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**SURFACE WEATHERABILITY OF GLASS-FIBER-REINFORCED
POLYESTER SHEETING. 1. EFFECT OF MODIFICATION OF RESIN
CHEMICAL COMPOSITION**

by R.S. Yamasaki

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RÉSUMÉ

On a soumis du polyester renforcé de fibre de verre (PRFV) à un test de vieillissement accéléré (cycle 2-0,67) pour déterminer l'effet de modifications de la composition chimique de la matrice de résine. Le genre et le taux de dégradation de la surface a été surveillé au microscope électronique à balayage. Dans le cas des PRFV à base de résine de polyester d'usage courant (anhydride o-phthalique et propylèneglycol), les modifications chimiques ne changeaient pas de façon significative la nature de la détérioration superficielle, bien qu'elles en faisaient varier le moment d'apparition. La durabilité globale moyenne du PRFV a été améliorée de 60 % par substitution de néopentylglycol au propylèneglycol, de 30 % par incorporation d'une plus grande quantité d'anhydride maléique, et de 20 % par remplacement simultané de l'anhydride et du glycol respectivement par de l'acide isophtalique et du néopentylglycol. Par inférence, le remplacement de l'anhydride par de l'acide isophtalique a réduit de 40 % la durabilité du PRFV à base de néopentylglycol.

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Surface Weatherability of Glass-Fiber-Reinforced Polyester Sheeting. I. Effect of Modification of Resin Chemical Composition

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ABSTRACT: An accelerated weathering test (2 to 0.67 cycle) has been applied to glass-fiber-reinforced polyester (GRP) to determine the effect on surface durability of modifying the chemical composition of the resin matrix. The nature and rate of induced surface degradation were monitored by scanning electron microscopy. For GRP based on general purpose polyester resin (o-phthalic anhydride-propylene glycol-maleic anhydride-based) the nature of surface damage was not significantly influenced by chemical modification, although the time of initiation was altered. The average overall durability of GRP improved 60% by substitution of propylene glycol with neopentyl glycol, 30% by incorporation of a greater amount of maleic anhydride, and 20% by replacement of both anhydride and glycol with isophthalic acid and neopentyl glycol, respectively. By inference, replacement of anhydride with isophthalic acid reduced the durability of neopentyl glycol-based GRP by 40%.

KEYWORDS: composite materials, surface properties, glass fibers, polyester laminates, resin chemical composition, accelerated weathering test, scanning electron microscopy

Glass-fiber-reinforced polyester (GRP) sheets used on the exterior of buildings undergo surface degradation as a result of weathering. Efforts are being made at the Division of Building Research, National Research Council of Canada, to improve their durability by varying the resin composition. Normally such investigations require long-term exposure to natural weathering conditions. Yamasaki and Blaga [1,2] concluded, however, that by using an accelerated weathering test (AWT) (2-h xenon arc radiation followed by 0.67 h cold water spray cycle in a Weather-Ometer®) the degradation occurring under natural weathering conditions (that is, fiber ridging, cracking of resin adjacent to fibers, fiber pop-out, and isolated surface microcracking followed by network microcracking) can be progressively simulated in a relatively short time. Such damage was produced as a result of hydrolytic or ultraviolet degradation or both of the resin phase in the presence of alternating stresses induced by cyclic variation of moisture and tempera-

ture [1,2]. To improve durability it was suggested that resin with less permeability to moisture and greater resistance to hydrolytic and ultraviolet degradation should be used.

Review of the literature suggests that hydrolytic and ultraviolet stability of general purpose GRP (propylene glycol-phthalic anhydride-maleic anhydride-based resin) can be improved by the replacement of propylene with neopentyl glycol, greater stability being conferred by the identical (methyl) groups on a carbon atom [3]. Substitution of a phthalic by an isophthalic group should provide greater resistance to water [4]. Finally, increased ratio of unsaturated (such as from maleic anhydride) to saturated acid should result in increased molecular weight and hence greater resistance to chemicals and probably to weathering factors [5]. Thus, the objective of this work is to apply AWT to determine the effect of modifying the chemical composition of the resin matrix on the surface durability of GRP sheeting.

Experimental Procedure

Four GRPs differing only in the chemical composition of the resin matrix and specifically developed for solar collector covers were used (Table 1).

TABLE 1—Description of GRP sheet material.

GRP Designation	Chemical Composition of Resin	Composition and Processing
GRP A1-GP	o-phthalic anhydride-propylene glycol-maleic anhydride-based (general purpose)	substrate composed of 86% resin and 14% chopped glass roving (XC 129AA) by volume. Resin ultraviolet-stabilized
GRP C1-NP	o-phthalic anhydride-neopentyl glycol-maleic anhydride-based	with Tinuvin P® was produced by condensing glycol with both unsaturated and saturated acids and cross-linking with 40% styrene. GRP sheeting was fabricated by a continuous process and heat-cured without promoter.
GRP F1-INP	isophthalic acid-neopentyl glycol-maleic anhydride-based	
GRP B1-HU	greater proportion of maleic anhydride than for A1-GP formulation	

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Duplicate GRP panels (165 by 55 by 1.5 mm) chosen at random from samples cut from 1.2- by 2.4-m sheeting were subjected to an accelerated weathering test using the 2 to 0.67 cycle in a xenon arc Weather-Ometer (Atlas Model 65WR) [2].

Surface degradation was assessed with a scanning electron microscope (SEM) (Cambridge Stereoscan® Model 2A) operated at 20 kV and using a tilt angle of 45°. Specimens were prepared for SEM examination by ultrasonic cleaning before coating with carbon and gold to render them conductive.

At appropriate intervals duplicate GRP panels were removed and surveyed with an optical stereomicroscope. Where indicated, 15- by 15-mm specimens were cut and examined in detail by SEM to determine both the nature and rate of induced surface degradation, using as a basis the duration of exposure leading to the inception of approximately two to three incidents of surface damage per 200 mm² of the panel area. This allowed assessment of the effect of modifying the chemical composition of the resin matrix on the progressive degradation of GRP.

Results and Discussion

Fiber Pop-Out

Close monitoring of the surface degradation of GRP A1-GP showed that the first change to occur is fiber ridging [1]. This is followed by cracking of resin at either the peak or the trough of the ridges and eventual spalling, so that glass fibers become essentially free of the substrate, producing so-called fiber pop-out. Such damage is illustrated in Fig. 1b.

Close observation and comparison of surface degradation of the other three GRPs with that of GRP A1-GP disclosed that all undergo the same sequence of surface damage leading to fiber pop-out, each stage being similar. Figure 1b-e demonstrates each stage and similar damage. The differences in chemical composition of the resin matrices of the GRPs did not significantly influence the nature of surface damage because the mechanism inducing such degradation is probably common to all. It involves gradual embrittlement of resin by ultraviolet radiation and moisture accompanied by alternating stresses induced at the glass-resin interface by changes in moisture content and temperature [6].

To determine whether modification of the resin composition affects the resistance of GRPs to fiber pop-out, their durability was compared as shown in Table 2. In the following discussion the effect of composition on surface durability is assessed in relation to GRP A1-GP (o-phthalic anhydride-propylene glycol-maleic anhydride-based resin). Incorporation of neopentyl glycol in the resin matrix improved the resistance of GRP C1-NP to fiber pop-out by about 10%. Substitution of both o-phthalic anhydride and propylene glycol by isophthalic acid and neopentyl glycol, respectively, reduced durability of GRP F1-INP by 30%. In effect, substitution of isophthalic for o-phthalic reduced the resistance of the neopentyl glycol resin by about 40%. Finally, incorporation of a greater proportion of maleic anhydride impaired the durability of GRP B1-HU by approximately 20%.

Erosion

Observation of surface degradation of GRP A1-GP by optical microscope revealed that the clear resin surface was developing a haze (Fig. 2a). Close examination with an SEM at 2000X disclosed that the original smooth surface was being eroded, hidden features

(a) GRP A1-GP, control
(b) GRP A1-GP, 115 days exposure
(c) GRP C1-NP, 98 days exposure
(d) GRP F1-INP, 56 days exposure
(e) GRP B1-HU, 72 days exposure

FIG. 1—Fiber ridging, cracking of resin adjacent to fibers and fiber pop-out in each of the GRPs, with resin matrix of modified chemical composition, induced by AWT.

becoming visible in the process (compare Fig. 2b and c). With further exposure the surface became very rough (Fig. 2d). Examination of other GRPs revealed similar progressive erosion (Fig. 3a-c) accompanied by increasing opacity of the surface. Such a development is an important consideration in application of GRP as a solar cover since it impairs the transmittance of solar radiation, as evidenced by a decrease in solar energy transmittance (ASTM Test for Solar Energy Transmittance and Reflectance [Terrestrial] of Sheet Materials [E 424]) of GRP A1-GP from an initial value of 82 to 75% after 109 days of exposure.

The time to inception of erosion, however, varied with resin composition, as shown in Table 2. Compared to GRP A1-GP made with o-phthalic anhydride-propylene glycol-maleic anhydride-based resin the resistance to erosion improved by approximately 70% for neopentyl glycol-based GRP C1-NP, by 25% for isophthalic acid-neopentyl glycol-based GRP F1-INP, and by 35% for GRP B1-HU containing more maleic anhydride. Comparison of C1-NP with F1-INP again demonstrated that substitution of iso-

TABLE 2—Effect of modification of chemical composition of resin matrix on rate at which surface degradation of GRPs is induced by AWT.

GRP Designation	Modification of Resin	Fiber Pop-Out	Erosion	Duration of Exposure to First Occurrence of Degradation (Days)	
				Surface Microcracking	
				Isolated	Network
GRP A1-GP	none (reference)	85	64	109	115
GRP C1-NP	neopentyl glycol	95	110	125	244
GRP F1-INP	isophthalic acid, neopentyl glycol	56	81	111	180
GRP B1-HU	more maleic anhydride than in A1-GP	69	87	114	163

- (a) (1) control
 (2) 109 days exposure
 (optical microscope)
 (b) control (SEM)
 (c) 65 days exposure (SEM)
 (d) 163 days exposure (SEM)

FIG. 2—Appearance of erosion of GRP A1-GP induced by AWT.

phthalic acid for o-phthalic anhydride decreases durability of the neopentyl glycol GRP.

Surface Microcracking

Towards the latter part of the exposure period GRP A1-GP underwent isolated surface microcracking. On further exposure, this

- (a) GRP C1-NP, 262 days exposure
 (b) GRP F1-INP, 189 days exposure
 (c) GRP B1-HU, 163 days exposure

FIG. 3—Advanced state of erosion of GRPs induced by AWT.

proliferated to a network (Fig. 4a). The other three GRPs also sustained surface microcracks that were randomly oriented and similar in shape, size, and depth (Fig. 4b-d). These results show that differences in resin composition were not sufficient to affect significantly the characteristics of cracks formed in GRPs.

Inception of a network of surface microcracks varied with the resin matrix composition (Table 2). With GRP A1-GP as the reference, resistance of GRPs to network surface microcracking improved by about 100% by incorporating neopentyl glycol, by 60% by using both isophthalic acid and neopentyl glycol, and by 50% by increasing the amount of maleic anhydride in the resin matrix. By inference, replacement of the anhydride with isophthalic acid reduces the durability of the neopentyl glycol-based GRP by 40%.

Previous investigations [1,2] show that fiber pop-out and surface microcracking of acrylic-modified general purpose GRP can be attributed mainly to the effect of hydrolytic and ultraviolet degradation, respectively, accompanied by physically induced stress. As

(a) GRP A1-GP, 223 days exposure
 (b) GRP C1-NP, 262 days exposure
 (c) GRP F1-INP, 262 days exposure
 (d) GRP B1-HU, 223 days exposure

FIG. 4—Advanced network of surface microcracking of GRPs induced by AWT.

suming that a similar degradation mechanism applies to GRPs studied here, present findings suggest that replacement of propyl by the neopentyl group, primarily, improved the resistance of general purpose GRP to ultraviolet degradation. Substitution of phthalic with isophthalic group probably reduced the durability of neopentyl-based GRP to both hydrolytic and ultraviolet degradation. Finally, incorporation of a greater proportion of maleic anhydride decreased and increased the resistance of general purpose GRP to moisture and ultraviolet radiation, respectively.

Conclusions

By application of the accelerated weathering test (2 to 0.67 cycle) the effect of modifying the chemical composition of the resin matrix on the surface durability of GRP can be evaluated. For GRP based on general purpose polyester resin (o-phthalic anhydride-propylene glycol-maleic anhydride-based) the nature of surface degradation, which is characterized by erosion as well as by fiber pop-out and surface microcracking, is not significantly influenced by the chemical modifications under study. The time of initiation of such damage is, however, altered. The average overall durability of GRP improves by 60% with substitution of propylene glycol with neopentyl glycol, by 30% with incorporation of a greater amount of maleic anhydride, and by 20% with replacement of both anhydride and glycol by isophthalic acid and neopentyl glycol, respectively. By inference, replacement of anhydride with isophthalic acid reduces the durability of neopentyl glycol-based GRP by 40%.

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