

Effect of Coupling Agent and Absorbed Moisture on the Tensile Properties of a Thermoplastic RRIM Composite

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SYNOPSIS

The effect of introduction of a silane coupling agent and absorbed moisture (i.e., equilibrium hygroscopic state) on the tensile properties of a thermoplastic reinforced reaction injection molding (RRIM) composite, having a fiber volume fraction of 0.33, was evaluated. The composite was produced by anionically polymerizing caprolactam monomer within a continuous strand (swirl) glass fiber mat using a RRIM method. In addition to the expected strong dependence of the composite tensile stiffness and strength on introduction of 1.5 wt % (based on the total weight of glass fibers) of γ -amino propyl triethoxy silane coupling agent, the effect of the mode of application of the coupling agent on the resultant composite properties, under tensile loading, was observed to be insignificant in the dry state but quite important in the wet state. Microscopic examination of the fracture surfaces revealed a three-stage tensile failure mechanism that is associated with debonding at low strains of the fibers, fiber failure (at the weakest point), and pull-out of the fibers resulting in catastrophic failure, at the ultimate tensile strain, of the composite.

INTRODUCTION

Thermoplastic reinforced reaction injection molding (RRIM) composite sheet materials are finding increasing applications in the automotive and other vehicular industries as metal replacement parts because of the adaptability of the RRIM process to thermoplastic structural composites.¹⁻⁴ In these target applications, the materials are subjected to different kinds of mechanical stresses and various corrosive environments.⁵ Consequently, a physical understanding of the behavior of these materials, under a variety of corrosive environments is highly desirable.

The work reported here is part of a long-range research program that deals with the production of structural thermoplastic composite sheet material that could be thermoformed into a prescribed shape (or used as-polymerized) using a reinforced reaction injection molding method.⁶⁻⁸ In this method,⁶ a con-

tinuous strand (swirl) glass fiber mat is placed in a mold prior to injection of the reactive polymerization mixture containing caprolactam monomer and catalyst. The production method and the behavior of the materials (at four levels of fiber volume content) under impact and dynamic mechanical loading conditions have been described previously.⁶⁻⁸ The properties of the present composite system, which comprises polyamide 6 matrix and glass fibers, are particularly susceptible to humid environments.

The primary aim of this communication is to report the effect of moisture (equilibrium hygroscopic state) on the tensile stress-strain behavior of the composite with a fiber volume fraction (V_f) of 0.33, as well as to explain the observed failure mechanisms. Additionally, it shows how a reactive silane coupling agent may be incorporated into the RRIM process (without adversely affecting the in-mold polymerization reaction) to reduce the deleterious effect of moisture on the properties of the composite under static loading conditions. This information will provide a basis for the interpretation of the relationships between processability, property, and performance (under wet conditions) of the composite in the target applications.

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EXPERIMENTAL

The composite ($V_f = 0.33$) was produced in sheet form (4 mm thick) by polymerizing caprolactam monomer in situ within a mat of swirl-type continuous glass strand mat compressed to the final thickness of composite required and containing the required volume fraction of glass. Initially, it was observed that the commercial "sizing" (or coating), which comprises an epoxy compatible binder and coupling agent, on the glass fibers greatly inhibited the polymerization reaction.⁶ No commercial continuous glass strand mat containing a compatible sizing with the RRIM process used to fabricate the composite could be obtained, therefore the sizing on the glass mat was removed by heating it in a muffle furnace at 600°C (to constant weight) before it was incorporated into the matrix to produce the uncoupled composite used here. A more detailed description of the composite fabrication method is reported elsewhere.⁶ In the latter experiments a reactive silane coupling agent (γ -amino propyl triethoxy silane) was applied to the composite system, by treating the reactive polymerization mixture with 1.5 wt % (based on the weight of the glass mat used) of the coupling agent, to produce the coupled composite of this study. Preliminary investigations showed that

a 1.5 wt % silane loading, an amount significantly greater than the usually recommended monolayer (i.e., 0.1–0.5 wt %) for glass-fiber-reinforced plastics,^{9,10} was required for optimum performance of the present composite system. The heat-cleaned glass mat was either exposed to moisture in the atmosphere for at least 72 h or soaked in water overnight and dried, to constant weight, in a vacuum oven at 100°C prior to treatment with the coupling agent. This pre-fiber treatment leads to the generation of reactive surface hydroxyl groups (silanols) on the glass fibers to an extent that depends on the degree of exposure to moisture.⁹

Rectangular shaped test samples (with smoothed edges) of dimensions 150 × 10 × 40 mm were cut from the molded composite sheet, dried in a vacuum oven at 100°C to constant weight, and stored in a dessicator until required for testing. Water-saturated samples were prepared by immersing the previously dried samples in boiling water until constant weight was achieved. The samples were then immersed in cold water at room temperature for at least 2 weeks to afford the wet samples used here. The moisture content was expressed as a percentage of the dry weight. The tensile stress-strain properties of the dry and wet (coupled and uncoupled) composite were obtained by means of a universal testing ma-

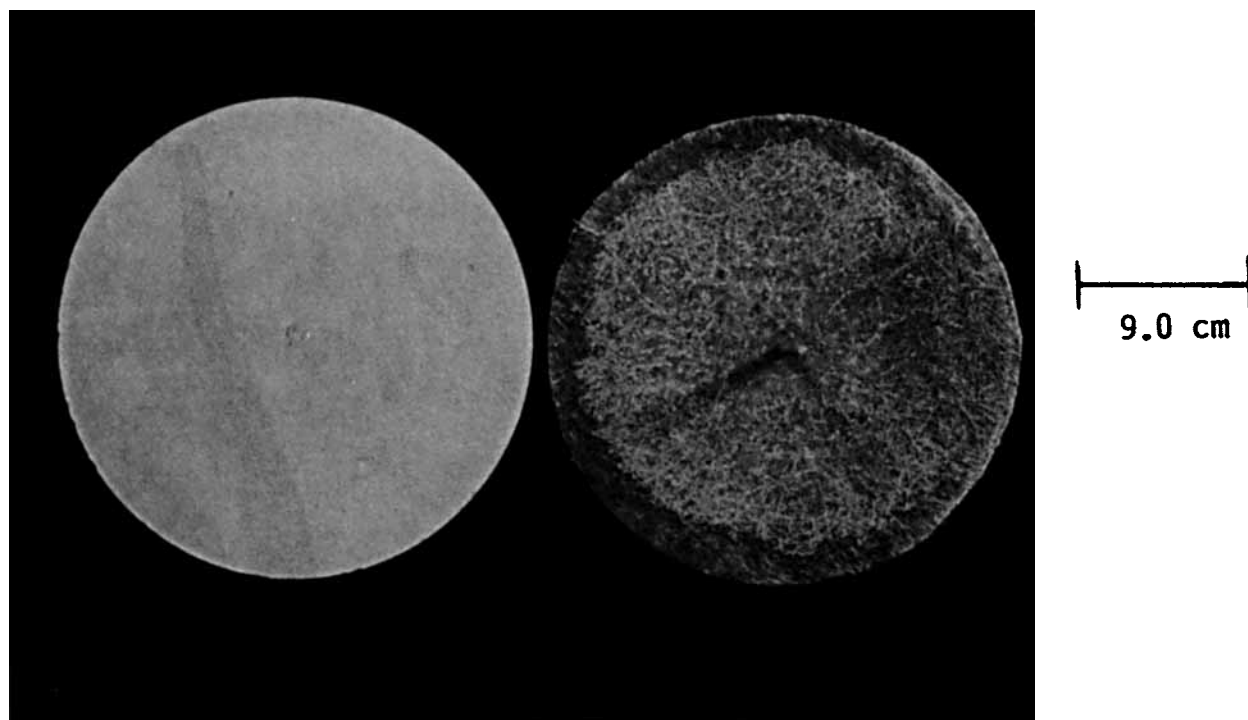


Figure 1 Molding using "sized" and "unsized" glass fiber mats. Note that the white sheet (free of any surface defects) contains heat-cleaned (unsized) glass fibers.

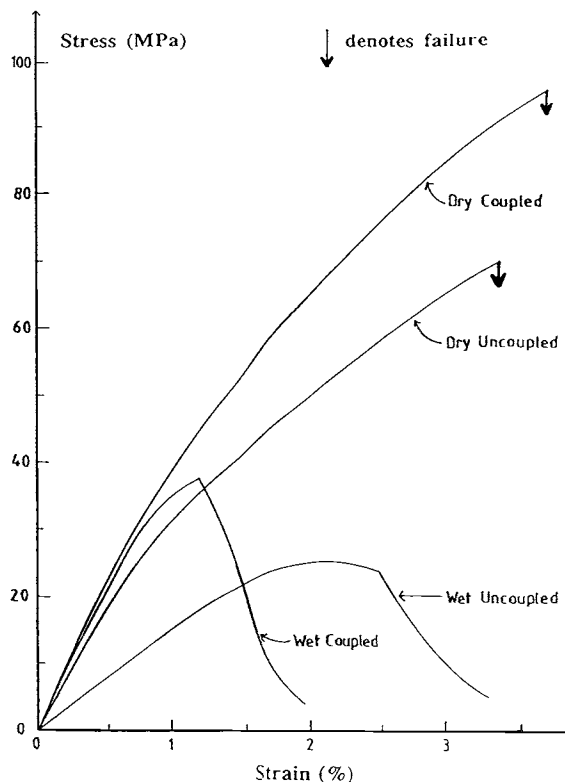


Figure 2 Typical tensile stress-strain curves of the composites showing effect of coupling agent and absorbed moisture.

chine (Instron 1122) operating under the following conditions: crosshead speed 20 mm/min, gauge length 50 mm. The samples were tested inside a constant-temperature cabinet maintained at 20°C. The stress-strain data obtained represent the mean values of at least five samples.

A microscopic study of the fracture surfaces was done by means of optical and scanning electron microscopy as described previously.⁷

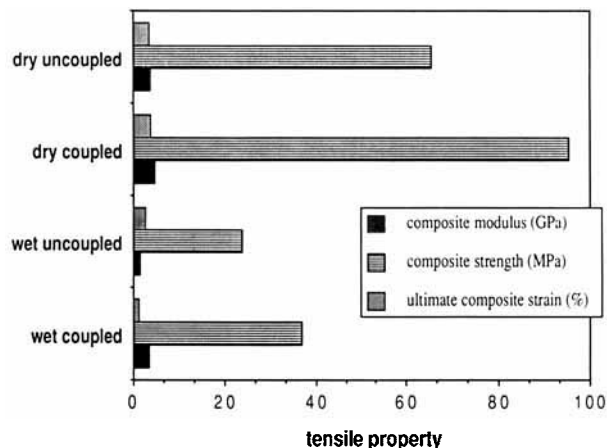


Figure 3 Effect of coupling agent and absorbed moisture on the Young’s modulus, strength (or peak stress), and ultimate strain of the composites.

RESULTS AND DISCUSSION

As mentioned earlier, it was observed that the commercial sizing on the glass fibers significantly inhibited the polymerization reaction so heat-cleaned glass mat was used. Figure 1 shows the detrimental effect of the “sizing” in the molded composite. Note that the white sheet (free of any surface defects) contains the heat-cleaned glass mat. It is pertinent to note that, for optimum performance, silane coupling agents are traditionally applied to glass fiber surfaces from aqueous solutions during commercial processing.⁹ One of the main inhibitors of the anionic polymerization of lactams (as used here) is water, so an aqueous coupling agent solution was not used. In this work, the coupling of the fibers and matrix polymer, using pure γ -amino propyl triethoxy silane, was carried out in situ in a mold containing heat-cleaned glass mat that was pre-exposed to different amounts of water as described above.

Table I Effect of Coupling Agent and Absorbed Moisture on Tensile Stress-Strain Data of the Composite ($V_f = 0.33$)^a

Composite	Young’s Modulus (GPa)	Strength (MPa)	Ultimate Strain (%)	Moisture Content (wt. %)
Dry uncoupled	3.74	65.3	3.38	—
Dry coupled	4.68 (4.34)	95.4 (94.1)	3.71 (3.99)	—
Wet uncoupled	1.41	23.9	2.52	6.9
Wet coupled	3.54 (3.61)	36.8 (45.8)	1.26 (1.68)	6.0

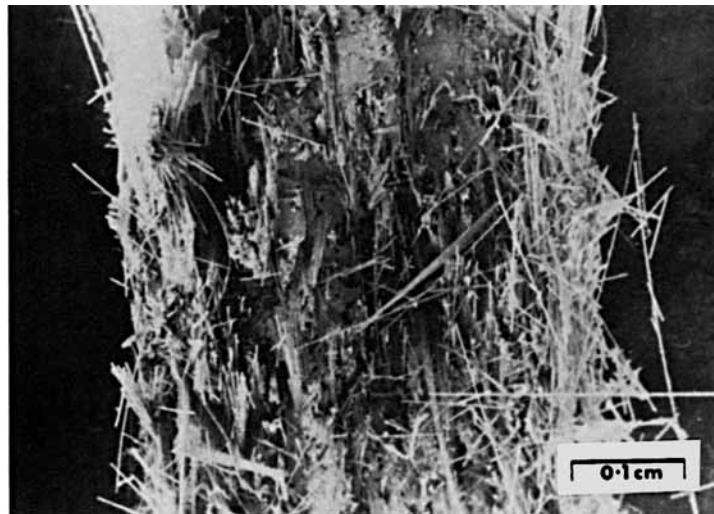
^a Values in parenthesis were obtained from the composite samples containing glass mat that was initially soaked in water before coupling.

Figure 2 shows typical stress-strain plots for dry and wet coupled and uncoupled composite at 20°C. The curves for the dry materials are essentially viscoelastic with a clearly defined failure stress whereas the wet materials exhibited gross yielding with no precise fracture point so the ultimate (peak) stress was taken as the composite strength for the latter materials. In the wet materials most of the failure occurred at the fiber-matrix interface with the fibers

left bridging the crack plane. Fractographic evidence for this failure mechanism (discussed later) was obtained on microscopic examination of the fracture surfaces. The Young's modulus, strength, and ultimate strain for the dry and wet coupled and uncoupled composites are listed in Table I and plotted together in Figure 3 for easy comparison. It can be seen from this figure that the application of the coupling agent increased the composite strength from



(a) Uncoupled



(b) Coupled

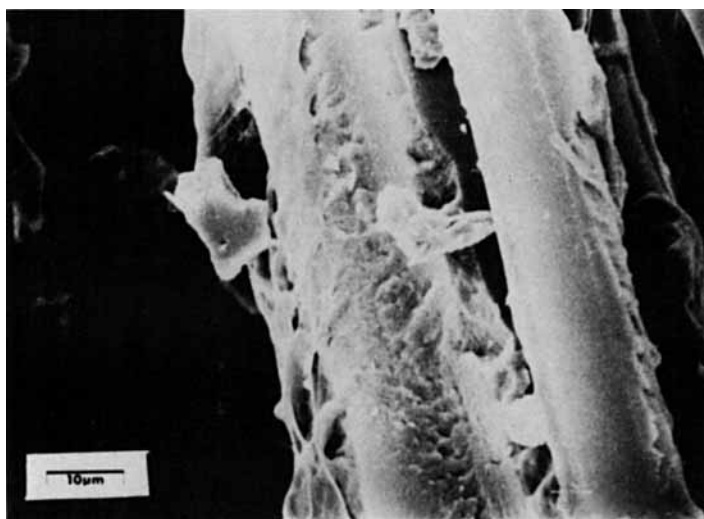
Figure 4 SEM photomicrograph of composite fractured surface showing extent of fiber pull-out: (a) uncoupled; (b) coupled.

65.0 MPa (dry uncoupled) to 95.0 MPa (dry coupled). The modulus increased from 3.74 GPa (dry uncoupled) to 4.68 GPa (dry coupled) and the ultimate strain was relatively unaffected. These values suggest that the coupling agent effectively improved the interfacial adhesion between the fibers and the matrix, which is highly desirable for the effective transfer of load from the matrix to the fiber under tensile loading.¹⁰ The introduction of about 7.0 wt

% moisture decreased the composite strength from 65.0 MPa (dry uncoupled) to about 24.0 MPa (wet uncoupled) and from 95.0 MPa (dry coupled) to about 37.0 MPa (wet coupled). This observed deleterious effect of moisture on the tensile properties of the composite are ascribed to dewetting or debonding of the fibers especially at large strains and the well-known plasticizing action of water on the polyamide 6 matrix.¹⁰ Other researchers have ob-



(a) Uncoupled

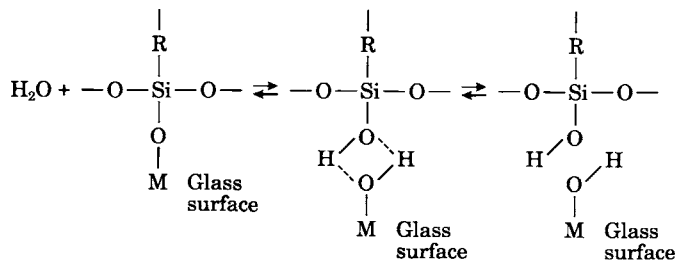


(b) Coupled

Figure 5 SEM photomicrograph showing effect of coupling agent: (a) uncoupled; (b) coupled.

served similar moisture effects on the properties of other composite systems.^{11,12} A mechanism has been

proposed by Plueddemann¹³ to explain this phenomena according to the following reaction scheme:



Note: R = organofunctional alkyl group capable of reacting with the matrix polymer and M—O = metallic oxides on the glass surface.

Water may also separate at the fiber–matrix interface as liquid water causing the growth and propagation of large cracks consequently reducing the tensile properties of the composite.^{9,10,12} The effect of the coupling agent on the composite modulus was observed to be less significant relative to its effect on composite strength, indicating that the fiber–matrix interfacial conditions are less critical for modulus (low strain behavior) of the present composite. Moisture decreased the modulus from 3.74 GPa (dry uncoupled) to 1.41 GPa (wet uncoupled) and from 4.68 GPa (dry coupled) to 3.54 GPa (wet coupled). Additionally, application of the coupling agent was observed to significantly improve the modulus of the wet composites.

In an effort to optimize the performance of the coupling agent in the composite by the generation of relatively more hydroxyl groups (silanol) on the surface of the glass fibers, the glass mat, which was soaked in water overnight and dried in vacuo, was coupled as usual and samples were tested at 20°C. These silanols are known to enhance the bonding at the fiber–matrix interface of a glass-fiber-reinforced plastic composite.⁹ The results obtained are the values in parenthesis in Table I. As expected, this treatment was observed to improve the wet properties of the composite slightly relative to the wet properties of the composite made in the usual fashion, i.e., initially exposing the heat-cleaned glass mat to the atmosphere and subsequently treating it with the polymerization reaction mixture containing the coupling agent. The dry composite properties



0.5 cm

Figure 6 Debonding or dewetting action of water. Note fibers bridging the crack plane.

were relatively insensitive to the method of application of the coupling agent (see Table I). Other types of coupling agents are currently being tested for compatibility with the present composite system.

A fractographic study of the tensile fracture surfaces of the composites was carried out, using scanning and optical microscopic methods, to explain and clarify the observed composite failure mechanisms. This information assists in understanding

the failure micromechanisms of the composite, which will in turn provide a useful tool in the eventual commercial exploitation of the materials for the target applications. The application of the coupling agent was observed to reduce the fiber pull-out considerably and markedly improved the adhesion between the fibers and the matrix (see Figs. 4 and 5). In both the coupled and uncoupled materials, the introduction of about 7 wt % moisture led to the

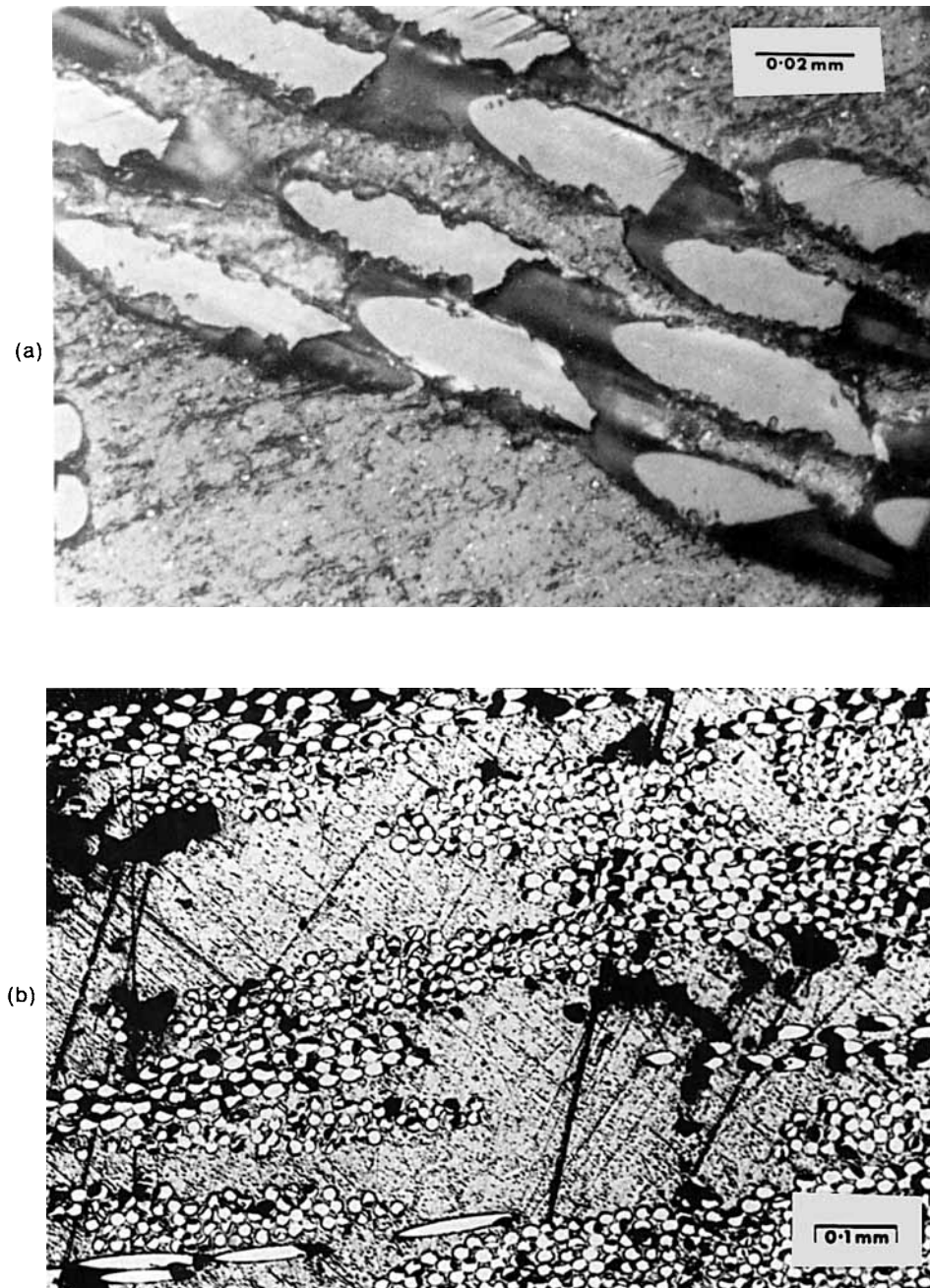


Figure 7 Cross section of fractured surface showing (a) failure at the fiber-matrix interface (uncoupled) and (b) fiber orientation distribution (note polymer-rich regions).

destruction of the fiber–matrix interfacial adhesion thus leaving the fibers bridging the crack plane upon tensile testing (see Fig. 6). The uncoupled materials failed predominantly at the glass fiber–matrix interface [Fig. 7(a)] and no micromatrix cracking was observed. This is probably due to the relatively poor interfacial adhesion between the fibers and matrix polymer. In these materials, the failure is by a de-

bonding mechanism at low strains, and the debonded fibers fail at their weakest points, and pull-out results in catastrophic failure of the composite at the ultimate strain of the composite. This failure mechanism is further supported by the snapping noise heard during tensile testing of these materials and the gross fiber pull-out observed on the fracture surface [see Fig. 4(a)]. Figure 7(b) is an optical mi-

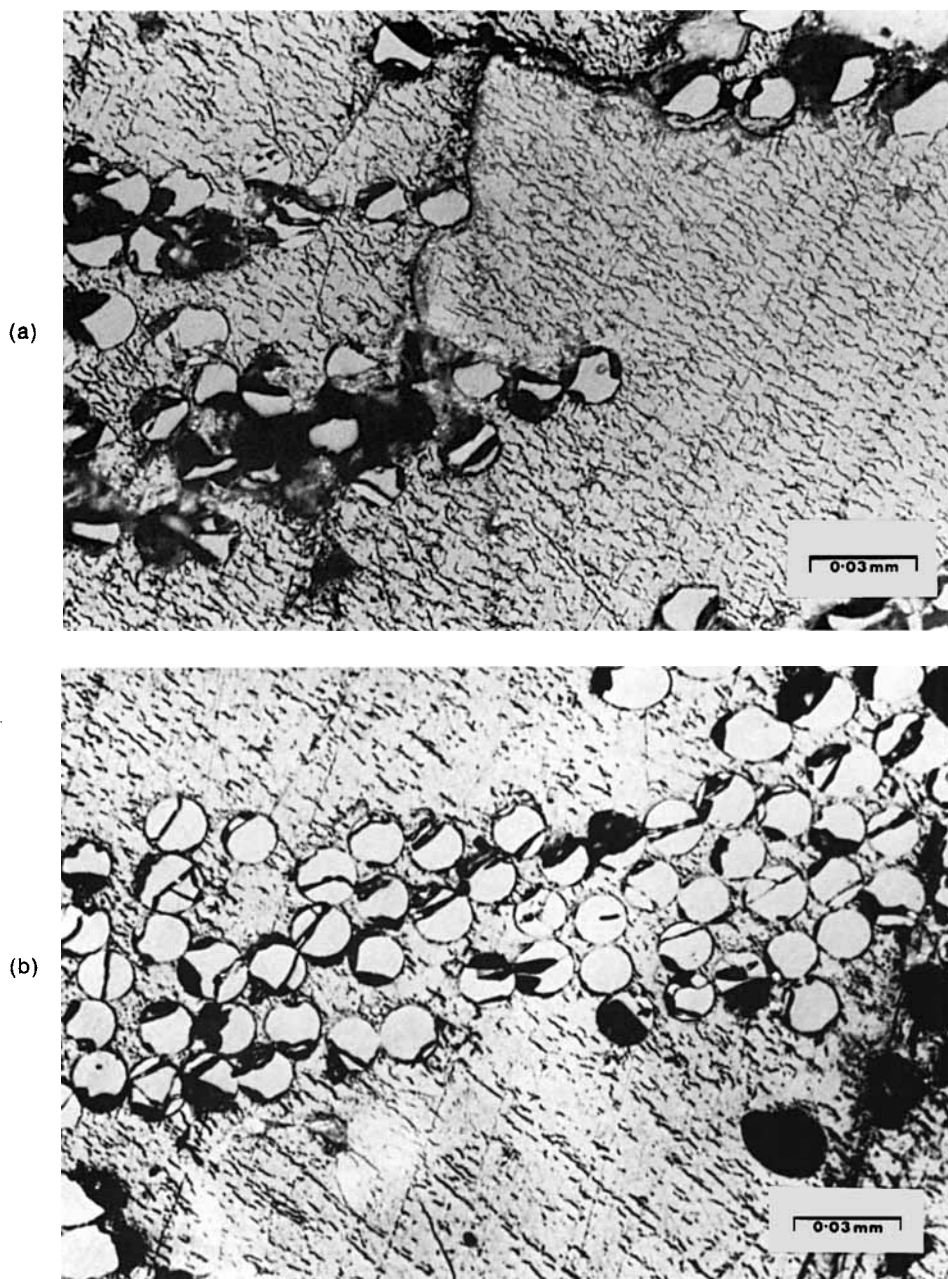


Figure 8 Cross section of fractured surface of the coupled composite showing (a) transverse matrix cracking (note micromatrix cracks) and (b) crack running through the fibers (note trans-fiber failure and micromatrix cracks).

crograph of the microstructure of these materials showing the fiber orientation distribution (note the polymer-rich regions).

It is important to note that a similar three-stage failure mechanism have been observed by Hull and co-workers¹⁰ for dry polyester resin reinforced with chopped strand glass fiber mat as follows: (i) linear elastic behavior up to a strain of 0.3%, deviation from this behavior being due to the onset of cracking or debonding of the transversely oriented fiber bundles; (ii) onset of resin cracking at a strain of 0.7% corresponding to the most pronounced change in slope in the stress-strain curve; (iii) further debonding, shear cracking, and resin fracture at composite ultimate strain of 1.5–2.0%. (Note that the unreinforced polyester resin had a strain to failure of about 2%.)

All of these stages have been observed for the dry coupled composite of this study. The three stages are clearly evident from the stress-strain curve for the dry coupled composite shown earlier in Figure 2. The material behaves in a linear elastic manner up to a strain of about 0.3%, and the most pronounced change in slope occurs at a strain of about 1.5% and has been ascribed to matrix cracking between the fiber bundles. Evidence for this mechanism can be seen in Figure 8(a). This evidence is further supported by the observation that the detrimental effects of moisture on the elastic modulus (low strain behavior) was less critical than its effect on the strength (ultimate or large strain behavior) of the coupled composite (see Fig. 3). The last stage, which occurs at a strain of 3.0–3.7%, is attributed to fiber fracture, shear cracking (micromatrix cracking), and further debonding of the fibers until complete failure of the composite. Figure 8(b) shows crack propagation through the fibers and micromatrix cracking. The failure mechanisms of the present composites under impact loading conditions, reported elsewhere,⁷ are somewhat similar to those reported here.

CONCLUSIONS

The moisture conditioning procedure (i.e., equilibrium hygroscopic state) used here was rather severe and may be well removed from the practical service conditions that the composite is likely to experience in the target applications. However, the results suggest that the incorporation of 1.5 wt % γ -amino propyl triethoxy silane coupling agent into the RRIM

process (as used here) for the composites improved both the dry and wet properties of the composite and the method of application of the coupling agent appear to be insignificant in the dry state but quite important in the wet state. The tensile failure mechanism of the present composite appear to follow a three-stage mechanism that may be associated with debonding at low strains of the fibers, fiber failure (at the weakest point), and pull-out of the fibers resulting in catastrophic failure, at the ultimate tensile strain, of the composite.

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REFERENCES

1. P. Beardmore, J. J. Harwood, K. R. Kinsman, and R. E. Robertson, *Science*, **208**, 833 (1980).
2. S. Christensen and L. P. Clark, "Thermoplastic Composites for Structural Applications: An Emerging Technology," 31st. International SAMPE Symposium, April 7–10, 1986, p. 1747.
3. D. Reinhard, "Reinforced Thermoplastic Composites in Transportation Applications," SAE Transactions, Paper No. 880153, Detroit, Michigan, February 29–March 4, 1988, p. 53.
4. A. E. Johnson and J. R. Jackson, "RRIM for Automotive Bodywork—An Evaluation of its Dynamic Performance in Comparison with Metals and SMC," 37th Ann. Conf. SPI, January, 1982.
5. F. N. Cogswell and M. Hopprich, *Composites*, **14**(3), 251 (1983).
6. J. U. Otaigbe and W. G. Harland, *J. Appl. Polym. Sci.*, **36**, 165 (1988).
7. J. U. Otaigbe and W. G. Harland, *J. Appl. Polym. Sci.*, **37**, 77 (1989).
8. J. U. Otaigbe, *Polym. Eng. Sci.*, **31**(2), 104 (1991).
9. H. Ishida and J. L. Koenig, *Polym. Eng. Sci.*, **18**(2), 128 (1978).
10. D. Hull, *An Introduction to Composite Materials*, Cambridge University Press, Cambridge, U.K., 1981.
11. J. R. Vinson, Ed., *Advanced Composite Materials—Environmental Effects*, ASTM-STP 658, American Society for Testing and Materials, Philadelphia, 1978.
12. O. Ishai, *Polym. Eng. Sci.*, **15**(7), 486, 491 (1975).
13. E. P. Plueddemann, Ed., *Mechanism of Adhesion through Silane Coupling Agents*, *Composite Materials*, Vol. 6, Academic Press, New York, 1974, pp. 174–216.

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