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Aggregation structure and molecular motion of (glass-fiber/matrix nylon 66) interface in short glass-fiber reinforced nylon 66 composites

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Abstract

Aggregation structure and thermal molecular motion of an adhered polymer layer on a glass-fiber (GF) surface after a removal of nylon 66 from a short glass-fiber reinforced nylon 66 were studied on the basis of photoacoustic spectroscopy–infrared spectroscopy (PAS–IR), pyrolysis–gas chromatography (Py–GC), X-ray photoelectron spectroscopy (XPS) and scanning viscoelasticity microscopy (SVM). PAS–IR, Py–GC and XPS measurements of the GF surface showed the presence of strongly adhered nylon 66 layer on the surface of aminosilane-treated GF. The glass transition temperature, T_g, of the adhered nylon 66 layer on the glass-fiber surface was directly evaluated on the basis of SVM measurement. In the case of the GF treated with an aminosilane coupling agent and a sizing agent, the magnitude of T_g at the (GF/nylon 66) interfacial layer was higher than that of the matrix nylon 66 due to the effective restriction of thermal molecular motion of nylon 66 at the (GF/nylon 66) interfacial layer. It is reasonable to consider that the sizing agent affects the strong interfacial interaction between a glass-fiber surface and matrix nylon 66 with covalent bond formation accompanying the network structure formation.

Keywords: Nylon 66; Glass-fiber reinforced composite; Interface

1. Introduction

Polymer composites are widely used as high performance structural materials. In engineering applications, metal parts have been replaced by thermoplastic composites reinforced with short glass-fibers because of reasonable cost and weight reductions. It is important to improve the mechanical properties as well as the long-term reliability of glass-fiber (GF) reinforced composites. In the case of glass-fiber reinforced composites, micro-failure occurs at an (GF/matrix resin) interface, which is generated by stress concentration. Therefore, the mechanical properties of composites are strongly influenced by the mechanical strength of (GF/matrix) interface [1–7]. Silane coupling agents are widely used for various surface treatments of glass-fibers. The surface treatment of glass-fiber by coupling agent induces higher strength and fracture toughness. Several theoretical models of interface strengthening such as chemical bonding [4], interpenetrating network [5–7] and so forth, have been proposed. However, the models at the (GF/matrix) interface have not been verified yet with actual experimental analysis, especially for thermoplastic composites.

There have been some reports on chemical structure at the (GF/matrix) interface [4–13]. Ishida and Koenig [5,7,8] had studied the interaction of resin and/or silane coupling agents at the glass-fiber surface by using a Fourier transform infrared spectroscopy (FT-IR) and proposed the existence of multilayer structure of the silane coupling agent. Ikuta et al. [9] reported that the change in chemical structure of the matrix resin around silane-finished glass-fibers was observed by using FT-IR and the silane affected the curing process of the thermosetting resin over the region greater than the thickness of the silane interphase. Wang and Jones [10–13] studied the interaction between aminosilane and epoxy resin at the E-glass plate or fiber surface by means of time-of-flight secondary ion mass spectrometry (TOF-SIMS) and X-ray photoelectron spectroscopy (XPS). They confirmed the formation of multilayer of aminosilane on the glass-fiber surface. They also found that the monolayer of epoxy resin was chemically bound to the aminosilane through covalent bonds between the epoxy end groups of the resin and the amino groups of the silane coupling agent. However, little attention has been paid to the effect of sizing

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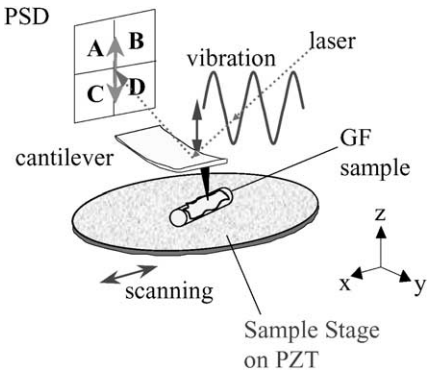

Fig. 1. Schematic representation of SVM measurement.

agents with respect to (GF/matrix) aggregation structure of commercial thermoplastic composites. Furthermore, thermal molecular motion of the interfacial layer on the glass-fiber surface of the thermoplastic composites has not been sufficiently discussed.

Scanning force microscopy (SFM) is a new technique to evaluate the surface morphology of materials based on the various forces acting between cantilever tip and sample surface such as van der Waals, electrostatic, frictional forces and so on [14,15]. In our previous studies [16–19], the surface molecular motion of monodisperse polystyrenes (PS) with different molecular weights has been investigated on the basis of scanning viscoelasticity microscopy (SVM). Fig. 1 shows the schematic representation of the SVM measurement. SVM is carried out in a repulsive force region of the force curve, and the sinusoidal modulation of the tip indentation is applied to the polymer surface [18]. SVM measurement provides the information about the dynamic viscoelastic properties at the polymer surface by measuring the force amplitude and the apparent phase lag between imposed displacement and detected force signals. Although thermal molecular motion at the polymer surface has been analyzed by using SVM, the composite interface has not been extensively studied yet. If the glass transition temperature at the (GF/matrix) interface can be directly evaluated on the basis of SVM measurement, the information on thermal molecular motion at the interfacial region can be obtained. The investigation of interfacial molecular motion at the composite interfaces can attract great attention for the improvement of composite performance.

The purpose of this study is to investigate the aggregation structure of the polymer layer on the glass-fiber surface after a removal of weakly adhered nylon 66 from the short glass-fiber reinforced nylon 66 composites on the basis of PAS–IR, Py–GC and XPS. Furthermore, thermal molecular motion of the interfacial layer adhered on the glass-fiber surface was studied on the basis of temperature-dependent SVM.

2. Experimental

2.1. Materials and glass-fiber preparation

The composite specimens were injection-molded from nylon 66 containing 33 wt% glass-fiber reinforcements that are commercially treated with various chemical agents. Table 1 shows the surface treatments of glass-fiber reinforcement, the tensile strength and fatigue strength of composites. Surface non-treated glass-fiber (non-treated GF), surface aminosilane-treated glass-fiber (CP_1-GF, CP_2-GF) and surface aminosilane-treated glass-fiber with sizing agent ((CP + SZ)-GF) were used. Then, the aminosilane treating concentration for CP_2-GF is higher than that for CP_1-GF. The sizing agent used was maleic anhydride dispersion-based sizing agent. The diameter of the E-glass-fiber was 10 μm. The matrix of nylon 66 was removed from the (GF/nylon 66) composites with phenol at 313 K. Phenol was selected because it could dissolve the matrix nylon 66 well without corroding the interfacial layer on the glass-fiber surface. The matrix nylon 66 weakly attached to the glass-fiber surface was almost completely removed by repeating the extraction treatment with phenol. Then, the glass-fibers recovered from the composites were washed with methanol and were dried under vacuum at 323 K.

2.2. Characterization of aggregation structure on glass-fiber surface

The amount of adhered layer on the glass-fiber surface after a removal of nylon 66 from the composites was measured by ignition loss (Ig. Loss), ΔW of glass-fibers at 913 K for 1 h according to JIS standard R3420. Also, the pyrolysis products of adhered nylon 66 layer bonded to the glass-fiber surface was investigated by pyrolysis–gas chromatography (Py–GC) analysis at 863 K using HP5890

Table 1
Surface treatments of glass-fiber reinforcement, tensile strength and fatigue strength of (GF/nylon 66) composites

GF/nylon 66 sample	Chemical treatments of GF surface	Tensile strength at 296 K (MPa)	Cycles to failure under tension–compression fatigue at 303 K, 10 Hz and 70 MPa (cycles)
Non-treated GF	Non-treated	110	2.0×10^3
CP_1-GF	Aminosilane (low conc.)	143	4.7×10^3
CP_2-GF	Aminosilane (high conc.)	188	3.0×10^4
(CP + SZ)-GF	Aminosilane + sizing agent	193	1.8×10^5

(Hewlett Packard Co. Ltd) with JHP-3S (Japan Analytical Industry Co. Ltd).

The morphology of the glass-fiber surface was observed with atomic force microscopy (AFM). The AFM equipment was SPA 300 (Seiko Instruments Industry Co. Ltd) with a SPI 3700 controller. Contact-mode AFM observation was carried out at 293 K in air under a repulsive force region. A commercially available silicon nitride (Si_3N_4) tip on a rectangular cantilever with the bending spring constant of 0.09 N m^{-1} (Olympus Co. Ltd) was used.

The adhered polymer layer on the glass-fiber surface was analyzed by photoacoustic spectroscopy–infrared spectroscopy (PAS–IR). PAS–IR was measured in He atmosphere with FT/IR-500 (Jasco Co. Ltd). The spectra were recorded at a resolution of 4 cm^{-1} throughout the spectra range from 3500 to 1500 cm^{-1} with the total of 128 scans.

The coverage ratio of the glass-fiber surface with adhered nylon 66 was evaluated on the basis of XPS. The XPS spectra were obtained with VG ESCALAB 200-X (VG Scientific Co. Ltd), by using a Mg Kα X-ray source operating at 15 kV and 20 mA. The core electron spectrum of neutral carbon at 285.0 eV was employed as a reference for the calculation of a binding energy. The relative surface concentration of atoms were calculated from the integral intensity of each element in the narrow scan spectra.

2.3. Direct measurement of thermal molecular motion of interfacial layer on glass-fiber surface

Thermal molecular motion of the adhered nylon 66 layer on the glass-fiber surface was directly investigated on the basis of temperature-dependent SVM measurement. The glass transition temperature, T_g, of the adhered nylon 66 at the (GF/matrix) interface was evaluated as the temperature at which the temperature-dependence of the apparent phase lag between imposed displacement and detected force signals started to increase, in other words, the onset temperature. The specimens used for SVM measurement were the glass-fibers after a removal of nylon 66 from the composites with phenol. The SVM equipment was SPA 300HV (Seiko Instruments Industry Co. Ltd) with SPI 3800 controller and modulation system. Temperature-dependent SVM measurement was carried out in a temperature range from 273 to 450 K under vacuum and a repulsive force of ca. 1 nN. The modulation frequency and the modulation amplitude were 4 kHz and 1.0 nm, respectively. A silicon nitride (Si_3N_4) rectangular cantilever with the bending spring constant of 0.09 N m^{-1} (Olympus Co. Ltd) was used. Both sides of the cantilever were coated with gold in order to minimize a bending curvature of the cantilever due to different thermal expansion coefficients between Si_3N_4 and gold.

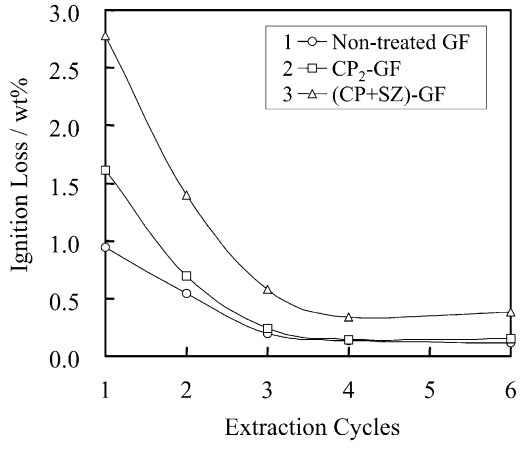

Fig. 2. Extraction cycle dependence of weight loss, ΔW by ignition loss for various (GF/nylon 66) composites.

3. Results and discussion

3.1. Preparation of glass-fiber surface strongly adhered with nylon 66

The matrix nylon 66 is usually removed from the short glass-fiber reinforced nylon 66 composites with various solvents, such as formic acid, *m*-cresol and phenol, in order to obtain the glass-fiber surface strongly or chemically adhered with nylon 66. In this experiment, phenol was selected so as to dissolve the matrix nylon 66 selectively without corroding the interfacial layer of nylon 66 on the glass-fiber surface. It was confirmed with FT-IR that the aminosilane coupling agent was not detected in the solution even after phenol extraction. Fig. 2 shows the extraction cycles dependence on the ignition loss, ΔW for the various (GF/nylon 66) composites. The amount of adhered layer on the glass-fiber after a removal of matrix nylon 66 from the composites became to be constant by repeating the extraction treatment after three cycles. This clearly indicates that the matrix nylon 66 weakly attached to the glass-fiber surface was almost completely removed by the extraction treatment with phenol. Then, glass-fiber surface strongly or chemically adhered with nylon 66 was obtained. Fig. 2 apparently showed that the amount of adhered nylon 66 on the glass-fiber surface depended on the surface treatments of GF. The amount of adhered nylon 66 layer was highest for the composite with (CP + SZ)-GF in comparison with the ones with non-treated GF and CP_2-GF. Therefore, it seems reasonable to consider that the strongly adhered nylon 66 layer can be formed on the glass-fiber surface, especially for the case of the composite with (CP + SZ)-GF.

3.2. Morphology of adhered nylon 66 layer on glass-fiber surface

The AFM observation was carried out under a repulsive force region. Fig. 3 shows AFM images on the glass-fiber surface for the various (GF/nylon 66) composites under a repulsive force of ca. 0.1 nN. AFM image was not dependent on the reference force in the repulsive force region of

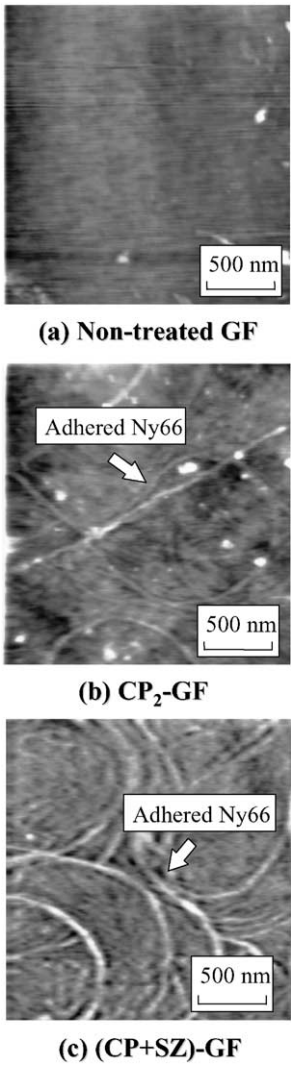

Fig. 3. AFM images of glass-fiber surface for various (GF/nylon 66) composites.

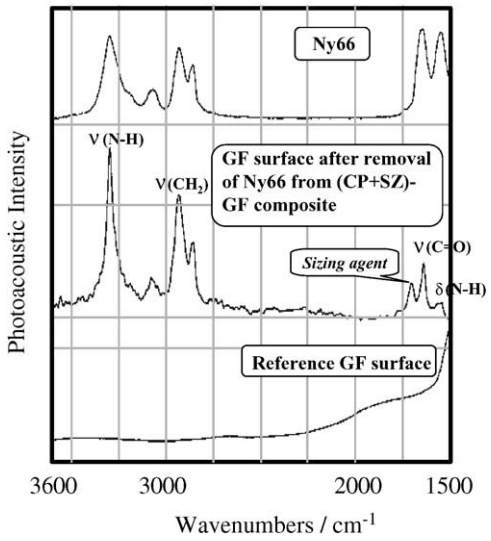

Fig. 4. PAS–IR spectra of matrix nylon 66, glass-fiber surface of (CP + SZ)-GF and reference glass-fiber without any treatments of coupling agent or sizing agent.

0.1–5 nN. In the case of the non-treated GF, the smooth glass-fiber surface was observed, since the strongly adhered layer was scarcely formed on the GF surface. On the other hand, in the case of the composites with CP_2-GF and (CP + SZ)-GF, the strongly adhered layer was observed on the glass-fiber surface as shown in Fig. 3(b) and (c). The fibrous texture was probably formed by crystallization during the solvent evaporation after extraction process. The disappearance of fibrous texture above 533 K suggested the melting of fibrous crystalline aggregates.

3.3. Aggregation structure of interfacial layer on glass-fiber surface

In order to characterize the chemical composition on the glass-fiber surface, the glass-fiber surface was analyzed by FT-IR spectrometer with photoacoustic detector. IR spectra with extremely high signal-to-noise ratios can be obtained by using the high sensitivity PAS–IR spectrometer. Fig. 4 shows the PAS–IR spectra of matrix nylon 66, the glass-fiber surface of (CP + SZ)-GF and the reference glass-fiber without any treatments of coupling agent or sizing agent. The IR spectrum of nylon 66 in the region of 3500–1500 cm^{-1} shows several characteristic bands at ca. 3300 cm^{-1} due to hydrogen-bonded N–H stretching, ca. 1640 cm^{-1} due to amide I, C=O stretching and ca. 1545 cm^{-1} due to N–H bending, respectively. Though the reference GF did not exhibit any characteristic absorption peaks of nylon 66, the (CP + SZ)-GF surface exhibited the characteristic bands of nylon 66, even after a removal of matrix nylon 66 from the composite. Furthermore, the sharp PAS–IR band for the C=O stretching was detected at ca. 1700 cm^{-1} due to an existence of maleic anhydride dispersion-based sizing agent. Fig. 4 clearly indicates that the strongly adhered nylon 66 grafted onto the glass-fiber surface in the (CP + SZ)-GF composite was formed with sizing agent. Therefore, it is reasonable to consider that the sizing agent induces the reaction of aminosilane with the matrix nylon 66 at the (GF/nylon 66) interface.

The amount of the nylon 66 component in the adhered layer on the glass-fiber surface was characterized on the basis of Py–GC measurement. Since the most abundant species in the pyrolysis products of nylon 66 is cyclopentanone [20,21], the amount of strongly adhered nylon 66 was calculated from that of cyclopentanone generated upon volatilizing nylon 66 adhered on the glass-fiber surface at 863 K. The amount of cyclopentanone was calibrated using nylon 66 dissolved in hexafluoroisopropanol (HFIP). Table 2 shows the amount of adhered nylon 66 layer on the glass-fiber surface on the basis of Ig. Loss and Py–GC. In the case of non-treated GF, the weight loss, ΔW at 913 K was measured. However, the cyclopentanone was not detected by Py–GC at 863 K. This means that nylon 66 did not exist

Table 2
Amount of adhered nylon 66 layers on glass-fiber surface based on Ig. Loss and Py–GC

GF/nylon 66 sample	Amount of adhered nylon 66 layer on GF surface	
	ΔW by Ig. Loss (wt%)	Amount of cyclopentanone by Pr–GC (wt%)
Non-treated GF	0.13	0
CP_1-GF	0.14	0.15
CP_2-GF	0.14	0.19
(CP + SZ)-GF	0.37	0.38

on the non-treated GF surface but the volatilizing material. The amounts of adhered nylon 66 layer of CP_1-GF, CP_2-GF and (CP + SZ)-GF were ca. 0.15, ca. 0.19 and ca. 0.38%, respectively. It is apparent that the amount of adhered nylon 66 layers on the aminosilane-treated GF with sizing agent was higher than that of the ones without sizing agent. Under assumption of the uniform coverage of glass-fiber surface with nylon 66, the average thickness of adhered nylon 66 layers can be calculated from the surface area and volume of a glass-fiber. The average thickness of the adhered nylon 66 layer on a glass-fiber surface for CP_1-GF, CP_2-GF and (CP + SZ)-GF was calculated to be ca. 9, ca. 11 and ca. 22 nm, respectively. Since the remaining nylon 66 on the glass-fiber surface after the extraction treatment with phenol should be strongly adhered to the glass-fiber surface, it is reasonable to consider that the nylon 66 layer is grafted onto the aminosilane-treated glass-fiber surface with sizing agent and also, the maleic anhydride dispersion-based sizing agent induces the reaction of aminosilane with matrix nylon 66.

The XPS spectra were obtained in order to characterize the relative atomic concentration at the glass-fiber surface. For XPS measurements, the glass-fibers were recovered after the extraction of matrix nylon 66 with phenol from the composites. Table 3 shows the relative atomic composition of all elements for various glass-fibers based on XPS measurements. The phenol-cleaned E-glass-fiber was used as a reference glass-fiber. Fig. 5 shows the schematic representation of relative atomic composition for the glass-fiber surface. The constituent elements of E-glass-fiber are oxygen, silicon, aluminum, calcium, boron and sodium as shown in Fig. 5. Since hydrocarbons commonly exist as

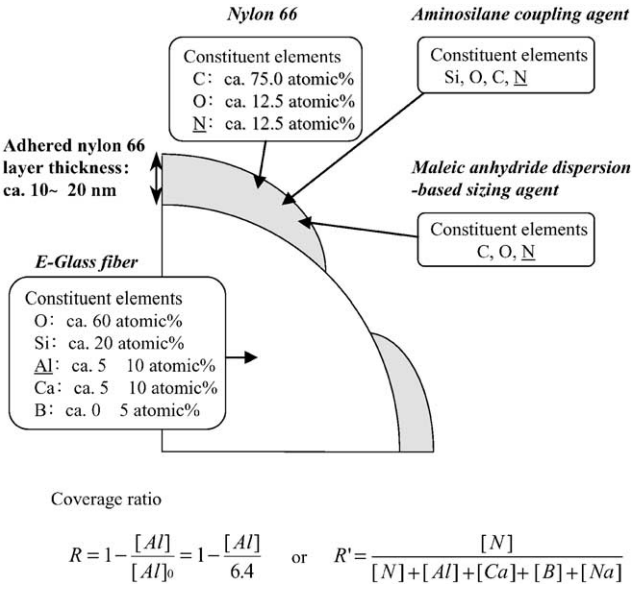

Fig. 5. Schematic representation of relative atomic surface composition for glass-fiber surface.

contaminations on the glass-fiber surface, the carbon was also detected on the E-glass-fiber surface. Also, non-treated GF is composed of a silica-rich surface as indicated by the high silicon and oxygen concentrations as mentioned in Table 3. Furthermore, the surface carbon and nitrogen concentrations were low for the non-treated GF. Therefore, these results apparently indicate that the small amount of nylon 66 adhered on glass-fiber surface for non-treated GF. On the other hand, in the cases of CP_1-GF, CP_2-GF and (CP + SZ)-GF, the surface carbon and nitrogen concentrations were higher than that for non-treated GF and also, the silicon and aluminum surface concentration were lower than that for non-treated GF. The presence of a significant amount of nitrogen concentration indicated that the strongly adhered nylon 66 layer with aminosilane coupling agent and/or sizing agent was formed on the glass-fiber surface. Since a higher amount of the nylon 66 layer was present on (CP + SZ)-GF compared with CP_1-GF and CP_2-GF, the silicon and aluminum concentrations of (CP + SZ)-GF became relatively lower than those of CP_1-GF and CP_2-GF.

The aluminum was detected by XPS due to one of the constituent elements of E-glass-fiber. Therefore, the

Table 3
Relative atomic composition of all elements and coverage ratio for various glass-fibers based on XPS measurement

GF/nylon 66 sample	Relative atomic composition (at.%)								Coverage ratio	
	C	N	O	Si	Al	Ca	B	Na	R	R'
Non-treated GF	14.4	1.2	51.7	21.0	6.1	2.9	2.0	0.9	0.05	0.09
CP_1-GF	48.9	7.9	26.7	11.0	2.8	1.6	1.0	0.1	0.56	0.59
CP_2-GF	61.2	10.0	18.8	6.9	1.8	1.0	0.4	–	0.72	0.76
(CP + SZ)-GF	71.5	10.9	14.0	2.7	0.6	0.3	–	–	0.91	0.92
Reference GF	12.5	0.8	51.6	22.3	6.4	3.3	2.6	0.5	0	0.06
Nylon 66	76.0	12.0	11.9	–	–	–	–	–	–	–

coverage ratio on the glass-fiber surface with adhered nylon 66 was examined on the basis of the concentration of aluminum. Here, the coverage ratio corresponds to the incompletely covered surfaces with nylon 66, the partially covered surfaces with nylon 66 and/or the presence of very thin layer of nylon 66 through which photoelectron can escape. Two following assumptions were made in order to calculate the coverage ratio on the glass-fiber surface with adhered nylon 66. The first assumption was that the coverage ratio on the glass-fiber surface with adhered nylon 66 was 0% when the surface aluminum concentration for the reference E-glass-fiber was 6.4 at.% as shown in Table 3. The second one was that the surface aluminum concentration on the glass-fiber was 0 at.% when the glass-fiber surface was completely covered with adhered nylon 66 over ca. 10 nm thickness through which photoelectron cannot escape. The coverage ratio on the glass-fiber surface with adhered nylon 66, R was calculated by Eq. (1)

$$R = 1 - \frac{[\mathrm{Al}]}{[\mathrm{Al}]_0} = 1 - \frac{[\mathrm{Al}]}{6.4} \quad (1)$$

where [Al] and $[Al]_0$ are the surface aluminum concentration of the composite sample and the reference E-glass-fiber, respectively. Also, the coverage on the glass-fiber surface with adhered nylon 66, R' was calculated from the aluminum, calcium, boron, sodium and nitrogen concentrations on the basis of XPS measurement, as given by Eq. (2).

$$R' = \frac{[\mathrm{N}]}{[\mathrm{N}] + [\mathrm{Al}] + [\mathrm{Ca}] + [\mathrm{B}] + [\mathrm{Na}]} \quad (2)$$

where [Al], [Ca], [B], [Na] and [N] are the aluminum, calcium, boron, sodium and nitrogen concentrations, respectively. The coverage ratio, R and R' for the various glass-fibers are shown in Table 3. Fig. 6 shows the relationship between the coverage ratio, R on the basis of the surface aluminum concentration and R' on the basis of the surface nitrogen concentration. Since the relationship between R and R' followed a linear relation, the accuracy of the coverage ratio on the basis of XPS measurement is high. The coverage ratio increased with an increase in the amount of adhered nylon 66 layer measured by Py–GC as mentioned in Tables 2 and 3. It was revealed from Table 3 that about 90% of the glass-fiber surface was covered with the adhered nylon 66 layer due to the presence of both the aminosilane coupling agent and sizing agent in the case of (CP + SZ)-GF. It seems reasonable to consider that the maleic anhydride dispersion-based sizing agent induces the interfacial strong adhesion of nylon 66 on the glass-fiber surface and the formation of network structure due to grafting reaction between aminosilane and matrix nylon 66.

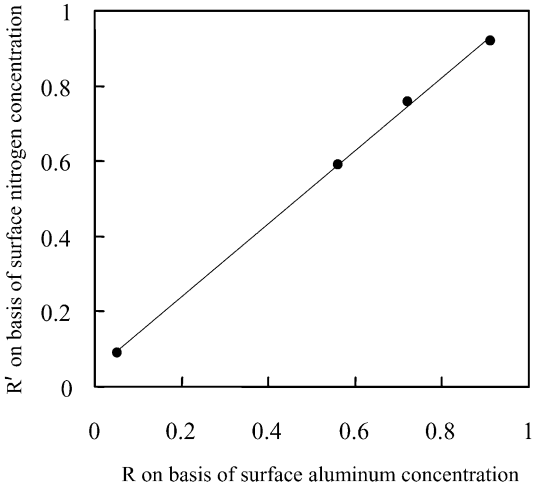

Fig. 6. Relationship between coverage ratio on glass-fiber surface with adhered nylon 66, R (based on [Al]) and R' (based on [N]).

3.4. Thermal molecular motion of interfacial layer on glass-fiber surface

SVM was carried out in a repulsive force region of the force curve, and the modulation of the tip indentation was applied sinusoidally to the glass-fiber surface. Then, the dynamic viscoelastic properties at (GF/nylon 66) interface could be directly evaluated by measuring the force amplitude and the apparent phase lag between stimulation displacement and response force signals. Therefore, thermal molecular motion of the adhered nylon 66 layers on the glass-fiber surface after a removal of weakly adhered nylon 66 from the composites was directly investigated on the basis of the temperature-dependent SVM. Fig. 7 shows the temperature dependence of the apparent phase lag

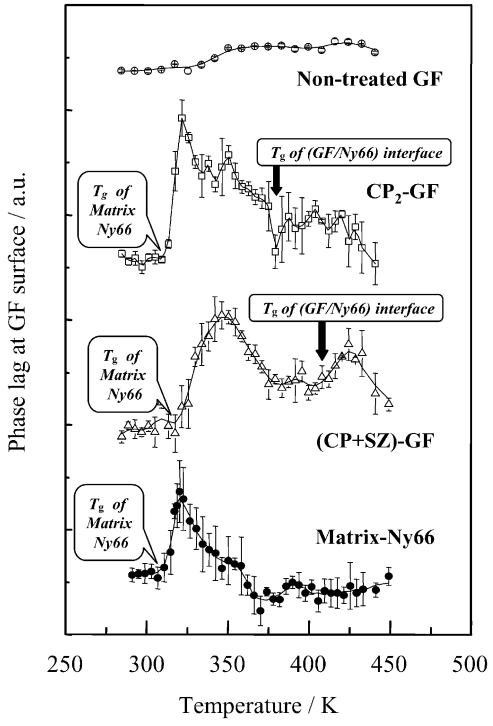

Fig. 7. Temperature dependence of apparent phase lag between stimulation deformation and response force signals at surface for non-treated GF, CP_2-GF, (CP + SZ)-GF and matrix nylon 66.

between stimulation deformation and response force signals at the surface for non-treated GF, CP_2-GF, (CP + SZ)-GF and matrix nylon 66. The glass transition temperature, T_g, of nylon 66 was evaluated as the temperature at which the temperature-dependence of the apparent phase lag between imposed displacement and detected force signals started to increase, that is, the onset temperature. The T_g observed at ca. 315 K could be ascribed to the micro-Brownian motions of the matrix nylon 66 (α_a-absorption). The non-treated GF showed no obvious viscoelastic absorption peak at the 273–453 K temperature range. In the case of the CP_2-GF, the T_g ascribed to the micro-Brownian motions of the matrix nylon was observed as steep increase in phase lag at ca. 315 K, and the T_g ascribed to the adhered nylon 66 layer was observed as slight increase in phase lag at ca. 375 K. In the case of the (CP + SZ)-GF, the two onset temperatures at ca. 320 and ca. 390 K were assignable to the micro-Brownian motions of the matrix nylon 66 and the strongly adhered nylon 66 layer to the GF surface, respectively. Since T_g of the matrix nylon for CP_2-GF and (CP + SZ)-GF was similarly observed at ca. 315–320 K, there is not any substrate effect on the measured surface T_g even though the thickness of the adhered nylon 66 layer is as thin as 10 nm. Fig. 7 apparently indicates that the T_g of adhered nylon 66 on the glass-fiber surface is remarkably higher than that of the matrix nylon 66 due to an effective restriction of thermal molecular motion of nylon 66 at the (GF/nylon 66) interfacial layer. Fig. 8 shows the schematic representation of the (GF/nylon 66) interfacial layer for non-treated GF, CP-GF and (CP + SZ)-GF. In the case of non-treated GF, the hydrogen bonds are present between glass-fiber and matrix nylon 66, but the matrix nylon 66 weakly attached to the glass-fiber surface is almost completely removed with phenol. On the other hand, in the case of CP-GF and (CP + SZ)-GF, the hydrogen bonds and the covalent bonds are present between glass-fiber and matrix nylon 66 due to the effective restriction of thermal molecular motion of nylon 66. Especially, the maleic anhydride dispersion-based sizing agent induces the cross-linking reaction between the amine groups of aminosilane and the amine or amide groups of nylon 66 during melting process and the formation of the covalent bonds and network structure on the glass-fiber surface. Therefore, these network structures also increase the interfacial adhesion and aid stress transfer between glass-fiber and matrix nylon 66 in composite. Thus, it seems reasonable to conclude that thermal molecular motion at (GF/nylon 66) interface is restricted due to the presence of the covalent bonds and hydrogen bonds with the formation of network structure, since the multifunctional sizing agent can form cross-links between aminosilane coupling agent and matrix nylon 66.

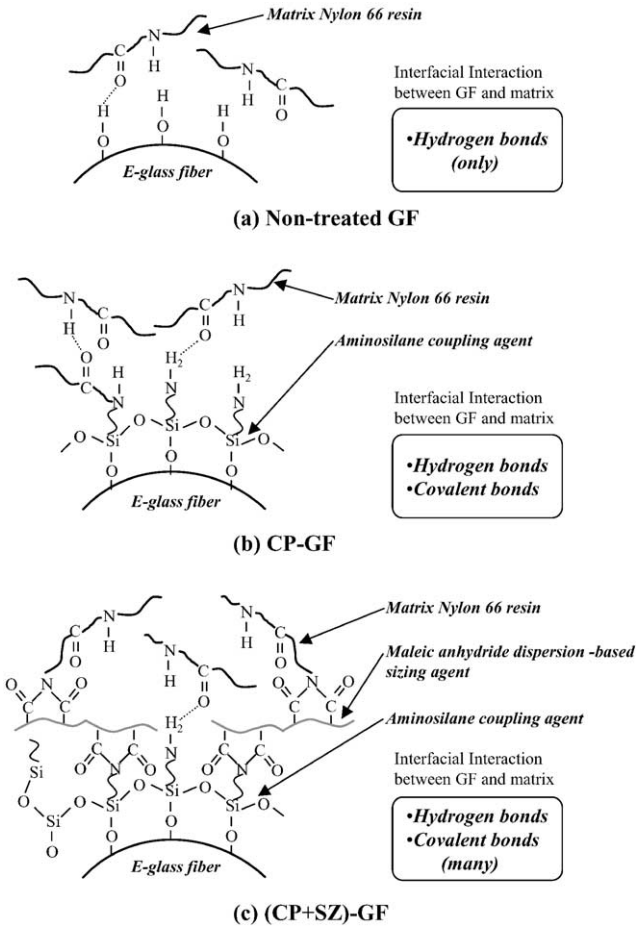

Fig. 8. Schematic representation of (GF/nylon 66) interfacial layer models for non-treated GF, CP-GF and (CP + SZ)-GF.

4. Conclusion

The aggregation structure on the glass-fiber surface after a removal of nylon 66 from short glass-fiber reinforced nylon 66 were studied on the basis of PAS–IR, Py–GC and XPS. It was revealed that the strongly adhered nylon 66 grafted onto the aminosilane-treated glass-fiber surface with sizing agent was formed. The direct information of thermal molecular motion at the composite interfaces could be obtained on the basis of SVM. The T_g at (GF/nylon 66) interfacial layer are higher than that of the matrix nylon 66 due to the effective restriction of thermal molecular motion of nylon 66 at the (GF/nylon 66) interfacial layer. It was concluded that the sizing agent affects the strong interfacial interaction between glass-fiber surface and matrix nylon 66 with the covalent bond formation accompanying network structure formation.

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