agent distinctly brings about the unique tensile properties for the SPP/silanized FC composite. In the case of the composites with IBTMS, the Young's moduli have a large margin of error as compared with those with APTMS and with APTES. In addition, the tensile strengths are lower, and the elongations at break are higher and also have a large margin of error. These tensile behavior is due to weaker interface strength
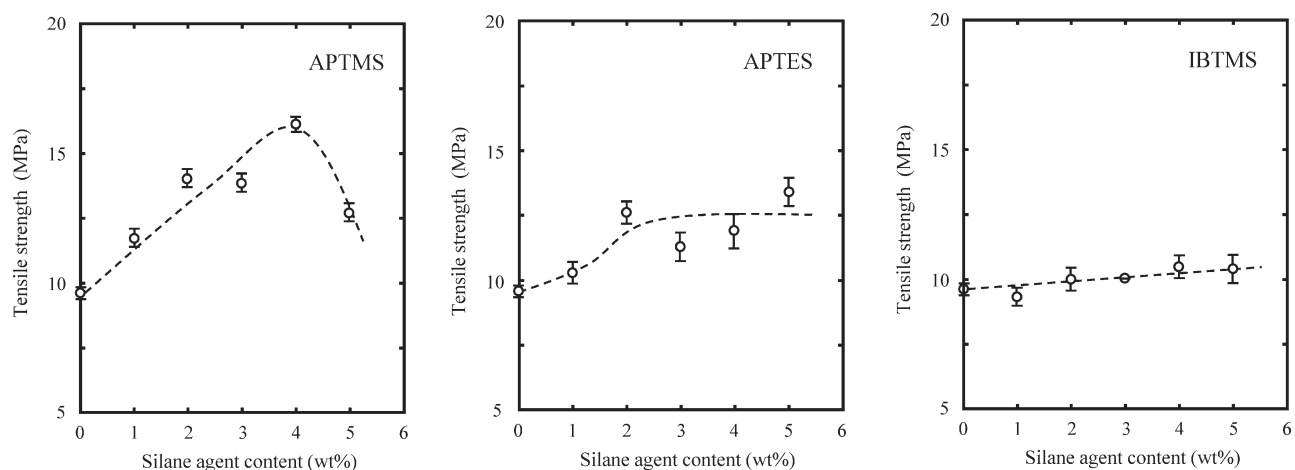

Figure 7 Tensile strengths of SPP (70 wt %)/silanized FC (30 wt %) composites with various contents of APTMS, APTES, and IBTMS silane agents, respectively: SPP (100 wt %) = 14.2 ± 0.2 MPa.
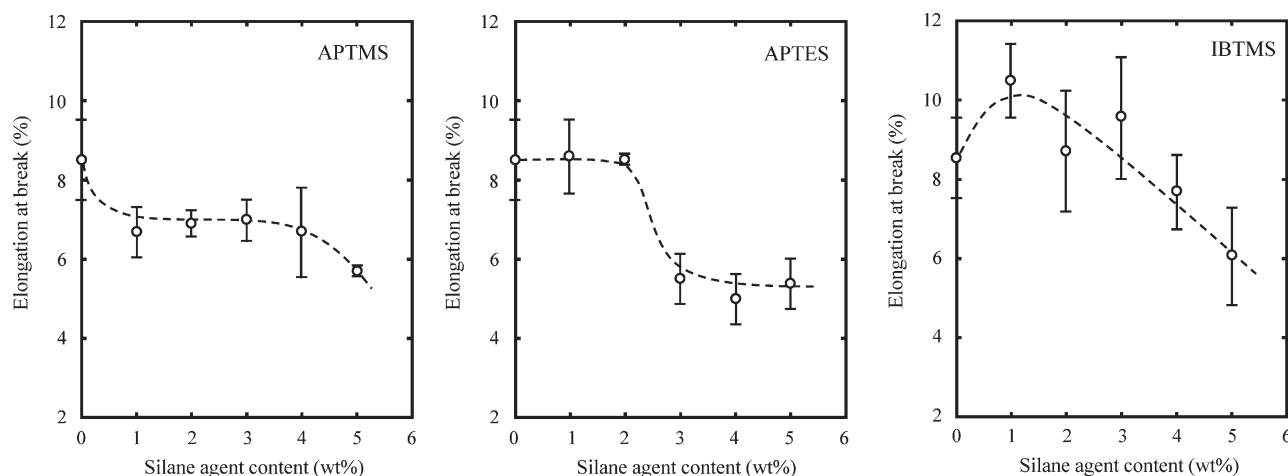
Figure 8 Elongations at break of SPP (70 wt %)/silanized FC (30 wt %) composites with various contents of APTMS, APTES, and IBTMS silane agents, respectively: SPP (100 wt %) = 200 over %.

between the SPS and the silanized FC with IBTMS. As mentioned above, the reactivity between the FC and IBTMS is lowest, resulting that the amount of the linked IBTMS is considerably small even with the 5 wt % solution. Therefore, the interface has many defects (i.e., naked FC point). The poor tensile properties are due to the lower coverage although the composite shows better compatibility. In addition, it is difficult to produce the polymeric silanol structure (see "Structure B2" in Fig. 2) because of the existence of the sterically bulky isobutyl group. The polymeric silanol formation can be estimated by the Si/O atomic ratio obtained by the XPS measurements.[25] The Si/O atomic ratios are 0.42 and 0.11 when the FC is treated with the 5 wt % APTMS and the 5 wt % APTES, respectively (see Table I). These atomic ratios are much higher than that of the 5 wt % IBTMS. The ratio of 0.33 is theoretically expected in the absence of intermolecular silanol formation. Considering from the higher Si/O atomic ratio, there certainly exists the polymeric silanol structure on the surface of the silanized FC with APTMS. In the case of the silanized FC with the 5 wt % APTES, the ratio is considerably lower, suggesting that the amount of polymeric silanol formation is smaller. Whereas, the ratio (0.06) with the 5 wt % IBTMS is much lower, suggesting that there hardly exists the polymeric silanol formation. The tensile strength of the monomeric silanol structure (Structure A2) must be inferior to that of the polymeric one because the applied stress concentrates on the only one ether linkage. The less tensile strength is due to the bulky chemical structure of IBTMS.

CONCLUSIONS

With the aim of improving compatibility between SPP and FC, the effects of chemical structure of sil-

ane coupling agent on the reactivity for the surface hydroxyl group on the FC were studied by XPS measurement. Among the three kinds of the silane coupling agent, APTMS showed the highest reactivity with the surface hydroxyl group on the FC. By comparing with the reactivities with APTES and with IBTMS, it was found that the linear silane compound with methoxyl group, e.g., APTMS, is suitable for the reaction. Although the morphology of the SPP/FC composite is hardly affected by the difference in the kinds of the silane coupling agent, the tensile properties were considerably different. In particular, in the case of using higher silane coupling agent solution (over 3 wt %), the chemical structure of silane coupling agent certainly affected the tensile properties of the SPP/silanized FC composites. In the case of the SPP/silanized FC composites with IBTMS, the Young's moduli had a large margin of error as compared with those with APTMS and with APTES. In addition, the tensile strengths were lower, and the elongations at break were higher and also had a large margin of error. The unique tensile behavior was due to the poor interface strength between the SPS and the silanized FC with IBTMS. It was found that the tensile properties of the SPP/silanized FC composite were distinctly affected by the reactivity between the surface hydroxyl group on FC and the silane coupling agent.

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