Simplification and Application of Single Fiber Fragmentation Test on Silylated Polyester–Glass Fiber Composites

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ABSTRACT: Single fiber fragmentation test (SFFT) was used to investigate the interfacial adhesion in glass fiber-unsaturated polyester composites. A simplified approach was developed for SFFT based on determination of the maximum number of fragments on the fiber at the end of the test. This approach does not involve length measurements and shortens the experiment time to a few minutes. By using a digital camera attached to the microscope, photographs of the coupon were taken during the test, and the number of fragments within the gauge length were counted later. This method allows quick, quantitative comparison of different fibers and matrices. The test samples were prepared by using commercial polyester resin and E-glass fibers having different commercial sizings. SFFT results were in excellent agreement with the macromechanical test done on samples prepared with the same glass fiber and same polyester. The crack modes and debonding phenomena were examined from the microscopic images. Atomic force microscopic (AFM) images of the fiber were examined to get detailed topographic information about fiber surfaces. To improve interfacial adhesion, commercial unsaturated polyester was reacted with 3-aminopropyltriethoxy silane via Michael Addition reaction on the maleate double bonds of the polyester. The resulting silylated polyester was characterized by H^1 NMR spectroscopy. The results of SFFT showed that the maximum numbers of fragments increased 23% on using silylated polyester. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 748–755, 2010

Key words: adhesion; composites; mechanical properties; polyester; interfaces

INTRODUCTION

In industrial applications, composite performance is generally assessed by macroscopic tests that measure various mechanical properties of large test samples. Macromechanical tests always involve high data spread, usually due to differences in fiber volume fraction of and inclusion of voids in the test samples. As an alternative to this approach, researchers have attempted to use micromechanical tests to measure the performance of a composite. Among the micromechanical testing methods for evaluating fiber–matrix interface properties of fiber-reinforced composites, the single fiber fragmentation test (SFFT) has attracted special attention since the method was introduced by Kelly and Tyson.[1] The applicability of this technique for measuring the interfacial properties of composites has been verified experimentally by Schultz and Nardin.[2-4] The fragmentation test is now widely used for measuring the effect of different glass sizing on the interfacial adhesion strength because of its simplicity in specimen preparation, ease of testing, wealth of information obtained in terms of the damage processes and reproducibility of the results.

However, SFFT is still far from a routine test for industrial applications. In this work, SFFT has been modified by simplifying the testing apparatus, using microscope photography and simplifying the data evaluation to be able to compare different fibers and matrices. Briefly, a single fiber is embedded in a polymer matrix coupon and a strain is applied to the coupon in the direction of the fiber. With increasing load, the coupon elongates and the fiber fractures into shorter and shorter fragments until the stress transfer across the interface is insufficient to cause further fracture of the fiber. Fragmentation of the fiber during the experiment is observed by a conventional optical microscope; therefore, the test requires the matrix to be transparent.

The maximum number of fiber fragments in a given gauge length depends on the fiber strength and the adhesion forces that exist between the fiber and the matrix. When the adhesion forces are low, the maximum number of the fragments is low, as the fiber slides within the coupon. On the other hand, when the fiber–matrix adhesion is high, the number of fiber fragments will be high because the adhesive forces act more efficiently and transfer the

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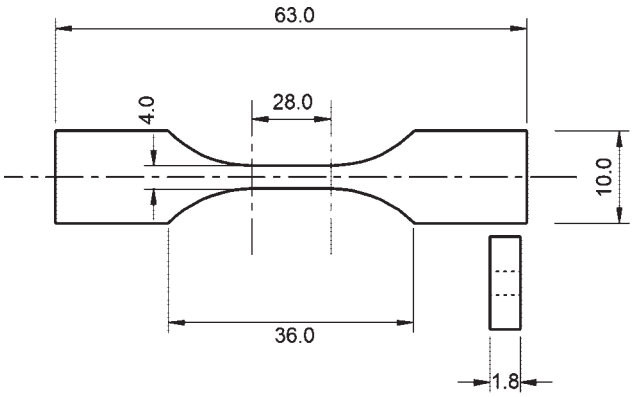

Figure 1 Dumbell-shaped specimen for SFFT (dimensions in mm).

stress onto the fiber surface. Ultimately, a point is reached where no additional fiber fractures can be induced irrespective of the amount of applied strain. The number of fragments reaches a plateau and the average length of the fiber fragments at this point is called the critical length.

The test has the advantage that there is no need to measure any force or any elongation accurately. The test does not measure force at all. It measures only the number of fragments that are produced within a given gauge length of the sample. The strain is however roughly measured so that the experiment is carried out within the elongation limit of the sample. By using a polarizer in the microscope and by adjusting the light intensity, the fragments can be easily seen and photographed.

Micromechanical investigations have often modeled the fiber surfaces as homogeneously coated. A better understanding of fiber surface is obtained by atomic force microscopy (AFM), which shows the actual topographic silhouette of surfaces. It also allows inferring interface properties directly.[5]

Mäder[6] compared the surfaces of unsized and sized glass fibers. It was observed that the surface of unsized glass fiber is relatively even and homogeneous, but the surface of sized glass fibers showed distinct size droplets on the surfaces. This is an important observation: if the sizing wets the fiber surface, a larger proportion of the fiber surface is covered by the sizing, and a more homogeneous coating is obtained, leading to a better interfacial adhesion. Such considerations are very important for a glass fiber manufacturer.

A matrix polymer, which contains silanol groups as pendant groups, is expected to bind to such uncovered areas on the glass fiber and provide a better interfacial strength. To test this conjecture, commercial polyester was reacted with an aminosilane via Michael Addition reaction.[7] The amount of aminosilane was adjusted in such a way that only one third of the unsaturation of the polyester was consumed, so there should be a sufficient amount of double bonds at the end of this reaction to be used in the curing process.

We report here our SFFT results using different commercial glass fibers with commercial unsaturated polyester and the silylated unsaturated polyester of our own synthesis.

EXPERIMENTAL

Chemicals and apparatus

Unsaturated polyester with the commercial name CE 92 containing 38% styrene as a reactive diluent produced by Cam Elyaf A.Ş., İstanbul, Turkey, was used. This resin is composed of maleic anhydride, phtalic anhydride, and a mixture of diols. Commercial E-glass fibers were obtained from their respective manufacturers.

Sources of other chemicals used are methyl ethyl ketone peroxide (MEKP) from Akzo Nobel, Cobalt naphthenate from Akzo Nobel, 3-aminopropyl trimethoxysilane (A1100) from Hüls-Degussa, and hydroquinone from Merck.

A silicone mold with eight dumbbell-shaped cavities, microstraining device, Baistolscope Bristoline Microscope (200X), and a Digital camera were used for the SFFT. The dimensions of the coupons used for SFFT are shown in Figure 1.

H^1-NMR spectra were recorded on a Varian 400 MHz NMR instrument operating at a frequency of 399.986 MHz. The spectra were reported as ppm (δ). AFM was performed using an universal scanning probe microscope (USPM) (Ambios Technolgy, Santa Cruz, CA). Phase-mode imaging was performed using a silicone nitride cantilever probe with nominal resonance frequency of 170 kHz and a nominal tip radius of 5–10 nm. Samples were prepared for AFM investigation by mounting the glass fibers in epoxy potting compound. Macromechanical tensile tests were done on a Zwick universal testing machine, according to ASTM D638. The results shown are an average of six test coupons.

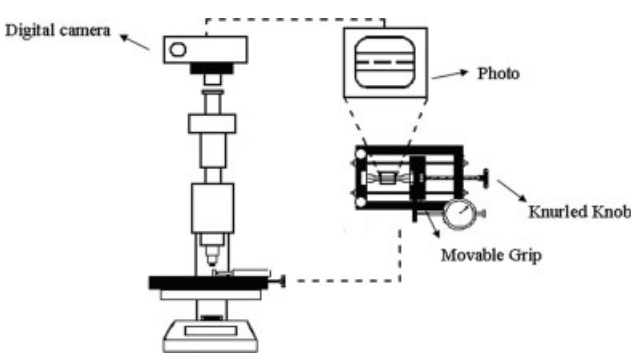

Figure 2 Schematic illustration for testing system.

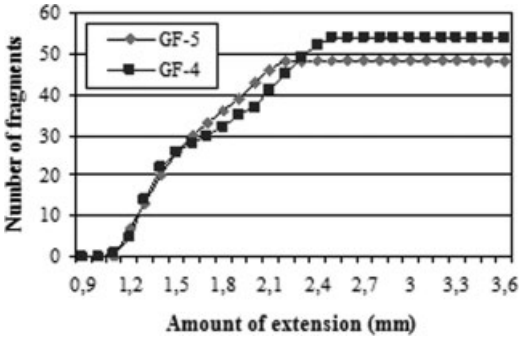

Figure 3 Number of fragments as a function of extension for the specimens with GF-5 and GF-4.

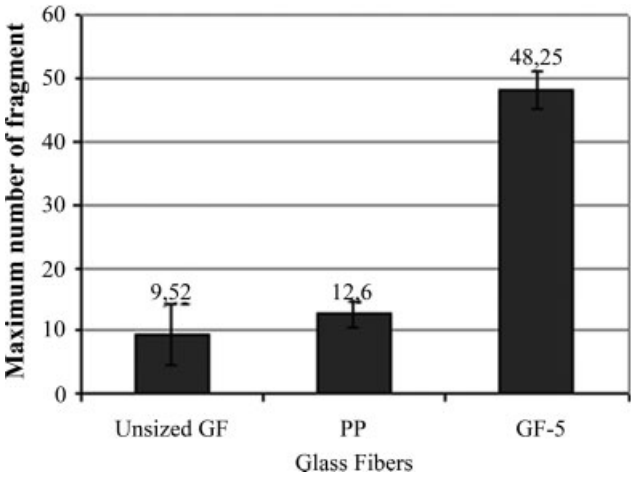

Figure 4 SFFT results: maximum number of fragments for unsized GF, PP, and GF-5.

Sample preparation and testing

Fiber lay-up process is the most challenging step. Fibers are placed into the slots cut into the silicone mold one by one and the ends are glued to the mold with one drop of cyano acrylate glue. Twelve milliliter of unsaturated polyester was mixed first 0.0382 g of Co-naphthenate and then 0.174 g of MEKP. The mixture was transferred into the mold and mold was cured in air, at room temperature, for one day. The test coupons can be easily removed from flexible silicone mold without using any mold release agent.

Before testing a sample the coupon was marked with two ink marks, spaced 25-mm apart. This is the gauge length under observation during the test. The sample was attached to the microstraining device and was placed under the microscope, which was equipped with a digital camera.

The setup is shown in Figure 2. Then strain was applied to the specimen manually, in controlled increments of 0.5 mm. The fragments were counted, and strain was applied again by turning the knob by 0.5-mm increments in elongation and this process was continued until the number of fiber breaks within gauge length reached a constant. Photomicrographs were taken at each increment and accurate fragment counts were obtained from the pictures. SFFT test was made for each of the eight specimens, and the maximum numbers of fragments within the gauge length were averaged.

TABLE I
Comparison of Macromechanical Test and SFFT Results

Fiber	Macromechanical test results (normalized for fiber fraction) (kPa)	SFFT results
GF-1	141	51.42
GF-2	162	65.20
GF-3	143	59.60
GF-4	140	54.00
GF-5	138	48.00

Aminosilylation of unsaturated polyester

To 50 g of commercial unsaturated polyester containing 38% styrene, 0.5 g of hydroquinone, and 4.0 g of 3-aminopropyl trimethoxysilane was added. The mixture was stirred at room temperature for one night under dry conditions. The product was characterized by ^{1}H NMR.

^{1}H NMR ($CDCl_3$) δ: 0.6 (—CH_2—Si—); 1.2 (—Si—O—CH_2—CH_3); 1.28 (—O—$CHCH_3$—CH_2—O—); 1.29 (—NH—CH_2—CH_2—CH_2—Si—); 3.62 (—NH—CH_2—CH_2—CH_2—Si—); 3.8 (—O—$CHCH_3$—CH_2—O—); 4.4 (—O—$CHCH_3$—CH_2—O—); 5.21 (—CH=CHaHb); 5.66 (—CH=CHaHb); 6.66 (—CH=CHaHb); 6.83 (—O(C=O)CH=CH(C=O)O—); 7.30–7.39 (aromatic protons of styrene); 7.45, 7.66 (aromatic protons of phthalate group).

For the curing reaction, 12 g aminosilylated polyester, was mixed with 0.153 g of Co-naphthenate and then 0.695 g of MEKP with stirring. Curing reactions were carried at room temperature for one day. The presence of the aminosilane pendant group extended the gel time from 15 to 22 min, but the overall cure was not affected.

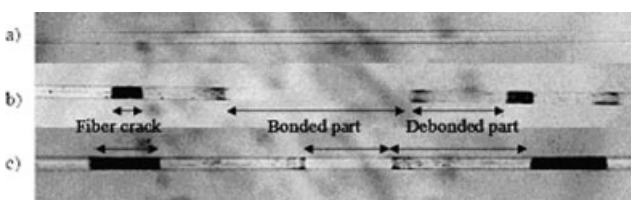

Figure 5 Fragmentation process of the specimen with GF-5: (a) at the beginning of the process, (b) in the middle of the process, and (c) at the end of the process.

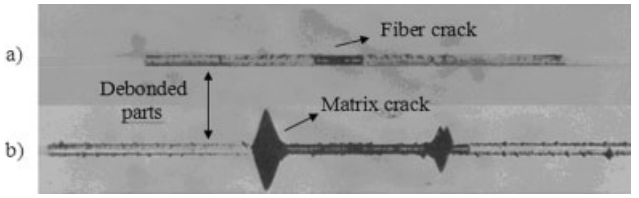

Figure 6 Different fragmentation modes of GF-5 (a) and GF-3 (b).

RESULTS AND DISCUSSIONS

Glass fiber used in SFFT

The same commercial polyester resin was used with different commercially available glass fibers for SFFT. No information is available on the composition of the sizing on the fibers. However, all of the fibers were optimized for unsaturated polyester and had a diameter of 15 μm. For sake of identification, the different glass fibers are named GF1, GF2, GF3, etc. During the test, as the sample is elongated, the number of fragments increase, but as the fragment length approaches the critical length, the number of fragments reaches a constant number. The number of fragments within the gauge length at this point is used as the indication of interfacial strength. Figure 3 shows the actual data obtained for GF5 and GF4 samples. The average of maximum numbers of fragments for GF-5 and GF-4 were 48.00 and 54.00, respectively. We conclude that GF-4 fiber, which gave higher value of maximum number of fragments, has higher interfacial adhesive strength than the specimen with GF-5 fibers.

Comparison of SFFT results with the Macromechanical test results

The same fiber and matrix combinations were used to make large test samples and were separately tested by using standard macromechanical tests done according to ASTM D638. The glass content of each batch of samples was determined by combustion analysis of the laminate. The ultimate tensile strength values obtained from the macromechanical tests were normalized for glass fiber content, as there was inevitable fiber content differences in the large samples. All fibers were 1200 tex and 15 μm diameter. The results of the tensile strength test and

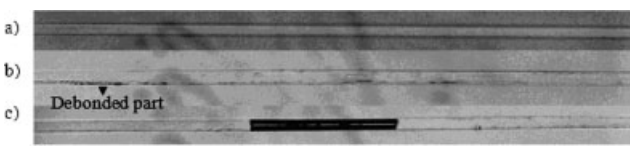

Figure 7 Fragmentation process for PP fiber: (a) initial state, (b) after the first elongation, and (c) after the first fragmentation.

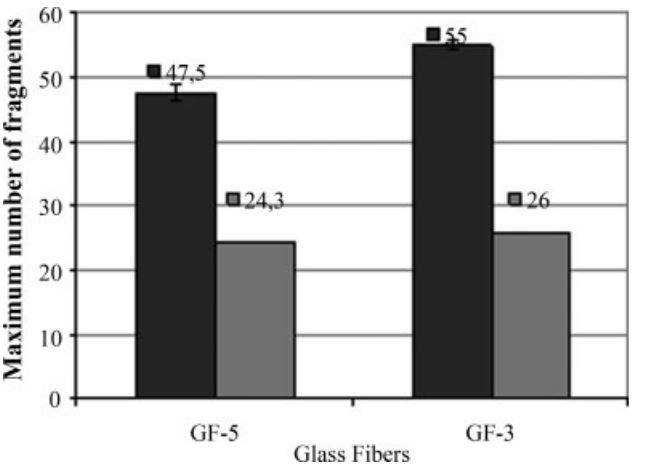

Figure 8 Comparison of single fiber (dark bar) and multifiber (light bar) fragmentation test results.

of the SFFT of the same fiber are shown in Table I. The SFFT and tensile strength test results are in excellent agreement. Furthermore, the percent improvements measured are found to be consistently higher with the SFFT than with the tensile strength test. The overall sensitivity of the SFFT is higher, and we conclude that SFFT can measure the smaller improvements better than macromechanical tests.

In separate tests, we observed that the data spread of the results for different tex strands obtained by using macromechanical test was very high. It should be noted that higher tex strands include more fibers and wetting of fibers in high-tex strands by the liquid resin is more difficult.

Thus, the simplified SFFT proved to be a precise, easy, and cheap method to compare interfacial adhesive strengths between glass fibers and polymers for industrial applications. The absolute value of the adhesion strength cannot be determined by the simplified method used in this work, but different fibers can be compared with good precision.

SFFT results for unsized and improperly sized fibers

SFFT was applied to samples made with glass fiber with sizing optimized for polypropylene (PP)resin, unsized glass fiber (unsized GF), and glass fiber optimized for unsaturated polyester (GF-5). It is expected that when (PP) fiber and unsized fiber is used with a polyester matrix, SFFT should show a

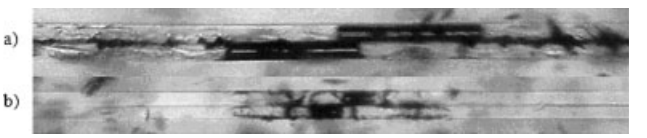

Figure 9 Multifiber test samples: (a) GF-5 and (b) GF-3.

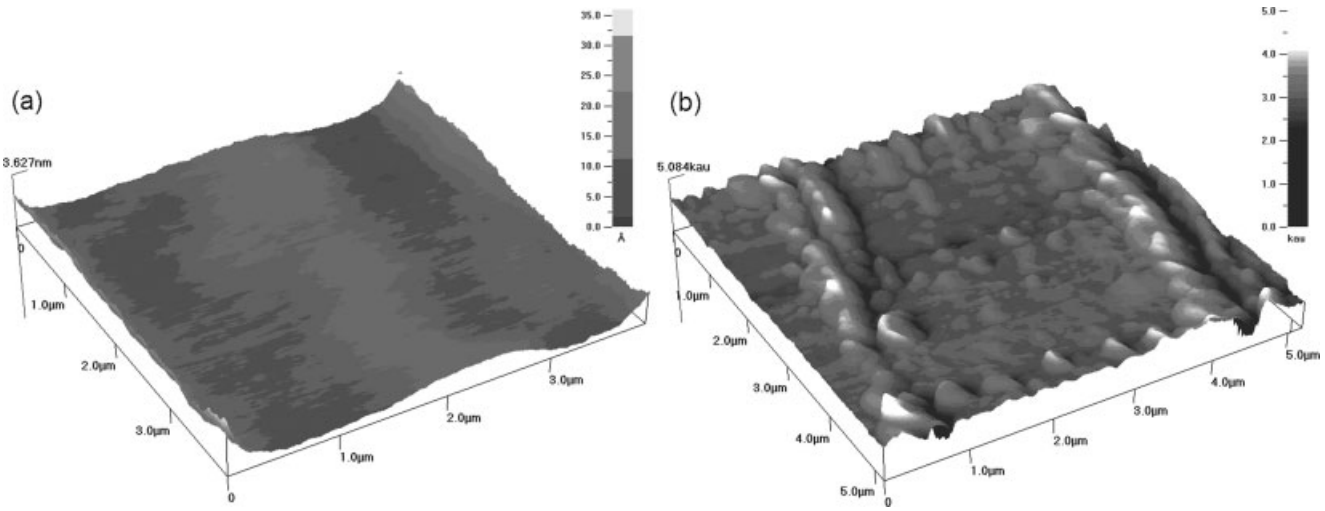

Figure 10 AFM image of (a) unsized and (b) sized glass fiber.

very low interfacial adhesion. GF-5, which has a sizing optimized for polyester, should show a high interfacial adhesion.

Figure 4 shows the SFFT results as 9.5, 12.6, and 48.3 for unsized GF, PP, and GF-5 respectively. This result is the expected behavior for unsized glass fiber and improperly sized fiber. Thus, SFFT test proves to be a quick screening test for choosing a fiber that is suitable for a given matrix.

Observation of different modes of fractures and debonding phenomena

Fracturing process during SFFT was monitored by a digital camera for the sample with GF-5. Figure 5 shows the pictures taken during the test. Figure 5(a) shows a part of fiber GF-5 at the beginning of the process. It has no fragments. Figure 5(b) shows the same part of the fiber during the test with two fractures and Figure 5(c) shows the same fractures but with longer gap. When critical fragment length is reached, the cracks simply got bigger without any further fracturing of the fiber.

The mode of cracks can be different for different fibers depending on the bond quality between the fiber surface and the matrix. Figure 6 shows photographs of the two modes of cracks observed during SFFT. With a relatively weak interphase bonding, initial small fiber break is followed by debonding around the crack. Figure 6(a) shows GF5 after fragmentation. The fiber debonds at the interface and does not cause a matrix crack. Figure 6(b) shows GF-3, which has a stronger interfacial adhesion: the fiber fragments and causes matrix cracks at the site of the crack.

Debonding around the fiber is not always observed after fiber crack. If the bond is very weak as in the case of PP sample, which has a size optimized for polypropylene matrix, debonding between two phases can be immediately seen after very small load application, as seen in Figure 7(b). The fiber crack gaps are very long because the fiber fragments can easily slide in the matrix, and there is no evidence of matrix cracks.

Multiple fiber fragmentation test results

Moon and McDonough have published their resuls on a multiple fiber technique for the SFFT.[8] We also made an attempt to see if a multiple fiber sample could be tested by the same procedure. Interfiber spacing is difficult to control in these experiments. The average numbers of the cracks of the two fibers were taken as the test result. Figure 8 shows the SFFT results for two fibers when the test is done with one fiber and with two fibers. The maximum number of fractures and the relative number of cracks between different fibers do not agree.

With more than two fibers the SFFT gave unexpected results. Figure 9(a,b) belong to GF-5 and GF-3, respectively. We observe that, when one fiber fractured, this caused more stress on the second one and second fiber also fractured at a point very close to the first fracture, an observation that is also mentioned in the article by Moon and McDonough. In conclusion, using multiple fibers in a fragmentation test has disadvantages because breaks in one fiber caused breaks in the adjacent fiber. With these results, we conclude that the multifiber test results cannot be relied on.

AFM results

Atomic force microscopy was used to get phase-mode images using a silicone nitride cantilever probe with a nominal resonance frequency of

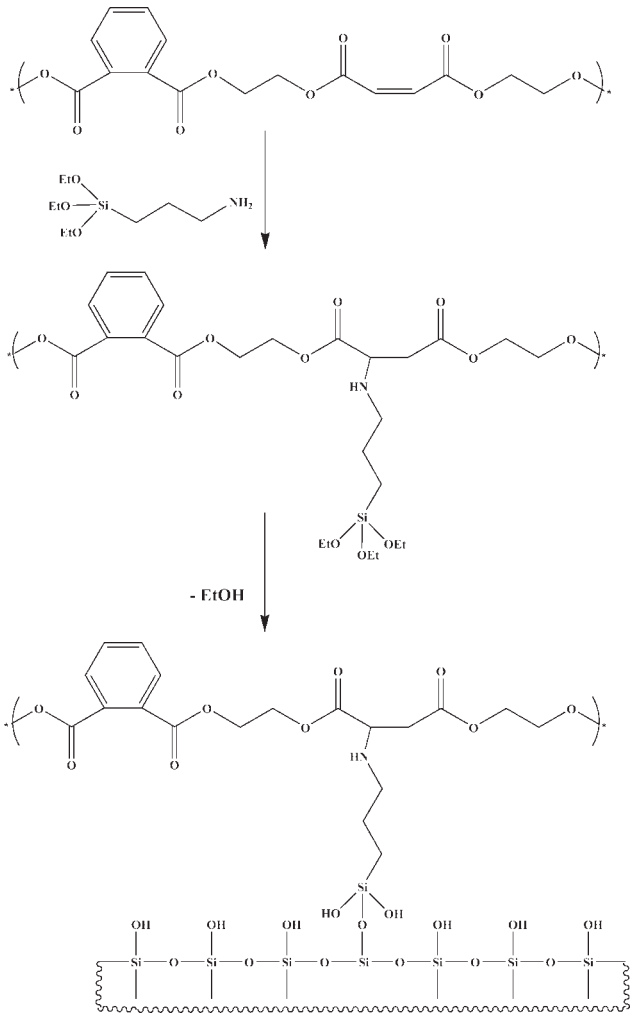

Figure 11 Addition of 3-aminipropyl triethoxysilane to UPE, followed by the proposed coupling of the product to glass fiber surface.

170 kHz and a nominal tip radius of 5–10 nm. The topographic images of unsized and sized glass fiber surfaces are shown in Figure 10.

The surface of unsized glass fiber is flat and uniform, whereas the sized glass fiber has a higher roughness factor and shows sizing droplets on the surface distributed heterogeneously. The droplet size probably corresponds to the micelle size of the emulsion used to deposit the sizing mixture on the glass fiber by the manufacturer and it is clear that these droplets have not coalesced and formed a continuous film on the fiber. There are some areas on the surface of the glass fiber with no visible sizing and presumably the wetting of these regions by the matrix resin will be difficult. On the basis of these AFM images, we developed improved polyester that has its own silane coupling agent as a pendent group to get better interphase adhesive strength by targeting the unsized areas on the glass fiber surface.

Michael addition of aminosilane to unsaturated polyester

Glass fiber sizings applied by the fiber manufacturer, contain a number of substances called coupling agents that are responsible for the coupling reaction between the glass surface and the matrix polymer. These compounds have alkoxy silane groups at one end that can be hydrolyzed to silanol groups, and these are capable of reacting with the glass surface. The coupling agents also have a suitable functional group at the other end which is capable of reacting with the matrix polymer (9). It is clear that if, in addition to the glass surface, the matrix polymer also contains silane type coupling agents, a

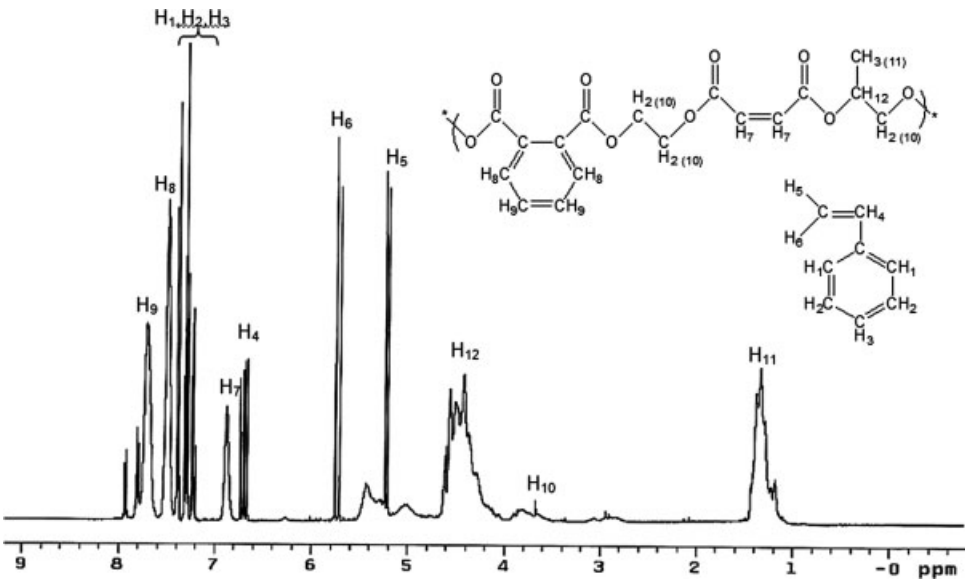

Figure 12 1H NMR spectrum of commercial polyester.

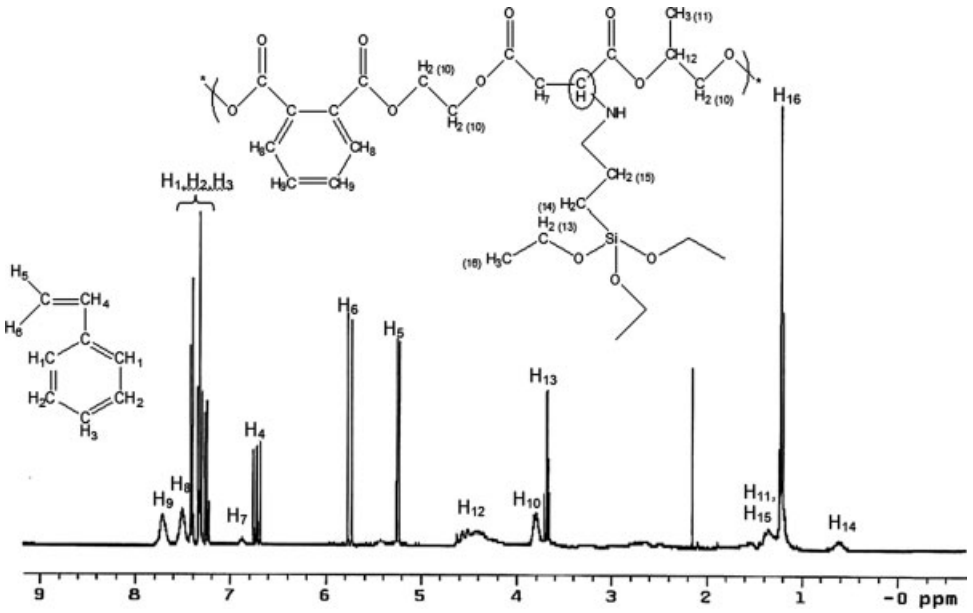

Figure 13 1H NMR spectrum of 3-aminopropyltriethoxysilylated polyester.

stronger bond between the matrix and the glass fiber would be obtained. With this goal in mind, we set out to synthesize an unique polyester containing silanol pandant groups.

Commercial unsaturated polyesters are condensation polymerization products of phthalic anhydride, maleic anhydride, and diols such as ethyleneglycol and propylene glycol. The maleate double bonds on the polymer backbone are α,β unsaturated esters, which makes them susceptible toward nucleophilic attack via Michael addition reaction by primary amines. Figure 11 shows the Michael reaction between 3-aminopropyltriethoxysilane and a typical unsaturated polyester and the proposed coupling chemistry between the new functionalized polyester and the glass fiber surface.

The reaction was run with the aminosilane as the limiting reagent so that only one third of the total unsaturation of polyester was consumed. The rest of the unsaturation was used in the curing process. It was found that the Michael reaction could be carried out in the styrene solvent, which is already present in commercial unsaturated polyesters. The reaction was carried in completely dry conditions at room temperature to prevent premature hydrolysis of the ethoxy groups on the silane. To prove that the reaction proceeds only through a Michael addition, commercial unsaturated polyester was reacted with 3-aminopropyltrioxy silane in 1 : 1 ratio of silanes to double bonds so that all double bonds were depleted in the reaction, and the disappearance of all the maleate double bonds of the polyester was confirmed by NMR spectroscopy. Figure 12 shows the ^{1}H NMR spectrum of commercial polyester and Figure 13 is the ^{1}H NMR spectrum of 3-aminopropyltriethoxysilylated commercial polyester. After the reaction, the decrease in the intensity of the peak at 6.83 ppm, belonging to the protons of maleic double bond, and appearance of ethyl group protons indicates that the reaction proceeds via Michael reaction.

SFFT samples were made using UPE that was aminosilylated to an extent of 1 : 3 and with two different glass fibers GF-5 and unsized glass fiber. The sample with GF-5 fiber showed a very different mode of fragmentation when the load was applied. As shown in the Figure 14, there were too many fragments and they were not distinguishable enough

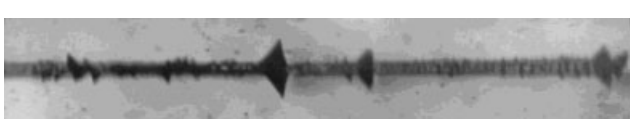

Figure 14 Micrograph of GF-5 - aminosilylated polyester sample after the load was applied.

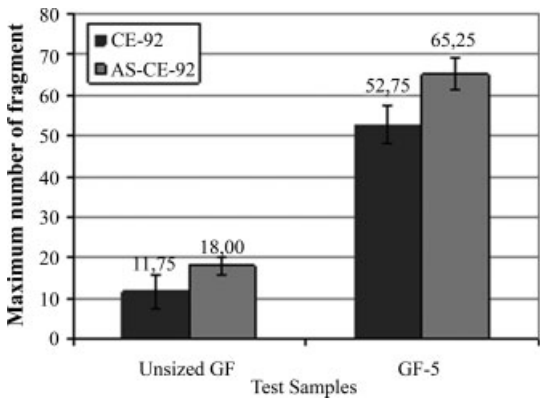

Figure 15 SFFT results for unsized GF and GF-5 with commercial UPE and aminosilylated UPE.

TABLE II
Comparison of SFFT Results Using Commercial UPE (UPE) and Aminosilylated UPE(AS-UPE)

Sample	SFFT results	Improvement achieved (%)
GF-5/UPE	52.75	23.70
GF-5/AS-UPE	65.25	
UGF/UPE	11.75	53.19
UGF/AS-UPE	18	

to count. Matrix cracks that were not related to fiber could be observed. Only the fragments which were obvious were counted.

SFFT results of the samples with aminosilylated UPE were compared with the samples tested before. As shown in Figure 15, the samples in which aminosilylated polyester was used gave higher number of fragments, and the improvement was more dramatic when unsized glass fiber was used. Table II shows the calculated percent improvements. For GF-5, it was found as 23.70%, and for unsized glass fiber, it was found as 53.19%. This proves that the new silylated polyester is in fact capable of improving the interphacial adhesion strenth between the matrix and the glass fiber.

CONCLUSIONS

The single fiber fragmentation test provides an easy and cheap way to compare the adhesive strength between the fiber and the matrix. The results were compared with macromechanical test results and were found to be in good agreement.

SFFT was applied to test samples made with unsized glass fiber and glass fiber that had an incompatible size for unsaturated polyester. Because of the lack of covalent bonds in the interphase between fiber and matrix, these samples showed very low numbers of fragments. By the simplified method described here, different glass fibers can be very easily compared and classified.

The fiber/matrix adhesion has a strong influence on the failure modes in the fiber fragmentation test. It was observed that strong interphacial adhesion causes matrix cracks during fragmentation and that cracks on the fiber cause fiber-matrix debonding in the vicinity of the crack.

Test samples that included two glass fiber filaments showed a lower number of fragments. A single crack on one of the fibers caused the other to carry all the stress alone and the second fiber fragmented at a point close to the original fragment.

AFM images showed that on the surface of glass fiber, sizing material stayed as droplets, with unsized areas between these droplets. 3-aminopropyltriethoxysilane Michael Addition to unsaturated polyester gave a polyester that is itself capable of coupling to the unsized regions on the fiber. SFFT showed a big improvement in the interfacial adhesion when silylated UPE was used in the samples.

References

1. Kelly, A.; Tyson, W. R. J Mech Phys Solids 1965, 13, 329.
2. Schultz, J.; Nardin, M. J Adhes 1994, 45, 59.
3. Nardin, M.; Schultz, J. Compos Interfaces 1993, 1, 117.
4. Spragg, C. J.; Drzal, L. T. ASTM-STP Publication No. 04-012900-33, 1994.
5. Mäder, E.; Gao, S. L.; Kim, J. K. In Proceeding of EUROMAT99-Conference; Wiley-VCH: New York, 1999.
6. Mäder, E.; Gao, S. L. Composites 2002, 33, 559.
7. Moon, C. K.; McDonough, W. G. J Appl Polym Sci 1998, 67, 1701.
8. Witucky, G. L. J Coatings Tech 1993, 65, 57.