

Ionomer. I. The Effect of Woven Glass Mat Reinforcement on Tensile Properties

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ABSTRACT: An investigation was conducted on ionomer polymer. The ionomer pellets were molded into a thin sheet before fabrication into composites. The reinforcing agent used was woven glass mat. Before fabrication, the woven glass mat was treated with the following: 1. silane coupling agent for 5 min and dried at room temperature; 2. silane coupling agent for 5 min and dried in the oven at 110°C for 15 min; 3. Ultraviolet radiation for 5 min; and 4. silane (oven dried + ultraviolet). The composites were fabricated at various pressure, time, and temperature. An ideal processing condition was established, i.e., pressure = 5 MPa, temperature = 180°C, and the impregnation time = 30 min. The void contents of the composites were estimated using the ignition method and the tensile properties were measured. The results revealed that good impregnation of the matrix ionomer into the reinforcing agent can be achieved at 180°C. This was confirmed by low void content as compared with other test temperatures. Further clarification was through the tensile properties, which were higher than those at lower temperatures (120 and 150°C). The effect of fiber orientation was checked, and both 0 and 90° had identical strengths and moduli irrespective of the various fiber treatments. Apart from the void contents, the degree of impregnation was also checked based on the tensile strengths in 45, 25, and 60° fiber orientations. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1395–1400, 2001

Key words: ionomer; impregnation; woven glass mat; ultra violet; silane coupling agent

INTRODUCTION

Ionomer polymers are recently developed thermoplastic resins with ethylene as their major component. Ethylene is copolymerized with methacrylic acid which has been converted to methacrylate salt by neutralization in sodium (Na) or zinc (Zn) ion. The ionic aggregate (Na or Zn) serves as reversible crosslinking sites and results in high levels of resilience and impact resistance.^{1–4} The structure of ionomer is shown in Figure 1(a). Thermal analysis of ionomer by MacKnight and Taggart^{5,6} as well as Tadano, et al.⁷ have revealed two peaks correspond-

ing to ionization peak and melting peak. The model is represented in Figure 1(b).

Thermoplastics are known to have relatively high viscosities, which makes impregnation into reinforcing agents more difficult. Recently, various techniques for improving impregnation of matrix resin into the reinforcements have been developed. The techniques include commingling, cowoven fabric, film stacking, and coated yarn.^{8–11} However, the adoption of woven fabrics as a form of reinforcement in composite fabrication is attributed to their flexibility, toughness, high impact resistance, and ease of fabrication at low cost.^{12–14} Various fabric constructions including ordinary plain weave, twill, satin, and the more highly sophisticated honeycomb weaves have been used. The most successful of all is the plain woven fabric, in which the degree of com-

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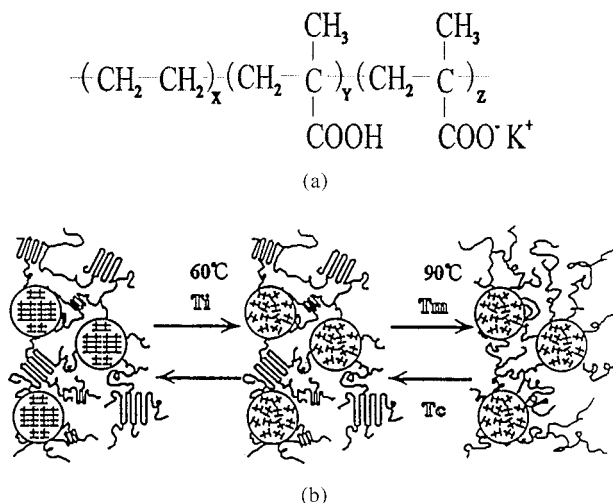


Figure 1 (a) Chemical structure of ionomer, (b) structural model.

compactness and stability in terms of slippage and distortion is achieved. In plain woven fabric, a warp yarn is made to interlace with the weft yarn in the order of 1 up 1 down. Because ionomers are primarily used for golf balls, packaging, and sporting footwear, further improvements in mechanical properties will make them more versatile, especially in the automotive industry. Fiber reinforced ionomer composites have not been well documented in the literature. Therefore, the aim of this investigation was to reinforce ionomer with woven glass mat and observe the effect of reinforcement on tensile properties. However, the impregnation condition of matrix ionomer may depend on surface treatment of the woven glass mat. Hence, the woven mat was treated with a silane coupling agent and ultraviolet (UV) radiation. A comparison between the tensile properties of untreated, silane-coupling treated, UV-irradiated and silane + UV-irradiated ionomer composites were made.

EXPERIMENTAL

Materials

Pellets of ethylene-based ionomer neutralized in 60% Zn were supplied by the Mitsui-DuPont Petrochemical Co. (Tokyo, Japan). The ionomer has a melting temperature (T_m) of 90°C, a glass transition temperature (T_g) of 50°C, and an ionization temperature (T_i) of 60°C. The glass fiber plain

woven mat was obtained from Asahi Chemical Co. (Osaka, Japan).

Woven Mat Treatment

The woven glass mat fabric was treated in silane coupling agent as well as UV radiation as follows: 1 wt % silane coupling agent was diluted in 99 wt % acetone and the glass mat was placed in the mixture for about 5 min. After this treatment, one of the samples was dried in the oven for 15 min at 110°C. The other sample was left to dry in the surrounding atmosphere.

The UV irradiation was performed by irradiating the woven glass mat for 5 min using an Ultra Violet Irradiation device (UVR-200G-SS2). The method described elsewhere¹⁵ is based on two factors^{16,17}: a significant oxidizing action caused by forming and decomposition of ozone (O_3) because of beam of dual wavelength (184.9 and 253.7 nm), and secondly, the scission of molecular chain because of the intense energy of deep wavelength UV rays. Two sets of samples were irradiated, i.e., normal glass woven mat and silane-treated (oven-dried) samples.

Fabrication

The ionomer pellets were compression molded into thin sheets at a temperature of 180°C and a pressure of 5 MPa. The thickness of the molded ionomer sheet was 1 mm. The reinforcing glass mat was sandwiched between the ionomer film. The sandwiched ionomer glass having a volume fraction of 90:10 was compression molded on a SHINTO compression-molding machine fitted with a cooling zone. The molding conditions were as follows: pressure = 3–7 MPa, impregnation time was varied between 20 and 40 min, and processing temperatures were 120, 150, and 180°C. After molding, the composite was quickly transferred to the cooling zone. The cooling medium is water, and it takes about 10 min to cool the sample to room temperature.

Estimation of void content in the sample was performed by the ignition method. In this case, the matrix ionomer resin was burnt off in an oven at 600°C for about 6 h. The void content was computed from the following relationship¹⁸:

$$\rho_{ct} = \left[\frac{W_c}{\frac{W_f}{\rho_f} + \frac{W_r}{\rho_r}} \right] \quad (1)$$

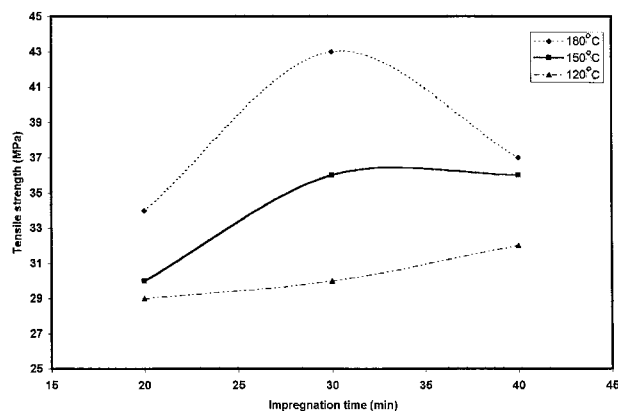


Figure 2 Tensile strength of woven glass mat reinforced ionomer composite versus impregnation time.

$$V = \left[1 - \frac{\rho_c}{\rho_{ct}} \right] \quad (2)$$

where W_f , W_r , and W_c are the weight fractions of fiber, resin, and composite, respectively; ρ_f , ρ_r , and ρ_c are the corresponding densities, and ρ_{ct} , the theoretical density of the composite.

Tensile Test

The tensile test sample was 2.2-mm thick and 127-mm wide. The gage length was 25 mm and the test was conducted on samples with different fiber orientation (0, 25, 45, 60, and 90°) at room temperature using a cross-head speed of 5 mm/min.

RESULTS AND DISCUSSION

Effect of Processing Variables

Variables such as processing temperature, pressure, and time are known to have some effects on composites during fabrication. Inadequate pressure, temperature, or impregnation time may affect the quality of the material. The variables as functions of tensile strength (0° fiber orientation) of the ionomer composites are plotted in Figures 2 and 3. As can be seen in Figure 2, the tensile strength was highest at 180°C with 30 min of impregnation time. Above 30 min, the strength reduced. This indicates that optimum tensile strength can be achieved below 30 min of impregnation time. At 150°C, the tensile strength is lower than that of 180°C. However, the tensile strengths of samples fabricated for 30 and 40 min,

which remains the same, indicates that impregnation at this temperature (150°C) is completed between 30 and 40 min, unlike at 180°C where it is completed at 30 min. In samples fabricated at 120°C, the tensile strength, which is the lowest of all three temperatures, increases with increasing impregnation time. This confirms that impregnation is incomplete at this temperature. The choice of processing temperature depends on the melting temperature (T_m) of ionomer, which is around 90°C.^{19,20} Because it is a copolymer of ethylene [$T_m = 135^\circ\text{C}$ and methacrylic acid ($T_m = 50^\circ\text{C}$)], a higher temperature beyond 120°C may be necessary during fabrication. Thus, the polymer molecules will move more rapidly under the influence of higher temperature, i.e., the chains untangle and tend to orient in the direction of flow. Tensile strength is plotted against impregnation pressure in Figure 3. The most ideal processing pressure in which maximum tensile strength is attained is 5 MPa. Apart from the tensile strength at 180°C being higher than that of 150°C, there is similarity between the two, i.e., tensile strength reduced above 5 MPa. Reduction of tensile strength (30-min impregnation time) at 7 MPa implies that the pressure is too high. At 120°C, the tensile strength reduces with increasing pressure. This unusual behavior is due to the temperature which is much too low.

A significant point is that attainment of full impregnation may be achieved in much less time in woven glass mat reinforced composites than in unidirectional (UD) composites. This is because of the spacing created between the adjacent fiber bundles that permits resin to flow more easily²¹ in glass mat reinforced whereas in UD, fibers are

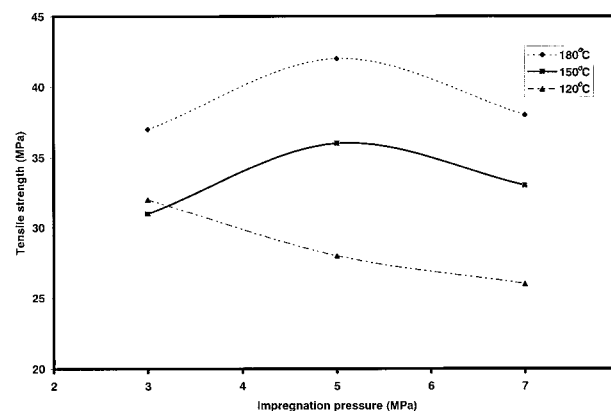


Figure 3 Tensile strength of woven glass mat reinforced ionomer composite versus impregnation pressure.

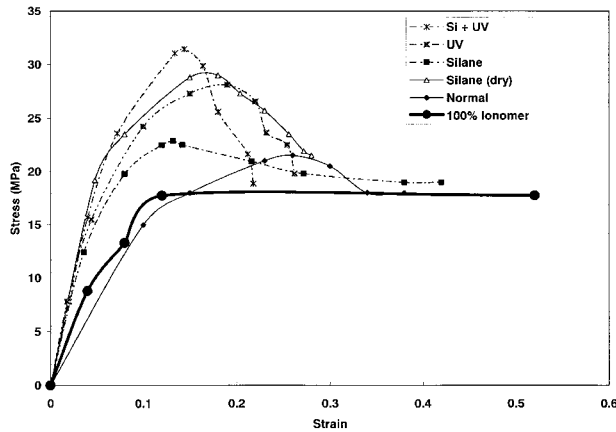


Figure 4 Stress-strain curves of woven glass mat reinforced ionomer composites at 45° fiber orientation.

more compact because of lack of spacing between them.

Degree of Impregnation

For a composite material to be of good commercial value, the impregnation conditions must be adequate. Having established the most suitable molding conditions, it is necessary to observe the impregnation of matrix resin into the reinforcing glass mat. This is studied via the tensile strength of 45° fiber orientation and void content. Unlike in UD composites in which the strength is influenced by the reinforcing fiber in the longitudinal direction (0°) and matrix resin in the transverse direction (90°), the situation is different with woven glass mat. In glass mat reinforced composites, both 0 and 90° had identical strengths, indicating that the fiber is effective in both directions. The effect of the matrix resin can only be felt in other fiber orientations, e.g., 45°. Figure 4 shows the stress-strain curves of ionomer composites (45°) with different fiber treatments. Also shown in Figure 4 is the stress and strain curve of unreinforced ionomer for comparison. Tensile strengths of the unreinforced ionomer and glass mat reinforced ionomer composites are identical, as observed in Figure 4. The similarity in tensile strength is an indication that the matrix ionomer influences the strength of the composite in the 45° direction. Different fiber treatments further enhance the impregnation of the composites. In this case, the woven glass mat treated with silane + UV had the highest tensile strength. This is followed by the silane- (dried at 110°C for 15 min) and UV-treated samples. Silane treatment has

been known to provide adhesion at the fiber-matrix interface. This is likely attributable to the covalent or hydrogen bonding at the interface. Improvement of impregnation of matrix ionomer into the reinforcing woven fabric after UV irradiation of the woven glass may be initiated by chemical reactions at the interface. In addition, all samples, irrespective of fiber treatment, are ductile with yield points. The unreinforced ionomer having a high elongation-at-break indicates that ionomer is a highly ductile polymer. Reinforcing the ionomer matrix reduces the elongation and the reduction depends on the fiber surface treatment. Another interesting feature is that the degree of impregnation can also be determined at 25 and 60° fiber orientations (Figs. 5 and 6). Because it is reasoned above that the matrix resin influences the tensile strength in 45° orientation, the same can be attested for 25 and 60° orientations because of comparability of tensile strengths.

The degree of impregnation of matrix resin into the reinforcement may also be checked by measuring the quantity of voids in the composites. A high degree of void is an evidence of poor impregnation and this will have an adverse effect on the quality of the final product. Figure 7 shows the void content as a function of impregnation time. It is seen in Figure 7 that the lowest processing temperature (120°C) is accompanied with high void content whereas the highest processing temperature (180°C) had the least quantity of voids. The void contents in samples processed at 180°C for 30 and 40 min were almost the same. Further reduction below this level (2.8%) may be difficult because of the presence of air entrapped during

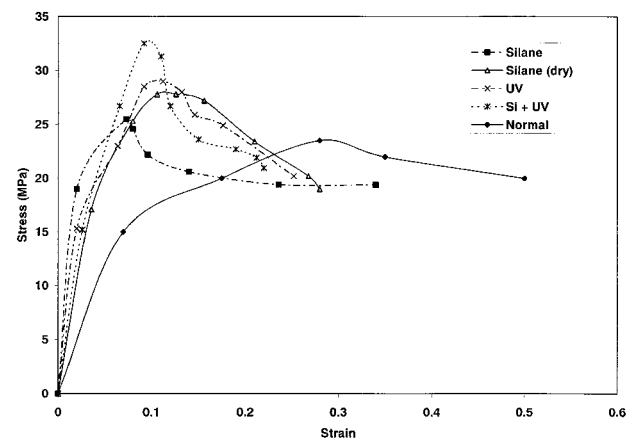


Figure 5 Stress-strain curves of woven glass mat reinforced ionomer composites at 25° fiber orientation.

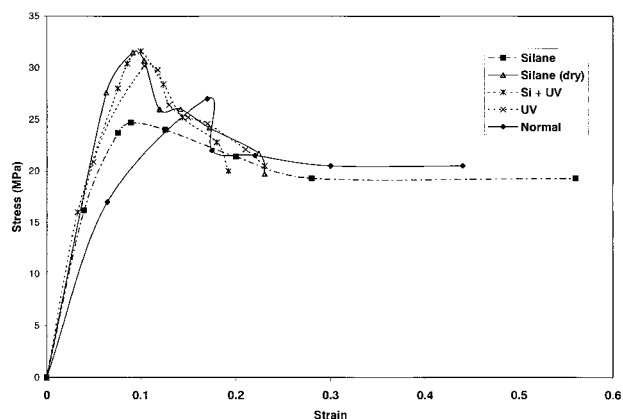


Figure 6 Stress-strain curves of woven glass mat reinforced ionomer composites at 60° fiber orientation.

consolidation, molecular entanglements, and other imperfections.^{22,23}

Tensile Properties

The tensile strengths of glass mat reinforced ionomer composites fabricated at 180°C for 30 min are shown in Figure 8. The woven glass mat contain different treatments, i.e., silane, silane (dry), UV, and silane + UV. The tensile strengths of all the different fiber treatments are compared in Figure 8. As expected, both 0 and 90° fiber orientations had identical tensile strengths, higher than those in other directions. However, higher tensile strengths in both 0 and 90° fiber orientations are not too sensational because one would expect higher values because of the strength of the reinforcing woven glass mat which is influential in both directions. Thus, the reason for the low

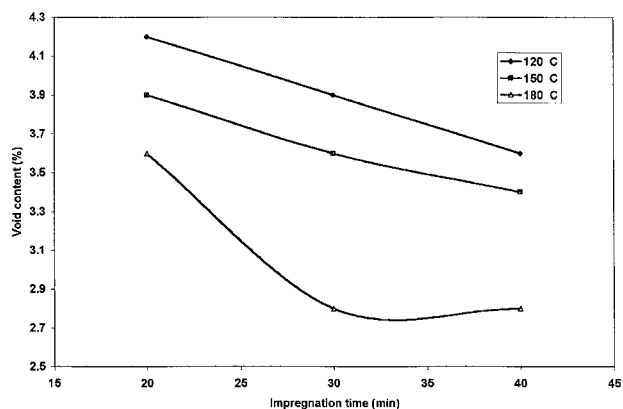


Figure 7 Void content as function of impregnation time.

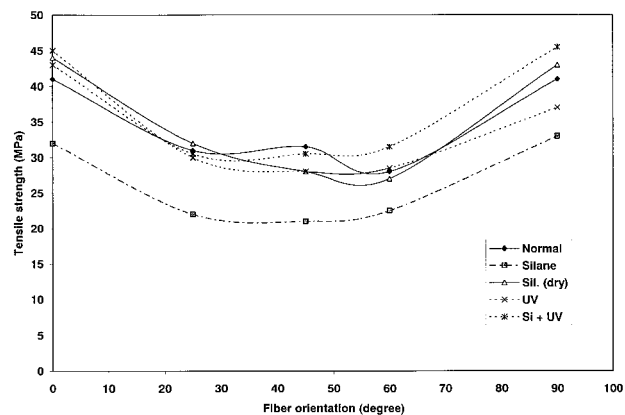


Figure 8 Tensile strength of woven glass mat reinforced ionomer composites as a function of fiber orientation.

strengths in these two directions is due to the volume fraction of the reinforcing glass mat. The volume fraction in this case is around 10%, which is rather low for a composite material. It is well documented in the literature that the higher the volume fraction, the higher the tensile strengths in both directions.²¹ In this investigation, the difference between the tensile strengths in 0 and 45° is less than 30%. Various fiber treatments were introduced particularly to modify the surface of the reinforcing woven glass mat. The purpose of such modification is to enhance adhesion at the matrix-woven glass mat interface. The various methods adopted are discussed above. The silane-treated sample (room temperature dry) had the lowest tensile strength at all fiber orientations whereas silane (oven dry) + UV treatment may be adjudged to be the best. The adhesion mechanism involved in this case will be analyzed in a subsequent investigation.

Fiber orientation has a stronger effect on modulus than in the strength of this ionomer composite. As shown in Figure 9, irrespective of various fiber treatments, the difference between the 0 and 45° samples is more than 100%, i.e.: normal, about 189%; silane (oven dry), 120%; silane (room temperature dry), 92%; UV, 193%; and Silane + UV = 200%. Fiber modification via various treatments also improves the modulus of the composites. As observed in Figure 9, the silane + UV treated composite had the highest modulus, particularly in 0 and 90° oriented samples. The modulus of the untreated sample is the lowest of all, indicating that surface modification of the woven glass mat can significantly improve the tensile

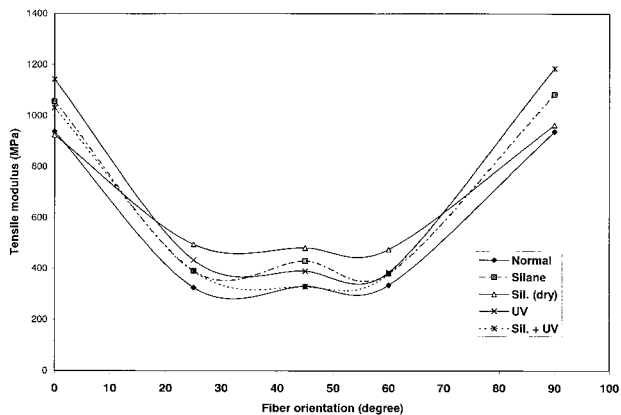


Figure 9 Tensile modulus of woven glass mat reinforced ionomer composites as a function of fiber orientation.

modulus of the composite irrespective of fiber orientation.

CONCLUSIONS

In this preliminary investigation on woven glass mat reinforced ionomer composites, it is shown that reinforced ionomer composites can compete with medium-range engineering polymers. Despite the fact that the volume fraction of the reinforcing agent was low (10%), a significant improvement of the tensile properties was achieved. The reinforcement is more effective in improving the modulus than the strength. Impregnation of matrix ionomer into the reinforcing agent was achieved at a moderate pressure (5 MPa) when compared with some other thermoplastics that may require higher pressures. Further improvement on impregnation as well as tensile properties was attained after subjecting the reinforcement to various treatments before fabrication. However, composites treated with silane + UV had the overall best properties.

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