

Influence of Silane Coupling Agents on the Interlaminar and Thermal Properties of Woven Glass Fabric/Nylon 6 Composites

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Abstract: In this study, the influence of silane coupling agents, featuring different organo-functional groups on the interlaminar and thermal properties of woven glass fabric-reinforced nylon 6 composites, has been by means of short-beam shear tests, dynamic mechanical analysis, scanning electron microscopy, and thermogravimetric analysis. The results indicate that the fiber-matrix interfacial characteristics obtained using the different analytical methods agree well with each other. The interlaminar shear strengths (ILSS) of glass fabric/nylon 6 composites sized with various silane coupling agents are significantly improved in comparison with that of the composite sized commercially. ILSS of the composites increases in the order: Z-6076 with chloropropyl groups in the silanes > Z-6030 with methacrylate groups > Z-6020 with diamine groups; this trend is similar to that of results found in an earlier study of interfacial shear strength. The dynamic mechanical properties, the fracture surface observations, and the thermal stability also support the interfacial results. The improvement of the interfacial properties may be ascribed to the different chemical reactivities of the reactive amino end groups of nylon 6 and the organo-functional groups located at the ends of the silane chains, which results from the increased chemical reactivity in order chloropropyl > methacrylate > diamine.

Keywords: interlaminar property, dynamical mechanical property, woven glass fabric/nylon 6 composite, silane coupling agent.

Introduction

An introduction of interphase by use of coupling or sizing agents to a fiber-reinforced polymer composite material not only provides the ability to control the interfacial characteristics at the interface between the fiber and the matrix in a composite, depending on the chemical and physical interaction involved, but also contributes to improving various properties of a composite material.¹⁻⁴

The chemical bonding at the fiber-matrix interfaces is critically important to understand the interfacial strength in a fiber-reinforced polymer matrix composite. Especially, an application of silane-based sizing interphase onto glass fiber surface not only protects the fiber from possible surface damages on handling, but also significantly improve the adhesion between the reinforcing fibers and thermosetting or thermoplastic polymer matrix.^{2,5-9} The chemical bonds can

be formed between the chemical groups at the fiber surface and in the polymer matrix resin. For instance, the hydroxyl groups in the silanols [Si(CH₃O)] of a silane coupling agent and the hydroxyl groups at the glass fiber surface can form the chemical bonds. The organo-functional groups located at the end of silane chains with the other end anchored at the glass fiber surface may form the chemical bonds with reactive amino end groups in the nylon 6 molecular chains. Silane compounds with different organo-functional groups may importantly influence the chemical reactivity and the bonding strength between inorganic glass fiber and organic polymer resin.⁵

The experimental approaches for examining the interfacial properties between reinforcing fiber and matrix are largely divided into two categories. The one is to indirectly use a simplified fiber-matrix specimen for the interfacial measurement of a composite material. The typical examples are single fiber pull-out test, single fiber microbonding test and embedded single fiber fragmentation test.¹⁰⁻¹² These methods use a model composite composed of a single filament fiber

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as representative reinforcing fiber and of a thermoplastic or thermosetting resin as representative matrix to mimic the practical composite material with corresponding fibers and matrix. The test results may provide useful information on predicting the interfacial property of a composite. The other is to directly use a real composite specimen in the interfacial measurement. The typical examples are short-beam shear test,^{13,14} microindentation test^{13,15} fracture toughness test¹⁶ and dynamic mechanical analysis.¹⁷⁻¹⁹ These methods are also widely used because they may provide practical information on the interfacial properties of a composite material. All the methods above-mentioned may give quantitative information. Also, qualitative interpretation on the interfacial phenomenon may be obtained from microscopic observations of the fiber-matrix fracture surfaces of a composite.

Consequently, the objective of the present study is to investigate the effect of various silane coupling agents with different organo-functional groups on the interlaminar and thermal properties of glass fabric/nylon 6 composites through short-beam shear test, dynamic mechanical analysis, fracture surface observations, and thermal stability test.

Experimental

Materials. E-glass woven fabrics with plain texture (KN 1800-HS, Kangnam Chemical Co., Korea) were used as reinforcing fibers in this work. The 'as-received' fiber surface is commercially sized but the information has not been released from the manufacturer. The average diameter of a continuous single fiber filament in the fabric is about 16 μm . The thickness per ply of the 'as-received' fabric is 0.18 \pm 0.02 mm. Pellet type nylon 6 resin (Grade MC100L), supplied in the pellet form from Kanebo Gohsen, Ltd., Japan, was used as matrix resin. Glass fabrics and nylon 6 were sufficiently dried in an oven prior to fabrication of each composite specimen.

Four silane coupling agents with different organo-functional groups, supplied from Dow Corning Corp. U.S.A., were used to explore their effects on the interlaminar and dynamic mechanical characteristics of woven glass fabric/nylon 6 composites. The commercial sizes on the glass fiber surface

were completely desized at 400 °C for 45 min prior to sizing treatment in the present study. The sizing content of 1.0 wt% has been used throughout this work. Table I summarizes the chemical structure and name of silane-based coupling agents with different organo-functional groups.

Fabrication of Woven Glass Fabric/Nylon 6 Composites. Woven glass fabric/nylon 6 composites were fabricated in a compressive molding machine using a film stacking method. A number of nylon 6 films were prepared repetitively by melting at 228 °C for 30 seconds and then naturally cooling in between two clean and smooth stainless steel plates using a hot press. A number of glass fabrics and nylon 6 films were stacked alternately in a steel mold. The nylon 6 films interleaved between the glass fabrics were remelted, sufficiently impregnated and consolidated under given melting and cooling cycles. The composites were fabricated by melting at 228 °C for 5 min, pressing at 1,000 psi for 1.5 min, and then naturally cooling down to ambient temperature. The applied pressure was 1,000 psi during processing. The dimensions of the composite fabricated were 50 \times 50 mm. The thickness of each composite specimen was prepared according to individual test requirements. The average thickness per ply in a composite is about 0.32 mm. The ratio of the resin to the fiber in the composite is 6 : 4.

Analysis. A thermogravimetric analyzer (TGA 951, TA Instrument) was used to examine the content of the commercial size of 'as-received' glass fibers and the thermal stability of the composites. A heating rate of 10 °C/min was used purging a N₂ gas of 50 cc/min.

The short-beam shear tests of the composites were conducted according to ASTM D-2344 using a UTM (Instron 4467). The crosshead speed was 1.3 mm/min and the span-to-depth ratio was 5. Ten specimens from each composite were used to have the average value of interlaminar shear strength.

The storage modulus, loss modulus and $\tan \delta$ of the composites were measured in the vertical mode using a dynamic mechanical analyzer (DMA 983, TA Instrument). The heating rate of 2 °C/min was used with purging a N₂ gas of 50 cc/min. Use of the slow rate is to minimize the possible thermal lag between the program temperature and the com-

Table I. Four Silane-based Coupling Agents Used in the Present Study

No	Trade Name	Chemical Name Chemical Structure	Organo-functional Group
1	Z-6020	<i>N</i> -2-Aminoethyl-3-aminopropyl-trimethoxysilane $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$	Diamine
2	Z-6030	3-Methacryloxypropyltrimethoxysilane $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$	Methacrylate
3	Z-6040	3-Glycidoxylpropyltrimethoxysilane $\text{OCH}_2\text{CH}(\text{CH}_2\text{O})_3\text{Si}(\text{OCH}_3)_3$	Epoxy
4	Z-6076	3-Chloropropyltrimethoxysilane $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$	Chloropropyl

posite specimen temperature. A fixed frequency of 1 Hz and the oscillation amplitude of 0.25 mm were used.

The delamination pattern after the short-beam shear test and the fracture pattern of each composite specimen were observed using a scanning electron microscopy (SEM, JEOL JSM-5900).

Results and Discussion

In the present work, TGA thermograms for commercially sized and desized glass fabrics were studied to examine the sizing content in the 'as-received' fabric, as shown in Figure 1. The result informed that the commercial size starts to lose its weight around 150°C and is completely removed below 400°C due to decomposition of the sizing ingredients. The content of the commercial size is estimated to be approximately 1~2% of the total fiber weight used. It is known that commercial applications of silane coupling agents include silanes as an ingredient with additional reactive or nonreactive chemicals such as lubricants, antistatic agents, etc.⁵ Even though the silane is partial constituent of the formulations in the sizing system, this TGA result provides useful information to determine the concentration of silane coupling agents to be 1 wt% in the present study. It has been found from microscopic observations that sizing of 1 wt% does not alter significantly the appearance of the surface, as reported previously.¹² The thickness has been expected to be less than 0.1 μm. It is noted that the surface chemistry of glass fiber may be changed due to different interactions between the hydroxyl groups in the fiber surface and the hydroxyl groups of silanols in the silane coupling agents having different organo-functional groups onto the fiber surface, although the appearance of the surface does not change significantly.

Interlaminar Shear Strength. Composite laminate tests are often used to directly measure fiber-matrix adhesion in a fiber-reinforced polymer matrix composite. Short-beam shear test is one of the frequently used test methods because the fiber-matrix interface dominates the test results and the test method is relatively simple with minimum complication of specimen preparation.² Figure 2 compares the interlaminar shear strengths (ILSS) for glass fabric/nylon 6 composites sized with four silane coupling agents. The short-beam shear testing was done with removing the applied load as soon as the initial delamination between the fiber and the matrix takes place through the thickness in a composite right after the yield point in the stress-strain behavior. The averaged ILSS values were obtained from the maximum load of the stress-strain curve for each specimen using the following equation.

$$\tau_{max} = 3P_{max}/4b \cdot t$$

where τ_{max} is the ILSS, P_{max} is the maximum load, b is the width of the specimen, and t is the thickness of the specimen.

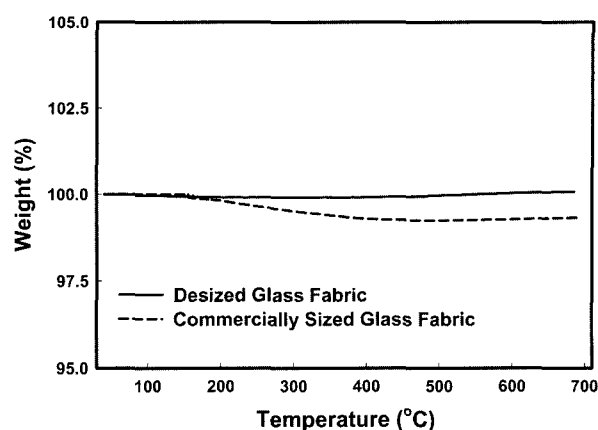


Figure 1. TGA result showing the weight change of commercially sized material in the glass fabric before and after desizing.

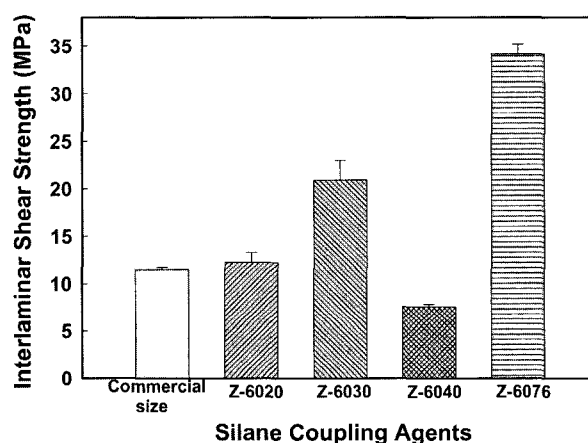


Figure 2. Interlaminar shear strengths for various silane-sized woven glass fabric/nylon 6 composites obtained by short-beam shear tests.

The ILSS value is the greatest with the Z-6076 that has chloropropyl organo-functional groups at the molecular ends. Comparing with the commercially sized composite, the ILSS is remarkably improved by 196%. The ILSS value in the case of the Z-6030 is significantly increased by 82%. It is also slightly increased by 6% in the case of the Z-6020. Such the improvement has been found similarly in the interfacial shear strength (IFSS) results studied for a single glass fiber system embedded in nylon 6 microdroplet using a microbonding test method in an earlier report.¹² Even though the percent improvement in the ILSS is relatively lower than that in the IFSS, the tendency of the improvement quite agrees with each other, with the exception of the Z-6040. The ILSS value of the Z-6040 is even lower than that of the commercially sized one. In the single fiber microbonding test, the composite sized with the Z-6040 exhibits a large increase of the IFSS by about 115%. The reason for

this discrepancy has been found from some possible causes occurred during the composite fabrication in the present work. There has been no wetting problem with the formation of the nylon 6 microdroplet on a single glass fiber filament prepared for microbonding tests. However, in the glass fabric/nylon 6 laminate prepared using the Z-6040 coupling agent only, it has been found that the glass fiber surface is not sufficiently wetted or impregnated with the nylon 6 resin under the same processing condition as used for fabricating other composites. Such the poor wetting is because the Z-6040 of relatively high viscosity puts the fiber filaments together. As a result, the resin cannot be properly impregnated into the individual filaments bound together, causing the incomplete fabrication of the composite with pores. Such the wetting problem obviously weakens the interfacial adhesion between the fiber and the matrix and results in the lowest value of ILSS. Therefore, the short-beam shear test

result suggests that the Z-6040 is not appropriate for applying on the fiber surface to make a glass fabric/nylon 6 composite although it increases the IFSS value, as found previously.¹²

Figure 3 shows the scanning electron microphotographs observed in the delaminated region after the short-beam shear test for various glass fabric/nylon 6 composites sized with different coupling agents. The photos were taken at the same magnification of $\times 1000$. Interlaminar failure was microscopically verified by the delamination pattern of variously sized composite specimens. The result indicates that the composite sized with the Z-6076 exhibits the strongest adhesion between the fiber and the matrix, resulting in the highest ILSS with a larger amount of the resin adhered to the glass fibers than in the other composite specimens, as seen in Figure 3(E). The composite sized with the Z-6040 in Figure 3(D) exhibits the weakest interlaminar failure leaving many debonded fibers behind. It is

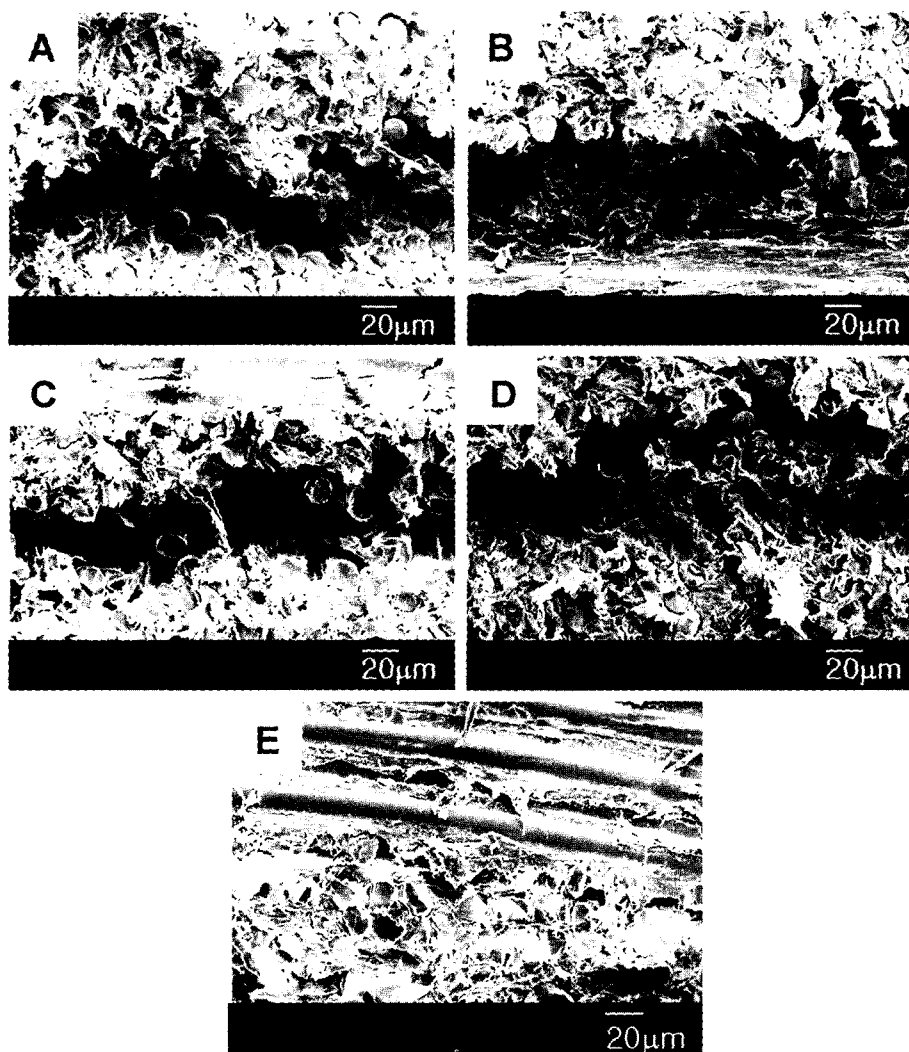


Figure 3. Scanning electron microphotographs ($\times 1000$) in the delaminated region after the short-beam shear test for woven glass fabric/nylon 6 composites sized with different coupling agents. (A) commercially sized, (B) Z-6020, (C) Z-6030, (D) Z-6040, and (E) Z-6076.

likely that the composite in Figure 3(C) (Z-6030) has the better adhesion than the composites in Figure 3(A) (commercial size) and 3(B) (Z-6020). These microscopic views also support qualitatively the ILSS measurements.

Fracture Surface. Qualitative information on the effect of silane coupling agents on the interfacial adhesion between the fiber and the matrix may be more apparently found from the fracture surface examination of each composite. Figure 4 represents the scanning electron microphotographs showing the fracture surfaces of nylon 6 composites reinforced with glass fabrics desized and sized with various coupling agents. The result indicates that the glass fabric/nylon 6 composite (E) sized with the Z-6076 exhibits the highest adhesion between the fiber and the matrix resulting in the greatest extent of the resin adhering on the pulled-out fiber surface upon fracture, reflecting a

ductile fracture pattern. As expected, Figure 4(D) microscopically demonstrates that use of the Z-6040 decreases the fiber-matrix adhesion in the glass fabric/nylon 6 composite, leaving a number of traces of clearly pulled-out fibers behind. It is also observed that there is a greater extent of the resin remaining on the fiber surface after fracture in Figure 4(B) (Z-6020) and 4(C) (Z-6030), compared with the commercially sized counterpart in Figure 4(A) (commercial size).

Dynamic Mechanical Behavior. Since dynamic mechanical analysis has been widely used as a powerful tool for studying the viscoelastic behavior of macromolecular structure and motion as well as polymer morphology, it has been increasingly utilized for characterizing the interfacial adhesion in fiber-reinforced polymer composite systems in terms of storage modulus, loss modulus, and $\tan \delta$.^{20,21} Figures 5 and 6 represent the dynamic mechanical behavior of glass/

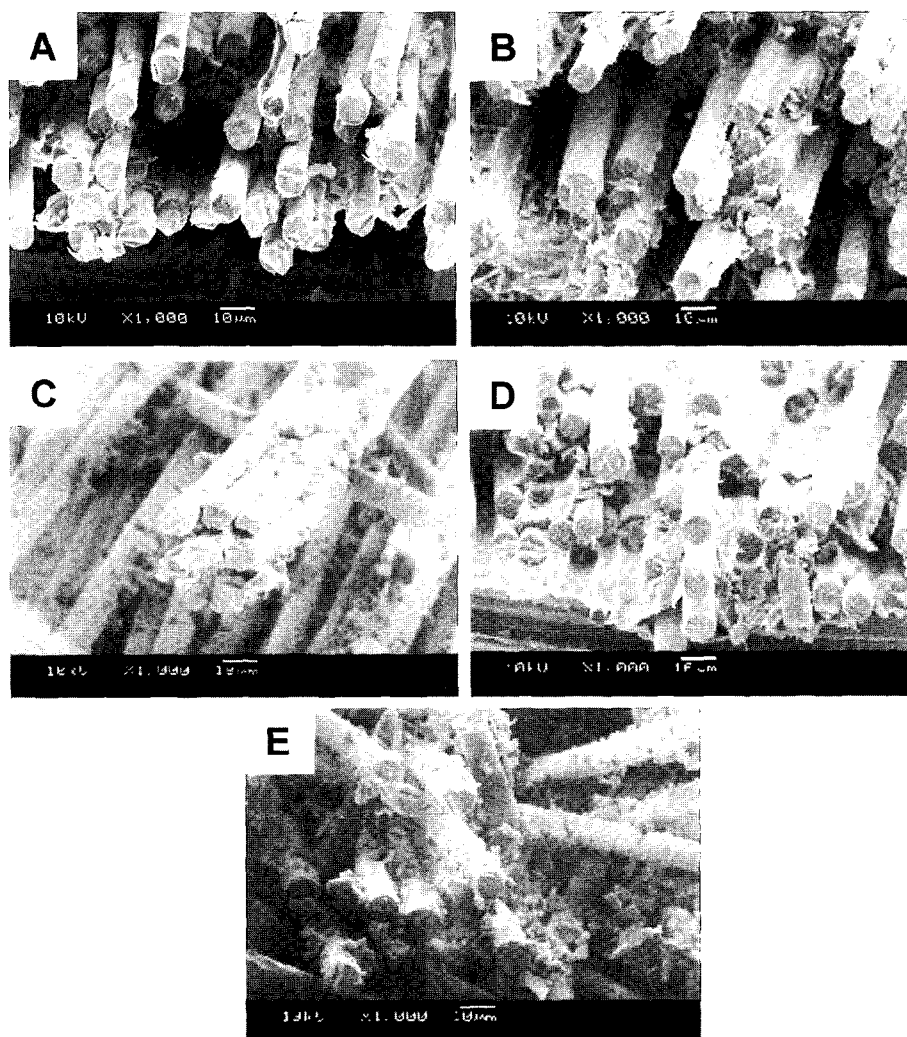


Figure 4. Scanning electron microphotographs showing the fracture surfaces of nylon 6 composites reinforced with various woven glass fabrics (A) commercially sized, (B) Z-6020, (C) Z-6030, (D) Z-6040, and (E) Z-6076. The scale bar indicates 10 μm at magnification of $\times 1000$.

nylon 6 composites fabricated using glass fabrics sized with four different silane coupling agents and also sized commercially for comparison. Figure 5 depicts the variation of the storage modulus as a function of temperature. The storage modulus of the composites sized with Z-6030 and Z-6076 is greater than that of the commercially sized counterpart. The composite sized with Z-6020 exhibits the comparable log E' values with the commercially sized one. However, the modulus of the composite sized with Z-6040 is the lowest. This dynamic mechanical result is quite consistent with the ILSS result. The lowest storage modulus for Z-6040 is attributed to the poor interfacial adhesion between the fiber and the matrix, as described earlier.

It is known that nylon 6 is a semicrystalline polymer having a glass transition temperature (T_g) of about 55 °C and melting point of about 225 °C. The T_g of nylon 6 is significantly enhanced by an incorporation of reinforcing glass fibers. The T_g s of the composites are observed to be in the range of

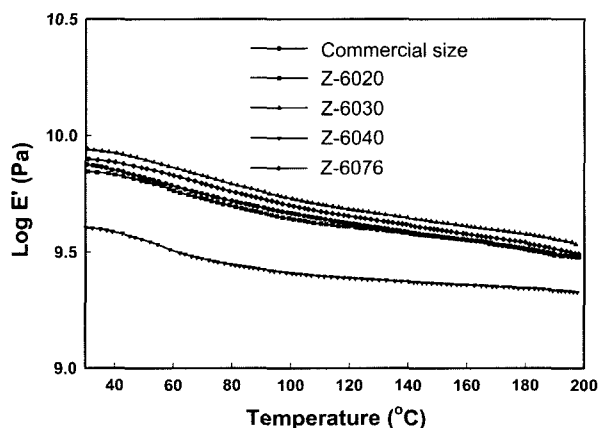


Figure 5. Variations of the storage modulus for woven glass fabric/nylon 6 composites sized with different silane coupling agents as a function of temperature.

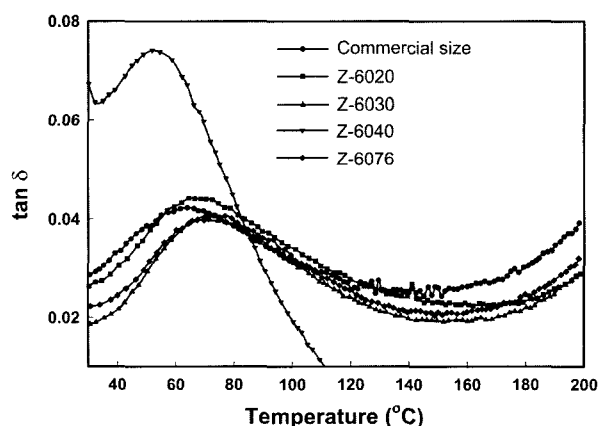


Figure 6. Variations of the $\tan \delta$ for woven glass fabric/nylon 6 composites sized with different silane coupling agents as a function of temperature.

60~70 °C depending on the silane coupling agents used. It is 5~15 °C greater than the T_g of nylon 6 without reinforcement. The T_g enhancement in the composite is because the molecular motion in the polyamide 6 chain is significantly restricted by the reinforcing fibers. Therefore, coupling agents with different organo-functional groups influence the T_g due to their different contribution to the fiber-matrix adhesion. The T_g in a fiber reinforced polymer composite, in general, increases with increasing the interfacial strength between the fiber and the matrix. The T_g can be normally determined from the maximum peak temperature of a $\tan \delta$ curve. Figure 6 shows the variation of the $\tan \delta$ as a function of temperature for the composites. The dynamic mechanical results show that the composite sized with the Z-6076 exhibits the greatest T_g while the one with the Z-6040 exhibits the lowest. The T_g of the glass/nylon 6 composites sized with the silane coupling agents used in this work is increased by 5~8 °C in comparison with the commercially sized one, except for the case of Z-6040. The reason for the lowest value of T_g in the case of the Z-6040 is found from the explanation described earlier.

Thermal Stability. The silane compounds with different chemical structures may have different thermal stabilities, influencing some possible integrity at the interfaces between the fiber and the matrix once the silane coupling agents are appropriately applied for the adhesion improvement. Figure 7 compares the thermal stability of the glass fabric/nylon 6 composites studied. All the composite specimens degrade beyond 350 °C, showing a dramatic weight loss, which is responsible for the nylon 6 resin. The composite sized with the Z-6076 exhibits the highest thermal stability. The result also indicates that the composites sized with the silane coupling agents used here have slightly improved thermal stability in the temperature range prior to degradation. This is due to the increased interfacial adhesion between the fiber and the matrix in the composites, which may somewhat

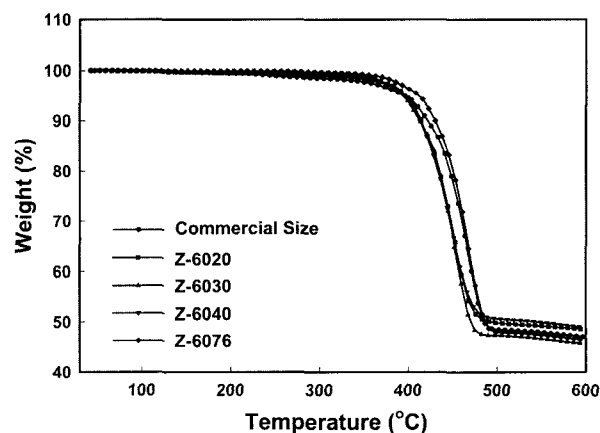


Figure 7. Thermal stability of woven glass fabric/nylon 6 composites sized with different silane coupling agents.

contribute to slightly deactivating and retarding the thermal degradation. However, one cannot expect exactly the effect of the sizing interphase at elevated temperature above the degradation. The thermal stability result indicates that the influence of the silane coupling agent on the thermal stability of glass fabric/nylon 6 composites is not distinguishable as much as found in the other examinations in this work.

Figure 8 illustrates proposed reaction schemes between the different organo-functional groups in the silane coupling agents and the amino groups in the nylon 6 resin occurring during the composite fabrication. It may be assumed that the trimethoxysilane groups located at the end of each silane coupling agent result in the same concentration of silanol groups upon hydrolysis, generating the corresponding number of -Si-O- linkages between the glass and silane coupling agent at the glass fiber surface. The organo-functional groups located at the other end can then react with the nylon matrix once a reactive functionality is present. In the present system, the chemical reactivity between the organo-functional groups located at the end of silane coupling agents with the other end anchored at the glass fiber surface and the reactive amino end groups of nylon 6 resin differs. Considering nucleophilicity and the unshared electron pair in the amino group, it is believed that the chemical bonds between the silane coupling agent and the nylon 6 can be formed with increasing frequency based upon the increased chemical reactivity in the order of chloropropyl > methacrylate >

diamine organo-functional groups. It is expected that the amino group in the resin may not react preferably with the diamine group in the Z-6020 coupling agent. Even though the glass fabric/nylon 6 composite has some difficulties in making an acceptable composite for the short-beam shear test in the case of Z-6040 due to insufficient wet-out between the reinforcing fibers and the resin and accordingly the ILSS of the composite sized with the Z-6040 is observed to be lower than that of other counterparts, it may be expected that the amino-epoxide reaction substantially takes place with the comparable reactivity with the Z-6030 having methacrylate groups, as found from the earlier result on the increased interfacial adhesion between the single glass fiber and the nylon 6 microdroplet in a microbonding testing system.

Conclusions

The interlaminar shear strengths of woven glass fabric/nylon 6 composites sized with silane coupling agents used in the work are significantly improved in comparison with the composite sized commercially. A silane coupling agent (Z-6076) with chloropropyl organo-functional groups shows the highest interfacial adhesion, followed by the Z-6030 with methacrylate group and by the Z-6020 with diamine group. The dynamic mechanical properties, the SEM observations of the fracture surfaces, and the thermal stability also support the interfacial result. Combining all the analyti-

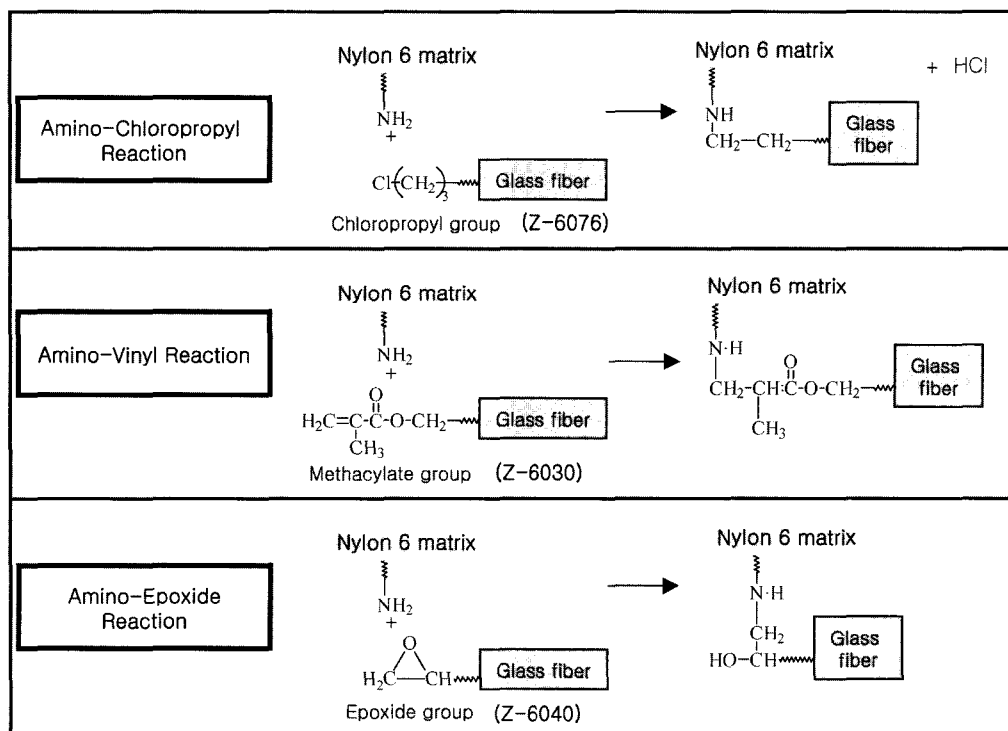


Figure 8. Proposed reaction scheme between the different organo-functional groups in the silane coupling agents and the amino groups in the nylon 6.

cal results, the fiber-matrix interfacial characteristics agree well with each other.

The improvement of the interlaminar shear strength may be interpreted in terms of different chemical reactivity between organo-functional groups located at the end of silane coupling agents with the other end anchored at the glass fiber surface and the reactive amino end groups at the nylon 6 resin. The possibility of the chemical bond formation between the silane coupling agent and the nylon 6 increases with increasing the chemical reactivity in the order of chloropropyl > methacrylate > diamine organo-functional groups.

In a fiber-matrix composite system, the solubility between the matrix and the sizing interphase apparently influence the interaction and chemical composition at their interfaces. Also, the interphase materials near the fiber surface may depend on the concentration of silane coupling agents, giving a gradient of properties with the distance from the fiber surface. The concentration effect will be discussed in a future paper.

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