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SURFACE WEATHERABILITY OF GLASS-FIBER REINFORCED POLYESTER SHEETING

II. EFFECT OF CONSTITUENTS

by R.S. Yamasaki

ANALYZED

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RÉSUMÉ

On a utilisé des essais de vieillissement accéléré (cycle 2-0,67) sur des polyesters renforcés de fibre de verre (GRP) pour évaluer l'effet des constituants sur la durabilité superficielle. La nature et la vitesse de la dégradation superficielle induite ont été déterminées au microscope électronique à balayage. Pour les GRP d'usage général (GRP(GP)), le remplacement de stratifils hachés par des mats de fibre hachée ne modifiait pas la dégradation superficielle. L'incorporation d'un voile de surfaçage du verre, pour avoir une couche superficielle riche en résine, augmentait par contre la résistance à la sortie des fibres de 100 %. De plus, le remplacement du styrène par un mélange styrène/méthacrylate de méthyle/agent de réticulation augmentait la résistance du GRP(GP) à la sortie des fibres, à l'érosion et à la microfissuration de 70 % en moyenne. Le remplacement de l'absorbant UV Tinuvin P par le Tinuvin 327 ne modifiait pas la durabilité des GRP à base d'éthylène-glycol, tandis que le remplacement du Tinuvin P par le mélange Tinuvin P/Tinuvin 144 dans les GRP à base de néopentyl-glycol améliorait la résistance à la sortie des fibres de 17 %, mais diminuait la résistance à l'érosion et à la microfissuration de 19 % et 12 % respectivement.

R. S. Yamasaki¹

Surface Weatherability of Glass-Fiber Reinforced Polyester Sheeting.

II. Effect of Constituents

REFERENCE: Yamasaki, R. S., "Surface Weatherability of Glass-Fiber Reinforced Polyester Sheeting. II. Effect of Constituents," *Composites Technology Review*, Vol. 4, No. 4, Winter 1982, pp. 125-129.

ABSTRACT: An accelerated weathering test (2 to 0.67 cycle) has been applied to glass-fiber reinforced polyester (GRP) to evaluate the effect of constituents on the surface durability of GRP. The nature and rate of induced surface degradation was assessed by scanning electron microscopy. For general-purpose GRP (GRP (GP)), replacement of chopped glass roving reinforcement with chopped glass mat reinforcement did not change the nature and rate of surface degradation. Incorporation of a glass surfacing veil, to provide a resin-rich surface layer, however, improved the durability of GRP (GP) to fiber pop out by 100%. Moreover, replacement of styrene with a styrene-methyl methacrylate cross-linking agent enhanced the resistance of GRP (GP) to fiber pop out, erosion, and surface microcracking an average of 70%. Substitution of an ultraviolet absorber Tinuvin P with Tinuvin 327 did not alter the durability of ethylene glycol-based GRP, while replacement of Tinuvin P with Tinuvin P/Tinuvin 144 in neopentyl glycol-based GRP improved the resistance to fiber pop out by 17% but decreased the durability to erosion and surface microcracking by 19 and 12%, respectively.

KEYWORDS: composite materials, composite structures, glass fibers, polyester fibers, ultraviolet absorbers, glass fiber reinforcement, glass surfacing veil, cross-linking agent, glass fiber reinforced polyester, surface weatherability, accelerated weathering test, scanning electron microscopy

In order to improve the weatherability of glass-fiber reinforced polyester (GRP) sheeting used on the exterior of buildings, the effect of various constituents on the surface durability of the GRP composite is under study. In a previous investigation [1], the effect of modification of the resin chemical composition on the surface durability of GRP was examined by using an accelerated weathering test (AWT) [2] to reduce the test period. In this paper the effects of glass surfacing veil and of different kinds of glass-fiber reinforcement, cross-linking agent, and ultraviolet (UV) absorber on the surface durability of GRP sheeting are reported.

Experimental Procedure

Seven GRPs, produced for evaluation as solar collector covers, were used. Their general compositions are given in Table 1.

Duplicate GRP panels (165 by 55 by 1.5 mm), chosen randomly from those cut from 2.4- by 1.2-m sheeting, were exposed to an ac-

celerated weathering test that used the 2 to 0.67 cycle in a xenon arc Weather-Ometer[®] (Atlas Model 65 WR).

Surface degradation was observed 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 being coated 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 the SEM to determine both the nature and rate of induced surface degradation, using as a basis the duration of exposure leading to inception of approximately two to three incidents of surface damage per 200 mm² of panel area. Every effort was made to take micrographs of representative damages since they may vary from location to location for each specimen.

Results and Discussion

The effect of exposure to accelerated weathering on GRPs is illustrated in Figs. 1 to 4, which show that all GRPs underwent a sequence of surface damages characterized by fiber ridging, resin cracking either at the peak or trough of the ridges, and eventual spalling that produced fiber pop out or release. In addition, these GRPs sustained progressive erosion that was followed by formation of isolated surface microcracks, which proliferated to form a network.

Effect of Forms of Glass Reinforcement

Glass fibers in various forms or configurations are added to polyester resins to improve their strength. This study included comparison of chopped glass fibers in the form of roving (three-dimensional ribbon) (Fig. 5a) and mat (two-dimensional network) (Fig. 5b) reinforcement that was incorporated in a general-purpose resin (GRP (GP)).

The results of exposure of GRP A1-GP incorporating chopped glass roving reinforcement and GRP A4-GP containing chopped glass mat reinforcement are illustrated in Figs. 1b, 2b, and 3b and 1c, 2c, and 3c, respectively. Comparison of corresponding damages, taking into account local variation of damages that occur on the same specimen, shows that substitution of roving reinforcement with mat reinforcement did not result in any significant alteration of the nature of damages that lead to fiber pop out, erosion, and surface microcracking.

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TABLE 1—Description of GRP sheet material.

GRP Designation	Constituents					Composition and Processing
	Reinforcement	Surfacing Agent	Cross-Linking Agent	Ultraviolet Absorber	Matrix Resin	
A1-GP	chopped glass roving	none	styrene	Tinuvin® P	O-phthalic anhydride-propylene glycol-maleic anhydride-based (general purpose)	substrate composed of 86% resin and 14% reinforcement, by volume. The resin was produced by condensing glycol with both unsaturated and saturated acids and cross-linking with 40% styrene or otherwise stated. GRP sheeting was fabricated by a continuous process and heat-cured without promoter.
A4-GP	chopped glass mat	none	styrene	Tinuvin P		
A6-GP	chopped glass mat	glass surface veil	styrene	Tinuvin P		
A5-GP	chopped glass roving	none	styrene-MMA	Tinuvin P		
A8-GP	chopped glass roving	none	styrene	Tinuvin 327		
C1-NP	chopped glass roving	none	styrene	Tinuvin P	O-phthalic anhydride-neopentyl glycol-maleic anhydride-based	
C4-NP	chopped glass roving	none	styrene	Tinuvin P/ Tinuvins 144		

To determine whether forms of glass reinforcement affected the resistance of the GRP to surface degradation, durations of exposure to inception of such damages were compared (Table 2). It is evident that resistance to fiber pop out and erosion improved by about 8%, which is not significant considering the experimental

variability. Further, the resistance to initiation of isolated and network surface microcracking remained unchanged.

These results show that changing the glass reinforcement from roving to a mat reinforcement did not significantly influence either the nature or rate of surface degradation of GRP (GP).

FIG. 1—Comparison of fiber ridging, cracking of resin adjacent to fibers, and fiber pop out induced by AWT.

FIG. 2—Comparison of an advanced state of erosion induced by AWT.

FIG. 3—Comparison of an advanced network of surface microcracking induced by AWT.

FIG. 4—Comparison of surface damages of GRP C1-NP and GRP C4-NP induced by AWT. (a), (b), and (c)—fiber ridging, cracking of resin adjacent to fibers, and fiber pop out. (d) and (e)—advanced state of erosion. (f) and (g)—advanced network of surface microcracking.

FIG. 5—Optical micrographs of forms of glass-fiber reinforcement or overlay in GRPs. (a) chopped glass roving reinforcement. (b) chopped glass mat reinforcement, and (c) surfacing veil.

Effect of Glass Surfacing Veil

The glass surfacing veil is a very thin, predominantly single-stranded, nonreinforcing glass fiber mat that is used to provide a smooth resin-rich surface by keeping the reinforcing mat away from the surface region.

Comparison of surface damage of GRP A6-GP, which incorporates the glass surfacing veil (Fig. 5c) with that of GRP A4-GP with no veil, reveals that the former generally sustained single-strand fiber pop out rather than multistrand fiber pop out (Fig. 1d and c) while other damages (Figs. 2d and c, 3d and c) were qualitatively similar. In Table 2 it is disclosed, however, that resistance to inception of fiber pop out by the glass-veil sheet was 100% greater than that of GRP A4-GP, probably because of the lower concentration

of glass fibers in the surface region (compare Fig. 5c and a), while resistance to other forms of damage was comparable. Thus, the glass surfacing veil improved the resistance of GRP (GP) to fiber pop out by about 100%.

Effect of Cross-Linking Agent

In the process of curing polyester resin, the unsaturated polyester is polymerized into a three-dimensional structure by reaction with a vinyl monomer cross-linking agent, such as styrene. The cross-linking agent influences the properties of the resin by controlling the structure. The effect of changing the cross-linking agent from styrene to styrene-methyl methacrylate (MMA) was

TABLE 2—Effect of constituents on the rate at which surface degradation of GRPs is induced by AWT.

GRP Designation	Constituent	Fiber Pop Out	Erosion	Duration of Exposure to First Occurrence of Degradation, days ^a	
				Isolated	Network
A1-GP	reference for GRPs A4, A5, A8	85	64	109	115
A4-GP	chopped glass mat	92	70	109	115
A6-GP	glass surfacing veil	189	72	109	120
A5-GP	Styrene-MMA	154	94	156	244
A8-GP	Tinuvin 327	92	66	109	115
C1-NP	reference for C4-NP	95	110	125	244
C4-NP	Tinuvin P/Tinuvin 144	111	89	125	214

^aMean for duplicate specimens. Individual values generally ranged within about 10%.

studied since polymethyl methacrylate is known for its durability to weathering.

Comparison of surface degradation of styrene-MMA-cured GRP A5-GP with that of styrene-cured GRP A1-GP shows that the nature of fiber pop out (Fig. 1e and b) and surface microcracks (Figs. 3e and b) were not significantly altered by the difference in the cross-linking agent, while in erosion of the former, the concentration and sharpness of the peaks were greater than for GRP A1-GP. Conversely, the resistance to induction of such degradation for the resin containing MMA improved significantly for each type of damage (Table 2), ranging from an increase of 43 to 112% for isolated and network surface microcracking, respectively, and an increase of 81% for fiber pop out, and 47% for erosion. Thus, incorporation of styrene-MMA increased the average surface durability of GRP (GP) by about 70%.

Effect of UV Absorber

UV absorbers are incorporated into polyester resin to improve durability by absorbing solar UV radiation. In this study, the effect of different UV absorbers on surface durability of GRP based on general-purpose and neopentyl glycol-based resins was investigated.

Tinuvin 327 Versus Tinuvin P in General-Purpose Resin—Examination of surface damages of GRP A8-GP and GRP A1-GP, incorporating Tinuvin 327 and Tinuvin P, respectively, discloses that their characteristics are similar (Figs. 1f and b, 2f and b, and 3f and b). As Table 2 reveals, time for initiation of surface damages was also comparable so that the two absorbers are similar in effectiveness.

Tinuvin P/Tinuvin 144 Versus Tinuvin P in Neopentyl Glycol-Based Resin—Comparison of surface degradation of neopentyl glycol-based GRP C4-NP containing Tinuvin P/Tinuvin 144 and GRP C1-NP with Tinuvin P shows that they are similar with some differences in surface microcracking (Fig. 4b and c, d and e, and f and g). The resistance of the former to initiation of such damage (Table 2) increased by about 17% for fiber pop out but decreased by 19 and 12% for erosion and network of surface microcracking, respectively.

Conclusions

Use of the accelerated weathering test (2 to 0.67 cycle), permitted evaluation of the effect of constituents on the surface durability of GRP. Replacement of chopped glass roving reinforcement with chopped glass mat reinforcement does not change the nature and rate of surface degradation of (GRP (GP)). Incorporation of a glass surfacing veil to provide a resin-rich surface layer, however, improves the durability of GRP (GP) to fiber pop out by 100%. Moreover, replacement of styrene with a styrene-methyl methacrylate cross-linking agent enhances resistance of GRP (GP) to fiber pop out, erosion, and surface microcracking by an average of 70%. Substitution of UV absorber Tinuvin P with Tinuvin 327 does not alter the durability of ethylene glycol-based GRP, while replacement of Tinuvin P with Tinuvin P/Tinuvin 144 in neopentyl glycol-based GRP improves resistance to fiber pop out by 17% but decreases durability to erosion and surface microcracking by 19 and 12%, respectively.

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