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Hayashi Award Winning Paper

Effect of glass filler surface treatment on flexural properties of polypropylene composites

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Abstract—The effect of glass particle surface treatment on the flexural properties of glass particle reinforced polypropylene composites was investigated. The glass particles used were glass beads, glass milled fibers (average length 26 μm), and glass cut fibers (average length 100 μm). The glass particles were treated with six kinds of silane coupling agents with different organic functional groups. The wettability of glass plates treated with these coupling agents was also estimated by measurement of contact angles using thirteen liquids. It was found that composite flexural properties correlated with wettability of the glass plate when both the glass particles and glass plate were treated with the same coupling agent. For the case where the organic functional group comprised an alkyl group, the composite flexural rigidity and strength decreased with increasing critical surface tension calculated from the contact angles of halogen-containing liquids.

Keywords: Polypropylene; glass filler; surface treatment; flexural properties; wettability.

1. INTRODUCTION

Polypropylene (PP) is widely used as a material for automobile and other applications due to its mechanical properties, thermal properties, cost performance, and recycling potential. PP is often reinforced by various inorganic fillers in order to increase the stiffness, strength, and dimensional stability at elevated temperature. Characteristics of such composites depend on the interface and interphase between organic matrix (PP) and inorganic fillers. Thus, design of the interface and interphase is of great importance.

The influence of the interface and interphase between PP and fillers on the mechanical properties of PP composites has been widely studied. For example, Avella *et al*. [1] investigated the influence of glass fibers on crystallization together with properties of homo PP and acrylic modified PP using nucleating agents. Thomason and van Rooyen [2, 3] studied the effect of thermal conditions on transcrystallization of PP at the fiber interface for various fibers. Regarding interfacial bonding, Daemen and den Besten [4] investigated the influence of sizing agents on mechanical properties of PP composites whilst Olsen and Hyche [5] proposed new coupling agents. However, there is a relative dearth of information concerning the effect of wettability on mechanical properties of PP composites.

In the present paper, the following have been investigated:

(1) The wettability of glass plates treated with six silane coupling agents with different organic functional groups.

(2) The influence of glass particle surface treatment on the flexural properties of PP composites.

(3) The relationship between the wettability of glass plates and flexural properties of composites whose glass particles were treated with the same coupling agents as for the glass plates.

2. EXPERIMENTAL

2.1. Materials

Polypropylene pellets were supplied by Chisso Co. (K1008, $M_{\mathrm{w}} = 190,000$, Melt Index $= 10$ g/10 min) whilst three types of glass particle were used for reinforcement as shown in Table 1. Soda-lime glass beads were supplied by Toshiba Balotieni Co.whilst E-glass milled fiber and E-glass cut fiber were supplied by Nittobo Co.. Glass beads and milled fibers were used either ‘as received’ or else following treatment with silane coupling agents whose organic functional groups were different from each other, as indicated in Table 2. Glass cut fibers were used following 1 h of heat cleaning at 350°C as they had already been treated with another silane when received. Silane coupling agents Nos 1–4 in Table 2 were supplied by Toray Dow Corning Silicon Co. and Nos 5 and 6 from Shin-etsu Silicon Co. The silane concentration in the coupling agent solutions, achieved by dissolving the respective silane in distilled water, was 1.0wt%. The glass particles were dispersed into the silane solution and then collected in a filter and dried at 110°C for 20 min. Following this, the particles were washed with an amount of methanol to remove the physiadsorbed silane from the glass surface [6].

PP composites were prepared as follows: PP pellets and glass particles were mixed using hot kneading rollers at 190°C for 3 min. The compound sheet was molded using a hot press at 210°C (2.06 MPa, 1 min.) after being preheated for 4 min. The pressed composite was transferred from the hot press mold to a cold press at approximately 25°C and pressed at 2.1 MPa.

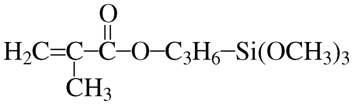
2.2. Determination of contact angles

Contact angles were determined using glass plates made of soda-lime microscope slide glass, whose cut size was 25 mm × 50 mm, and the dropping liquid

Table 1.
Glass fillers used for experiments

Filler	Grade	Formation	Pretreatment
Glass bead (GB)	GB731	average particle diameter: 30 μm	untreated
Glass milled fiber (GMF)	PFB-001	diameter: 9 μm, average length: 26 μm	untreated
Glass cut fiber (GCF)	SS05-404	diameter: 10 μm, average length: 100 μm	heat cleaned at 350°C, 1 h

Table 2.
Silane coupling agents used for surface treatment of glass

No.	Grade	Composition	
1	SZ6070	Methyltrimethoxysilane	$CH_3-Si(OCH_3)_3$
2	AY43-203M	n-Propyltrimethoxysilane	$n\text{-}C_3H_7-Si(OCH_3)_3$
3	AY43-210MC	n-Decyltrimethoxysilane	$n\text{-}C_{10}H_{21}-Si(OCH_3)_3$
4	AY43-216MC	n-Hexadecyltrimethoxysilane	$n\text{-}C_{16}H_{33}-Si(OCH_3)_3$
5	KBM903	γ-Aminopropyltrimethoxysilane	$H_2N-C_3H_6-Si(OCH_3)_3$
6	KBM503	γ-Methacryloxypropyltrimethoxysilane	 $H_2C{=}\underset{CH_3}{C}-\overset{O}{\overset{\Vert}{C}}-O-C_3H_6-Si(OCH_3)_3$

method [7, 8]. Liquids with volume 1.8 mm^3 were dropped vertically using a microsyringe and the contact angle was measured using a contact-angle goniometer (Model CA-DT·A, Kyowa Interface Science Co.). The glass plates were treated with the six types of silane coupling agents shown in Table 2 and 13 liquids were used for the wettability measurement, as shown in Table 3: n-decane, n-dodecane and n-hexadecane as group A; hexachlorobutadiene, tetrachloroethane, tricresylphosphate, α-bromonaphthalene, tetrabromoethane and methylene iodide as group B; dipropylenre glycol, ethylene glycol, formamide and distilled water as group C.

For each liquid, five drops were placed onto the glass plate and contact angle readings were taken from both sides of the liquid–air–solid interface at approximately 20°C. Contact angles were measured for four glass plates treated with the same coupling agent. Therefore, at least 40 readings were obtained for each combination of coupling agent and liquid. Averages of these readings were used for the Zisman plot in order to obtain the critical surface tension [7, 8].

2.3. Flexural testing

Three point bend tests were conducted in accordance with the JIS K7055 standard. Specimens of size 50 × 15 × 2 mm (length × width × thickness) and 32 mm span were loaded at a cross-head speed of 1 mm/min (Tensilon, Orientech Co.).

Table 3.
Surface tension values for various liquids

	Liquid	Composition	Surface tension dyne/cm (at 20°C) (10^{-3} N/m)
A	*n*-Decane	$CH_3(CH_2)_8CH_3$	23.9
	n-Dodecane	$CH_3(CH_2)_{10}CH_3$	25.4
	n-Hexadecane	$CH_3(CH_2)_{14}CH_3$	27.6
B	Hexachlorobutadiene	$CCl_2{=}CClCCl{=}CCl_2$	36.0
	Tetrachloroethane	$CHCl_2CHCl_2$	36.3
	Tricresyl phosphate	$(CH_3C_6H_4O)_3PO$	40.9
	α-Bromonaphthalene	$C_{10}H_7Br$	44.6
	Tetrabromoethane	$CHBr_2CHBr_2$	47.5
	Methylene iodide	CH_2I_2	50.8
C	Dipropylenre glycol	$(HOC_3H_6)_2O$	33.9
	Ethylene glycol	$HOCH_2CH_2OH$	47.7
	Formamide	$HCONH_2$	58.2
	Distilled water	H_2O	72.8

2.4. Microscopy

A scanning electron microscope (Type JSM-840, Nippon Densi Co.) was used to examine the surface of composites fractured in liquid N_2 whilst an optical microscope (Type BH-2, OLYMPUS Co.) was used to examine composite tensile fracture surfaces following three point bend testing.

2.5. Dynamic viscoelastic measurement

The composite $\tan\delta$ was measured as a function of temperature between -30 and 150°C at a heating rate of 2°C/min (DMS 200, Seiko Electronics Co.). The specimen size was $40 \times 5 \times 0.3$ mm (length × width × thickness) with a span of 20 mm. The displacement amplitude was 20 μm and a frequency of 10 Hz was used.

3. RESULTS AND DISCUSSION

3.1. Critical surface tension

Zisman plots for glass plates treated with six types of silane coupling agent and 13 different liquids has been shown in Fig. 1. The scatter in contact angles was typically 1–3 deg around the average angle, except for the case of glass plates treated with methyltrimethoxysilane where the data were more widely dispersed. For this latter case, the average of 40 readings, excluding those where the contact angles

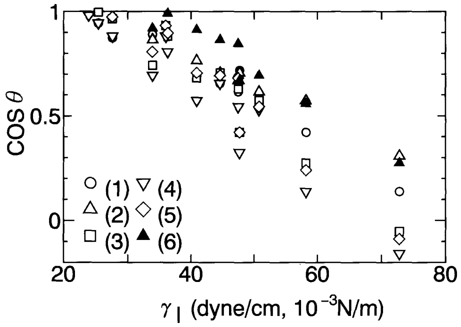


Figure 1. Zisman plot for glass plates treated by various silane coupling agents; (1) methyltrimethoxysilane, (2) *n*-propyltrimethoxysilane, (3) *n*-decyltrimethoxysilane, (4) *n*-hexadecyltrimethoxysilane, (5) γ-aminopropyltrimethoxysilane, and (6) γ-methacryloxypropyltrimethoxysilane.

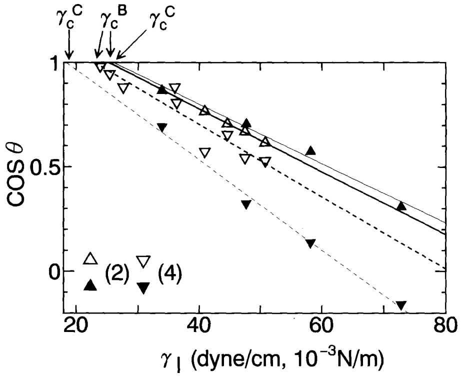


Figure 2. Wettability of glass plates treated by silanes; (2) *n*-propyltrimethoxysilane, (4) *n*-hexadecyltrimethoxysilane.

were observed spreading over the glass plates, has been used in Fig. 1. Contact angles of liquids that did not adhere to the glass plates were not included in the plots [9–13]. The surface tension [9–13] for each liquid (γ_l) has been presented in Table 3.

The critical surface tension (γ_c) was obtained from the $\cos\theta$ *vs.* γ_l plot which was approximately a straight line. For example, in Fig. 2 the $\cos\theta$ *vs.* γ_l plots of glass plates treated with *n*-propyltrimethoxysilane (△) contact angles for halogen-containing liquids, (▲) contact angles for hydrogen bond-containing liquids) and *n*-hexadecyltrimethoxysilane (▽) contact angles for hydrophobic- and halogen-containing liquids, (▼) contact angles for hydrogen bond-containing liquids) have been shown. Critical surface tensions calculated from the contact angles of halogen-containing liquids (B Group) (γ_c^B) and hydogen bond-containing liquids (C Group)

(γ_c^C) have been presented in Table 4. However, the critical surface tension calculated from contact angles of the hydrophobic liquids (A Group)(γ_c^A) have not been included as these liquids spread over the glass plates.

Table 4 shows γ_c^B to be different from that of γ_c^C. The surface polarity (in Table 4) of glass plates treated with different silane coupling agents are thus different from one other. Namely, the polarity of glass plates treated with methyltrimethoxysilane or *n*-propyltrimethoxysilane was hydrophilic as $\gamma_c^C > \gamma_c^B$ whilst the polarity of all other agents was hydrophobic as $\gamma_c^B > \gamma_c^C$. The polypropylene plate in Fig. 3 also indicates $\gamma_c^B > \gamma_c^C$. The reason why glass plates treated with methyl- and *n*-propyltrimethoxysilanes showed hydrophilic wettability is attributed to their organic functional groups not being so long as to inhibit hydrophilic wettability by OH groups existing in a crosslinking formation at the treated glass surface.

Table 4.
Critical surface tension (γ_c^B and γ_c^C) and surface polarity of slide glass treated by various coupling agents

Coupling agent	γ_c^B (dyne/cm, 10^{-3} N/m)	γ_c^C (dyne/cm, 10^{-3} N/m)	Surface polarity
Methyltrimethoxysilane	26.3	30.3	hydrophilic
n-Propyltrimethoxysilane	25.3	26.0	hydrophilic
n-Decyltrimethoxysilane	30.8	20.5	hydrophobic
n-Hexadecyltrimethoxysilane	27.2	18.4	hydrophobic
γ-Aminopropyltrimethoxysilane	31.6	24.3	hydrophobic
γ-Methacryloxypropyltrimethoxysilane	36.6	28.8	hydrophobic

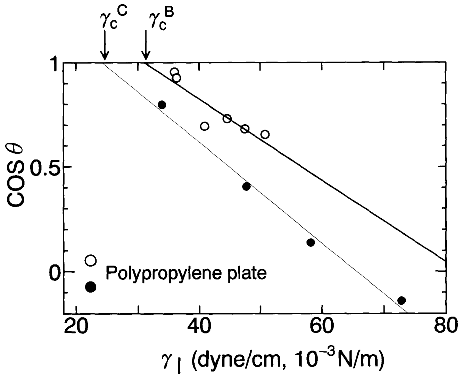


Figure 3. Wettability of PP plates.

3.2. Flexural properties

Figures 4, 5, and 6 present bending stress–deflection curves at room temperature for polypropylene composites filled with glass beads, glass milled fibers, and glass cut fibers, respectively. In these figures, GB0, GMF0, and GCF0 indicate untreated glass particleswhereas GB4, GMF4 and GCF4 indicate glass particles treated with *n*-hexadecyltrimethoxysilane which has an alkyl functional group. GB5, GMF5, and GCF5 indicate glass particles treated with γ-aminopropyltrimethoxysilane which has a polar functional group. The effect of the glass particle's shape on the bending yield stress and modulus tended to be in the order GB $<$ GMF $<$ GCF. The yield bending stress and the modulus for composites reinforced with surface treated glass particles with aminosilane (indicated by 5 in Figs 4–6) were higher compared to untreated glass particles (indicated by 0 in Figs 4–6) and those surface treated with hexadecylsilane (indicated by 4 in Figs 4–6). The yield deflection showed as an opposite trend. Such specific behavior of the surface treatment with aminosilane may be attributed to the interfacial adhesive strength between glass particles and matrix [14].

Figure 7 shows scanning electron micrographs of the fracture surface for PP composite reinforced with untreated glass beads (a), glass beads treated with aminosilane (b), untreated glass milled fibers (c), glass milled fibers treated with aminosilane (d), untreated glass cut fibers (e), and glass cut fibers treated with aminosilane (f). The surfaces of treated particles (b, d, and f) are rough, which indicates good adhesion between the particles and PP, whereas the surface of untreated glass particles (a, c, and e) was smooth, indicating no adhesion. Observation of composites filled with glass particles treated with other silanes, except for aminosilane, were almost the same as for untreated glass particles (a, c, and e).

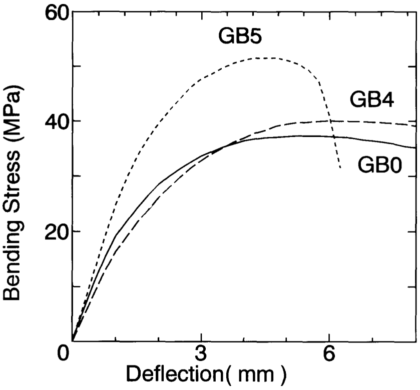


Figure 4. Bending stress–deflection curves for glass bead composites; GB0, 4, and 5 indicate glass beads untreated, treated by *n*-hexadecyltrimethoxysilane, and treated by γ-aminopropyltrimethoxysilane, respectively.

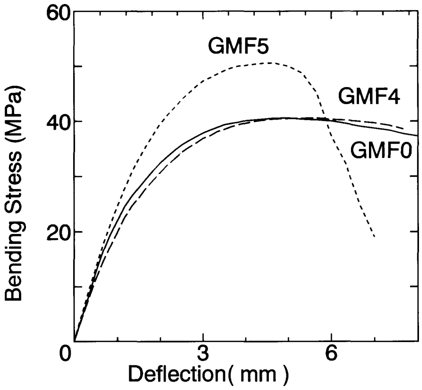


Figure 5. Bending stress–deflection curves for glass milled fiber composites; GMF0, 4, and 5 indicate milled fibers untreated, treated by *n*-hexadecyltrimethoxysilane, and treated by γ-aminopropyltrimethoxysilane, respectively.

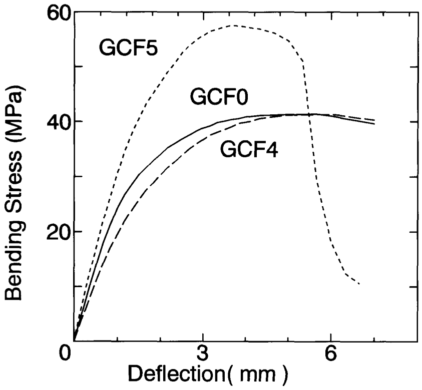


Figure 6. Bending stress–deflection curves for glass cut fiber composites; GCF0, 4, and 5 indicate cut fibers untreated, treated by *n*-hexadecyltrimethoxysilane, and treated by γ-aminopropyltrimethoxysilane, respectively.

Figures 8 and 9 illustrate plots of flexural modulus and strength *versus* glass particle aspect ratio, respectively. In these figures, (○), (△) and (□) indicate composites filled with glass particles untreated, treated with *n*-hexadecyltrimethoxysilane and γ-aminopropyltrimethoxysilane, respectively. Composite flexural modulus and strength increased glass particle aspect ratio. However, the rate of increase for flexural strength was less than that for flexural modulus. This may be due to the fact that interfacial strength between the glass particles and matrix is much weaker as the PP matrix is a hydrophobic polymer. It is also considered that the glass fibers used in the present experiment were shorter than the critical fiber length required for the appearance of the filling effect on strength [15]. In Figs 8 and 9,

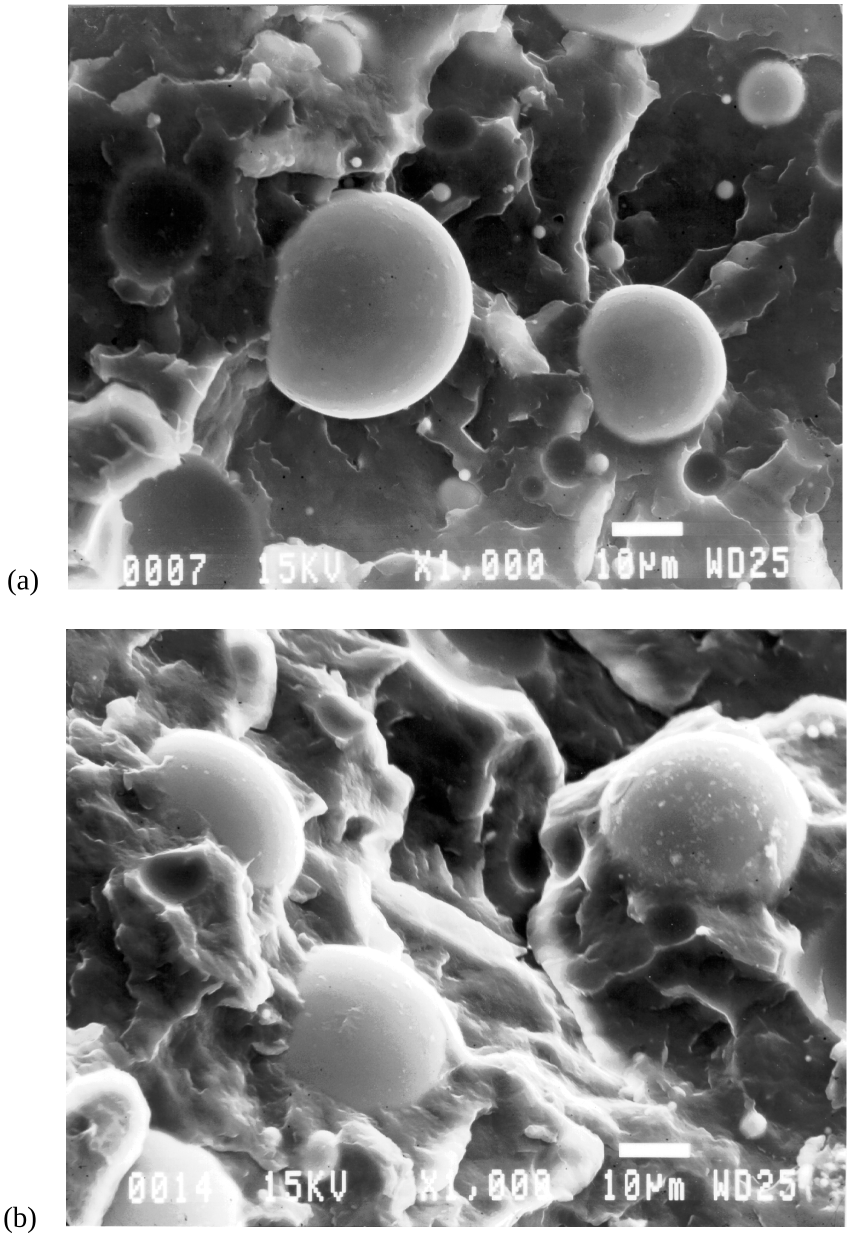


Figure 7. SEM micrographs taken from the fracture surface of composites; (a) GB0, (b) GB5, (c) GMF0, (d) GMF5, (e) GCF0, and (f) GCF5.

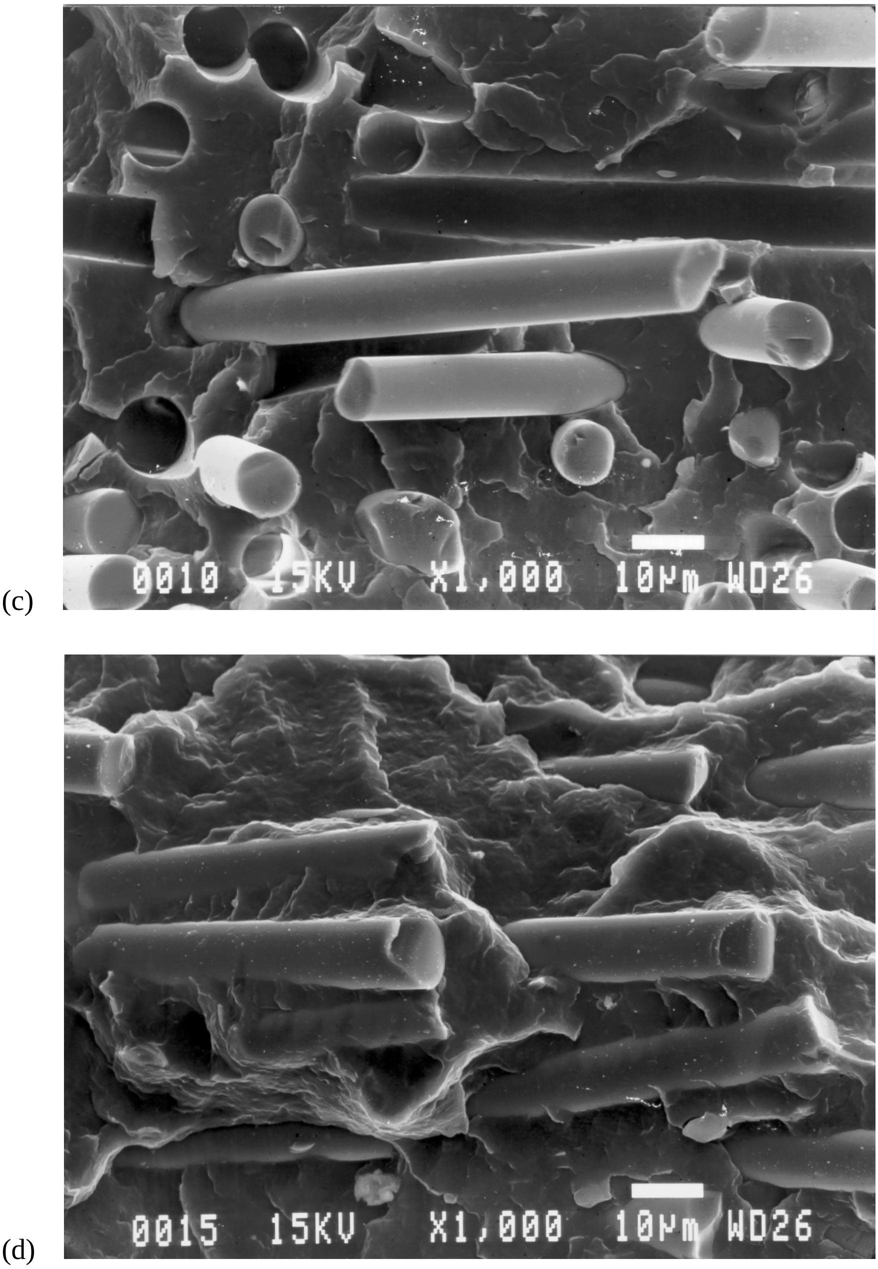


Figure 7. (Continued).

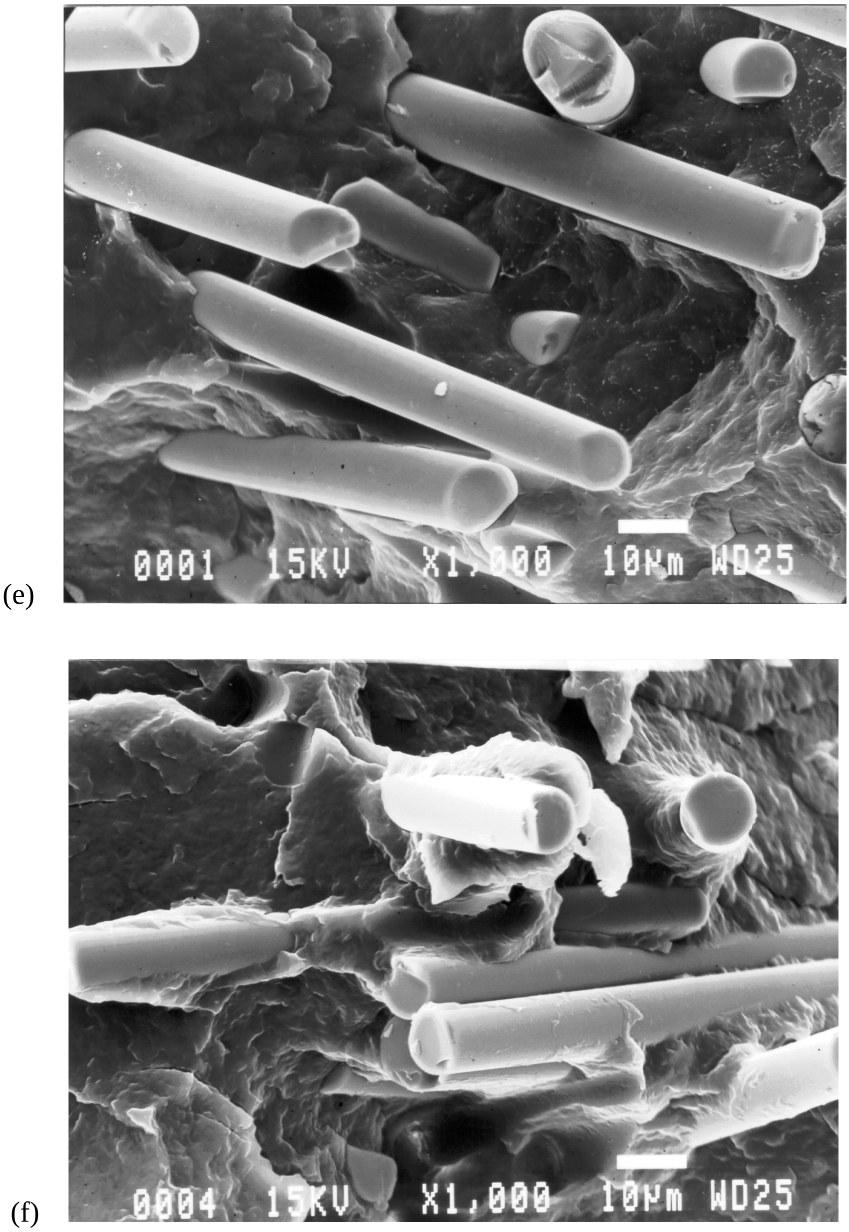


Figure 7. (Continued).

the composite filled with glass particles treated by aminosilane show the largest flexural modulus and strength and this may be the result of the interfacial adhesion.

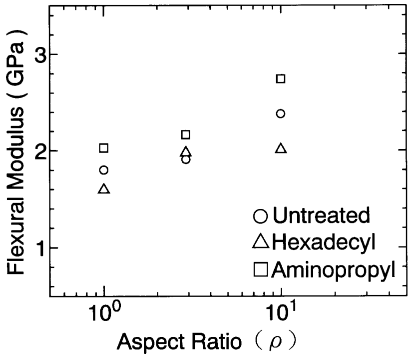


Figure 8. Effect of aspect ratio on flexural modulus for glass filled composites; (○) untreated, (△) treated by hexadecylsilane, and (□) treated by aminopropylsilane.

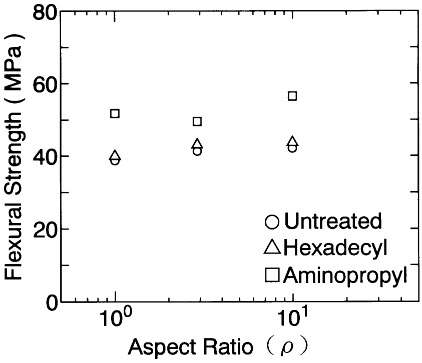


Figure 9. Effect of aspect ratio on flexural strength for glass filled composites; (○) untreated, (△) treated by hexadecylsilane, and (□) treated by aminopropylsilane.

3.3. Relationship between wettability and flexural properties

The infuluence of glass wettability on flexural properties was investigated by using the critical surface tension (γ_c^B) calculated from the contact angles of halogen-containing liquids on glass plates treated with silane coupling agents, because the surface polarity of PP was hydrophobic. Figure 10 shows the relationship between flexural modulus and γ_c^B with (○) and (●), (△) and (▲), and (□) and (■) indicating composite filled with glass beads, glass milled fibers, and glass cut fibers, respectively. The (○), (△), and (□) data indicate composites filled with glass particles treated with silanes having alkyl organic functional groups (methyl, *n*-propyl, *n*-decyl, *n*-hexadecyl) whereas (●), (▲), and (■) represent composites filled with glass particles treated with silanes having polar organic functional groups (γ-aminopropyl, γ-methacryloxypropyl). In the case of glass particles treated with silanes having organic functional groups ((○), (△), and (□) in Fig. 10), the composite flexural modulus decreased with increasing γ_c^B.

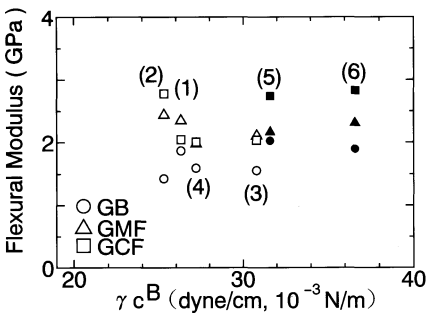


Figure 10. Flexural modulus versus critical surface tension (γ_c^B) calculated from Zisman plots for halogen-containing liquids.

It is supposed that the matrix flexibility around the particles increased with increasing wettability of the glass particles. When dispersing incompatible particles in the semi-crystalline polymer PP, crystal PP grows from the surface of particles and the interphase around the particle becomes the crystalline phase, so that the particles act as nucleating agents [1, 16]. On the contrary, increasing wettability of the particle surface may result in an amorphous interphase that is less rigid. However, in the case of glass particles treated with other silanes having polar organic functional groups ((●) (▲), and (■) in Fig. 10), the composite flexural modulus was higher in spite of γ_c^B having a larger value. These results may be explained by the good adhesion between PP and glass particles in the case of aminosilane, and by the incompatibility of the methacryloxy group with PP in the case of methacryloxysilane.

Figure 11 shows optical micrographs of tensile surfaces following three-point bending testing for the PP composite filled with; (a) untreated glass beads, (b) glass beads treated with *n*-hexadecyltrimethoxysilane, (c) glass beads treated with γ-aminopropyltrimethoxysilane and (d) glass cut fibers treated with γ-aminopropyltrimethoxysilane. In Figs 11a and b, relatively small cracks are observed, whereas in Figs 11c and d, wide growth of the crack was observed. Other specimens possessed similar fracture surfaces as for Figs 11a and b, apart from the γ-aminopropylsilane treatment. The composite filled with milled fibers treated with γ-aminopropylsilane showed a similar surface as for Figs 11c and d.

Figure 12 presents the relationship between flexural strength and γ_c^B. The composite flexural strength decreased with increasing γ_c^B for the case of glass particles treated with silanes having alkyl groups ((○) (△), and (□)). It is known that composite strength depends on the brittleness or ductility in addition to the interfacial adhesion. Composites filled with glass particles treated by silanes, except for aminosilane, were ductile and did not fracture as shown in Fig. 11.

Finally, the influence of wettability on the interphase mobility was examined from the relationship of tan δ with Figs 13, 14, and 15 showing tan δ measured at 10 Hz. The composites were filled with; glass beads (Fig. 13), glass milled

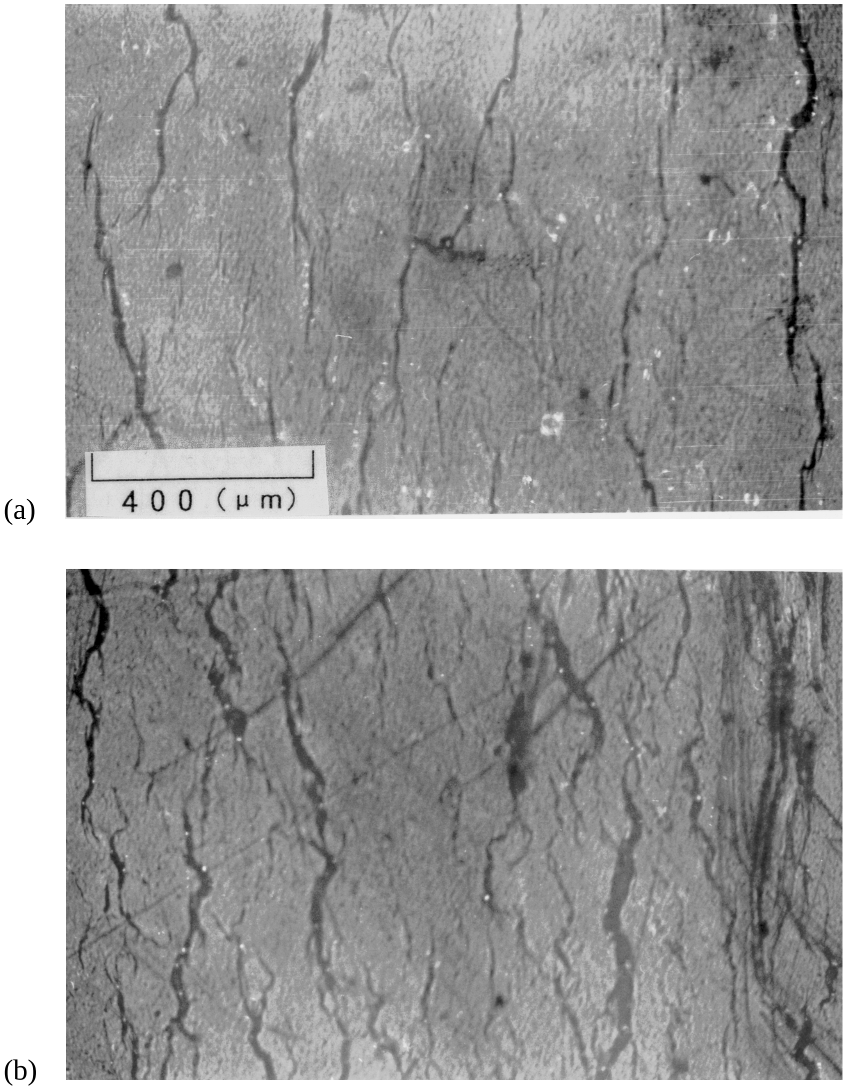


Figure 11. Photomicrographs of tension side views of specimens after bending test; (a) GB0, (b) GB4, (c) GB5, and (d) GCF5.

fibers (Fig. 14), and glass cut fibers (Fig. 15) whilst GB2, GMF2 and GCF2 (————), and GB3, GMF3, and GCF3 (— —) indicate glass particles treated with n-propyltrimethoxysilane and n-decyltrimethoxysilane, respectively. GB5, GMF5 and GCF5 (-----), represent glass particles which were treated with γ-aminopropyltrimethoxysilane. The $\tan\delta$ measured for PP composite filled with the glass particles treated with decylsilane (— —) was higher than for those with n-propylsilane (————) at the temperature above the glass transition temperature

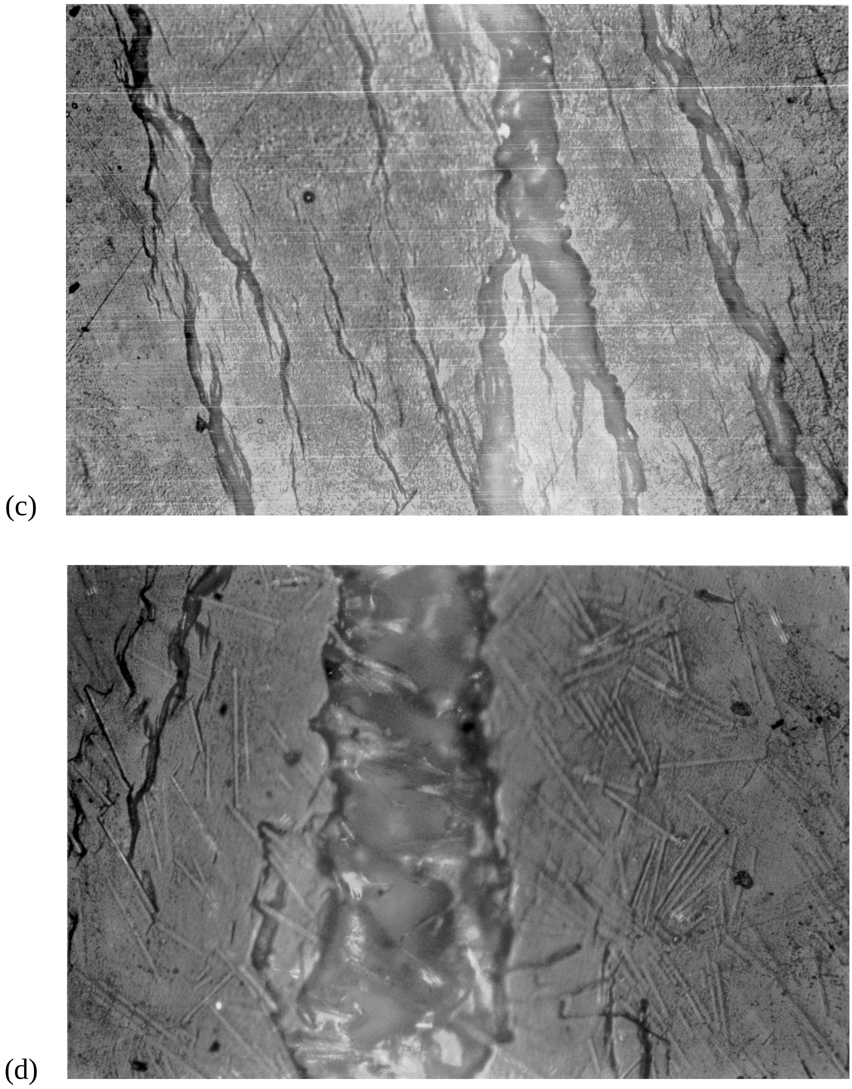


Figure 11. (Continued).

(T_g nearly equal to 0 °C). Higher $\tan\delta$ values indicate increased interphase mobility, which may be a result of increased wettability. The $\tan\delta$ measured for PP composite filled with glass particles treated with aminosilane (-----) was lower than with n-decylsilane though they showed the same wettability (γ_c^B), and is considered to result from the good interfacial adhesion.

It was also found that the $\tan\delta$ measurements for PP composite filled with glass particles treated with methylsilane and γ-methacryloxypropylsilane exhibit almost the same behavior as for n-propylsilane, and that the $\tan\delta$ for PP composite filled

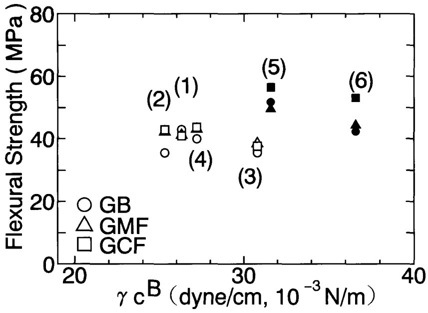


Figure 12. Flexural strength *versus* critical surface tension (γ_c^B) calculated from Zisman plots for halogen-containing liquids.

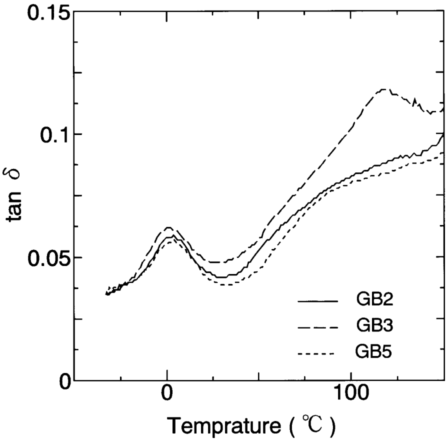


Figure 13. tan *δ* *versus* temperature for glass bead filled PP specimens; (————) GB2, (— —) GB3, and (- - - - -) GB5.

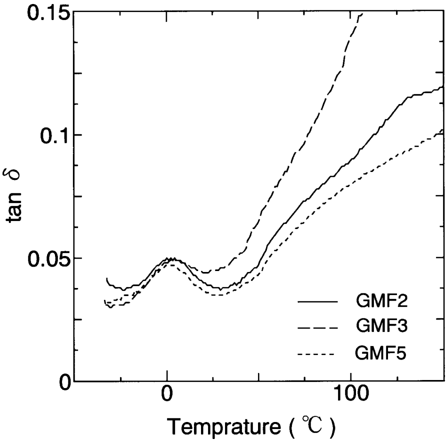


Figure 14. tan *δ* *versus* temperature for glass milled fiber filled PP specimens; (————) GMF2, (— —) GMF3, and (- - - - -) GMF5.

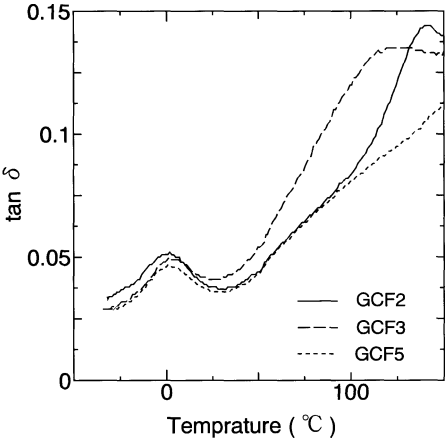


Figure 15. tan δ *versus* temperature for glass cut fiber filled PP specimens; (————) GCF2, (— —) GMF3, and (- - - - -) GMF5.

with glass particles treated with *n*-hexadecylsilane was slightly lower than that for *n*-decylsilane.

4. CONCLUSIONS

In this work, the following results were obtained:

(1) The wettability of glass treated with silane coupling agents depends on the composition of the organic functional group involved in the coupling agents.

(2) Composite flexural properties correlated with the glass plate wettability when both the glass particles and glass plate were treated with the same coupling agent. In the case where the organic functional group was an alkyl group, the composite flexural rigidity and strength decreased with increasing critical surface tension calculated from the contact angles of halogen-containing liquids.

(3) It was found from tan δ measurements that mobility of the interphase between matrix and glass particles increased with the increasing wettability in the case of poor interfacial adhesion.

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