Tensile Behavior of Glass-Fiber-Filled Polyacetal: Influence of the Functional Groups of Polymer Matrices

Kuniaki Kawaguchi,[1] Eiji Masuda,[1] Yoshihisa Tajima[2]

[1]*Research and Development Center, Polyplastics Company, Limited, 973, Miyajima, Fuji, Shizuoka 416-8533, Japan*
[2]*Technical Solution Center, Polyplastics Company, Limited, 973, Miyajima, Fuji, Shizuoka 416-8533, Japan*

ABSTRACT: We investigated the tensile behavior of glass-fiber-filled polyacetal [i.e., polyoxymethylene (POM)], focusing on the mutual influence of the functional groups in the POM matrices and the glass binder system. The different POM matrices were compounded with three kinds of glass fibers (20 wt %) treated with different glass binders, namely, epoxy resin, thermoplastic polyurethane (TPU), and a mixture of TPU and epoxy resin. A good correlation between the tensile strength and elongation at break was observed, regardless of the difference in the glass binders. The composites based on the modified POM matrix, which had both a carboxyl end group and a hydroxyl end group, improved the tensile properties noticeably in comparison with those based on the normal POM matrix. The composites were strengthened with an increase in the concentration of the functional groups. The results of scanning electron microscopy observations indicated that the fractured surfaces of a specimen having maximum tensile strength and elongation exhibited cohesion of the modified POM on the surfaces of the glass fibers. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 667–673, 2008

**Key words:** composites; interfaces; mechanical properties; modification

INTRODUCTION

Engineering thermoplastics have been used extensively as glass-fiber-filled composites because they possess high strength and increased stiffness.[1] Polyacetal [i.e., polyoxymethylene (POM) or acetal resin] is a major engineering thermoplastic, and its glass-fiber-filled composite has also been used in many industrial fields.[2] Several research groups have investigated the preparation and properties of glass-fiber-filled POM from theoretical and experimental points of view, including processing, fiber orientation, and composite properties.[3–13] Glass-fiber-filled POM offers lower creep, a higher deflection temperature, and reduced thermal expansion.[2] The interface between the glass fiber and the polymer matrix is very closely linked to the mechanical properties of the composite materials as well as the intrinsic characteristics of the matrix and the glass fibers because it allows for the efficient transfer of mechanical stresses within the composite materials. It is generally known that the application of a glass binder to a glass fiber surface improves the interfacial adhesion of the glass fiber/matrix in composites.[14] In comparison with other engineering thermoplastics, POM does not necessarily have good compatibility with glass binders because it possesses only a small number of functional groups, such as a hydroxyl end group in a POM copolymer prepared by cationic polymerization.[15]

In a previous work,[16] we carried out the cationic polymerization of 1,3,5-trioxane (TOX), 1,3-dioxolane (DOX), and a small amount of 2-hydroxyacetic acid (HAA) and performed melt blending of the resultant modified POM with thermoplastic polyurethane (TPU). The basic concept of the use of HAA as a functional monomer is to react a propagating oxycarbonium ion with a hydroxyl moiety of HAA in what is best described as a chain-transfer-type event to produce a carboxylic acid capped POM chain (Scheme 1). When the cationic active site undergoes chain transfer with both the hydroxyl and carboxyl end groups in HAA, the chain-transfer reaction is expected to generate an ester unit in POM. Furthermore, the generated protons during the chain transfer in these cases are capable of forming additional hydroxyl end groups in POM. The results of ^{1}H-NMR analysis indicated that HAA was almost incorporated into the modified POM and that the resultant carboxyl and hydroxyl end groups in the modified POM reacted with TPU during the melt blending. The results of scanning electron microscopy (SEM) observation and dynamic mechanical analysis indicated that a modified POM/TPU blend had good compatibility because of the interfacial reaction between the modified POM and TPU phase in the blend. The modified POM/TPU blend exhibited
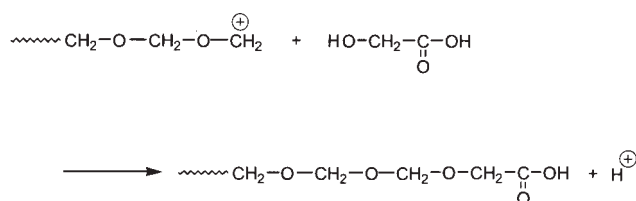
Scheme 1 Chain-transfer reaction of a propagating oxy-carbonium ion with a hydroxyl moiety of HAA.

higher Charpy impact strength, and its toughness was attributed to good compatibility between the two phases. The results provide possibilities for further and comprehensive improvements in the compatibility with glass binders and, therefore, the mechanical properties of glass-fiber-filled POM. Additionally, several modified POM samples have been prepared containing a variety of reactive groups as side-chain branches from the main polymer backbone and as terminal groups on the polymer chain.[17–23] Wissbrun[22] reported that a POM copolymer of TOX with epichlorohydrin as a comonomer reacted with thioglycolate to produce a modified POM with carboxylic derivatives. Hermann and Burg[23] prepared a POM copolymer of TOX with HAA methyl ester and reported that it incorporated carboxylic derivatives into POM. Such a series of modified POMs with various functional groups also have the potential to further improve the performance of POM composites.

In this study, we prepared different glass-fiber-filled POMs: a combination of different POM matrices and three kinds of glass fibers treated with different glass binders. As for the polymer matrices with new functional groups in the glass-fiber-filled POMs, we used the POM copolymer of TOX and DOX with a small amount of HAA. We investigated the tensile properties and fractured surfaces of the composites, focusing on the mutual influence between the functional groups in the POM matrices and each glass binder system to improve the performance of conventional POM composites.

EXPERIMENTAL

Preparation of glass-fiber-filled POM

We used a combination of polymer samples: normal POM samples (M90, M270, and POM-3) and a modified POM sample (POM-2). POM-2 was prepared by the cationic polymerization of TOX, DOX, and a small amount of HAA, and the preparation conditions for POM-2 are described in detail in the previous article.[16] POM-3 was prepared by polymerization with a small amount of water but in the absence of HAA. M90 and M270 were supplied by Polyplas-

tics (Shizuoka, Japan). Table I shows the characteristics of the initial polymer samples, and Table II shows the details of the prepared glass-fiber-filled POMs. The weight compositions of these polymers were selected on the basis of the calculation of the melt flow indices (MFIs) of the polymer matrices in glass-fiber-filled POMs, which were about 13–14 g/10 min. The prepared polymers were compounded with 20 wt % glass fibers with a twin-screw extruder at about 200°C and were formed into pellets. The screw rotational velocity was controlled to 120 rpm, and the residence time of the composites in the extruder was estimated to be about 2 min. Three kinds of short glass fibers (E-glass: aluminum–borosilicate glass treated with coupling agents and glass binders)—an epoxy resin coated glass binder (bisphenol A type; GF-a), a TPU coated glass binder (GF-b), and a coated glass binder that was a mixture of TPU and epoxy resin (bisphenol A type; GF-c)—and small amounts of stabilizers [pentaerythrityl tetrakis (3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate (Irganox 1010, Ciba Specialty Chemicals, Japan) and melamine (Mitsubishi Chemical, Japan)] were used in the compounding. The fiber diameters of GF-a, GF-b, and GF-c were 9, 9, and 10 μm, respectively, and each was in the form of 3-mm chopped strands. The average length of the glass fibers in these composites was confirmed to be about 0.5 mm, and the average aspect ratio of the glass fibers was calculated to be about 5×10^1.

Polymer characterization

To analyze the incorporation of DOX and HAA into the samples, ^{1}H-NMR spectra were obtained at 35°C on a Bruker Avance 400 spectrometer (Switzerland) operated at 400 MHz. The samples were purified by dissolution in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and reprecipitation with methanol before analysis, and they were prepared by dissolution in HFIP-d_2. The deuterated solvent was used to provide an internal lock signal. The chemical shift was referenced to tetramethylsilane as an internal standard. HAA was incorporated as a methylene–carboxylato unit ($-CH_2-COO-$), which was

TABLE I
Characteristics of the Polymer Samples

Sample	OH (mol %)[a]	HAA (mol %)[b]	DOX (mol %)	MFI (g/10 min)
M90	0.04	0	4.0	9.0
M270	0.04	0	4.0	27.0
POM-2	0.22	0.10	4.4	12.5
POM-3	0.30	0	4.2	37.0

[a] Hydroxyl end-group concentration.
[b] Methylene–carboxylato unit concentration.

TABLE II
Tensile Properties of the Glass-Fiber-Filled POMs

Composite	a-1	a-2	a-3	a-4	b-1	b-2	b-3	c-1	c-2	c-3	c-4
M90 (wt %)	47.8	54.7	24.5		47.8	54.7	24.5	47.8	54.7	24.5	
M270 (wt %)	31.9		15.5		31.9		15.5	31.9		15.5	
POM-2 (wt %)			39.6	79.7			39.6			39.6	79.7
POM-3 (wt %)		24.9				24.9			24.9		
Irganox 1010 (wt %)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Melamine (wt %)	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
GF-a (wt %)	20	20	20	20							
GF-b (wt %)					20	20	20				
GF-c (wt %)								20	20	20	20
Calculated OH[a] of the POM matrix (mol %)	0.04	0.12	0.12	0.22	0.04	0.12	0.12	0.04	0.12	0.12	0.22
Calculated HAA[b] of the POM matrix (mol %)	0	0	0.05	0.10	0	0	0.05	0	0	0.05	0.10
Calculated MFI of the POM matrix (g/10 min)	13.9	14.0	13.1	12.5	13.9	14.0	13.1	13.9	14.0	13.1	12.5
Tensile strength (MPa)	88	97	110	121	127	129	132	122	118	130	134
Elongation at break (%)	2.2	2.0	2.4	3.1	3.2	3.1	3.3	2.8	2.8	3.3	3.7

[a] Hydroxyl end-group concentration.
[b] Methylene–carboxylato unit concentration.

assigned to the signal at 4.29 ppm in the spectra. The molar compositions of DOX and HAA were determined against a monomer-repeating unit, as described in the previous article,[16] and the values of the initial samples are shown in Table I. The molar composition of HAA of the polymer matrix in the glass-fiber-filled POMs was calculated as the average molar composition of HAA, as shown in Table II.

To analyze the hydroxyl end group concentration[24,25] of the polymer samples, ^{1}H-NMR spectra were obtained at 45°C. The samples were trimethylsilyl-derivatized by dissolution in HFIP together with N,O-bis(trimethylsilyl) trifluoroacetamide and pyridine at room temperature and were held there for 0.5 h. The resulting products were dried with a nitrogen flow and prepared by dissolution in HFIP-d_2. The concentration of the hydroxyl end group, whose chemical shift was at about 0.2 ppm, was determined as a molar percentage versus a monomer-repeating unit, as described in the previous article,[16] and the values of the initial samples are shown in Table I. The hydroxyl end group concentration of the polymer matrix in the glass-fiber-filled POMs was calculated as the average hydroxyl end group concentration, as shown in Table II.

MFIs of the samples were measured at 190°C with a load of 2.16 kgf according to ASTM D 1238 on a melt indexer (Takara Kogyo Co., Japan), and the values of the initial samples are shown in Table I. The MFI of the polymer matrix in the glass-fiber-filled POMs was calculated as the logarithmic average of MFI, as shown in Table II.

The rheological data in the melt, namely, the storage modulus (G'), loss modulus (G''), loss tangent (tan δ), and complex shear viscosity (η^*) versus the angular velocity, were obtained with a Rheometric Scientific (USA) SR-200 dynamic stress rheometer. Small amounts of stabilizers were preblended with the polymer samples before the measurements. A dynamic frequency sweep was applied by sinusoidal stress of a constant peak amplitude over a range of frequencies. Experiments were performed at 190°C and 100 MPa (controlled stress) under a nitrogen atmosphere, and parallel-plate geometry was chosen for the investigation.

Evaluation of the tensile properties

Dumbbell specimens (4 mm thick) were injection-molded with a Toshiba IS80 (Japan). The cylinder nozzle temperature and molding temperature were 200 and 90°C, respectively. The tensile strength and elongation at break were measured according to ISO 527-1,2. An Autograph (Shimadzu Co., Japan) was used for tensile tests with a crosshead speed of 50 mm/min. The tests were performed at 23°C and 50% relative humidity, and the specimens were kept under the same conditions for more than 48 h before the tests.

Fractured surface observation

SEM observation was performed on a Hitachi S-4700 (Japan) at room temperature with an acceleration voltage of 5 kV. The fractured surfaces of the specimens, ion-sputtered with platinum and palladium in a vacuum, were used in the observation.
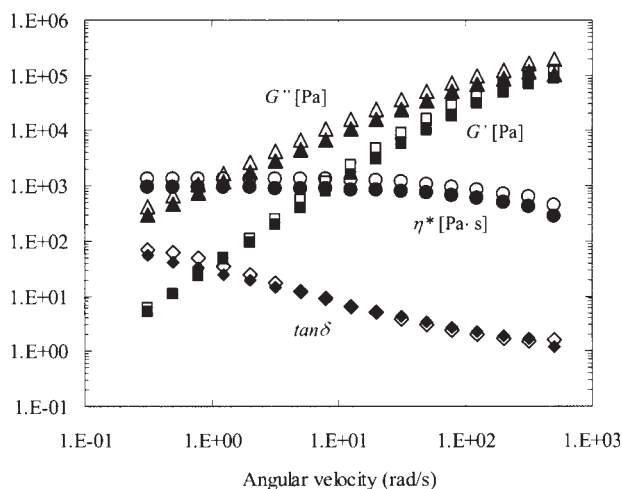
Figure 1 Plots of G', G'', tan δ, and η^* against angular velocity obtained at 190°C and 100 MPa (controlled stress) under a nitrogen atmosphere for the normal POM used in composite a-1 (filled symbols) and POM-2 (hollow symbols).

RESULTS AND DISCUSSION

Tensile properties of glass-fiber-filled POM

Figure 1 shows plots of G', G'', tan δ, and η^* against the angular velocity at 190°C for the normal POM used in composite a-1 and the modified POM (POM-2). There was no significant difference in the rheological behavior between the two samples. η^* of both samples remained constant (plateaued) when the angular velocity was below 10 rad/s. The rheological results indicated that the modified POM could classified as the linear POM type generally observed in conventional POM and that the HAA unit had little or no influence on the viscoelastic properties in the melt.

The prepared polymers were compounded with 20 wt % glass fibers with a twin-screw extruder at about 200°C, and the tensile properties of the glass-fiber-filled POM were investigated according to ISO 527-1,2. Table II shows the results of the tensile test of glass-fiber-filled POM composites having three kinds of glass fibers: GF-a [surface treatment: epoxy resin (bisphenol A type)], GF-b (surface treatment: TPU), and GF-c [surface treatment: a mixture of TPU and epoxy resin (bisphenol A type)]. We preliminarily investigated the tensile properties of an unfilled POM without glass fiber; the tensile strength at yield was 65.7 MPa and the elongation at break was 32.7% for POM-2. The compounding of glass fibers noticeably improved the tensile strength and lowered the elongation at break of the composites.[2] In Figure 2, a good correlation between the tensile strength and elongation for each glass-fiber-filled POM system can be observed, regardless of differences in the glass binders. The estimated MFI of the prepared

POM matrix was nearly the same, as shown in Table II, and no significant difference in the average aspect ratio of the glass fibers was observed in these composites. Therefore, the difference in the tensile strength of glass-fiber-filled POM can be attributed to the difference in the interfacial adhesion between the glass binder and the POM matrix.

Influence of the functional groups on the tensile behavior

The tensile behavior of the composites was investigated with a focus on the mutual influence of the functional groups in the modified POM and each glass binder system. As shown in Table II, a-1 exhibited much lower values of the tensile strength and elongation in comparison with b-1 and c-1. This indicates that the epoxy resin binder has relatively poor compatibility with the POM matrix, which has only a small concentration (0.04 mol %) of the hydroxyl end group. In contrast, the tensile strength of a-2 with a 0.12 mol % concentration of the hydroxyl end group was higher than that of a-1, and this indicates that the increased hydroxyl end group concentration contributed to a higher tensile strength. The tensile strength and elongation of a-3, which had a 0.12 mol % concentration of the hydroxyl end group and a 0.05 mol % concentration of the HAA unit, increased further compared with those of a-2. This indicates that the HAA unit, especially the carboxyl end group, is quite effective for the improvement of the tensile strength and elongation in the epoxy resin binder system. Composite a-4, having a 0.22 mol %
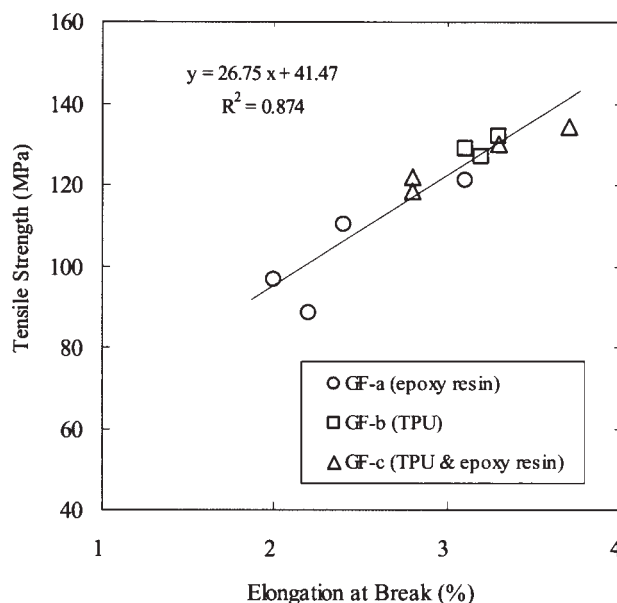

Figure 2 Correlation between tensile strength and elongation at break for each glass-fiber-filled POM system (20 wt % glass fibers).
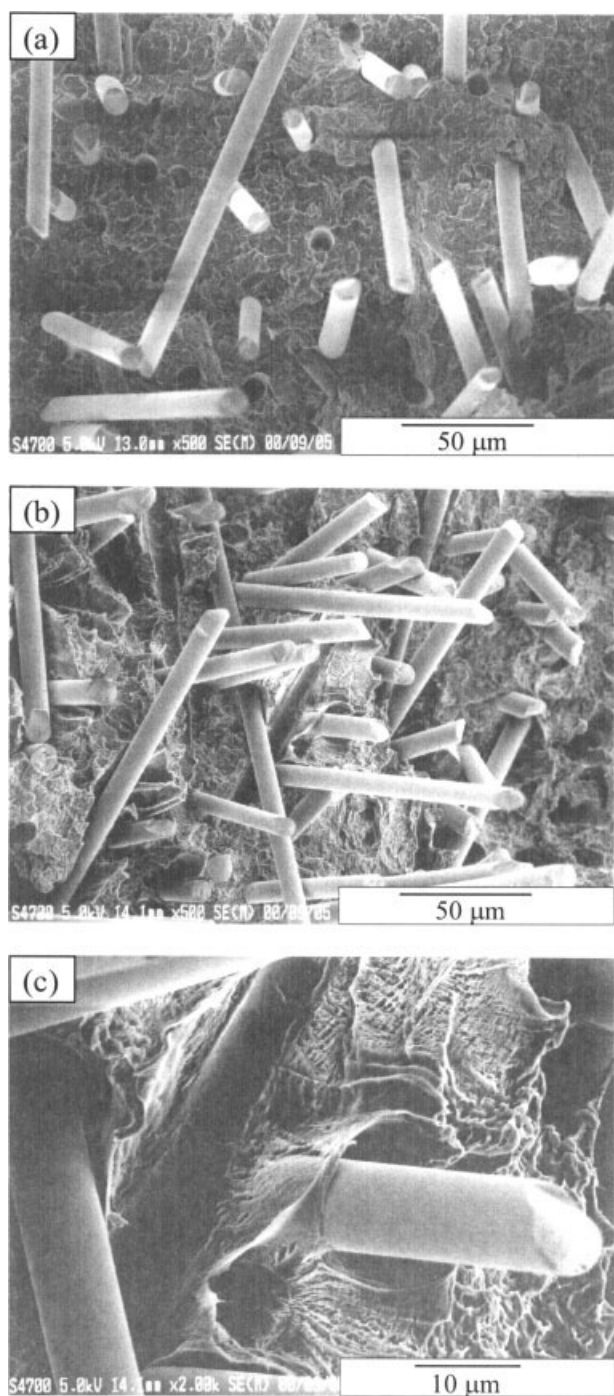
Figure 3 SEM micrographs of the fractured surfaces of specimens (a) a-1 and (b) a-4 and (c) a magnified photograph of (b).

concentration of the hydroxyl end group and a 0.10 mol % concentration of the HAA unit, showed even higher values of the tensile strength (121 MPa) and elongation (3.1%); the composite was strengthened by an increase in the concentration of the functional groups.
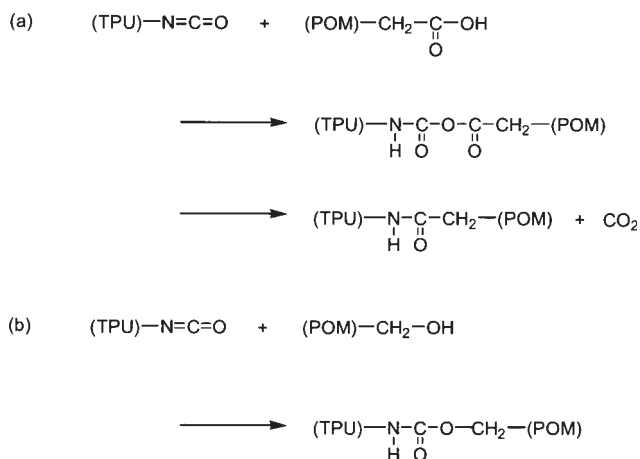
To investigate the correlation between the tensile properties and morphology of the POM/GF-a com-

posites, SEM observation was performed. Figure 3 shows SEM micrographs of the fractured surfaces of specimens a-1 and a-4. The glass fibers distributed in the POM matrix were observed in each micrograph. In a-1, several cylindrical cavities, which were formed by the glass fibers being pulled out during the fracture process, were clearly observed in the POM matrix [Fig. 3(a)]. This demonstrates that the interfacial adhesion between the POM matrix in a-1 and the glass binder of GF-a was so weak that it could not withstand the stress of the fracture. In contrast, in the case of a-4, the debonding of the interface between the glass fibers and the POM matrix was also confirmed [Fig. 3(b)], but the periphery of the glass fibers in the POM matrix appeared to be more ductile fracture features, as shown in the magnified photograph [Fig. 3(c)]. The results of SEM observation suggest that the interfacial adhesion between the glass binder and the POM matrix in a-4 was considerably stronger than that in a-1 during the fracture process, supporting the difference in the tensile strength and elongation. Epoxies have been identified as some of the most suitable functionalities to interact with nucleophilic end groups, such as carboxyl and hydroxyl end groups, in polyesters.[26,27] If we take into account the tensile behavior of the POM/GF-a composites with different POM matrices, it is conceivable that the epoxy resin binder (epoxy moiety) can provide a reaction site for the carboxyl and hydroxyl end groups in the modified POM during melt blending at elevated temperatures (Scheme 2).[26,28]

The tensile strength and elongation of b-1, on the other hand, were higher than those of a-1 (Table II). This indicates that the TPU binder has good compatibility with the POM matrix, which has a small number of the hydroxyl end groups. Chiang and Luor[9] also reported that the adhesion between POM
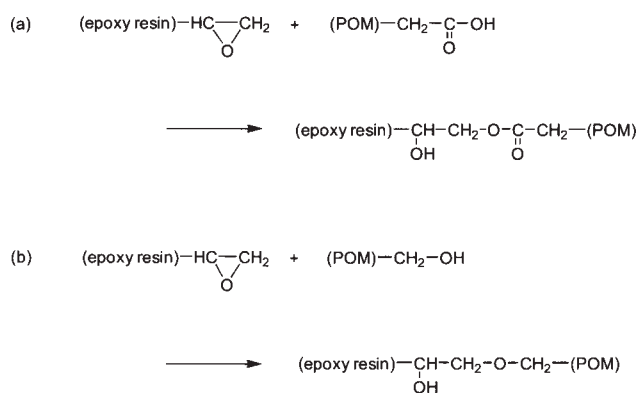
Scheme 2 Proposed reaction between the modified POM and epoxy resin binder during melt blending: (a) carboxyl end group in the modified POM versus epoxy resin binder and (b) hydroxyl end group in the modified POM versus epoxy resin binder.

(a)   (TPU)—N=C=O   +   (POM)—CH$_2$—C—OH
                                        |
                                        O

        $\longrightarrow$ (TPU)—N—C—O—C—CH$_2$—(POM)
                                  | || ||
                                  H O   O

        $\longrightarrow$ (TPU)—N—C—CH$_2$—(POM)   +   CO$_2$
                                  | ||
                                  H O

(b)   (TPU)—N=C=O   +   (POM)—CH$_2$—OH

        $\longrightarrow$ (TPU)—N—C—O—CH$_2$—(POM)
                                  | ||
                                  H O

Scheme 3 Proposed reaction between the modified POM and TPU binder during melt blending: (a) carboxyl end group in the modified POM versus TPU binder and (b) hydroxyl end group in the modified POM versus TPU binder.

(copolymer type) and the glass fiber was enhanced by a coating treatment with polyurethane. The tensile strength of the POM/GF-b composites increased in the following order: b-1 < b-2 < b-3. The tensile strength of the POM/GF-b composites was further increased with an increase in the concentration of the HAA unit or the hydroxyl end group to some extent in the TPU binder system. In the previous work,[16] we analyzed these functional groups in a modified POM/TPU blend (82/18 w/w) during melt blending (the residence time in a melt mixer was 5 or 10 min). In this case, a reduction of both the methylene–carboxylato unit and hydroxyl end group was detected in the modified POM/TPU blends, indicating that the modified POM reacts with the TPU interface in the blends. From the tensile properties of each POM/GF-b composite with different POM matrices, it is conceivable that the TPU (isocyanate moiety) binder can supply a reaction site for the carboxyl and hydroxyl end groups in the modified POM during melt blending at elevated temperatures, as shown in Scheme 3.[29] In this study, the residence time of the composites in the extruder was estimated to be about 2 min. Prolonging the residence time is expected to further enhance the interfacial reaction and, therefore, the adhesion properties of the POM/GF-b composites.[16]

The tensile strength of c-1 was relatively close to that of b-1 (Table II). This indicates that the TPU part in the glass binders of GF-c has good compatibility with the POM matrix, which has a small number of the hydroxyl end groups. The tensile strength of c-2, on the other hand, was somewhat lower than that of c-1; no noticeable effect of the hydroxyl end group concentration on the tensile strength was observed. Composite c-3 had a significantly higher

tensile strength and elongation than c-2, and this indicates that the carboxyl end group is quite effective for the improvement of the tensile strength and elongation; this is similar to the case of a-3. Composite c-4 showed the highest values of the tensile strength (134 MPa) and elongation (3.7%) among these composites; the composites were strengthened by an increase in the concentration of the functional groups. If we take into account the tensile properties, it is conceivable that, in the case of the POM/GF-c composites, both the TPU moiety[16,29] and epoxy moiety[26,28] can provide a concurrent reaction site for the carboxyl and hydroxyl end groups in the modified POM during melt blending at elevated temperatures (Schemes 2 and 3).

To further investigate the correlation between the tensile properties and morphology of the POM/GF-c composites, SEM observation was performed. Figure 4 shows SEM micrographs of the fractured surfaces of specimens c-1 and c-4. In c-1, from the observation of the periphery of the glass fibers in the POM matrix, the debonding of the interface between the glass fibers and the POM matrix was confirmed [Fig. 4(a)]. In contrast, the fractured surfaces of c-4 exhib-
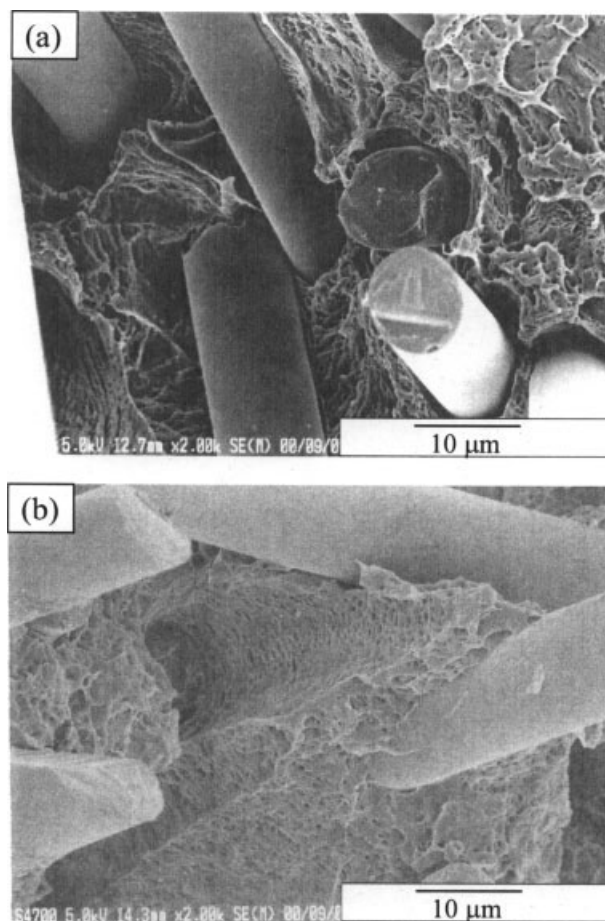

Figure 4 SEM micrographs of the fractured surfaces of specimens (a) c-1 and (b) c-4.

ited cohesion of the POM matrix on the surfaces of the glass fibers [Fig. 4(b)]. The results of SEM observation indicate that the strong interfacial adhesion between the glass binder of GF-c (both the TPU and epoxy resin binder) and the POM matrix in c-4 led to good reinforcement of the composite,[9] supporting the results of the highest values of the tensile strength and elongation.

CONCLUSIONS

The tensile behavior of glass-fiber-filled POM was investigated with a focus on the mutual influence of the functional groups in the POM matrices and glass binder system. The different POM matrices were compounded with three kinds of glass fibers (20 wt %) treated with different glass binders: epoxy resin (GF-a), TPU (GF-b), and a mixture of TPU and epoxy resin (GF-c). A good correlation between the tensile strength and elongation at break was observed, regardless of differences in the glass binders. Composite a-1 exhibited much lower values of the tensile strength and elongation than a-2 and a-3, and this indicates that the epoxy resin binder has relatively poor compatibility with the POM matrix, which has only a small number of the hydroxyl end groups. The glass-fiber-filled composites based on the modified POM matrix, which had both the carboxyl and hydroxyl end groups, noticeably improved the tensile properties in comparison with those based on the normal POM matrix, especially for the POM/GF-a and POM/GF-c composites. The composites were strengthened by an increase in the concentration of the functional groups in the POM matrix. The fractured surfaces of a specimen of c-4 having maximum tensile strength and elongation exhibited cohesion of the modified POM matrix on the surfaces of the glass fibers. It has been shown that modified POM improves the interfacial adhesion with the glass binders and, therefore, the performance of the glass-fiber-filled POM. On the other hand, much more work on an efficient characterization of the interface is necessary to further clarify the significance of the functional groups of POM and to explore the variations of interfacial adhesion.

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