IMPROVEMENT OF RESIN IMPREGNATION INTO GLASS CLOTH BY SILANE TREATMENT IN RESIN TRANSFER MOLDING

Nobuo Ikuta, Tohru Morii, Seiwa Ohori, Minoru Yasueda

Department of Materials Science and Engineering
Shonan Institute of Technology
1-1-25, Tsujido-Nishikaigan, Fujisawa, Kanagawa 251-8511, Japan

SUMMARY: An evaluation method was proposed for resin impregnation using resin transfer molding of unsaturated polyester matrix composites with silane-treated glass cloth. The determination of whitening of the composite was carried out as a parameter of incompleteness of resin impregnation. The change of whitening with silane concentration was compared with the bending modulus as a parameter of chemical reinforcement. The materials used were unsaturated polyester resin as a matrix and methacryloxypropyltrimethoxysilane as a silane coupling agent for glass cloth. Resin transfer molding produced 4 plies of glass cloth laminates by impregnating the resin. The silane-treated glass cloth repressed whitening above 0.026 w/w % of silane solution, while the chemical reinforcement due to silane gave no appearance below 0.2 w/w% from the bending test of the laminates. The large difference between the concentrations suggested that silane has a couple of functions, that is, chemical reinforcement and physico-chemical resin wettability.

KEYWORDS: physico-chemical property, silane, resin impregnation, interfacial effect, resin transfer molding, whitening, bending modulus

INTRODUCTION

Silane coupling agents have been employed for reinforcement of interface between glass fiber and resin. This effect is well known to depend on the chemical function of silane with bifunctional groups to glass fiber and to resin. We have already examined the relationship of the chemical function and the interfacial reinforcement [1-3]. Siloxane network coming from silane deposit linked to glass fiber surface is necessary to raise up the interfacial strength between glass fiber and resin effectively. This means that no chemical reinforcement occurs with diluter silane solution in the treatment. Silane monolayer gives no interfacial reinforcement. We need 20 - 30 silane molecules at 1 nm^2 of glass fiber surface for the reinforcement to be coming from the siloxane networks of silane deposit linked to the glass surface.

On the other hand, in a dilute silane solution, silane seems to give not chemical reaction but resin wettability. In practice, industrial process shows that silanes are effective on the improvement of resin impregnation onto glass filament in glass cloths and mats. However, such an impregnation effect has not been clarified in relation to resin wettability.

In this study, we have proposed an evaluation method for resin impregnation using resin transfer molding of unsaturated polyester matrix composites with silane-treated glass cloth. The determination of whitening of the composite has been carried out as a parameter of incompleteness of resin impregnation. The change of whitening has been compared with that of the bending modulus as a parameter of chemical reinforcement. This phenomenon should not be related to the surface tension of silane-treated glass cloth.

EXPERIMENTAL

The materials were used as follows: Resin as a matrix was unsaturated polyester resin (Polymal 5250, Takeda Chemical Industry Ltd.) One and half parts of hardening agent (Parcure HO, Nippon Oil and Fats Ltd.) and 0.3 parts of catalysis (Paroyal TCP, Nippon Oil and Fats Ltd.) were mixed with resin. Reinforcing fiber was heat-cleaned E-glass cloths supplied from Nittobo Co. Ltd. Silane was methacryloxypropyltrimethoxysilane (MPS) purchased from Shin Etsu Chemical Co.

In silane treatment, glass cloth was first dipped into different concentrations of aqueous MPS solution. Uptakes of silane solution was weighted to know the amounts of MPS on glass fiber. The glass cloth with silane solution was then heated at 100 °C for 10 min.

A mold in a transfer machine (TIC-26, Toho Machinary Co. Ltd.) had a twin of rectangular cavities. As shown in Fig. 1, a couple of four sheets of glass cloth were prepared to fit the size of each cavity. Liquid resin was transferred into the cavities and cured under 80 °C for 20 min. The molding conditon was summarized in Table 1.

After curing, the whitening of the molding product was evaluated from light transmittance at 680 nm of wavelength using a UV-visible spectrometer, UBEST-35, Nippon Bunko Co. The three points bending test was performed using a universal testing machine, Autograph AGS-50, Shimadzu Co., Ltd. to evaluate the interfacial effect on reinforcement.

The surface tension of glass cloth was determined to water and liquid resin of UP using a Wilhelmy type of surface tension instrument (WET-6000, Rhesca Co., Ltd.) The glass cloth was immersed into each liquid for 280 sec to measure the static surface tenstion.

RESULTS AND DISCUSSION

Table 1: Molding condition of resin trasfer molding

Upper Mold Temperarure / °C	80
Lower Mold Temperature / °C	80
Molding Pressure / MPa	19.6
Transfer Pressure / MPa	4.9
Resin Transfer Time / sec	8
Curing Time / min	20

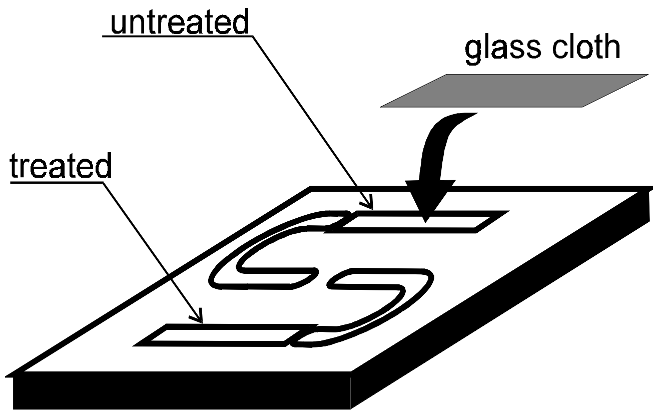

Fig. 1: Four plies of glass cloth in each cavity of a transfer mold

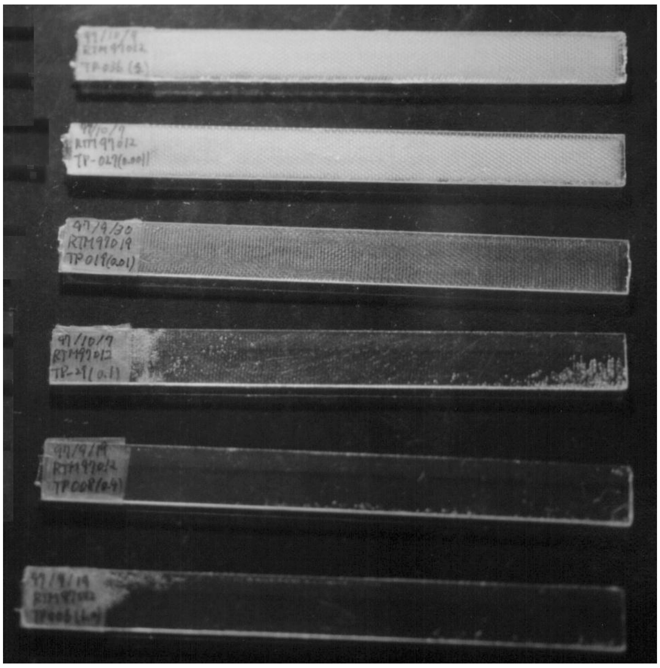

Fig. 2: *Appearance of molding products of glass cloth laminates with different amounts of silane; silane concentration was 0, 0.001, 0.01, 0.1, 0.4, 1.0 w/w % of MPS (from the upper product)*

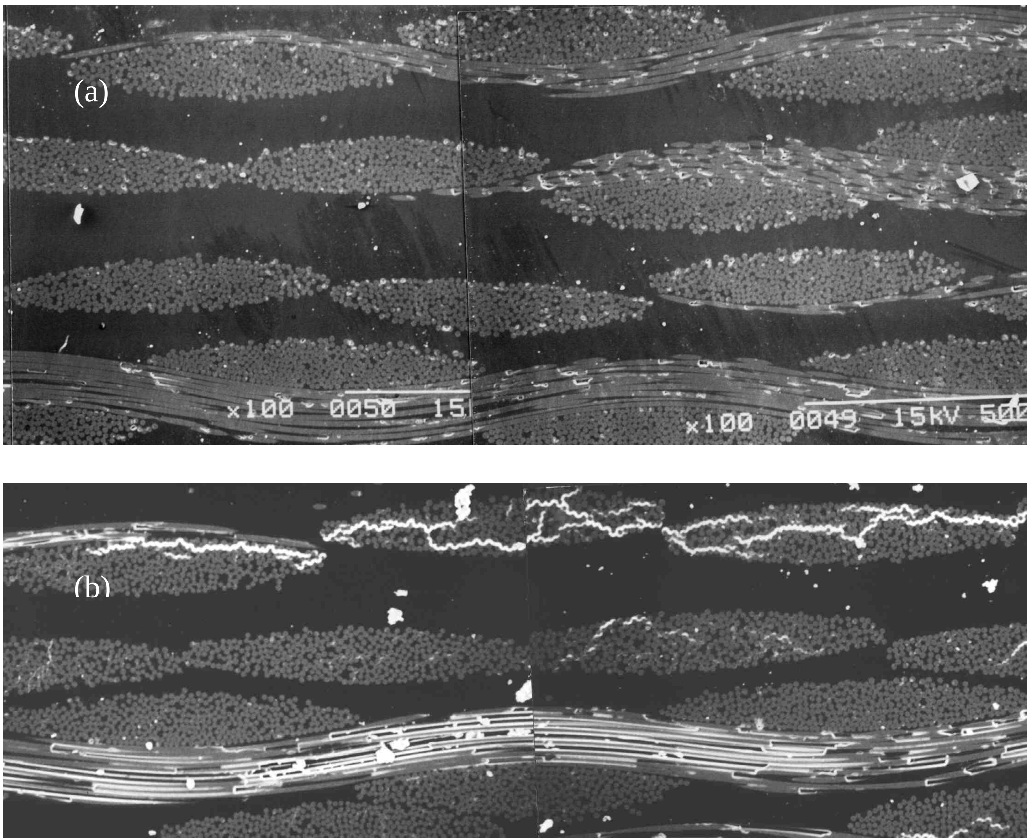

Fig. 3: *SEM observation of cross-section of laminate composites with silane-treated glass cloth (a) and untreated glass cloth (b)*

Depression of Whitening by Silane Treatment

The whitening was observed over the molding composite of the untreated glass cloth laminates. On the other hand, glass cloth treated with more than 0.01 w/w% of MPS showed transparent products, as shown in Fig. 2. The cross-section of the laminates was observed by scanning electron microscopy to know the difference of resin impregnation between untreated and silane-treated glass cloth laminates. As shown in Fig. 3 (a), silane-treated glass cloth laminates made resin impregnated into each yarn of glass cloth. In addition, resin was found to attach to each glass filament. On the other hand, silane-treated glass cloth laminates also resin impregnated into glass cloth, but filament was not closely surrounded by resin, as shown in Fig. 3 (b). Such a status meant micro-void at the surface of glass filament in the yarns of the cloth laminates, and this resulted into the whitening of glass cloth laminates. As a result, whitening in this case was reduced to the subject on an interfacial phenomenon due to silane treatment of glass fiber. In other words, the whitening came from defective of resin contact to glass filament.

Change of Whitening and Elasticity with Silane Concentration

Light transmittance at 680 nm of wavelength was measured for glass cloth laminates at different concentration of silane solution to see the quantitative relation between whitening and silane concentration. The transmittance was remarkably raised above 0.026 w/w %, as shown in Fig. 4.

In order to compare the interfacial effect of silane on whitening with interfacial reinforcement by silane treatment, the same laminate composites after the measurement of light transmittance was subjected to bending test. As shown in Fig. 5, the change of bending modulus with silane concentration was significantly different from the change of whitening. It should be noted that the bending modulus was remarkably lower than that of untreated glass cloth laminates. This phenomenon was possible to derive from the interfacial strength, as

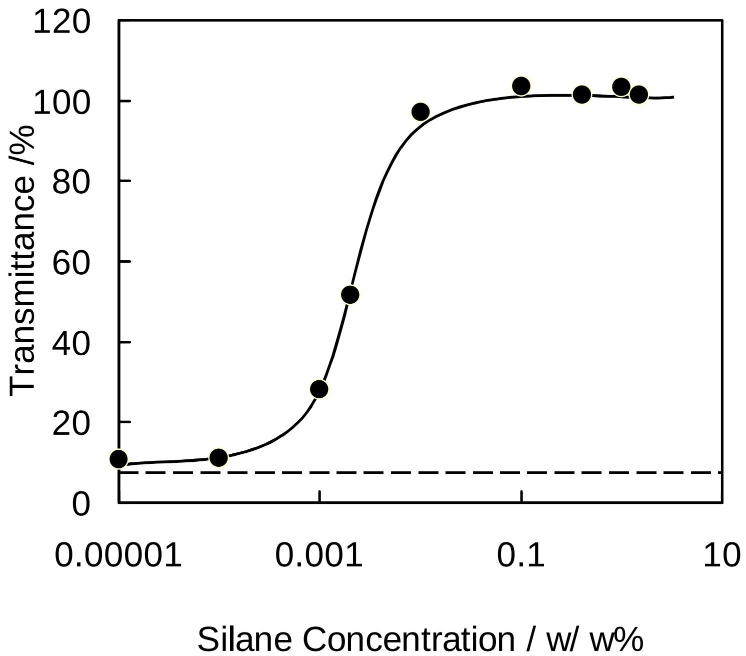

Fig. 4: Change of light transmittance (680 nm) of glass cloth laminates with MPS concentration in silane treatment; (---) for untreated glass cloth

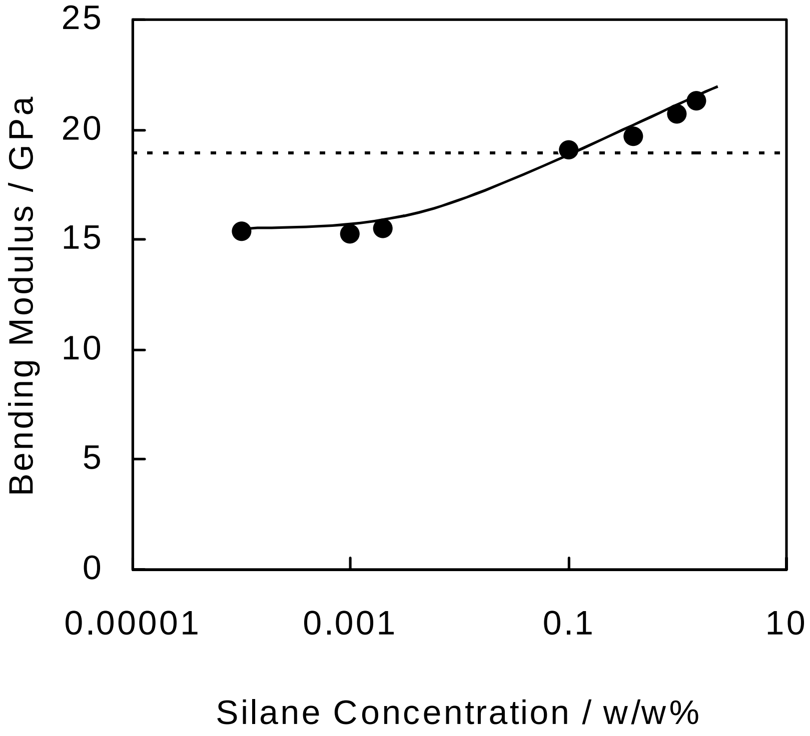

Fig. 5: Change of bending modulus of cloth laminates with MPS concentration in silane treatment; (---) for untreated glass cloth

described in the previous paper [1]. A small amount of silane on glass fiber gave no interfacial reinforcement, but play a role in lubrication. In this meaning, the interfacial reinforcement was produced above approximately 0.2 w/w% of silane concentration, compared with the bending modulus of untreated glass cloth laminates. This concentration was reasonable as a reference of the interfacial strength in the previous paper [1]. As a result, this concentration was different from that on whitening, 0.026 w/w%. This significant difference of critical concentration between whitening and reinforcement suggested that the mechanism of whitening due to silane was different from silane reinforcement.

The concentration of 0.026 w/w % gave a covering coat of silane molecules over the surface of glass filament from the estimation of uptake of silane molecules and surface area of glass filament. This meant that the organic property due to silane deposit on glass fiber raise up resin wettability.

Surface Wettability of Silane-treated Glass Cloth to Resin

It has been popularly said that the effect of silane on whitening depends on the surface

Table 2: Relative surface tension of glass cloth by silane treatment to water and liquid resin of UP

Liquid Medium	Water	Ethylene Glycol	UP (r. m.)	UP (100 °C)
Relative Surface Tension*1	0.43	0.80	0.97	0.92

*1 (Surface Tension of Silane-treated Glass Cloth)/(Surface Tension of Untreated Glass Cloth) wettability of resin to fiber due to surface tension. In order to examine the effect of silane on surface wettability, the surface tension of silane-treated and untreated glass cloth was measured to some kinds of liquid; water, ethylene glycol, and liquid resin of UP. Relative surface tension was determined from the ratio of surface tension with silane treatment. As summarized in Table 2, water showed a large gap between silane-treated and untreated glass cloth. This is because the organic surface due to silane depress the wettability of water. Other liquids gave little difference between them. Relative surface tension increased in order of polarity of liquid medium; water, ethylene glycol, liquid resin. However, the relative surface tension counld not be beyond one, even if the viscoelasticity of liquid resin was lowered at high temperature. This result exhibited that organic property due to silane molecule was impossible to elevate resin wettability due to surface tension. This meant that that the whitening effect should be taken into consideration other factors such as viscoelasticity and hardening shrink of resin.

CONCLUSION

Silane coupling agents has a couple of functions; chemical reinforcement at interface and improvement of resin wettability. In order to examine the difference between them, the improvement of resin wettability has been quantitatively evaluated using resin transfer molding. Whitening of molding products is a suitable parameter for inferior productivity. From the measurement of whitening, effective silane concentration is found to be significant lower in improvement of whitening than that in interfacial reinforcement. This means that the resin wettability by silane is different from chemical reinforcement. However, the effect of silane on resin wettability cannot be explained by the surface tension of glass cloth to liquid resin. It seems to depend not on statical surface energy, but on dynamic viscoelasticity and hardening shrink of resin.

REFERENCES

1. N. Ikuta, Z. Maekawa, H. Hamada, H. Ichihashi, E. Nishio, and I. Abe, “Controlled Interphases in Composite Materials”, Ed., H. Ishida, pp. 757 - 764 (1990).

2. N. Nishida, N. Ikuta, H. Hamada, and. Z. Maekawa, *Chem. Express*, **18**, 337-340 (1993).

3. N. Ikuta, T. Hori, H. Naitoh, Y. Kera, E. Nishio, and I. Abe, Composite Interfaces, 1, 455 – 462 (1993).