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

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SYNOPSIS

In order to increase the chemical bonding force between fiber and resin, several kinds of organometallic coupling agent (such as titanate, zirconate, and zircoaluminate) were chosen and added in the BMI resin formulation, which possess the same solvent system with those coupling agents. The DSC analysis technique was used to find the best curing condition, and TGA was used to investigate the thermal stability property of the best curing condition. For the purpose of analyzing the bonding structure, ESCA surface element analysis techniques was applied in this study. Beside that, the mechanical properties of tensile, flexural, and short-beam shear strengths were measured for the effect of adding coupling agents, and the SEM of fracture surfaces were taken to study the fractural analysis. The results showed that composites with the application of organometallic coupling agents of [RO–Ti (OX–R'NH$_2$)$_3$] structure in the treatment of BMI resin were highly thermal stable. Also, it was shown that the mechanical strengths of composites fabricated by pretreatment of the carbon fibers with coupling agents were higher than those fabricated by adding coupling agents in resins, but there was no obvious improvement of mechanical properties with higher concentration of coupling agents. However, the SEM showed that the adhesion between fiber and resin can actually be improved by adding proper amount of coupling agents in the BMI resin formulation.

INTRODUCTION

In general, synthetic resin, ceramic, metal, and carbon are used as the matrix of carbon fiber composites. Epoxy resin is the most popularly used one. Bismaleimide (BMI) contains an imide group, so it possesses a better heat resistance than epoxy resin. The crosslinking of BMI is an addition reaction in which no small molecular evaporative substances is produced, so that nonvoid material can be obtained.[1] Therefore, the use of BMI in advanced composite material is worth developing.

Because the manufacturing techniques of composites are constantly improved, the mechanical properties of composites are becoming better and better. Accordingly, the study on adhesion between fiber and resin is becoming very important.[2,3] The study on improving the adhesion between epoxy resin and carbon fiber, which has been treated by coupling agent (such as Ti, Zr, and Zr/Al), is already investigated.[4,5] The resulting composites possess excellent physical properties, except for the wet-hot resistance. To address this disadvantage, some new types of organometallic coupling agents were selected that contains an amine functional group with better heat resistance. This functional group will easily react with an unsaturated double bond of BMI. Solvent of the selected coupling agent is the same as that of BMI, thus, not only the chemical bonding between carbon fiber and BMI is increased[6,7] but the wet-hot resistance and the mechanical properties of composites can be improved.
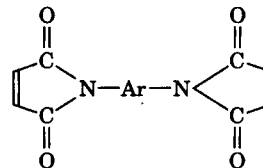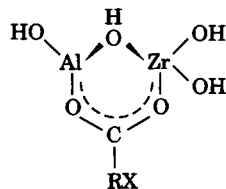
EXPERIMENTAL

### Materials

The following materials were used: Carbon cloth (Torayca 6K #1010), titanate coupling agent [Ken-

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React Co. (T_1 is [RO–Ti(OXR$_1$NH$_2$)$_3$]), (T_2 is [RO–Ti(OXR$_2$NH$_2$)$_3$])], zirconate coupling agent [Ken-React Co. (Z_1 is [RO–Zr(OXR$_1$NH$_2$)$_3$]), (Z_2 is [RO–Zr(OXR$_2$NH$_2$)$_3$])], and zircoaluminate coupling agent, (Cavedon Chemical Co.). A_3 is

Where R_2 is an aliphatic group, and R_1 is an aromatic group, and X is a binder functional group; BMI (bismaleimide) resin; Technochemic Co. (Germany), Compimide 183, hardener; 2-Methylimidazole (2-MI).
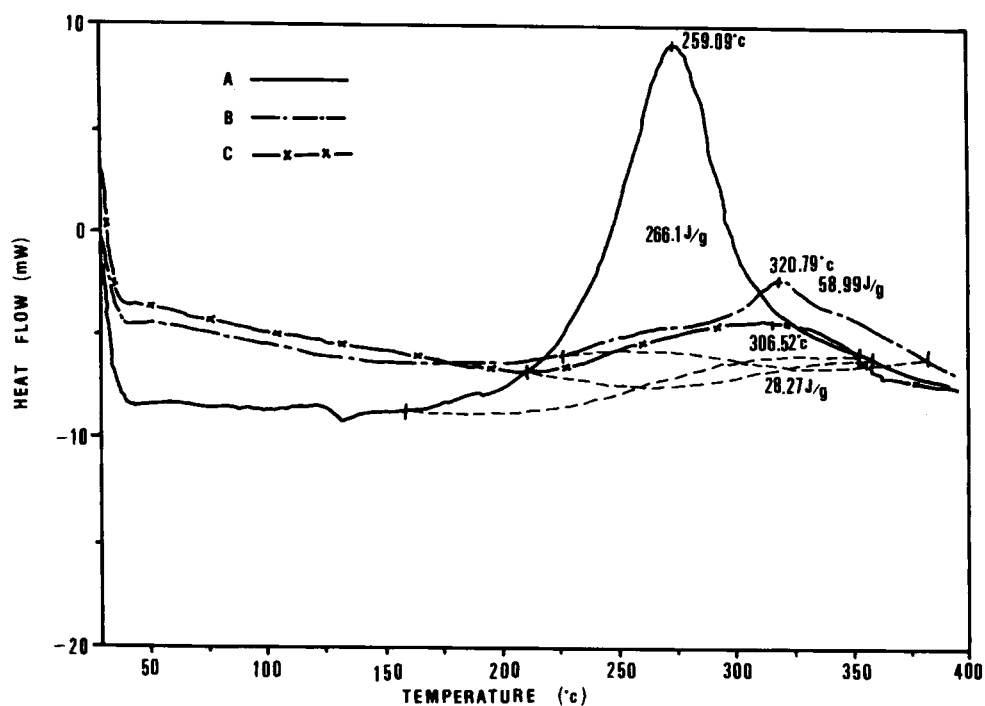
Figure 1   DSC curves of BMI (A) pure resin (B) resin with hardener, (C) post-cure.

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

Specimen	Thermal Cracking Temperature (°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

1. Treatment of carbon fiber: To desize the carbon fiber, put it in a Soxhlet extractor with chloroform and reflux at 70°C for 48 h. Extracted carbon fiber cloth is put in various coupling agents that are dissolved with IPA for 24 h. Then rinse the cloth with IPA and tap water, and vacuum dry at 60°C for 30 min.

2. Preparation of BMI–carbon fiber composites: The resin matrix studied was a high-temperature-type compimide 183 BMI resin. BMI resin was mixed with the solvent (dimethyl formamide) and then added to the hardener (2-methylimidazole) and the diluent (isopropanol), which were mixed according to the established proportion.[4] When the resin solutions were well mixed, the carbon fiber cloth were impregnated with the BMI resin. The fabrication of composites is according to the
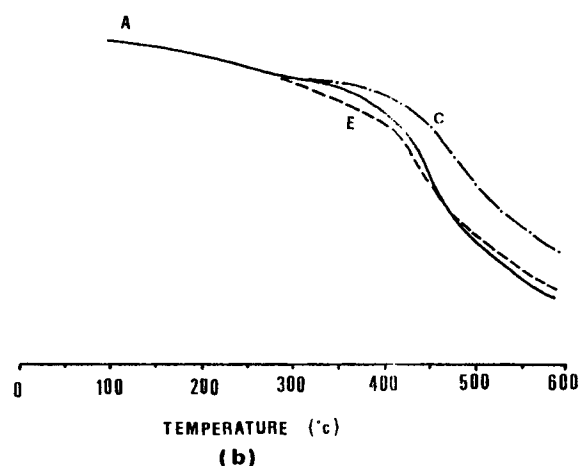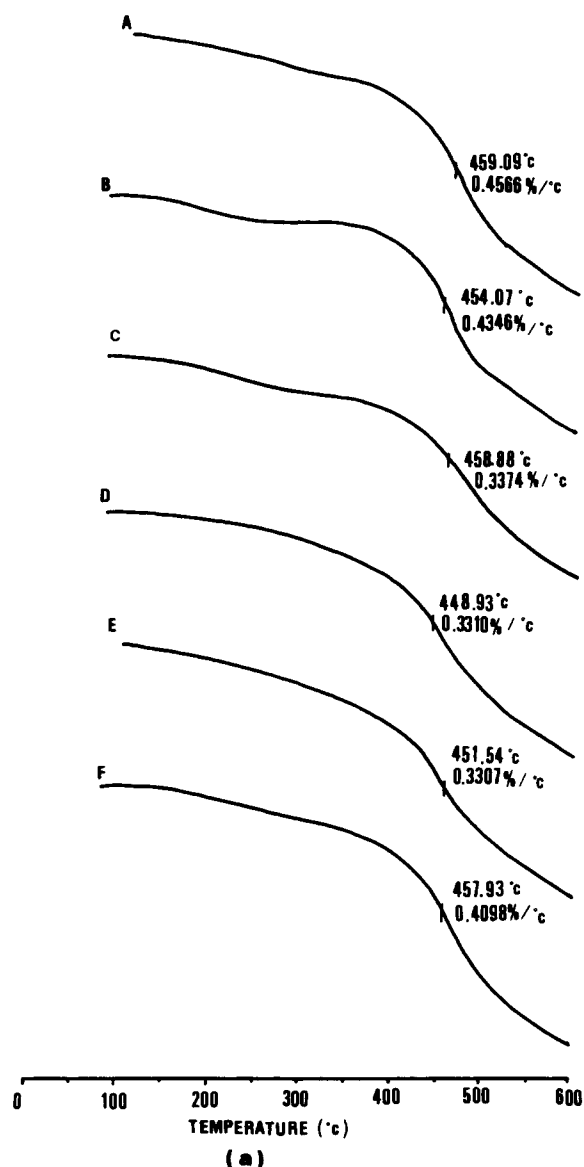

Figure 2 (a) (b) TGA curves of BMI with various coupling agents. (A) curing resin with hardener; (B) Z_1; (C) T_1; (D) Z_2; (E) T_2; (F) A_3.

Table II Relationship of Carbon Fiber Treated with 0.2 wt % Mixed Solution Consisting of Different Coupling Agents on Shear Strength and Percentage of Increase Strength of Their Composites

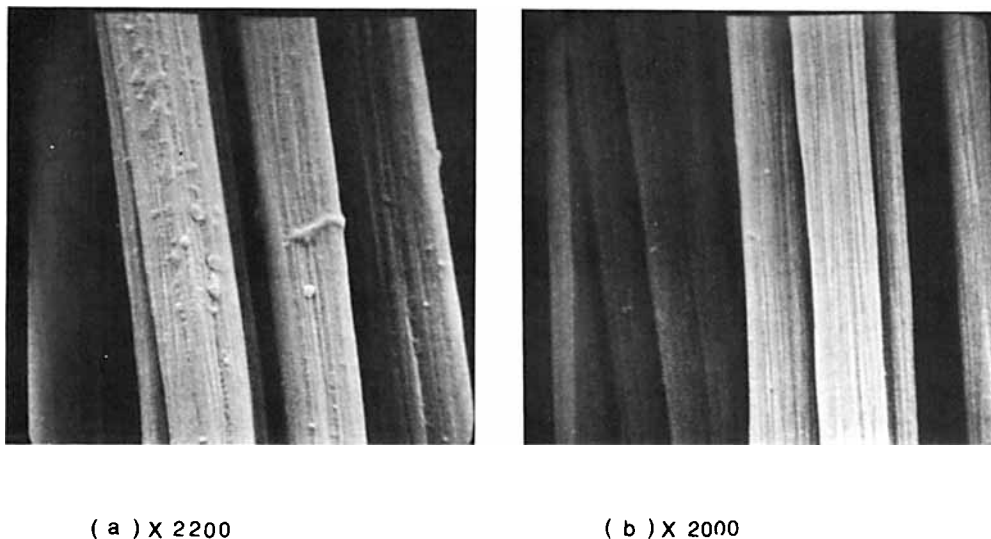| Specimen	Test Item Shear Strength (MPa)	Test Item Percentage of Increase Strength (%)
Untreated	18.91	—
Z_1	22.69	19.98
T_1	23.07	21.99
Z_2	22.52	19.09
T_2	24.39	28.97
A_3	24.01	26.96

(a) X 2200   (b) X 2000

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

following processes: Put the impregnated cloth in the vacuum oven. The temperature of oven is 110°C and the time for evacuation is 100 min. The cloths will impregnate with resins sufficiently. The prepreg sample was put in a matched metal die at 150°C for 5 min under atmosphere pressure. The temperature of hot-press is 180°C, apply 40 kg/cm^2 pressure for 2 h; then the pressure was released and cooled to room temperature. The post-cure temperature is 200°C and the time is 2 h.

3. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA): DuPont model 9900; 10°C/min; temperature 30°C ~ 400°C; N_2 gas amount flowing 100 cm^3/min.

4. Electron spectroscopy for chemical analysis (ESCA): Perkin-Elmer PHI 1950 model; 12 kV; 250 W; depth is 20 Å if Mgk α is target.

5. Shear strength: ASTM D2344-76; Instron, crosshead speed 2 mm/min; span length/thickness = 4/1. Adamel Lhomargydivision d'Instrument, SA.

Table III Relationship of Carbon Fiber Treated with 0.2 wt % Mixed Solution Consisting of Different Coupling Agents on Flexural Strength and Percentage of Increase Strength of Their Composites

	Test Item	
Specimen	Shear Strength (MPa)	Percentage of Increase Strength (%)
Untreated	182.3	—
Z_1	218.7	19.96
T_1	220	20.68
Z_2	216	18.48
T_2	238.8	30.99
A_3	223.5	22.60

Table IV Relationship of Carbon Fiber Treated with 0.2 wt % Mixed Solution Consisting of Different Coupling Agents on Tensile Strength and Percentage of Increase Strength of Their Composites

	Test Item	
Specimen	Shear Strength (MPa)	Percentage of Increase Strength (%)
Untreated	351.3	—
Z_1	435.6	23.99
T_1	449.6	27.98
Z_2	432	22.97
T_2	456.69	30
A_3	442.6	25.98

6. Flexural strength: ASTM D790; three-point bending method; span length/thickness = 16/1.
7. Tensile strength: ASTM D3039; room temperature; crosshead speed 2 mm/min.
8. Scanning electron microscopy (SEM): Cambridge steroscan S4-10 type and S360 type.

RESULTS AND DISCUSSION

DSC Analysis of BMI Added with Coupling Agent Curing Reaction

Figure 1 shows that the curing degree of BMI with 0.2 phr 2-MI is 78% at 180°C for 2 h. Then post-curing at 200°C for 2, 3, and 4 h, the curing degrees all reach 90%.

TGA Analysis of BMI Added with Coupling Agent

After curing BMI, which is added with various coupling agents, TGA was used to measure the heat stability, and the results are shown in Figure 2. From the figure we know that when Ti, Zr coupling agent is added to BMI, the thermal cracking temperature will decrease slightly due to these organometallic coupling agents containing neoalkoxy group, which has thermal stability.[8] At about 100–200°C, there is a little weight loss because a little water and impurity exist in BMI. Table I shows that the decrease of
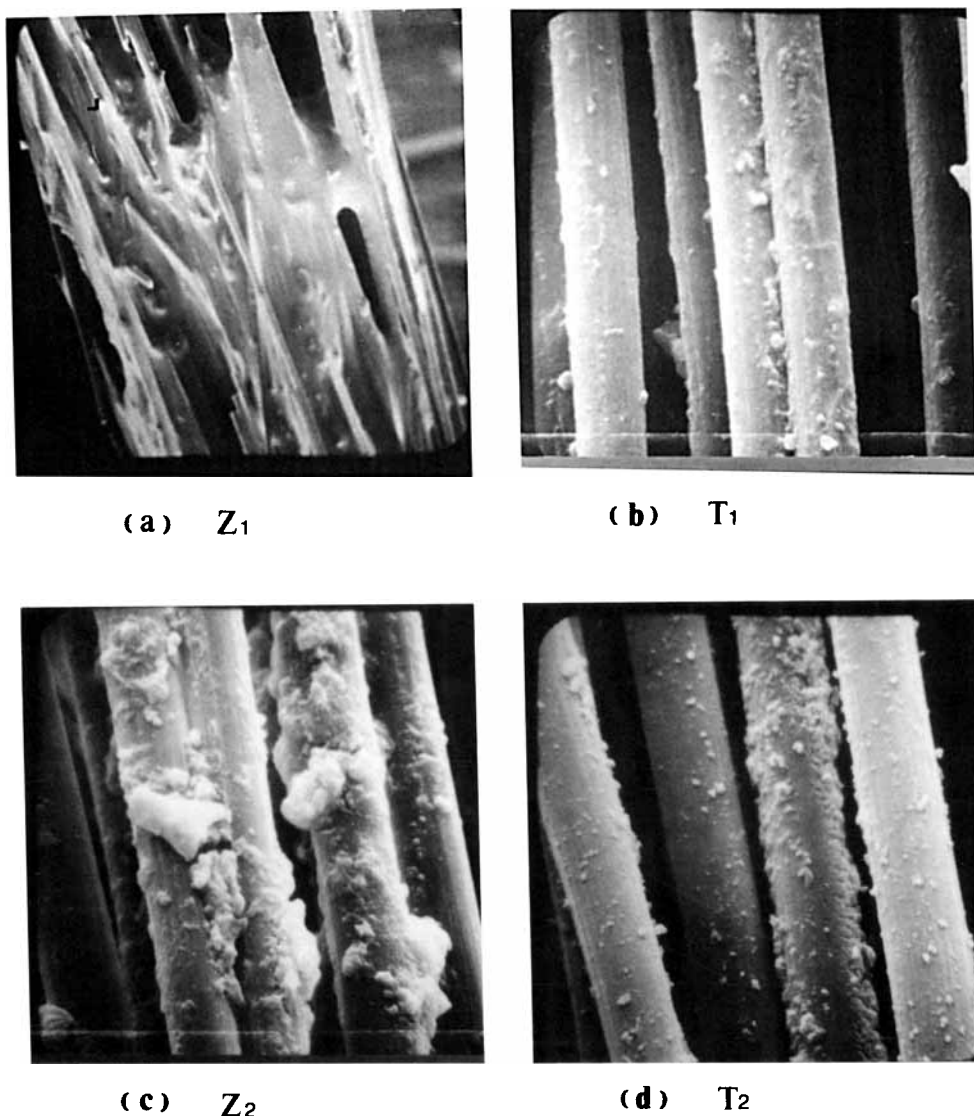

(a) Z_1 (b) T_1

(c) Z_2 (d) T_2

Figure 4   Scanning electron micrograph of the surface of carbon fiber treated with various coupling agents (0.2 wt %): (a) Z_1, (b) T_1, (c) Z_2, (d) T_2 (X 2200).

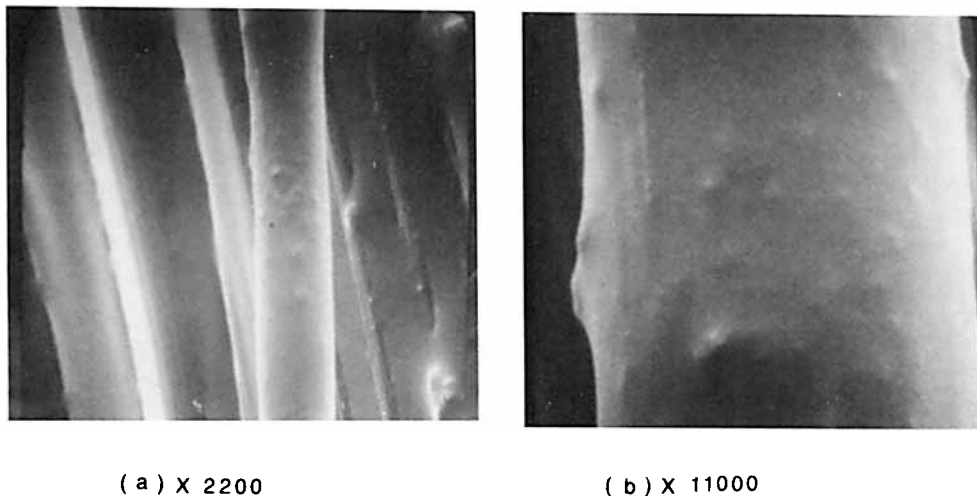(a) X 2200   (b) X 11000

Figure 5   Scanning electron micrograph of the surface of carbon fiber treated with 0.2 wt % A_3 coupling agent.

thermal cracking temperature and the weight loss of T_1 coupling agent are the smallest, followed by Z_1, Z_2 coupling agent, and then A_3 coupling agent. Therein, the Ti, Zr coupling agent containing the aromatic group (T_1, Z_1) is greater than that containing the aliphatic group (T_2, Z_2). Thus, the composites made of BMI in which Ti coupling agent is added have excellent heat stability.

Carbon Fiber Treated with Coupling Agent

1. Figure 3 shows the surface of carbon fiber before and after desizing. The surface of carbon fiber treated with Zr or Ti coupling agent treatment will have different outlooks, as shown in Figure 4. Among Zr coupling agent treatment, Z_1 has the property of stickiness such that many fibers are stuck together. As of Z_2, due to XR' ($— C_2H_4 — NH — C_2H_4 —$) in its molecular structure, it will attach on fiber surface easily and form clusters.

2. In Ti coupling agent treatment, the resulting outlook of fiber surface does not vary too much. Due to the molecular structure of T_1, which contains XR' ($— C_6H_4 —$), bigger, beanlike clusters are formed. As of T_2, small and uniform beanlike clusters are formed due to XR' ($— C_2H_4 — NH — C_2H_4 —$) in its molecular structure. In general, the molecular structure will not have as much influence on Ti coupling agents as on Zr coupling agents.

3. With A_3 treatment, the molecular structure is different from the latter and will smoothly attach on fiber surface (see Fig. 5) because it has better dispersion and reduced viscosity.[9]

Table V   Element Composition of the High-Resolution ESCA Spectra for Various Coupling Agents of Treatment (%)

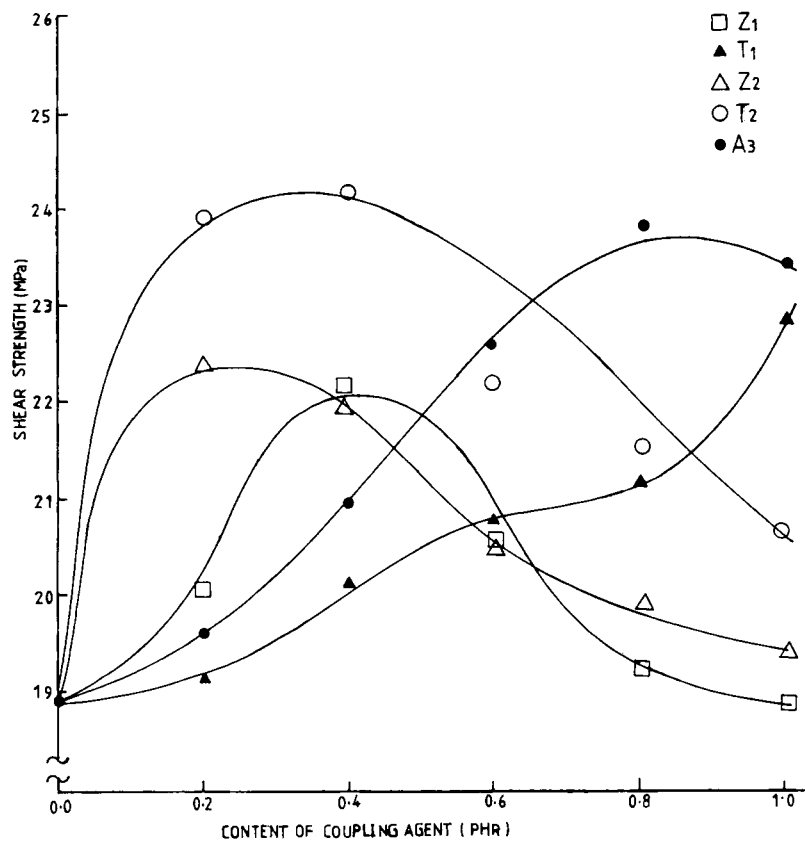| Sample	XPS Surface Stoichiometrics						
	O	C	ZR	AL	C/O	ZR/O	AL/O
Untreated	22.2	77.7	—	—	3.5	—	—
Z_1	28.1	71.5	0.3	—	2.54	0.0106	—
T_1	31.5	68.4	—	—	2.17	—	—
Z_2	29.8	69.4	0.6	—	2.33	0.0201	—
T_2	32.9	67.0	—	—	2.04	—	—
A_3	23.4	71.7	0.3	4.4	3.06	0.0128	0.1880

Figure 6 The effect of the coupling agent concentration on the shear strength of CFRP.
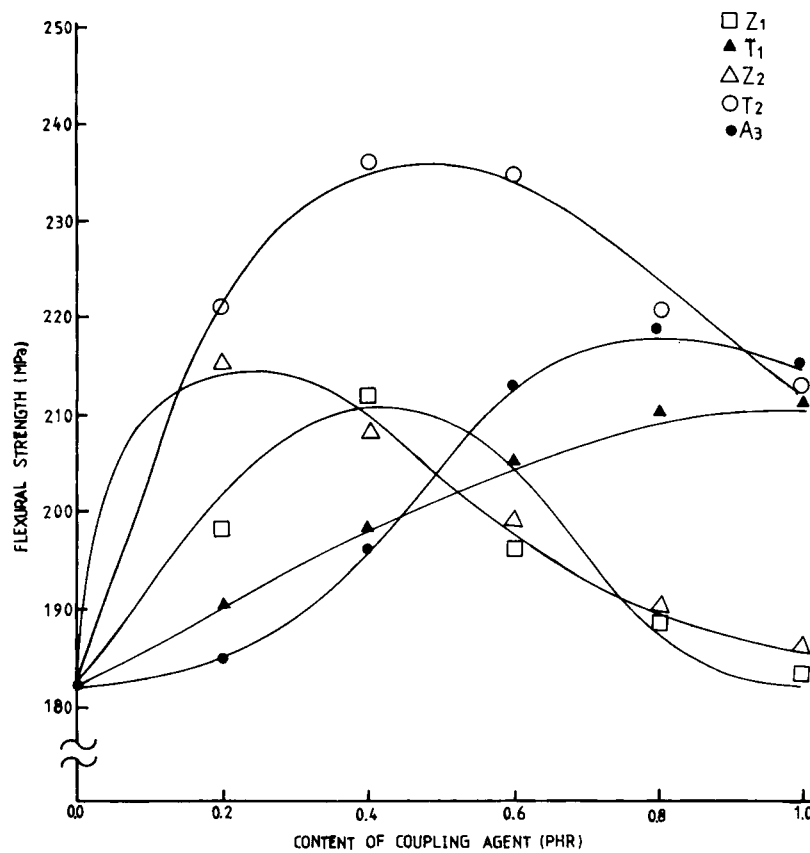

Figure 7 The effect of the coupling agents concentration on the flexural strength of CFRP.

Mechanical Properties of Composites of Coupling-Agent-Treated Carbon Fiber

Table II shows that the shear strength of composites of treated carbon fiber increases much more than of untreated carbon fiber. Among all, T_2 has the best result such that the shear strength of treated increases 28.97% more than that of untreated. In terms of the effect on increasing shear strength, Ti coupling agent is most effective, and then followed by A_3 and Zr coupling agent.

Table III shows the relationship of carbon fiber treated with various coupling agents on flexural strength, which is similar to the shear strength (Ti $> A_3 >$ Zr). Take T_2, the best flexural strength of 238.8 MPa can be obtained, which is 30.99% more than the untreated one.

The relationship of carbon fiber treated with various coupling agents on tensile strength is shown in Table IV. Even Z_2, which has the least increase of tensile strength, increases 22.97%.

From the above, we know that the improvement of mechanical properties is due to the increased surface area and increased oxygen content of fiber surface (see Table V), which can improve the interface between matrix and carbon fiber.[10-12] Therein, the adhesion of Ti coupling agent is better than that of A_3 coupling agent, due to the ether linkage or hydrogen bond between fiber and coupling agent while Ti coupling agent only has the ether linkage.[4] Also, due to the steric hindrance of the molecular structure which the radius of the atom of Zr element is bigger than that of Ti element. Moreover, the binding energy of Ti element (560 eV) is higher than that of
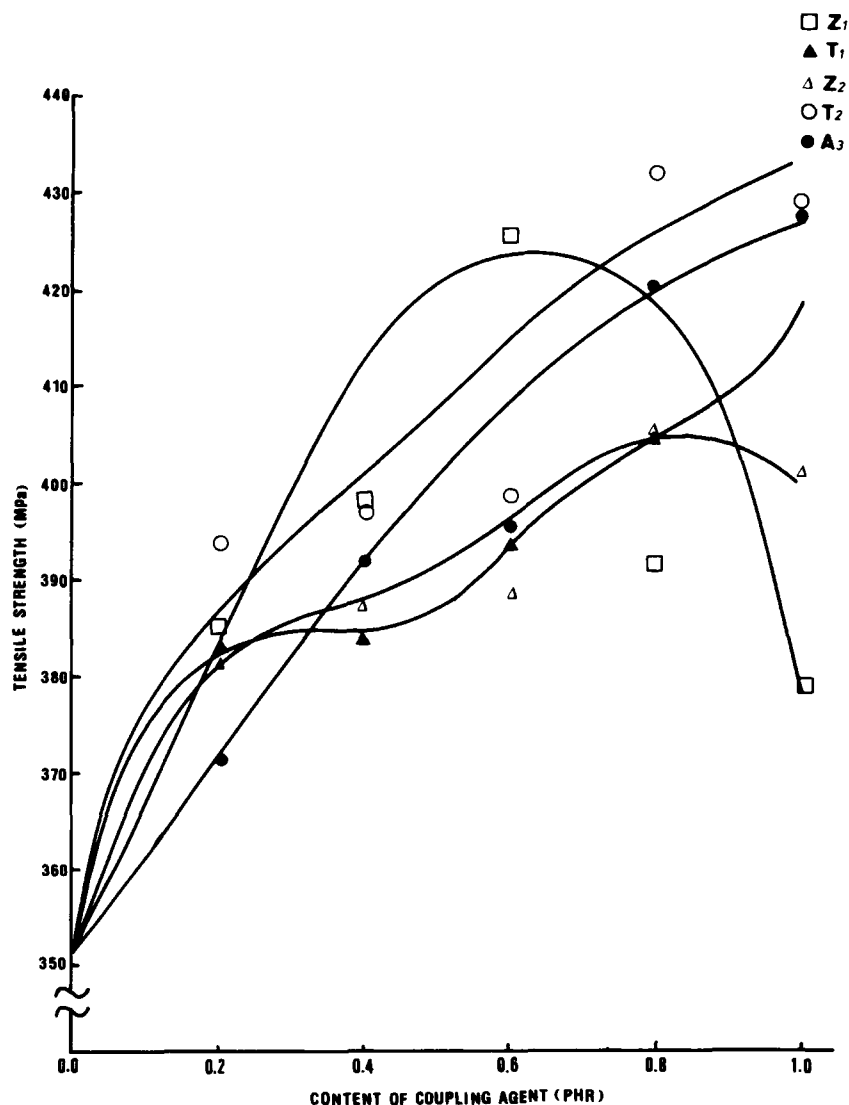

Figure 8 The effect of the coupling agent concentration on the tensile strength of CFRP.

Zr element (186 eV). Thus, at the same ether linkage between fiber and coupling agent, the adhesion of Ti coupling agent is greater than that of Zr coupling agent. Again, the oxygen content on the surface of the carbon fiber, which was treated with the A_3 coupling agent, is the least while it has the most Zr, A_1 elements, which create the coodinate covalent complex. Hence, the adhesion of A_3 coupling agent is better than that of Zr coupling agent.

Mechanical Properties of Composites in which Coupling Agent Is Directly Added to BMI

Figure 6 shows that the shear strength can be effectively increased only by 0.2 phr of T_2 or Z_2. This is due to the aliphatic molecular structures of T_2 and Z_2, which make them easily attached to the fiber surface. As of A_3 and T_1, the shear strength does not have obvious increase until the content is 0.8–1.0 phr because of their larger molecular structure and high viscosity with the same concentration.

Figure 7 shows the effect of the coupling agent concentration on the flexural strength of composites. T_2 is the most effective and the maximum flexural strength of 235.5 MPa is reached with a content of 0.4 phr, which is 29.19% more than without adding coupling agent. The reason is the same as before and T_2 is most effective is that its wettability between fiber and resin is better than other coupling agents.[13]

Figure 8 shows that, in most cases, the tensile strength increases as content of coupling agent increases. For example, when the content of A_3 is increased to 1.0 phr, the tensile strength increases about 23%. As the content of coupling agent increases, the wettability between fiber and resin is increased and it enables resin to penetrate evenly into the spaces between fiber and fiber.[4] This is the main reason for tensile strength being increased.

ESCA of Coupling-Agent-Treated Carbon Fiber

The main purpose of coupling agent surface treatment of carbon fiber is to increase carbon fiber surface area and surface activity, where the latter is more important. Usually, surface activity increases as the content of oxygen increases.

After carbon fiber is treated with Zr coupling agent, we can see from Figure 9(b) and 9(d) that Zr coupling agent has reacted with the fiber surface. The ESCA spectra of Figure 9(f) shows the reaction of A_3 coupling agent. However, from the ESCA spectra of Figure 9(c) and 9(e), we cannot see Ti. This is due to the hydrolysis of Ti or reactions of other functional groups, which hide Ti.[14,15]

Table V shows the carbon fiber treated with Ti or Zr coupling agent. The oxygen content, which is measured by semiquantative method, of fiber surface has an obvious increase. Using T_2 coupling agent will have the best result, with the oxygen content increasing to 48.19%. We agreed that with the content of oxygen increase the mechanical properties of composites were improved.[10-12] Also, the oxygen content on the surface of the carbon fiber, which were treated with the A_3 coupling agent, is the least while it has the most Zr, Al elements, which create
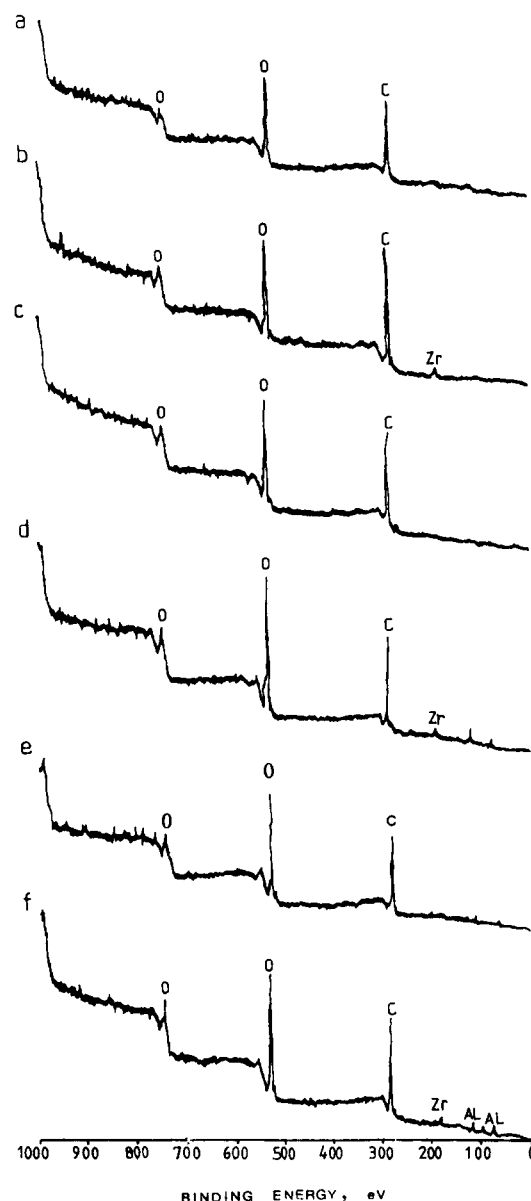

Figure 9 ESCA spectra of carbon fiber treated with various coupling agents: (a) untreated; (b) Z_1, (c) T_1, (d) Z_2, (e) T_2, (f) A_3.
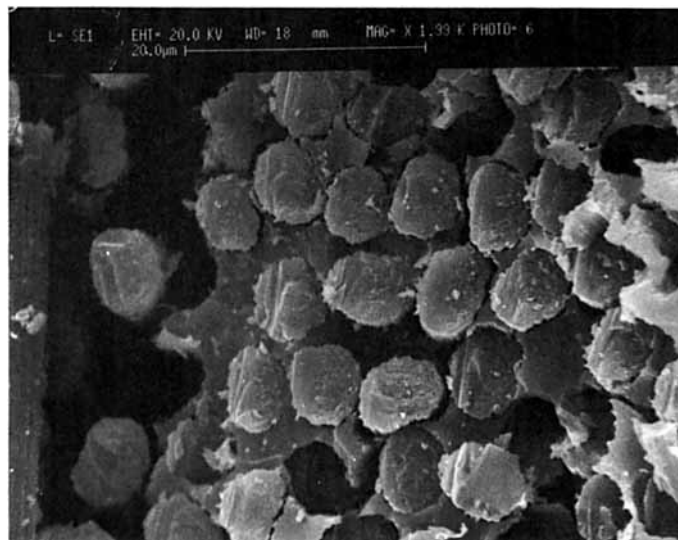
(a)   Z₁

(b)   T₁

Figure 10   Scanning electron micrograph of the fracture surface of CFRP flexural specimens with various coupling agents treated: (a) Z_1, (b) T_1, (c) Z_2, (d) T_2, (e) A_3 (X 2000).

the coodinate covalent complex. Thus, the adhesion of A_3 coupling agent is better than that of Zr coupling agent.

Observation of Fracture Surface

Figure 10 shows the SEM of the fracture surface of composites of BMI reinforced carbon fiber, treated with various coupling agents.

Figure 10(a) shows the fracture surface of Z_1

treated where not much resin is left; so we know that its adhesion is weak. Also, some fibers are being pulled out. Therefore, the flexural strength is not as good as others. From T_2 treated fracture surface, we can see that the resin is evenly distributed and attached on carbon fiber [see Fig. 10(d)]. This kind of fracture, which takes place at an instant and results with smooth fracture surface, is called tensile failure. Thus, treatment with T_2 will produce the greatest flexural strength.
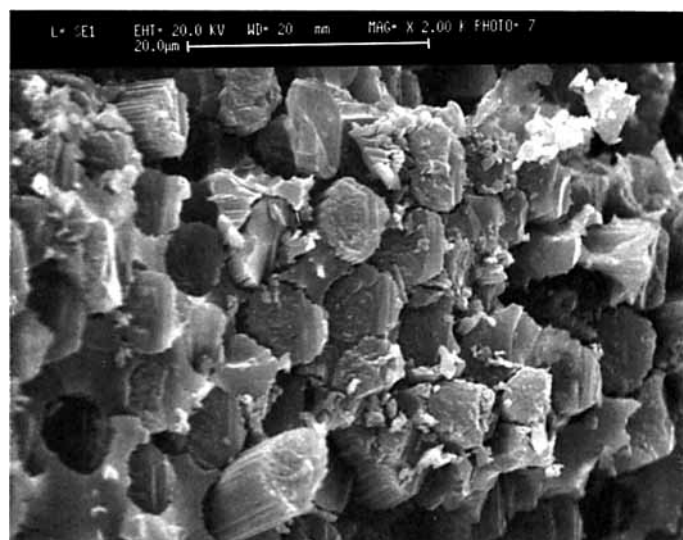
(c) Z$_2$
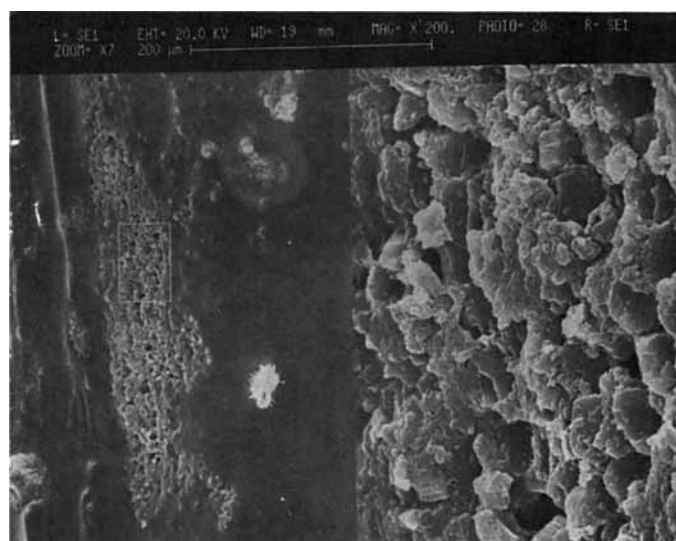
(d) T$_2$

Figure 10 (Continued from the previous page)

CONCLUSION

1. From DSC and TGA analysis of BMI added with coupling agent, we obtain the best curing condition, which is 180°C × 2 h and the post-curing, which is 200°C × 2 h.
2. In terms of the mechanical properties of composites of coupling-agent-treated carbon fiber, the order is Ti > A$_3$ > Zr.

3. When coupling agent is directly added to BMI, in most cases, the tensile strength of composites increases as content of coupling agent increases (0.2–1.0 phr). However, the viscosity of Z$_1$ coupling agent is so high that the 0.6-phr concentration is its top.
4. Both surface-treated carbon fiber and directly added to BMI with these coupling agents have the same adhesive effect. Also, the mechan-
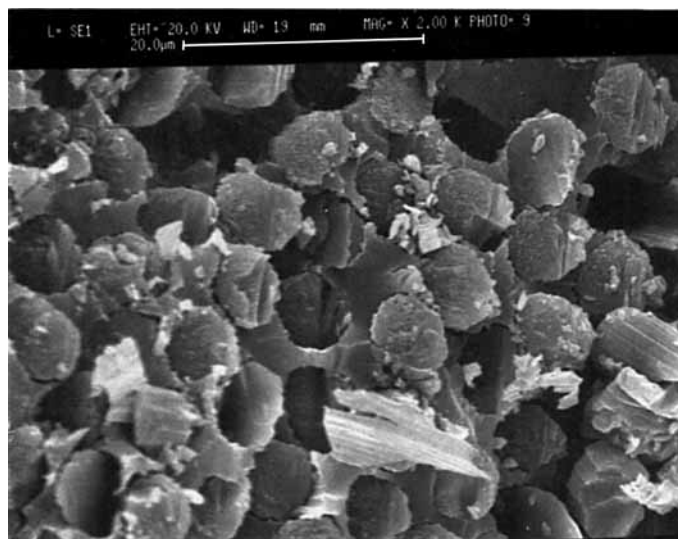
(e)   A₃

Figure 10   (*Continued from the previous page*)

ical strengths needed to reach the same level as those coupling agents directly added to BMI should use more, but it could reduce the processing.

5. ESCA shows that BMI added with coupling agent of [RO–Ti (OX–Ti(OX–R'NH₂)₃] type will result with greater adhesion.

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