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Publisher's version / Version de l'éditeur:

Polymer Engineering and Science, 12, 1, pp. 53-58, 1972-01

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WEATHERING STUDY OF GLASS-FIBER REINFORCED POLYESTER SHEETS BY SCANNING ELECTRON MICROSCOPY

by
A. Blaga

Reprinted from

POLYMER ENGINEERING AND SCIENCE
Vol. 12, No. 1, January 1972
p. 53

Research Paper No. 501
of the
Division of Building Research

OTTAWA
January 1972

Price 10 cents

NRCC 12270

LA MICROSCOPIE ELECTRONIQUE A GRILLE ET L'ETUDE DU VIEILLISSEMENT NATUREL DES FEUILLES DE POLYESTERS RENFORCES A FIBRES DE VERRE

SOMMAIRE

Démonstration des principales étapes de la désagrégation par les intempéries des matériaux composites en polyesters renforcés à fibres de verre. Séquence chronologique: les fibres forment des crêtes saillantes; rupture de la couche de résine recouvrant les fibres saillantes ou les fibres près de la surface; écaillage de la résine à l'endroit de la faille et érosion subséquente; proéminence de la fibre et formation d'un réseau de microfissures. On croit que la désagrégation est causée par un genre de fatigue du matériel composite assujetti aux tensions des change-
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Weathering Study of Glass-Fiber Reinforced Polyester Sheets by Scanning Electron Microscopy

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Division of Building Research
National Research Council of Canada
Ottawa, Canada

Evidence is presented of the main steps in the physical breakdown of glass-fiber reinforced polyester (GRP) composites on outdoor weathering. The chronological sequence is fiber ridging, rupture of the resin layer covering ridging fibers or fibers running close to the surface, spalling of the resin at the site of failure and subsequent erosion, fiber prominence and formation of a network of microcracks. Breakdown is believed to be caused by a type of stress fatigue imposed on the composite by cyclic variation of humidity and temperature in conjunction with solar radiation, and by the action of water and oxygen. The under side of the exposed GRP sheeting shows only incipient breakdown, indicating that solar radiation is an important factor. Countermeasures suggested to reduce breakdown include techniques to keep fibers away from the surface, use of resins with better thermal and moisture characteristics, and use of resin formulations with the best light stability.

INTRODUCTION

Change in appearance is the most significant effect of outdoor weathering on glass-fiber reinforced polyester (GRP) sheets and usually takes the form of changes in color, loss of gloss, surface resin erosion and fiber prominence (1-5). All are serious symptoms of chemical or physical breakdown of the composite material and are not acceptable to the user. If the impairment is severe, mechanical and other end use properties are seriously affected so that the material cannot fulfil the function for which it was intended.

Appearance is very important for such applications of GRP sheeting as corrugated roofing, carports, glazing, skylights, and translucent sidewalls. It is the purpose of this paper to report a study of the process of physical breakdown as it affects appearance of GRP sheets on exposure to outdoor weathering. Scanning electron microscopy (SEM), a fairly new technique, proved to be invaluable for this purpose. The instrument has a large depth of focus at high magnification and thus the image has a tridimensional character. The specimen detail resolution (150Å) is considerably better than that of the optical microscope (2500Å). Although the transmission electron microscope has a higher resolution (5Å), it requires very thin (about 1000Å) specimens or replicas. The very rough topography of the weathered surfaces or insolubility of the GRP samples renders either of these techniques impractical. The scanning electron microscope allows direct observation of the weathered surface with very little preparation of the specimen. This instrument has been used for several years in studying fracture surfaces (6-8), fiber orientations and spacing (9, 10), fatigue mechanism and interfacial properties (11, 12) in composite materials such as glass-fiber reinforced plastics and carbon-fiber composites. Recently, Crowder and Majumdar (13) used the scanning electron microscope to examine the surface of GRP sheets weathered for two years at Accra, Ghana. This publication reports a study of surfaces weathered for periods of up to five years.

EXPERIMENTAL

Glass-fiber reinforced polyester sheets were acquired on the open market from Canadian manufacturers and exposed at four Canadian sites, Ottawa, Halifax, Saskatoon and Esquimalt, British Columbia. The samples were non-gel-coated, translucent, flat or corrugated sheets (8 by 12 by 0.05-0.06 in.) in various colors or colorless. The GRP sheets contained 25% untreated reinforcing glass fiber (E-glass) in

Reprinted from Polymer Engineering and Science, vol. 12, no. 1, January 1972

the form of chopped strand mat and resin, fillers and pigments. The resin component (or binder) was a light-stabilized, acrylic-modified, general purpose polyester having the formulation 60% general purpose unsaturated polyester, 20% styrene, and 20% methyl methacrylate. The sheets were exposed on standard racks (ASTM-D1435-35) inclined at 45 deg to the horizontal facing south, with no background. On all sites the weather conditions are those of a temperate northern climate. The Ottawa and Saskatoon sites are typically rural, with high and low humidity, respectively. The Esquimalt and Halifax sites have, respectively, marine and marine-industrial climates. The weathering program was started in the fall of 1962 and terminated in the fall of 1969.

The scanning electron microscope was used to follow the progress of the physical breakdown of the surface of GRP sheets as a function of time. Specimens weathered for 16, 29, 47, and 62 months and the unexposed controls were examined. The specimens were taken consistently from the same exposed sample for each type of sheeting at the completion of the appropriate weathering period. The weathered specimens and controls were kept in the dark under standard laboratory conditions until 1970 when the electron micrographs were recorded. The various specimens were coated with metallic gold to prevent surface charging. Wire snips were used to cut them to the size and shape required for examination. The instrument, the Stereoscan Scanning Electron Microscope, Mark 2A, Cambridge Scientific Instruments Limited, was operated at 20 Kv. Although most of the various panels were examined with the electron microscope, the results discussed refer to colorless, translucent, flat sheeting weathered at Saskatoon. The remaining sheets, weathered at Saskatoon or at the other three sites, show similar results, so that remarks apply to all equally well.

DISCUSSION OF RESULTS

A number of selected scanning electron micrographs (*Figs. 1-12*) are presented to illustrate the processes and features of the physical breakdown of GRP sheets under outdoor weathering conditions in a temperate northern climate. *Figure 1* shows the surface microtopography of the control sample; the surface appears homogeneous and intact. *Figure 2* shows the exposed surface of a specimen weathered for 16 months. The micrograph reveals some pitting and particles lying on the surface; ridges can also be detected on the fiber. This fiber ridging may indicate incipient debonding of the fiber, with subsequent occlusion of air. The debonding is believed to be initiated by swelling of the matrix resin caused by absorption and chemical action of water. In their studies on the glass-resin bond, James and coworkers (14) indicated that this can take place.

Dimensional changes due to temperature variations may also be a contributing factor. The surfaces of samples weathered for 29 months are shown in *Figs. 3-6*. The micrographs reveal extensive littering of the surface with various particles and debris of

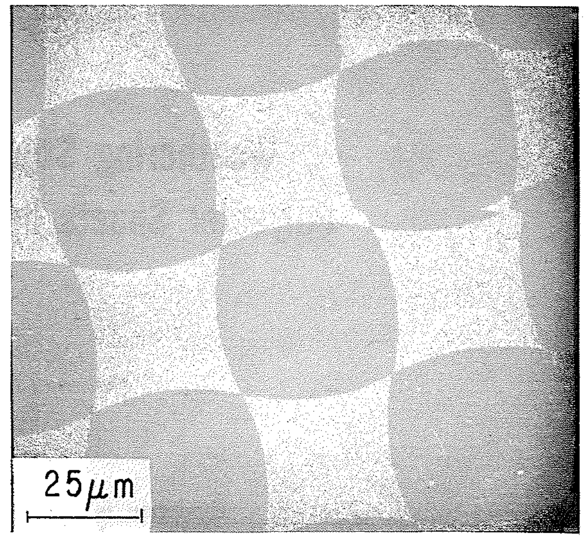

Fig. 1. GRP sheet. Control.

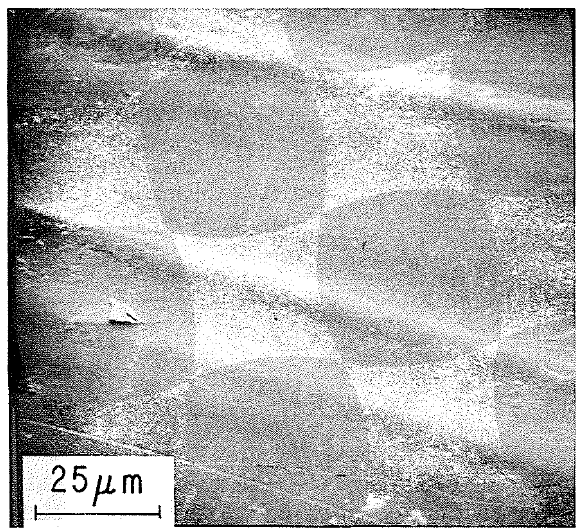

Fig. 2. GRP sheet weathered for 16 months.

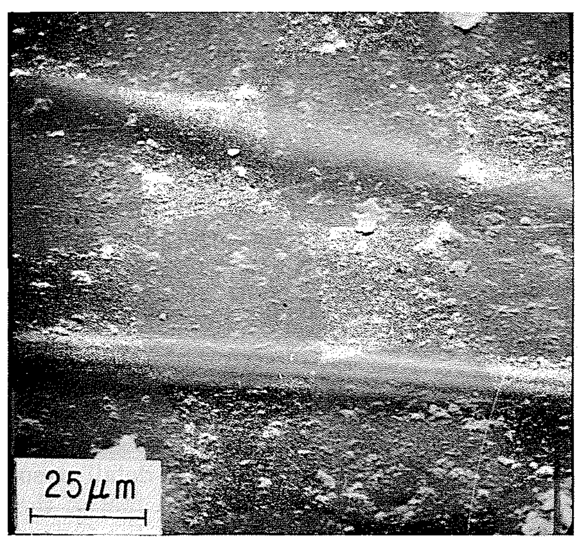

Fig. 3. GRP sheet weathered for 29 months.

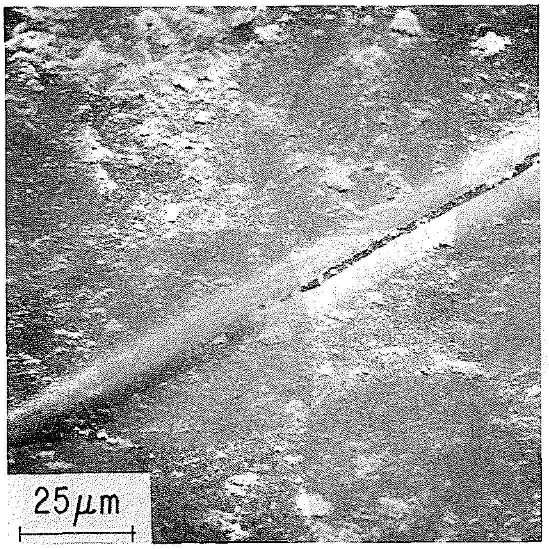

Fig. 4. GRP sheet weathered for 29 months.

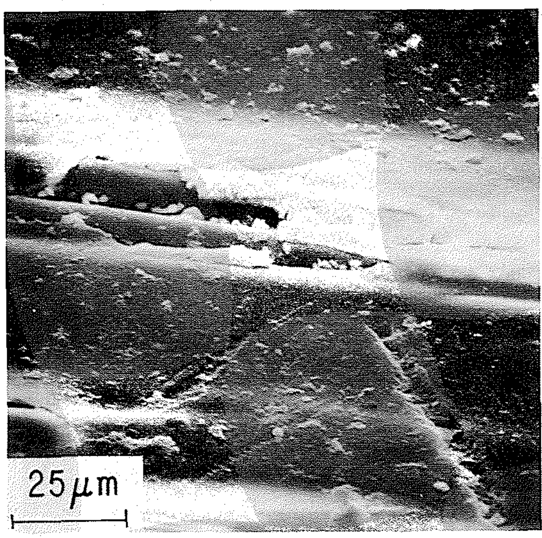

Fig. 5. GRP sheet weathered for 29 months.

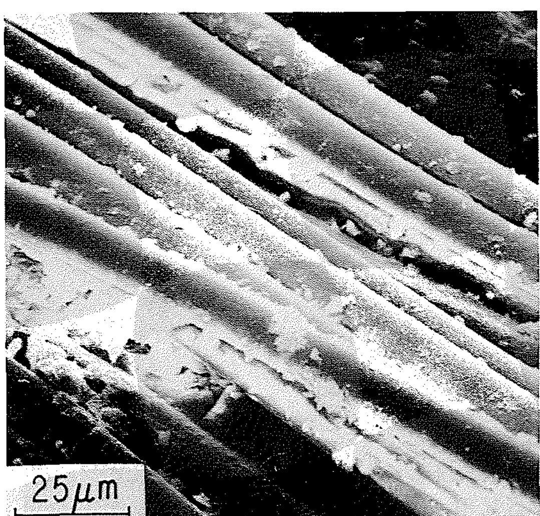

Fig. 6. GRP sheet weathered for 29 months.

what is probably resin material. At this stage the ridging of fibers is much more evident (*Fig. 3*). *Figures 4-6* display a sequence of events of great significance in the physical breakdown of GRP sheeting. These events result in the most common failure in glass-fiber reinforced plastics, the so-called "fiber prominence" (*Fig. 6*).

This failure is produced by a complex process of erosion that results from the interaction of the composite with the physical and chemical agents operating in the environment. The main environmental forces exerting a type of stress fatigue on the composite are the cyclic variations of temperature and humidity. The coefficient of thermal expansion of resin ($70\text{-}100 \times 10^{-6}/°C$) is considerably greater than that of E-glass ($4.9 \times 10^{-6}/°C$), so that resin expands and contracts to a greater extent. This produces relatively large, localized stresses at the glass-resin interface. Stresses may also be produced by differential cyclic swelling and shrinking of the resin and glass because of changes in moisture content within the composite. The point of initiation of damage is generally at the glass-resin interface where these localized repetitive stresses are operating during outdoor weathering; in combination with the chemical action of water, these stresses probably cause the destruction of the glass-resin bond (debonding of the ridging glass-fiber, *Fig. 3*). The next step is microscopic rupture of the resin layer surrounding the ridging fiber or that covering fibers running close to the surface (*Figs. 4, 5*). It is postulated that it is caused by stress fatigue. Hydrolytic scission of a high proportion of ester linkages in the resin, however, or even ultraviolet light initiated cleavage of covalent bonds may also occur and contribute to rupture.

As weathering progresses, localized spalling of the resin at the site of the failure takes place (*Fig. 5*). A contributing factor may be frost action, where the water present in voids or cavities formed by the above process freezes, expands, and mechanically disrupts the plastic component. As the ice melts and the resulting water eventually evaporates, it leaves bigger voids that make ingress of water easier, so that rate of damage increases with time. The chips or debris of resin produced by the action of these factors are carried away by wind and rainwater, although some microscopic debris or particles adhere to the surface of the weathered sheets. As will be seen, they play a role in the subsequent phase of the physical breakdown of the composite. Particles or debris are visible in most of the electron micrographs of the weathered surfaces.

The strands of fibers shown in *Fig. 6* are still held together and partly attached to their resin bed, although some filaments appear to be free of resin over most of their surface. As erosion progresses, the individual filaments become completely denuded and separate, lying free above the surface except for the end still embedded in the matrix (*Fig. 10*). *Figure 7* shows a fiber cross-over in a surface weathered for 47 months. The bed, or "clear mold" as it is called in fracture mechanics of composites (12), has flattened and its walls have been eroded away. The severity of the fiber prominence will increase with weathering time. The scattered fibers and voids diffuse the light instead of transmitting or reflecting it, giving an opaque appearance to the originally translucent sheet. In its advanced stages fiber prominence makes the GRP sheet unsightly, so that the material fails to meet one of its use requirements. If fiber prominence is very severe, it will also have a dramatic effect on mechanical properties.

Figures 8-11 illustrate, with different degrees of magnification, another type of failure occurring in GRP sheets during outdoor weathering. The surface of these samples shows a network of microscopic cracks. The severity of microcracking increases with weathering time, as shown by samples weathered for 62 months (*Figs. 10* and *11*).

The network of microscopic cracks divides the surface into small, mostly four-sided areas of varying size; the size of these four-sided areas decreases as weathering time increases, indicating that the areas split to form new cracks (*Fig. 11*). The surfaces of the areas show considerable defects such as round holes, depressions (former sites of departed particles), shallow cavities, blisters, microscopic particles of resin or impurities adhering to the surface or completely fused to it, and various other non-homogeneities. The microcracks are almost completely empty (*Figs.* 9 and *11*), containing only occasional minute particles of matter. While earlier workers (1-4, 15) sometimes referred to microcracks as crazes, they have none of the features of crazes as the latter term is currently understood (16, 17), i.e. sharply bound areas of oriented material mechanically continuous with the surrounding bulk polymer.

It is significant that microcracking of the exposed surface occurs only after fiber prominence has become quite extensive. It is believed that at this stage changes in the chemical structure make the matrix less able to withstand the cyclic forces exerted upon the system by the environment. The chemical changes may consist of hydrolytic scission of ester linkages, photo-oxidative and photolytic cross-linking. Hydrolytic scission of ester linkages results in carboxyl and hydroxyl end groups, which may accumulate in certain regions to create points of weakness. Photo-oxidative and photolytic cross-linking render the matrix resin increasingly more brittle. Thus, the matrix resin can no longer undergo reversible deformation. The various defects present on the surface may also play a role as stress concentrators. The nature of these cracks indicates that they are formed when the system is under multiaxial tensile stresses. These stresses have a gradient that decreases from the surface towards the bulk. The differential stresses are created during shrinking (loss of moisture) or contraction (cooling). For these reasons, the cracks are superficial, V-shaped, and divide the surface into small, fairly uniform polygonal areas.

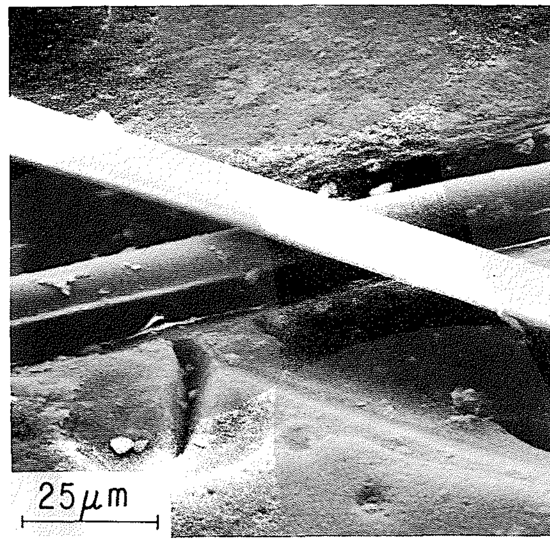

Fig. 7. GRP sheet weathered for 47 months.

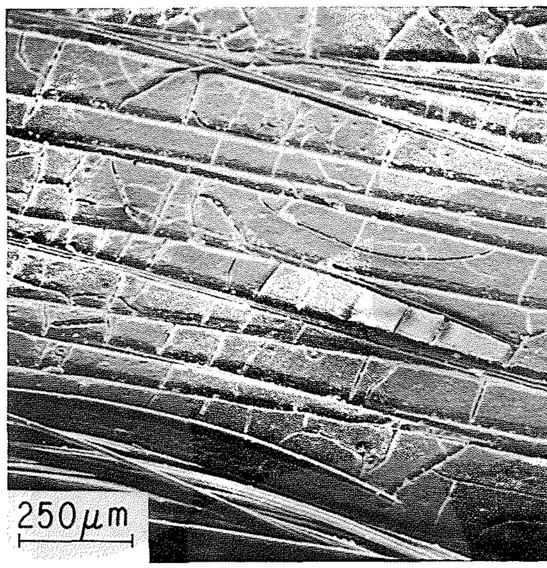

Fig. 8. GRP sheet weathered for 47 months.

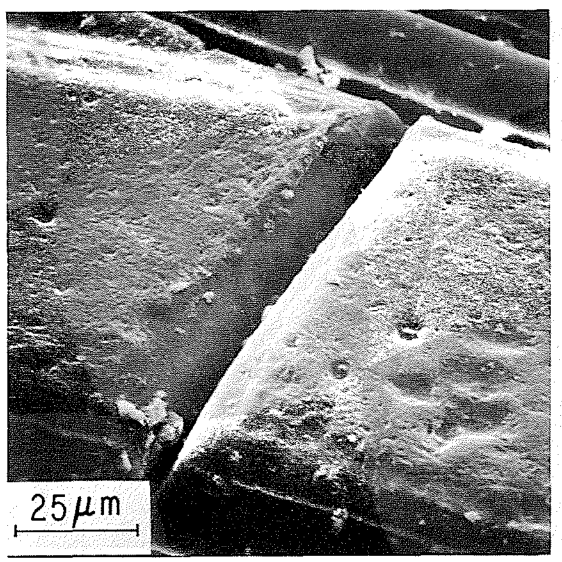

Fig. 9. GRP sheet weathered for 47 months.

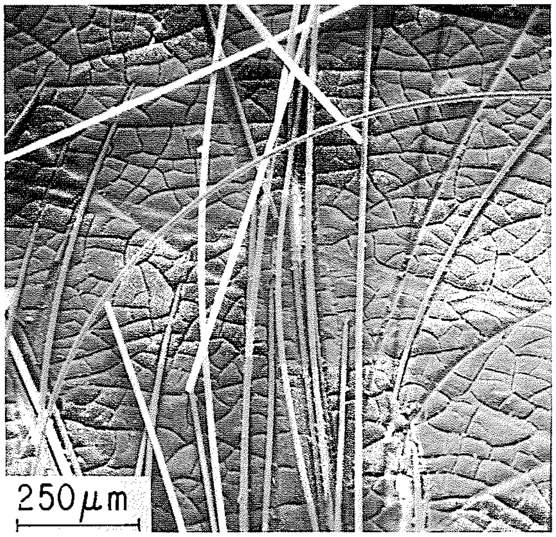

Fig. 10. GRP sheet weathered for 62 months.

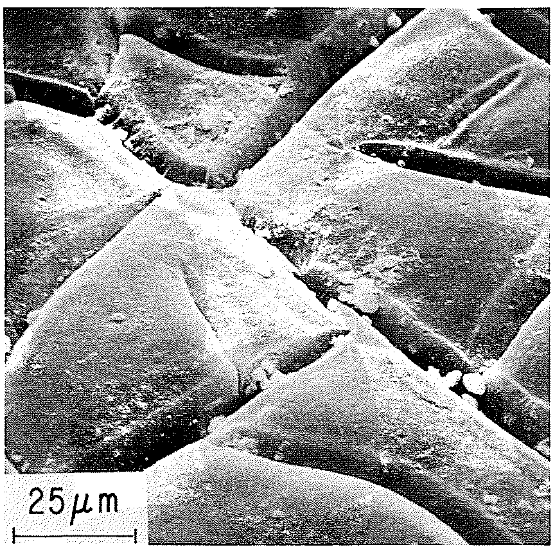

Fig. 11. GRP sheet weathered for 62 months.

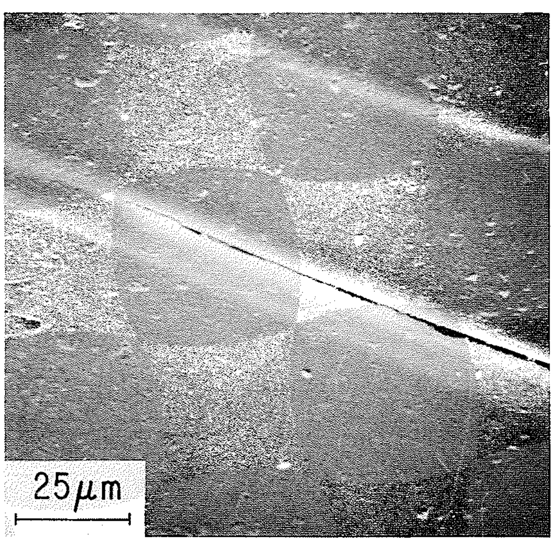

Fig. 12. The under side of GRP weathered for 62 months.

Examination of the under side (the unexposed surface) of GRP sheeting revealed little damage even after 62 months of weathering (*Fig. 12*). Some fiber ridging and rupture of the resin layers above the fibers close to the surface were detected, as were pitting, resin debris, and various particles adhering to the surface. The under side had not been subjected to the direct action of solar radiation, so that photolytic or photo-oxidative action was almost absent and thermal effects (caused by infrared radiation) were considerably reduced. This indicates that solar radiation is important in the physical breakdown of GRP sheets on weathering. The thermal effects have a dual role. First, they affect dimensional changes of the material; this may occur in the presence or absence of moisture. Second, they control the kinetics of the various chemical reactions that the material may undergo. It is thus understandable that the surface of the under side shows only signs of incipient breakdown.

This study suggests countermeasures to reduce the physical breakdown of GRP sheeting. One approach would employ techniques to keep the fibers away from the surface region. This could be accomplished by using a gel-coat or a uniformly thick layer of matrix resin above the fibers. Added improvement might be realized by the use of resin with the lowest possible coefficient of thermal expansion and better moisture characteristics (low moisture absorption, low rate of moisture absorption, etc.). Both methods reduce the stresses caused by variations of temperature and humidity in the environment and should confer upon the composite system better durability. Strengthening of the glass resin bond by the use of good coupling agents will also enable the composite to resist more effectively the localized stresses exerted at the interface. The most obvious method would be to use resin formulations with improved light stability, e.g., polyester resin having inherent stability in conjunction with compatible light stabilizers and the right combination of pigments.

CONCLUSIONS

On outdoor weathering for 5 years in a temperate northern climate, the exposed side of glass-fiber reinforced polyester sheeting shows two main types of failure, fiber prominence and microscopic cracking; both detract from its appearance. Microscopic cracking occurs only after extensive fiber prominence has been detected. Systematic pictorial evidence obtained by scanning electron microscopy illustrates the main steps involved in the process of physical breakdown of the composite. The chronological sequence of these steps is as follows: fiber ridging, rupture of the thin resin layer covering ridging fibers (or any fibers running close to the surface), spalling of the resin at the failure site and subsequent erosion, fiber prominence and formation of a network of microcracks. Breakdown is believed to be caused by a type of stress fatigue imposed on the composite by the cyclic variation of humidity and temperature in conjunction with solar radiation, and by the action of chemical agents (water, oxygen). The under side shows only signs of incipient breakdown, even after 5 years of weathering.

The evidence presented should contribute to understanding of the mechanism involved in the weathering of GRP and similar types of composite, an understanding that will help in devising effective countermeasures to reduce breakdown. This study suggests the use of techniques whereby fibers are kept away from the surface, use of resins with better thermal and moisture characteristics, treatment of the glass fibers with good coupling agents, and use of resin formulation with better light stability.

ACKNOWLEDGMENT

The author wishes to thank E. V. Gibbons who started the program of weathering of GRP sheeting, and P. J. Sereda who suggested the use of the scanning electron microscope to study weathered GRP. Thanks are also expressed to E. G. Quinn for producing the scanning electron micrographs.

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