

Studies of the Effects of the Organometallic Coupling Agents on Adhesion of the Glass Fiber–BMI Composites

S. CHOU,* H.-C. CHEN, and K.-S. LEE

Department of Textile Engineering, National Taiwan Institute of Technology, Taipei, Taiwan, Republic of China

SYNOPSIS

This work investigates the increase of adhesion between glass fiber and BMI. Five kinds of organometallic coupling agents of Ti, Zr, and Zr/Al are used to treat the fiber surface and then to reinforce BMI. A more efficient way is to mix the coupling agents directly into BMI and then reinforce by glass fiber. Then compare the adhesion of resulting composites, which are made by two methods described as above. As a result, the mechanical properties of the latter is slightly lower than the former. The Ti coupling agents are most effective, followed by Zr coupling agents and then Zr/Al coupling agents. Mixing Ti coupling agent directly into BMI, the degree of curing measured by DSC is 90%, the shear strength of the GFRP increases 31.9%, the flexural strength increases 30.8%, and the tensile strength increases 34.0%. Analyzing the chemical bonding by FT-IR, we found that choosing the organometallic coupling agent of type [RO–Ti (OX–R'NH₂)₃] and adding it to BMI can most effectively improve the adhesion. TGA shows that directly mixing coupling agent into BMI only changes a little of its thermal cracking temperature. Observed by SEM, we know that using coupling agent can promote adhesion between BMI and glass fiber.

INTRODUCTION

Since the innovation of the manufacturing techniques of polymer composites, the performance of composites have been improved. The study on interfacial adhesion of glass fiber and resin is also becoming important. Therefore, the interface of composites is sometimes called the heart of composites.¹ The failure of most composites due to the shear force occurs at the interface. The usage of coupling agents can improve the interfacial adhesion and hence the mechanical properties of composites.² The improvement on the interfacial adhesion of epoxy resin and glass fiber with coupling agent (such as silane) has been investigated extensively. The resulting composites possess better physical properties except the wet-hot resistance. At high temperature, however, the physical properties may be reduced and delamination occurs. To improve this disadvantage, new types of organometallic coupling agents and bis-

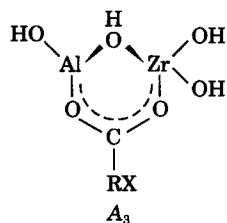
maleimide (BMI) were selected. These agents contain an amine functional group and show better heat resistance. This functional group reacts easily with the unsaturated double bond of BMI.³ Solvent of the selected coupling agent is the same as of BMI, thus, not only the chemical bonding between glass fiber and BMI is increased, the wet-hot resistance and the mechanical properties of composites is also improved.

EXPERIMENTAL

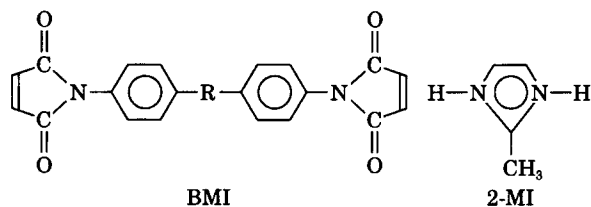
Materials

E-glass fiber cloth: 42 × 32 roving/in., and the roving is 1150 g/km; silane coupling agent *S*₁ (γ-Amino propyltriethoxy silane, Union Carbide Co.); titanate coupling agent *T*₁ ([RO–Ti–(OXR₁NH₂)₃], Ken-React Co.), and *T*₂ ([RO–Ti–(OXR₂NH₂)₃], Ken-React Co.); zirconate coupling agent *Z*₁ ([RO–Zr–(OXR₁NH₂)₃], Ken-React Co.), and *Z*₂ ([RO–Zr–(OXR₂NH₂)₃], Ken-React Co.); zircoaluminate coupling agent *A*₃, (Cavedon Chemical Co.):

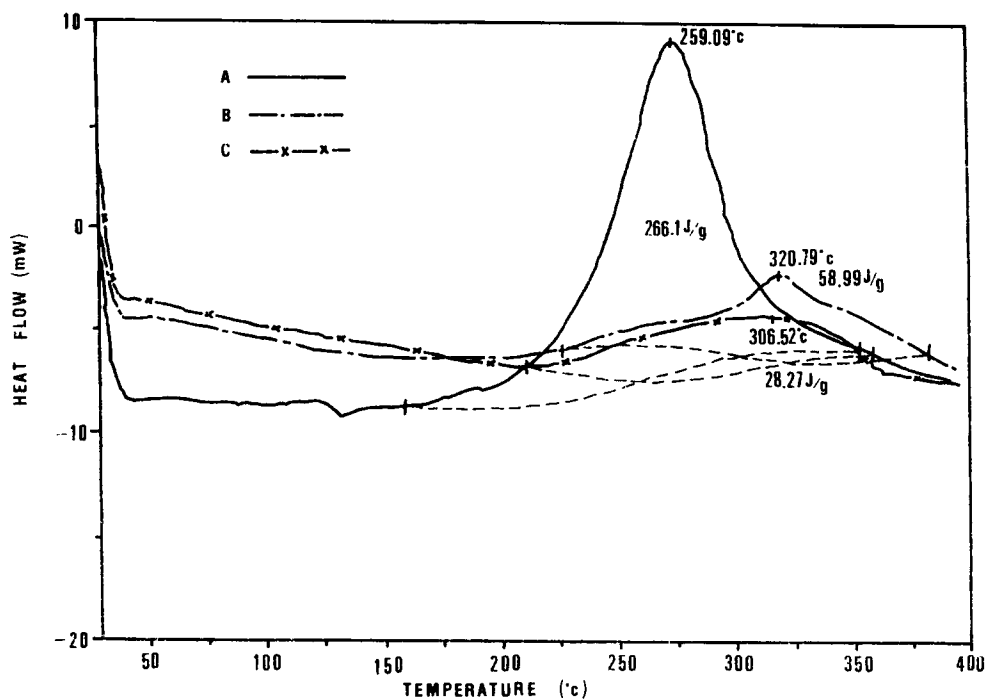
* To whom correspondence should be addressed.



resin is Compimide 183, and the hardener is 2-methylimidazole (2-MI) (both from Technochem Co., Germany).



where R_2 is an aliphatic group, R_1 is an aromatic group, and X is a binder functional group; The BMI



TEMPERATURE (°C)	180		200	
	TIME (hr)			
ITEM	2	2	3	4
$D_c = \frac{Q_o - Q_r}{Q_o} \times 100\%$ [6]	78	90	90	90

D_c : degree of curing
 Q_o : heat of reaction
 Q_r : residual heat of reaction

Figure 1 DSC curves of BMI: (A) pure resin, (B) resin with hardener, (C) postcure.

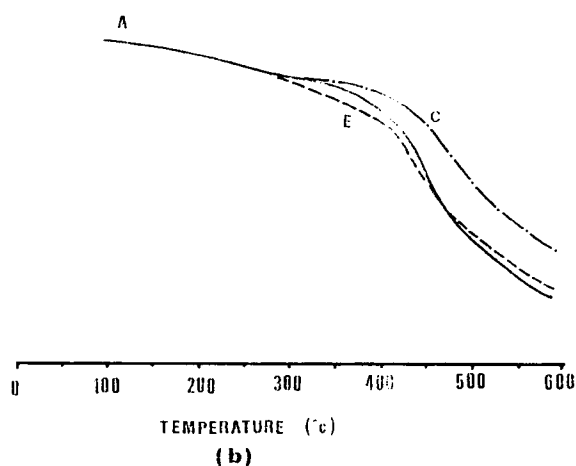
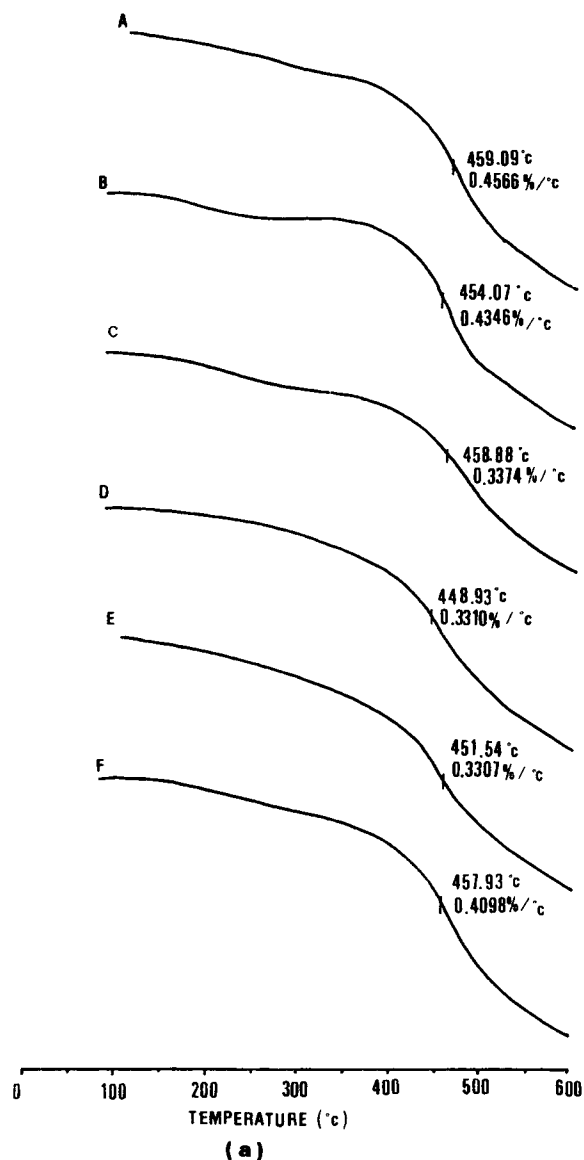


Figure 2 (a) (b) TGA curves of BMI with various coupling agents: (A) curing resin with hardener, (B) Z_1 , (C) T_1 , (D) Z_2 , (E) T_2 , (F) A_3 .

Table I The Relation of BMI Resin with Various Coupling Agents on Thermal Cracking Temperature and Percentage of Weight Loss

Specimen	Thermal Cracking Temperature ($^{\circ}\text{C}$)	Weight Loss at 600°C (%)
Untreated resin	460.13	52.67
Resin with 2-MI	459.09	51.33
Z_1 added	454.07	47.63
T_1 added	458.88	43.33
Z_2 added	448.93	48.67
T_2 added	451.54	50
A_3 added	457.93	52

Procedures

Desizing of Glass Fiber Cloths

The glass fiber cloths were immersed in 1% KNO_3 for 1 h, then dried in an oven at 110°C , followed by heat cleaning in a furnace at 350°C for 1 h for the complete desizing.

Surface Treatment of Glass Fiber Cloths

Preparation of Silane Coupling Agent: The silane coupling agent S_1 was hydrolyzed for 1 h in a 20% methanol aqueous solution, using acetic acid to adjust the pH. The cloths were then immersed in the solution for 1 h. Afterward, the cloths were taken out and dried at room temperature for one day, then dried in an oven at 80°C .

Preparation of Ti, Zr, and Zr/Al Coupling Agents: The coupling agent was dissolved in isopropanol as 0.2 wt % solution. The cloths were immersed in the solution for 24 h, then were taken out and rinsed with isopropanol and tap water, then vacuum dried at 66°C for 30 min.^{4,5}

Preparation of BMI-Glass Fiber Composites

BMI resin^{6,7} was mixed with the solvent (dimethyl formamide), and then the hardener (2-MI) and the

Table II Shear Strength and the Percentage of Increase of the Glass Fiber Composites Treated with 0.2 phr of Various Coupling Agents

Specimen	Shear Strength (Mpa)	% Increase of Strength
Untreated	14.75	—
Z_1	18.38	27.5
T_1	19.47	32
Z_2	19.02	28.9
T_2	18.98	28
A_3	17.85	21
S_1	17.73	20.2

diluent (isopropanol) were added according to the specified proportion.⁴ After the resin solution was well mixed, the glass fiber cloths were then immersed in the solution. To impregnate the cloths with resins sufficiently, the sample was put in a vacuum oven at 110°C for 100 min. The sample was then transferred to a matched metal die and heated at 150°C for 5 min under atmosphere pressure. Afterward, the die was hot-pressed at 180°C under a pressure of 40 kg/cm² for 2 h, then the pressure was released and cooled to room temperature. The sample was then postcured at 200°C for 2 h.

Testing of Mechanical Properties

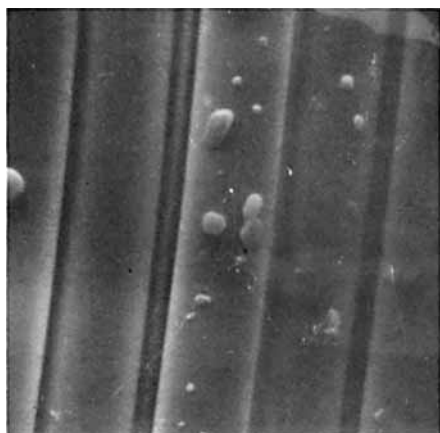
All specimens were prepared and tested according to the following ASTM methods: ASTM D3039 for

tensile test; ASTM D2344 for short-beam shear test; ASTM D790 for flexural test. The tensile test was conducted on a Material Test System (MTS) machine at a crosshead speed of 2.5 mm/min. The short-beam shear test was conducted on an Instron machine with a crosshead speed of 2 mm/min and a span-to-ratio of 4 : 1. The flexural test was conducted on the Instron machine with a crosshead speed of 2 mm/min and a span-to-ratio of 16 : 1.

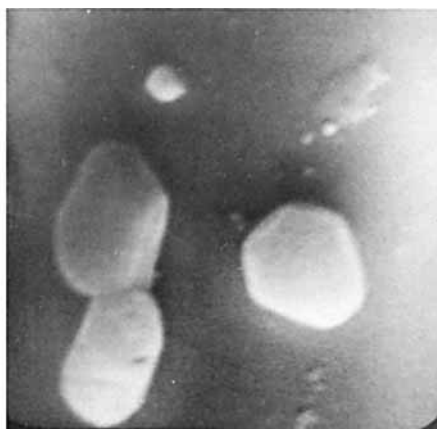
Thermogravimetric Analysis (TGA)

The samples were tested using a TGA (DuPont model 9900). The conditions were: 10°C/min, 30°C ~ 400°C, and the N₂ gas flow rate was 100 cm³/min.

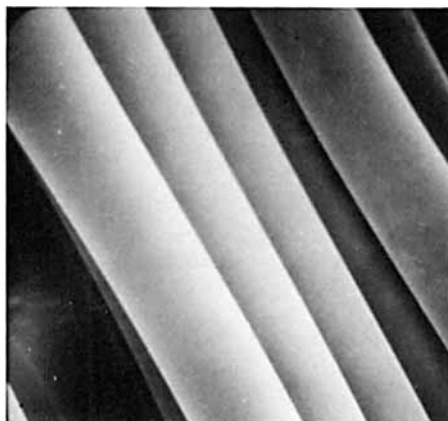
FTIR analysis was conducted using DP/F-3 model (Jasco).



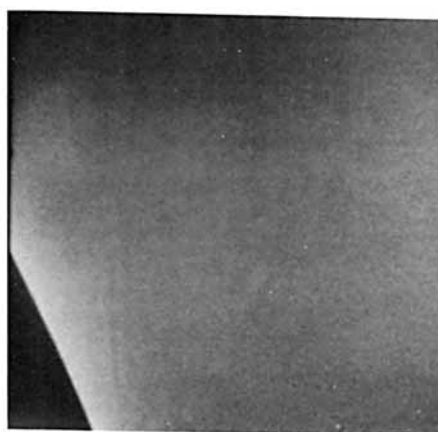
(a) X 2200



(a) X 11000



(b) X 2200



(b) X 11000

Figure 3 Scanning electron micrograph of the surface of glass fiber: (a) untreated, (b) after desizing.

Scanning electron microscopy (SEM) studies were performed using Cambridge Stereoscan S4-10 and S360.

RESULTS AND DISCUSSION

Differential Scanning Calorimetry (DSC) Analysis of BMI with Coupling Agent

Curing Reaction

Figure 1 shows that the curing of BMI with 0.2 phr 2-MI at 180°C for 2 h reached 78% degree of curing. After postcuring at 200°C for 2, 3, and 4 h, the curing degree reached no higher than 90%.

TGA Analysis of BMI with Coupling Agent

Figure 2 shows the results of the TGA curves for BMI samples with various coupling agents. When

Table III Flexural Strength and the Percentage of Increase of the Glass Fiber Composites Treated with 0.2 phr of Various Coupling Agents

Specimen	Flexural Strength (Mpa)	% Increase of Strength
Untreated	127.2	—
Z ₁	157.7	23.97
T ₁	166.4	30.8
Z ₂	165.6	30.18
T ₂	159	25
A ₃	152.6	19.9
S ₁	150	17.96

Ti and Zr coupling agents were added to BMI, the thermal cracking temperature only decreased slightly. There is a little weight loss at 100°C

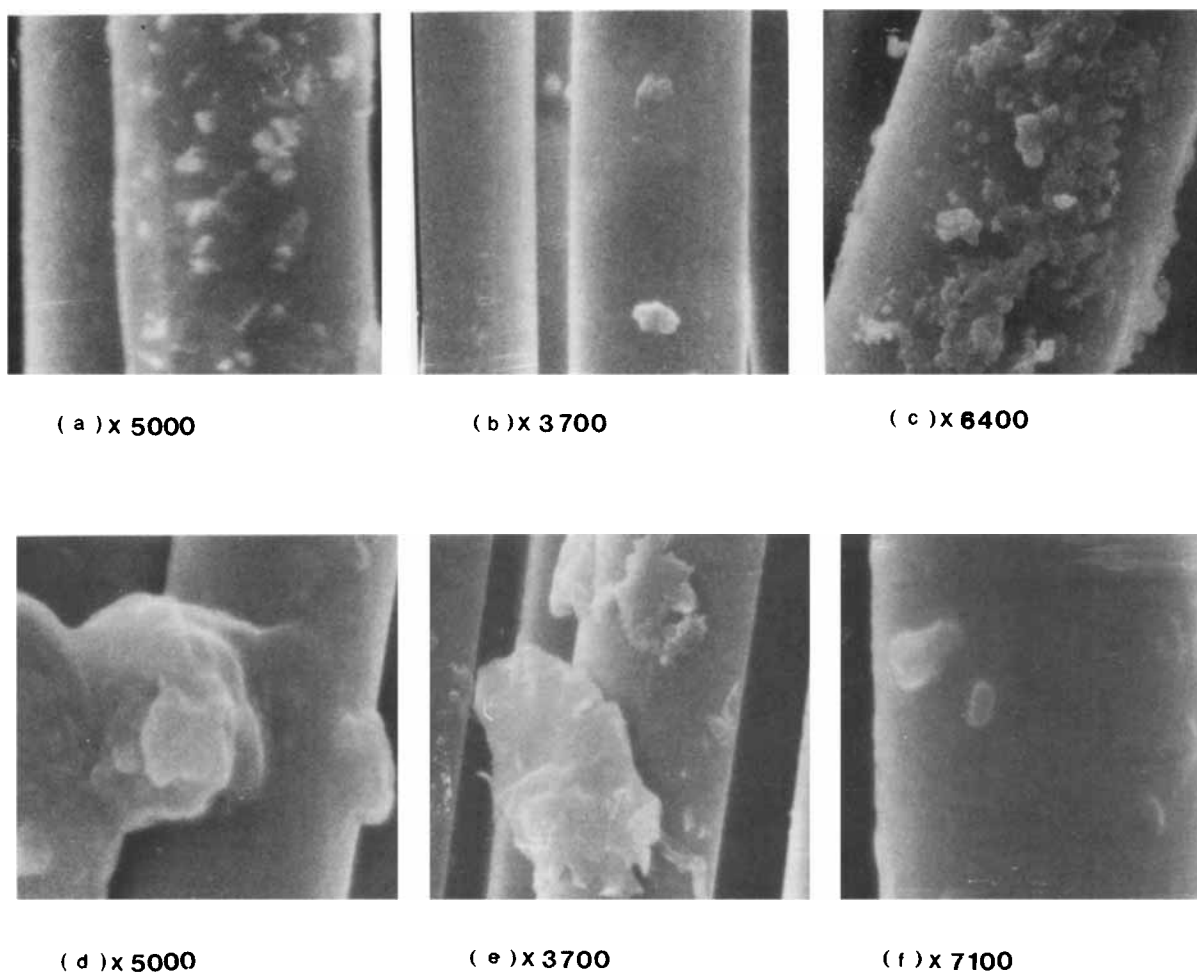


Figure 4 Scanning electron micrograph of the surface of glass fiber treated with various coupling agents (0.2 wt %): (a) S₁, (b) Z₁, (c) T₁, (d) Z₂, (e) T₂, (f) A₃.

Table IV Tensile Strength and the Percentage of Increase of the Glass Fiber Composites Treated with 0.2 phr of Various Coupling Agents

Specimen	Tensile Strength (Mpa)	% Increase of Strength
Untreated	238	—
Z ₁	306.9	28.9
T ₁	319	34
Z ₂	308.8	29.7
T ₂	302.7	27.2
Z ₃	300.4	26.2
S ₁	208.9	25.6

~ 200°C due to the small amount of water and impurity in BMI. Table I tabulates the decrease in the thermal cracking temperature as well as the weight loss at 600°C. Coupling agent T₁ shows the smallest weight loss, followed by Z₁, Z₂, T₂, and A₃. Therefore, the coupling agents containing the aromatic group (T₁, Z₁) show less weight loss than those containing aliphatic group (T₂, Z₂). Thus, the composites of BMI with T₁ coupling agent added show better heat stability.

Glass Fiber Before-After Coupling Agent Treatment

After the desizing, as shown in Figure 3, the sizing agent was completely removed from the glass fiber surface. The glass fibers were then treated with six coupling agents separately. Figure 4 (a) to (c) shows the surface after treatment with coupling agents S₁, Z₁, and T₁, respectively. For agents S₁ and T₁, the coupling agent reacted and attached evenly to the fiber surface. Figure 4(d) and 4(e) shows that the fiber surface after treatment with Z₂ or T₂, the agents were in the form of large clusters. This is because XR (i.e., —C₂H₄—NH—C₂H₄—) of T₂ and Z₂ are longer than that of XR (i.e., —C₆H₄—) of T₁ and Z₁. Figure 4(f) shows that after treatment with A₃, the fiber surface was covered with a layer of the agent. This is due to the structure of the coordinate covalent complex of A₃. In addition, the coupling agent A₃ has lower viscosity and hence better dispersion.⁸

Mechanical Properties of GFRP of Surface-Treated Glass Fiber

Table II shows that the glass fiber treated with T₁ coupling agent has the most increase in the shear

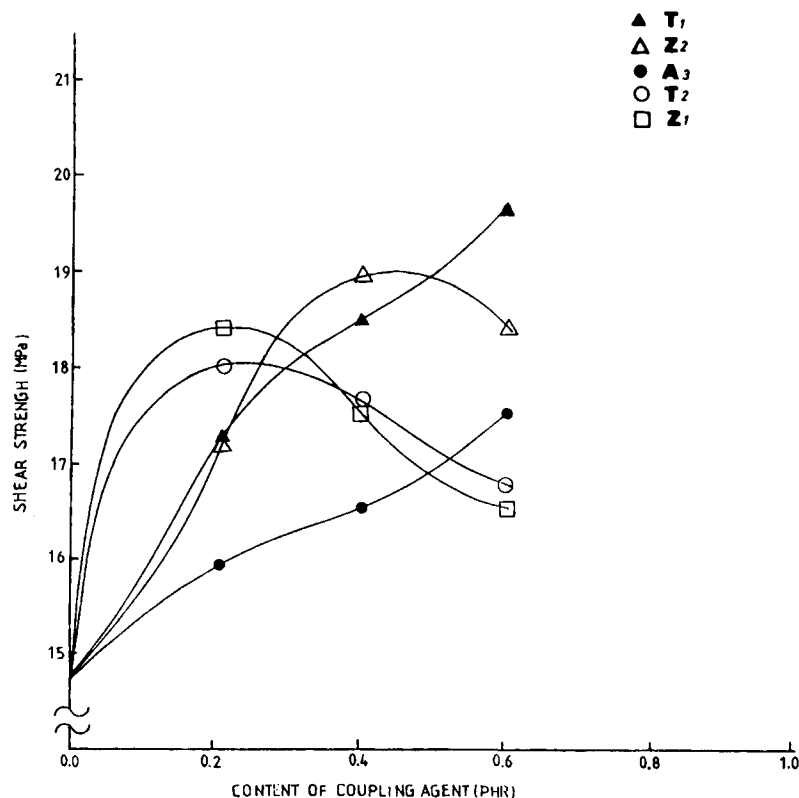


Figure 5 The effect of the coupling agents' concentration on the shear strength of GFRP.

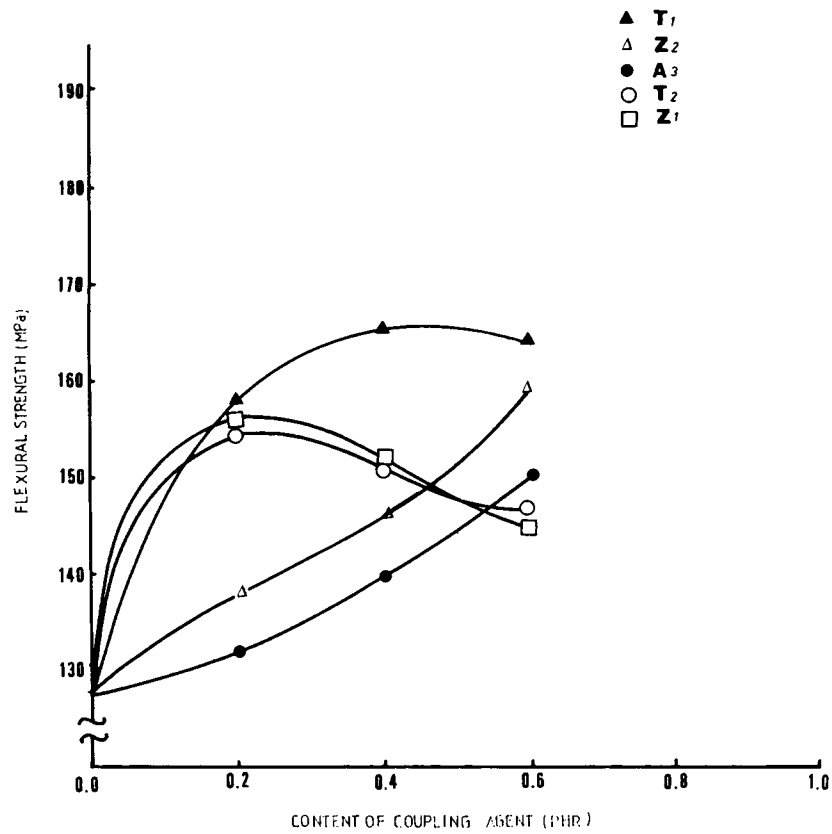


Figure 6 The effect of the coupling agents' concentration on the flexural strength of GFRP.

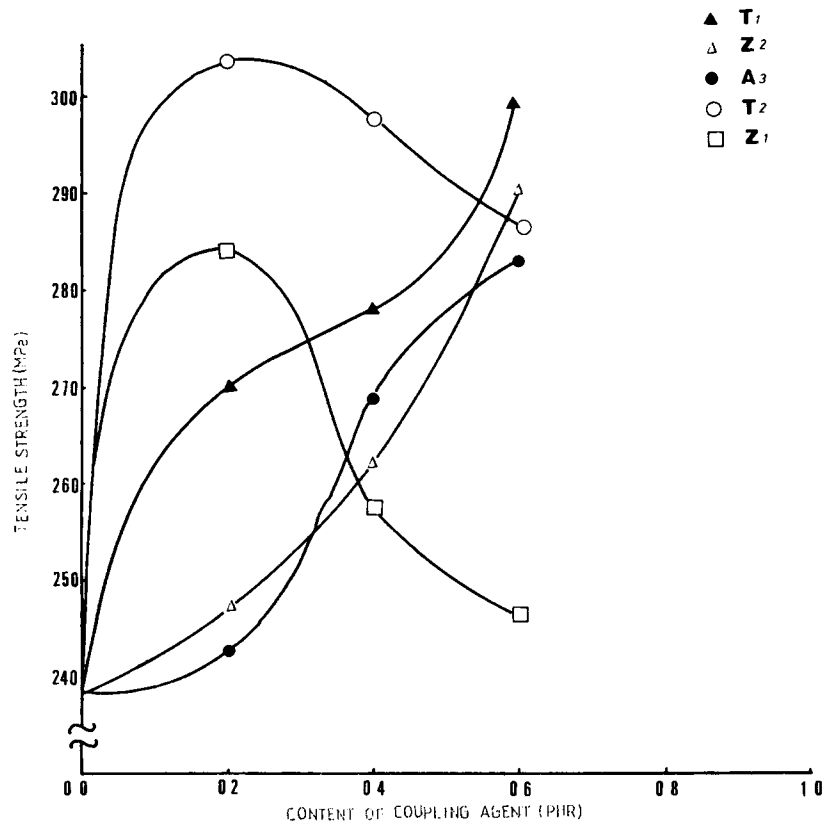
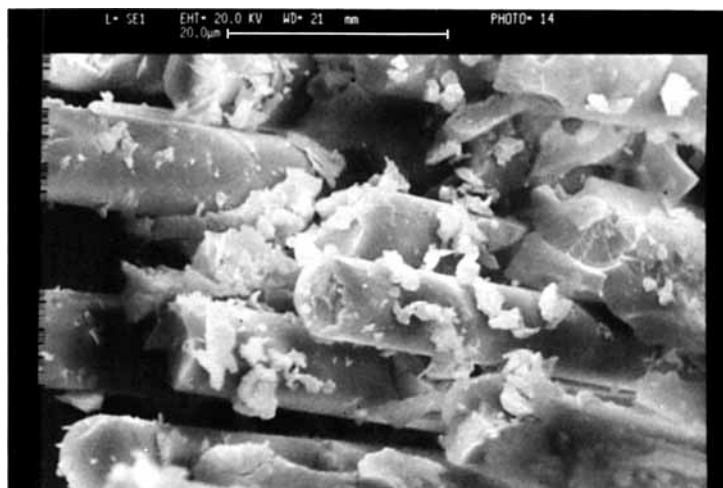


Figure 7 The effect of the coupling agents' concentration on the tensile strength of GFRP.



(a) UNTREATED

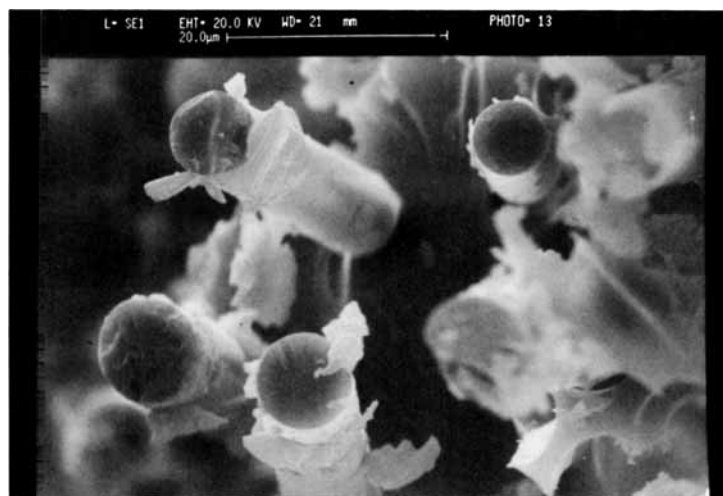
(b) Z_1 (0.2 phr)

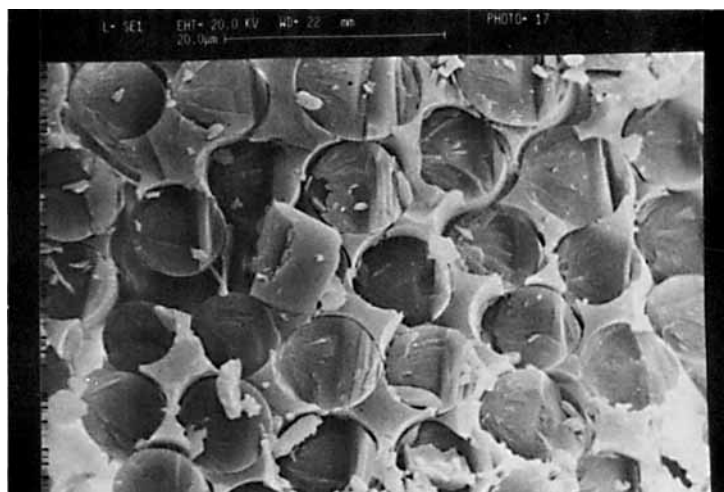
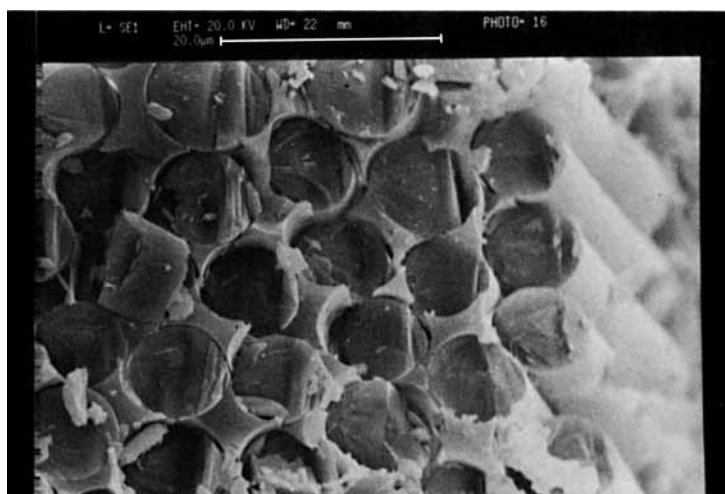
Figure 8 Scanning electron micrograph of the fracture surface of GFRP flexural specimens with various coupling agents treated: (a) untreated, (b) Z_1 (0.2 phr), (c) T_1 (0.4 phr), (d) Z_2 (0.6 phr), (e) T_2 (0.2 phr), (f) A_3 (0.6 phr).

strength (32%), followed by Z_2 (28.9%) and T_2 (28%). Silane coupling agent shows the least increase (20.2%). T_1 is the most effective because of its molecular structure XR has more polar. Moreover, the binding energy of Ti element (~ 560 eV) is higher than that of Zr element (~ 186 eV).¹¹

As shown in Table III, the order of the effectiveness of various coupling agents on the increasing of flexural strength is $T_1 > Z_2 > T_2 > Z_1 > A_3 > S_1$.

This is because Ti and Zr coupling agents can form covalent bonding with the glass fiber, while Zr/Al (A_3) coupling agent forms coordinate covalent complex. This order is the same as that of shear strength.

As indicated in Table IV, the glass fiber treated with T_1 coupling agent has the most increase in the tensile strength (34%), followed by Z_2 , Z_1 , T_2 , A_3 , and S_1 . This is because T_1 coupling agent forms uniform clusters on the fiber surface, and its molec-

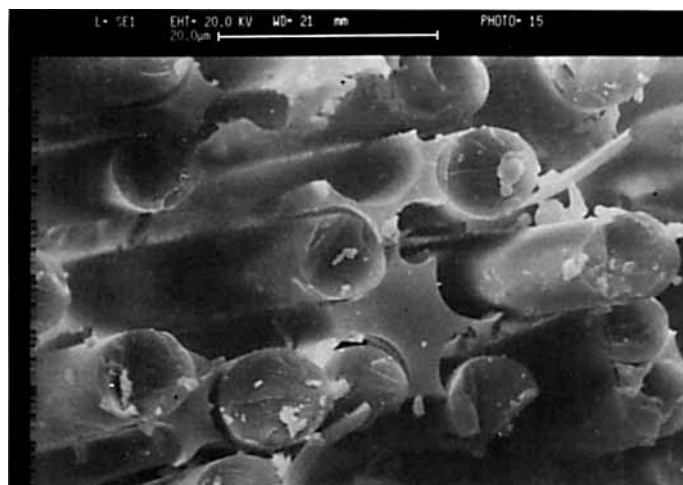
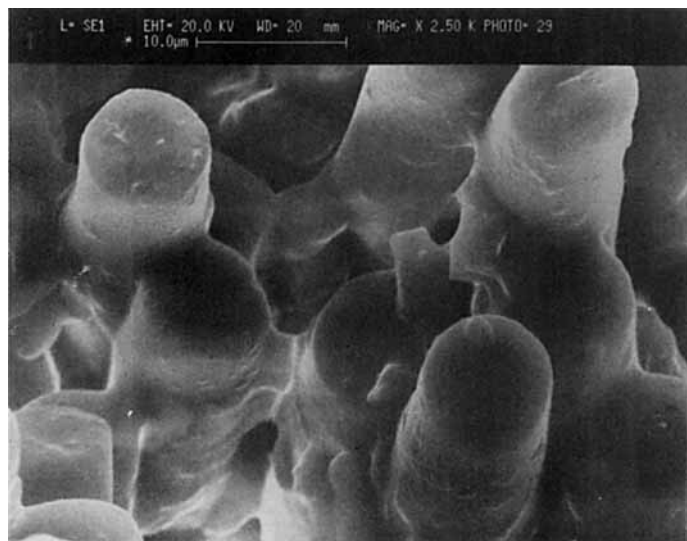
(c) T_1 (0.4 phr)(d) Z_2 (0.6 phr)**Figure 8** (Continued from the previous page)

ular structure XR has a polar long-chain group. Comparing the above-mentioned results, the mechanical properties have almost the same ranking of $T_1 > Z_2 > T_2 > Z_1$. And Z_1 has the poorest performance because it cannot form many clusters for anchoring, as shown in Figure 4(b). In addition, A_3 has coordinate covalent complex other than hydrogen bonds, while S_1 has only hydrogen bonds. Hence,

the mechanical strengths of composites treated with A_3 are stronger than those of S_1 .

Mechanical Properties of GFRP of Coupling Agent Added BMI

Figure 5 shows the effect of the content of coupling agent on the shear strength of GFRP, where T_1 (0.6

(e) T_2 (0.2 Phr)(f) A_3 (0.6 Phr)**Figure 8** (Continued from the previous page)

phr) is the most effective and the shear strength is increased by 31.9%. This is very close to the result of the GFRP with directly treating of 0.2 phr coupling agent. As of A_3 , with the content of 0.6 phr, the shear strength is increased by 18.6%. The dispersion of Z_1 and T_2 in the BMI was very well. The shear strength reached the maximum for only 0.2 phr of Z_1 or T_2 added. On the contrary the dispersion of T_1 and A_3 in BMI was poor. Thus the shear strength increased with the added amount of T_1 and A_3 .

Figure 6 shows the effect of the coupling agent content on the flexural strength of GFRP. With 0.4 phr of T_1 , the flexural strength increased by 30.5%. With more than 0.6 phr of T_1 , the flexural strength starts to decline slightly. However, with Z_2 or A_3 , the flexural strength increased with the content. Since Z_2 has chemical bonding and physical anchoring, the increase in the content improved the physical properties of BMI resin.

Figure 7 shows the effect of coupling agent content on the tensile strength of GFRP. The highest

tensile strength is increased by 28.9% with 0.2 phr of T_2 . With 0.6 phr of T_1 , the tensile strength is also increased fairly well. With more than 0.2 phr of T_2 or Z_1 , the tensile strength starts to decline.

From the preceding results, composites with 0.6 phr coupling agents mixed directly with BMI resin had almost the same mechanical properties as those composites with glass fiber surface treated with coupling agents. The optimum content is between 0.5 and 2.0 phr.⁹ In the case of adding the coupling agents directly to BMI resin, the hot-press process would transfer the coupling agent to the glass fiber surface. To get better mechanical properties, the amount of coupling agent added should be enough to contact sufficiently with glass fiber surface. On the other hand, adding too much coupling agent could lead to weaker mechanical properties. The

reason is that the residual coupling agent becomes lubricant to the BMI matrix.¹⁰

SEM of Fracture Surface

Figure 8 shows the SEM of the fracture surface of the composites with glass fibers treated with different coupling agents. The adhesion is improved after coupling agent treatment. Despite that the adhesion of resin on fiber surface is different, the fracture surface also shows a difference. For the composites of untreated glass fiber, Figure 8(a) shows that little resin is left on the fiber surface. This indicates that the strength of resin is stronger than shear strength of fiber surface and resin.

Figure 8(c) shows the fracture surface of the

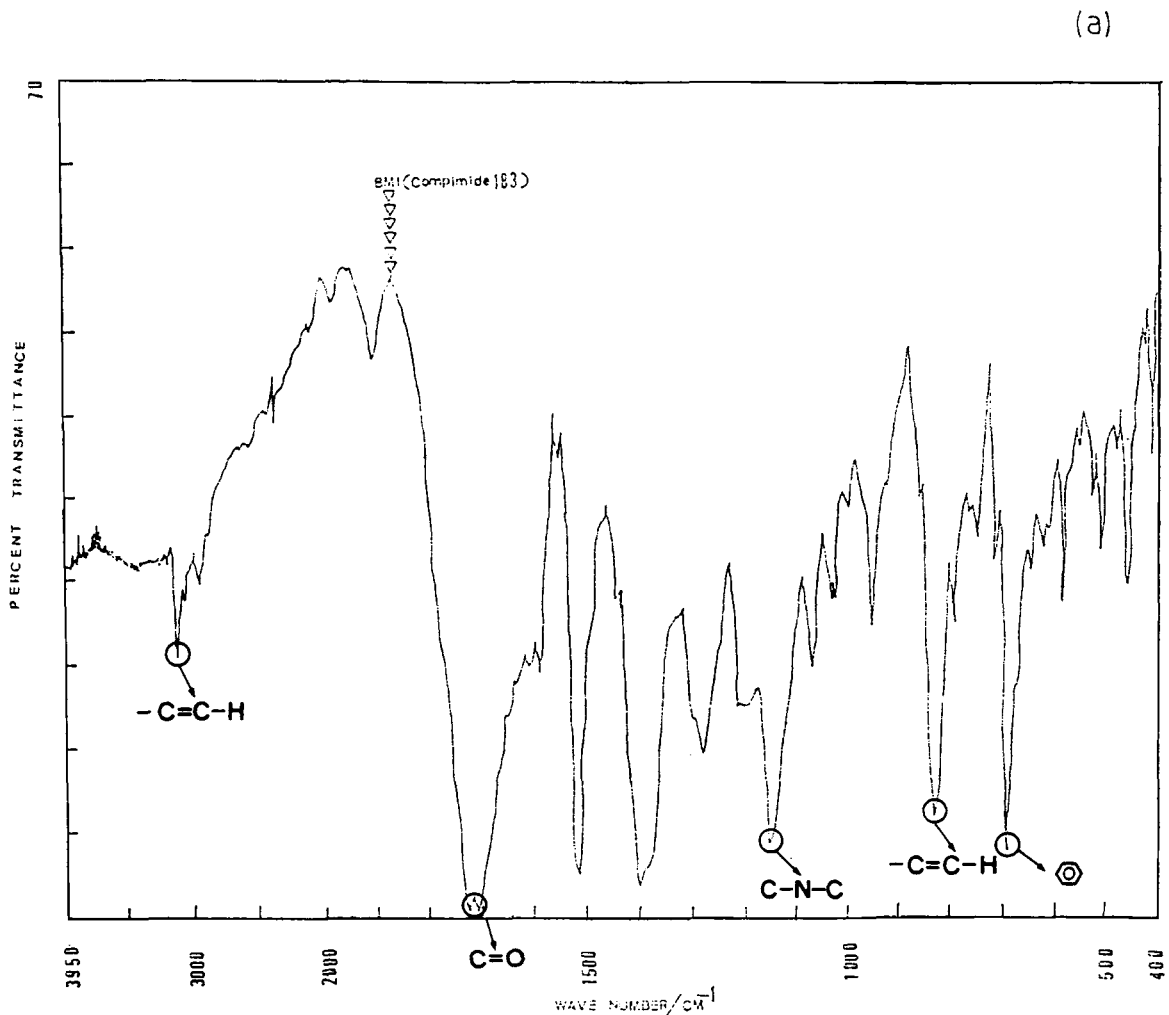


Figure 9 FTIR adsorption spectrum: (a) Compimide 183 resin; (b) Compimide 183 resin treated with (A) Z_1 ; (B) T_1 ; (C) Z_2 ; (D) T_2 ; (E) A_3 .

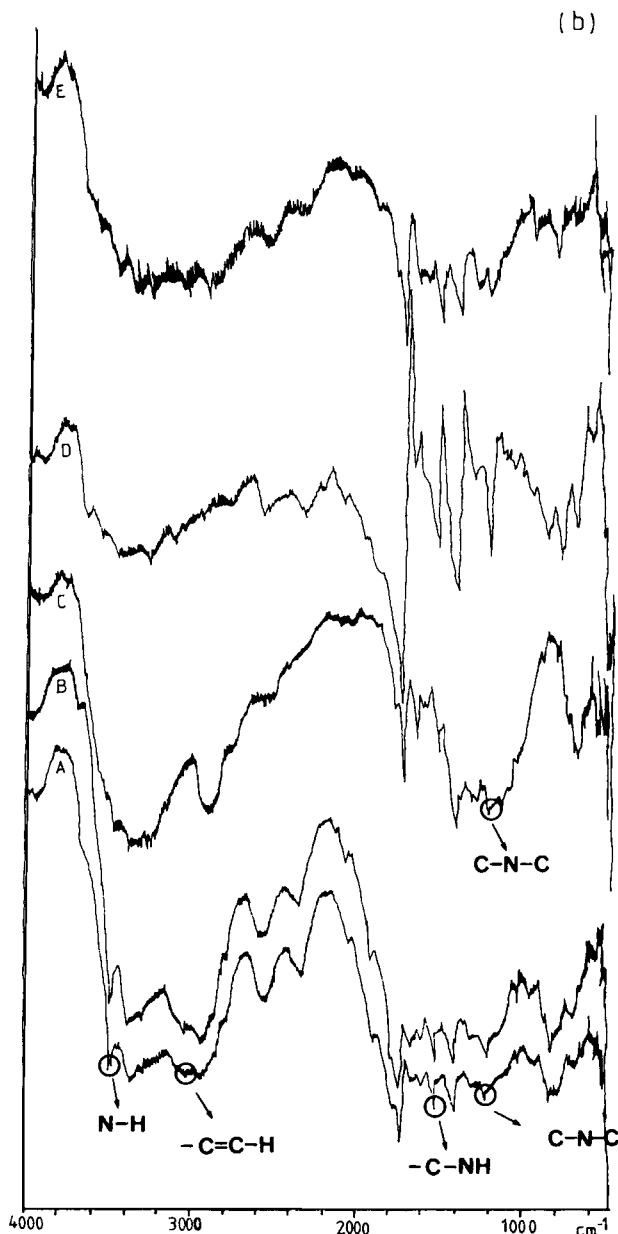


Figure 9 (Continued from the previous page)

composite with glass fiber treated with T_1 (0.4 phr). There is no pull-out of fiber on the fracture surface. This indicates that the shear strength of fiber-resin interface is stronger than the strength of resin. Glass fiber treated with Z_2 (0.4 phr) had similar effect to T_1 , as shown in Figure 8(d). When treated with A_3 coupling agent, the adhesion of resin is different from other coupling agents. This is because A_3 has a molecular structure that favors forming a thin layer on the fiber surface, as shown in Figure 8(f). This is due to its better dispersion and lower viscosity.

FTIR Analysis of BMI Resin

Figure 9 shows the FTIR absorption spectra of BMI with various coupling agents added. Before the curing of BMI (without mixing coupling agent), absorptions at 3100 and 830 cm^{-1} are the absorptions of $-\text{C}=\text{C}-\text{H}$, at 1770 and 1720 cm^{-1} are the absorptions of $\text{C}=\text{O}$, at 1150 cm^{-1} is the absorption of $\text{C}-\text{N}-\text{C}$ of maleimide, and at 710 and 675 cm^{-1} are the absorptions of benzene. After the curing of BMI (mixed with coupling agents), the absorption of $-\text{C}=\text{C}-\text{H}$ becomes weaker. At 710 and 675 cm^{-1} , the absorptions of benzene disappeared because benzene was reacted and a chemical shift occurred. There were new absorptions at 3430 cm^{-1} ($\text{N}-\text{H}$) and at 1520 cm^{-1} ($-\text{C}-\text{NH}$). At 1150 cm^{-1} , the absorption of $\text{C}-\text{N}-\text{C}$ of maleimide was reduced because the double-bond was opened. Because the *Michael addition* between unsaturated double-bond end group of BMI and amino group occurred, the addition of organometallic coupling agents of the type $[\text{RO}-\text{Ti}(\text{OX}-\text{R}'\text{NH}_2)_3]$ (i.e., T_1 and T_2) produced the best effects.

CONCLUSION

1. From DSC and TGA analysis of BMI added with coupling agent, the best curing conditions are at 180°C for 2 h, and the postcuring conditions are at 200°C for 2 h.
2. The mechanical properties were found to improve most effectively when the glass fiber was treated with 0.2 phr of T_1 coupling agent. Organometallic coupling agents are proved to be more effective than the commonly used silane coupling agent.
3. With proper amount of coupling agent added directly to BMI resin, the interfacial adhesion of glass fiber-BMI is increased.
4. From SEM observation, the composites of organometallic coupling agents treated glass fiber show excellent interfacial adhesion and no pull-out of fibers occurred.
5. The FTIR results show that the organometallic coupling agents of the type $[\text{RO}-\text{Ti}(\text{OX}-\text{R}'\text{NH}_2)_3]$ are the most effective when mixed directly with BMI resin.

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