

Mechanism of breakdown in the interface region of glass reinforced polyester by artificial weathering

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Laboratory studies were conducted to elucidate the mechanism of breakdown in the interface region of glass-fibre reinforced polyester (GRP) composites on outdoor weathering. GRP composites were subjected to the effects of moisture, temperature and radiation. Breakdown in the interface region occurred when the GRP sheets were aged in the presence of water and physically-induced stress (thermally and/or by moisture). The stresses involved are complex, the most predominant being axial shear stresses. Fracture characteristics of breakdown produced during laboratory ageing were very similar to those occurring on outdoor weathering.

According to the mechanism proposed, the resin in the interface region is subjected, during environmental ageing, to a stress-fatigue resulting from the differential dimensional changes between glass and matrix induced by moisture and/or temperature cyclic variations. Under the influence of alternating cyclic stresses and in conjunction with the chemical degradation of the matrix, the interface region undergoes cracking, fracture and fibre delamination. This type of breakdown may be referred to as environmental stress cracking.

1. Introduction

In a previous paper [1], scanning electron microscopy (SEM) was used to follow the breakdown of glass-fibre reinforced polyester (GRP) sheeting during outdoor weathering. To elucidate the mechanism of the breakdown, the scanning electron microscope has now been used to study the deterioration of GRP sheets subjected to artificial weathering.

If GRP composites are to achieve their expected extended use as engineering materials, the long-term environmental behaviour must be thoroughly explored and understood. Most of the existing commercial glass-fibre reinforced plastic composites undergo at least some deterioration when exposed to environmental factors such as heat, humidity, radiation, and chemical agents. Reports on the mode and mechanism of breakdown of these materials are relatively few and all are aimed at performance under specific environments, e.g., use in marine applications [2], performance under mechanically-induced stress-

fatigue [3, 4], and use under corrosive environments. These environments are different from those encountered in most GRP applications in buildings and constructions where these materials are used increasingly. Furthermore, most of these studies were performed on materials produced on an experimental basis. Hence there is little information on the deterioration of commercial or practical systems. The purpose of this paper is to report results of a study of the deterioration, in the glass-resin interface region, of GRP composites under conditions that are realistic and relevant to their use.

The role of environmental factors in the deterioration will be analysed and a breakdown mechanism proposed, thus permitting development of methods for evaluating performance of GRP sheets using accelerated conditions.

2. Experimental

2.1. Materials

The GRP test samples (0.12 to 0.13 cm thick)

TABLE I Conditions of artificial ageing*

No.	Ageing treatment	Humidity		Temperature		Remarks
		Level (%)	Duration (h)	Level (°C)	Duration (h)	
1	Variation of humidity and temperature in the presence of radiation. (Atlas Xenon Arc Weather-Ometer.)	100	4	12	4	Radiation off, water spray on. Radiation on†, water spray off. Details in Fig. 1.
		50	4	55	4	
2	Variation of humidity and temperature. (Aminco Climate Lab.)	100	7	56	7	Details in Fig. 2.
		25–100	5	11–56	5	
3	Constant humidity at constant temperature.	100	—	56	—	—
4	Variation of temperature in the absence of moisture‡.	0	—	56	7	Vessel contained some drying agent (P ₂ O ₅).
		0	—	11–56	5	
5	Variation of humidity at constant temperature.	100	8	56	—	—
		10	16	56	—	
6	Constant humidity at variable temperature‡.	100	—	56	7	Vessel contained a pool of water.
		100	—	11–56	5	

*With the exception of procedure 3, all the other treatments involved humidity and/or temperature cycling.

†Samples were exposed to radiation only in procedure 1.

‡Samples were placed in a closed vessel either at 0 (drying agent, P₂O₅) or 100% r.h. (in the presence of a pool of water) and subjected to temperature cycling in the Climate Lab as in Fig. 2.

were cut from commercial sheeting. The sheets were non-gel-coated, translucent, flat or corrugated, and of various colours (colourless, green, light green, coral, etc). They were reinforced with approximately 25% silane-treated glass-fibre (E-glass) in the form of chopped strand mat. The resin was a UV-stabilized, acrylic-modified general purpose polyester having the formulation: 60% unsaturated polyester, 25 to 35% polystyrene and 5 to 15% methyl methacrylate. The sheets were produced by the hand-lay-up process and cured at 85 to 90° C.

2.2. Methods of artificial weathering

To determine the mechanism of outdoor deterioration of GRP sheets and the role of the environmental (or weathering) factors in the process, test samples were subjected to various artificial weathering treatments as described in Table I. Additional details are given in Figs. 1 and 2.

2.3. Determination of sorbed water to estimate volume changes

To understand better the role of moisture in

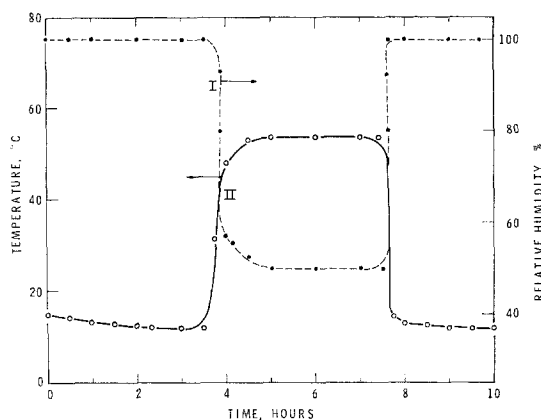


Figure 1 Humidity-temperature cycle (8 h) in The Atlas Xenon Arc Weather-Ometer. I. Humidity. II. Temperature of colourless GRP panel (exposed side).

the breakdown, the amount of water sorbed by GRP sheets during the various treatments was determined gravimetrically for each period of the cycle, e.g., low temperature and/or low humidity, and high temperature and/or high humidity. The

TABLE II Effect of environmental ageing on the amount of water* sorbed by, and on the breakdown of, GRP sheets

No.	Treatment	Sorbed water (wt %)		ΔSW^\dagger (wt %)	Occurrence of breakdown
		Low temp.	High temp.		
1	Variation of humidity (50 to 100% r.h.) and temp. (55 to 12° C); Radiation (Weather-Ometer).	0.14	0.01	0.13	Yes
2	Variation of humidity (25 to 100% r.h.) and temp. (11 to 56° C); (Climate Lab).	0.47	0.71	0.24	Yes
3	Constant humidity (100% r.h.) and const. temp. (56° C).	—	0.78	0.00	No
4	Variation of temp. (11 to 56° C); absence of moisture.	-0.35	-0.35	0.00	No
5	Variation of humidity (10 to 100% r.h.) and const. temp. (56° C).	—	-0.32 \ddagger 0.41 \S	0.73	Yes
6	Constant humidity (100% r.h.) and variable temp. (11 to 56° C).	0.77	0.78	0.01	Yes

*The sample gain or loss of weight is based on its weight at 50% r.h. and 23° C. Each value is the average of three determinations.

$\dagger \Delta SW$ designates the difference in the amount (wt %) of water sorbed by the GRP sheet at two levels of ageing.

\ddagger Water desorbed at 10% r.h.

\S Water sorbed at 100% r.h.

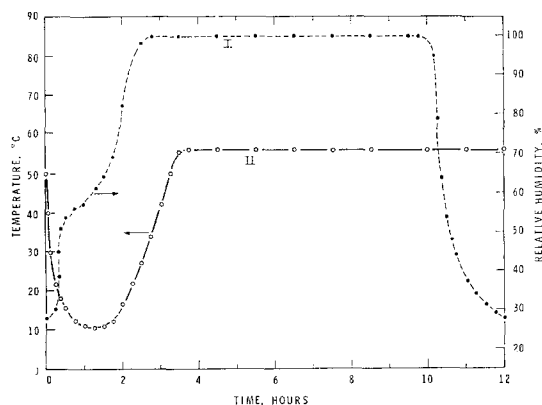


Figure 2 Humidity-temperature cycle (12 h) in the Amino Climate Lab. I. Humidity. II. Temperature.

determinations were effected after the samples had reached equilibrium with the environment (4 to 6 cycles), as indicated by constant gain or loss of water. Before weighing, the samples were wiped dry with absorbent paper.

Because the amount of water absorbed

*Failure, in this instance, signifies limited deterioration or damage.

(wt %) is only slightly larger than the vol % swelling [2], the difference in wt % between the two periods of the exposure cycle, ΔSW , is a good measure of the amount of swelling and shrinking of the GRP sheets (Table II).

2.4. Examination of the breakdown by scanning electron microscopy

The progress of the breakdown of the GRP sheets subjected to various laboratory treatments was followed with a scanning electron microscope, operated at 20 kV and a tilt angle of 45°. At appropriate intervals, samples were taken and coated with carbon and gold to make them conductive and prevent charging.

3. Results and discussion

As in outdoor weathering [1], two main stages of deterioration were observed in the breakdown of GRP sheets subjected to artificial weatherings. The first stage was characterized by occurrence of failure* in the glass-resin interface region exclusively. This type of deterioration invariably

leads to fibre prominence. Observations indicate that shape and colour did not have any significant influence on the mode of breakdown. The second stage involves the formation of a superficial network of microcracks in the matrix. This occurs when the sheets are exposed to radiation. Only the first stage of deterioration will be discussed. The results of the second stage of deterioration will be reported in a subsequent paper.

The term debonding will be used to describe the failure at the glass surface or within the coupling-agent layer, whereas failure in the resin layer adjacent to the coupling agent will be termed delamination.

3.1. Breakdown under variable humidity and temperature in the presence of radiation

Ageing of GRP sheets under conditions of cyclic variation of humidity and temperature in the presence of radiation (Table I, treatment 1) resulted in considerable surface deterioration in the glass-resin interface region. Physical stresses were provided mostly by thermal effects, the moisture contribution to stress being in opposition and relatively insignificant as indicated by the small difference (ΔSW) in the water sorbed and desorbed during a cycle (Table II). The breakdown features produced here were found to be qualitatively similar to, and included, those observed in all other treatments. In addition, this treatment simulated outdoor weathering most closely. For these reasons, breakdown in the Weather-Ometer will be described in detail to explain deterioration in artificial weathering. To illustrate the mode of breakdown a series of selected SEM micrographs are given in Figs. 3 to 13.

Observations show that the extent of degradation and the nature of physically-induced stresses will depend upon the ratio of resin to glass and the geometry of the localized composite system. In this respect, a GRP sheet can be viewed as consisting of resin-rich systems (or regions), glass-rich systems, and a number of intermediate systems. A resin-rich system may be defined as one in which the glass filament (glass fibre) is surrounded by a resin sleeve many times its diameter. It includes regions such as those between the bundles of multi-filaments, superficial fibres, and various single filaments. The glass-rich system comprises regions around and within the multi-filament bundles where the resin is located mostly in the interstices. Only

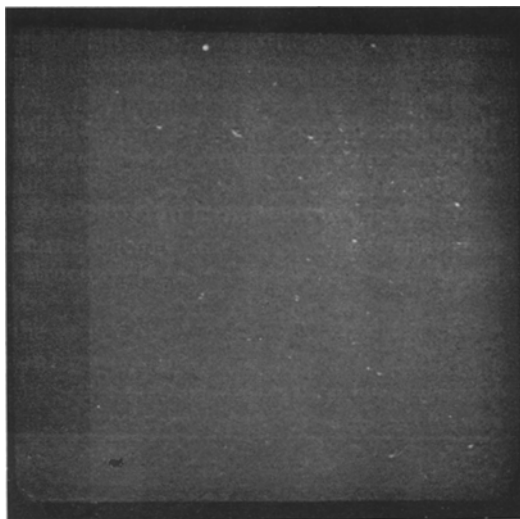


Figure 3 GRP sheet. Control ($\times 680$).

these two systems will be described to illustrate breakdown.

After a few days of ageing the resin layer above the superficial filaments formed ripples or round ridges (Fig. 4) in resin-rich as well as in glass-rich regions. These ripples are indicative of a permanent set resulting from plastic flow under the influence of radial compressive stresses. The ease of formation of these ridges depends upon the proximity of the filament to the surface, since the time of formation ranges from a few days for glass-filaments very near the surface



Figure 4 GRP sheet aged for 12 cycles in the Weather-Ometer ($\times 360$).

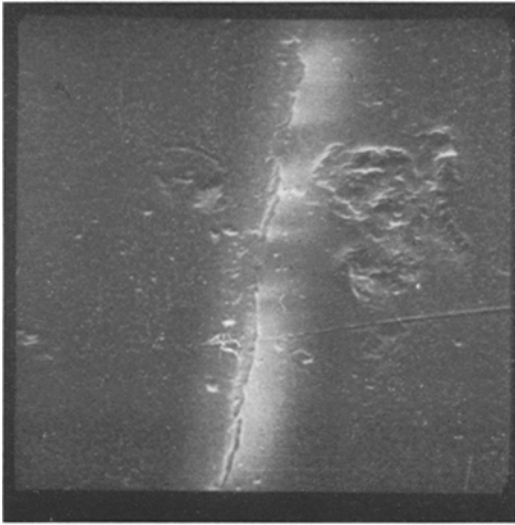


Figure 5 GRP sheet aged for 12 cycles in the Weather-Ometer ($\times 1300$).



Figure 6 GRP sheet aged for 15 cycles in the Weather-Ometer ($\times 2900$).

to 100 days or longer for those embedded relatively deep in the matrix.

3.1.1. Breakdown at single filaments

The next feature of breakdown is the rupture of the superficial resin layer (Fig. 5) at a ridging filament or above a filament close to the surface. At this point, the resin phase undergoes severe microfragmentation or spalling by a process of brittle fracture as evidenced by the presence of a multitude of irregularly shaped debris (Fig. 6). This suggests that the fracture occurs without prior plastic deformation. Most of the resin debris is then washed away by water during the water-spray period of the cycle, leaving an empty, long cavity (gap) parallel to the adjacent filament (Fig. 7). In most instances, the pattern of the fracture boundaries of the resin indicates that these failures occur under the influence of a definite set of predominating stresses, e.g., the failure shown in Fig. 6 was produced by stresses that were predominantly shear and radial tensile stresses. Fig. 8 shows an outstanding example of a site where the resin ruptured away in a brittle mode under the influence of considerable, predominantly shear stresses operating in the direction parallel to the filament axis (axial shear stresses). This is evidenced by the acute angle between the filament and the fracture boundaries of the resin, resulting in a saw-toothed pattern.

While the process of deterioration continues, the gap between the glass and the matrix widens

as the resin shrinks possibly because of cross-linking. The localized stresses are relieved so the process of breakdowns slows down. The glass filament remains attached to the matrix on one side, and no further delamination takes place at such a site even after 1250 cycles.

3.1.2. Breakdown at multi-filaments

Although the incipient step in the breakdown at

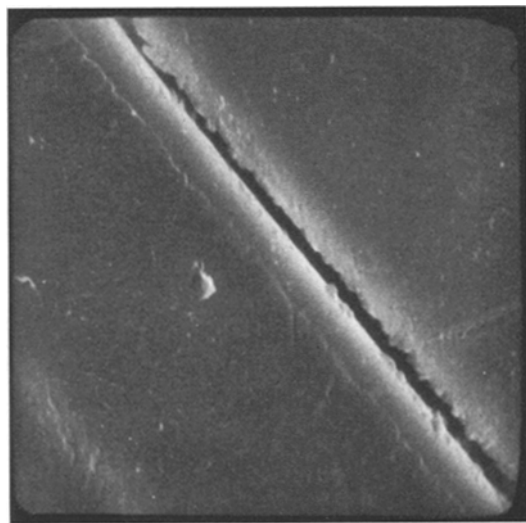


Figure 7 GRP sheet aged for 55 cycles in the Weather-Ometer ($\times 1300$).

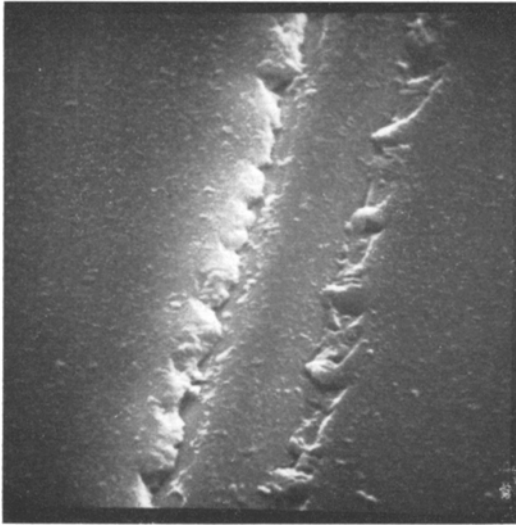


Figure 8 GRP sheet aged for 55 cycles in the Weather-Ometer ($\times 2900$).

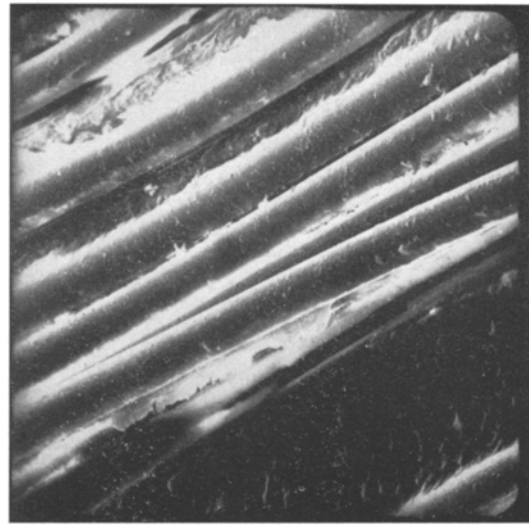


Figure 9 GRP sheet aged for 450 cycles in the Weather-Ometer ($\times 680$).

multi-filaments (bundle of multi-filaments) is the same as in the deterioration at single filaments, the other steps and features are different and more complex. Here, the cracking of the matrix also occurs parallel to the filaments, but it may take place on top of a ridging filament or between two ridgings. Once the process of deterioration is initiated, the rate of breakdown is fast and the extent much greater than at single filaments. The multi-filaments eventually become completely delaminated. The stresses involved in the breakdown appear to be predominantly radial tensile or occasionally radial compressive. Figs. 9 and 10 display stages of breakdown after 450 cycles (150 days) and 1200 cycles (400 days) of ageing, respectively. In Fig. 10, the glass filaments are completely delaminated as a result of spalling and gradual fracture of the matrix. Examination of the filaments at higher magnification shows that most of their surfaces are covered by a sheath of material having a rough surface (Fig. 11). Because the surface of the filament, *per se*, is smooth (Fig. 12), it may be concluded that the cleavage has occurred within the resin. Occasionally, however, some debonding (i.e., cleavage at the glass surface) was observed, as evidenced by the presence of islands of smooth areas on some delaminated filaments.

Delamination of the multi-filaments becomes extensive with ageing and results in a great number of fibres lying on the surface of the sheet but still retained, at some points, by the matrix.

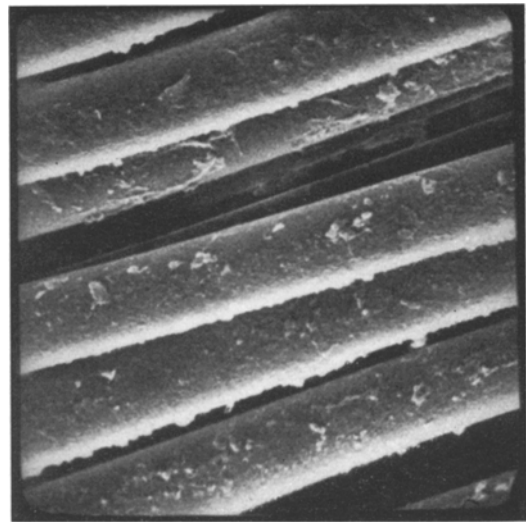


Figure 10 GRP sheet aged for 1200 cycles in the Weather-Ometer ($\times 1300$).

These scattered fibres, the very irregular surface of the fractured resin, and the microcavities diffuse the light instead of transmitting it, and thus render the originally translucent sheets more opaque. This type of failure impairs the appearance of GRP sheet and is commonly called fibre prominence.

3.1.3. Breakdown on the back side of the GRP sheets

The features of the breakdown on the back side

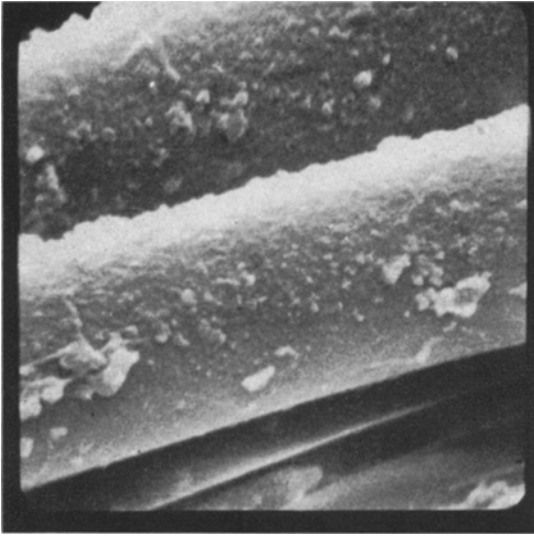


Figure 11 GFRP sheet aged for 1200 cycles in the Weather-Ometer ($\times 2900$).

of the GFRP sheets were qualitatively similar to those of the front side, but the rate of breakdown was much slower. This is understandable because the exposure conditions prevailing on the back side are less severe. During the transition between the radiation and the water-spray periods, the front side is subjected to a severe thermal shock caused by the cold (9°C) water striking the surface of the hot (55°C) sheet. This causes the surface temperature on the front side to decrease

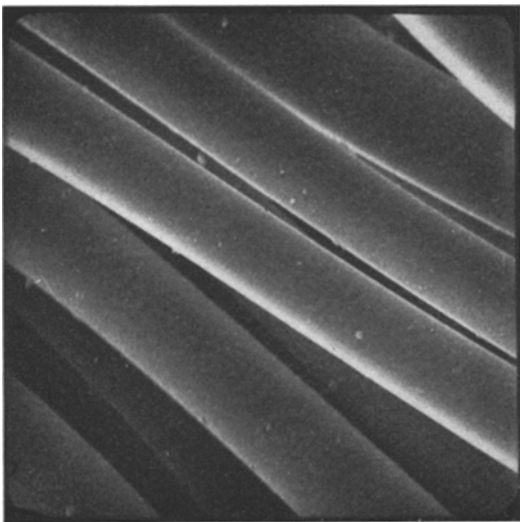


Figure 12 Filaments of chopped strand glass (E-glass) mat heated for 1 h at 650°C ($\times 1300$).

at a much faster rate than on the back side, producing thermally-induced stresses of corresponding magnitude. When the arc is turned on after the spray period the front side is subjected to another but lesser thermal shock. Furthermore, the direct actinic action of the radiation causes cross-linking in the resin of the front side rendering it more brittle than that of the back side, and thus more susceptible to fracture. Fig. 13 shows a failure at a multi-filament region on the surface of the back side of a sheet aged in the Weather-Ometer for 945 cycles (315 days).

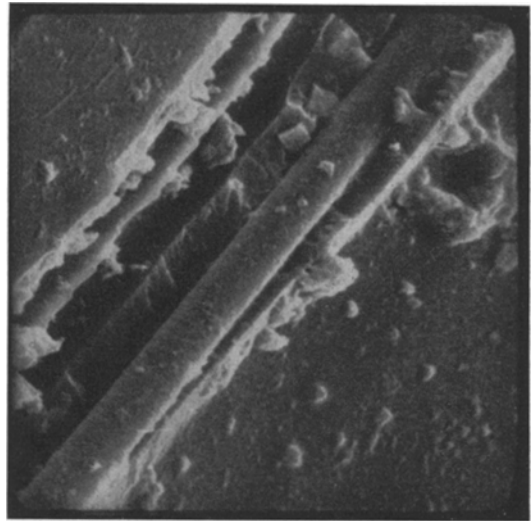


Figure 13 Back side of GFRP sheet aged for 940 cycles in the Weather-Ometer ($\times 680$).

3.2. Breakdown under variable humidity and temperature

In the Climate Lab, stresses are induced both thermally (11 to 56°C) and by moisture (Table I, treatment 2; Table II). The GFRP sheets subjected to this treatment showed breakdown features qualitatively similar to those produced in the Weather-Ometer, but the breakdown proceeded at a slower rate during the later stages of deterioration. In the Climate Lab, as in the Weather-Ometer, the rate of breakdown at single filaments prevailing in the early stages decreases with further ageing. A typical failure at a single filament after 270 cycles (135 days) is illustrated in Fig. 14. Fig. 15 illustrates an intermediate stage of breakdown in a multi-filament region.

This treatment would be useful to simulate

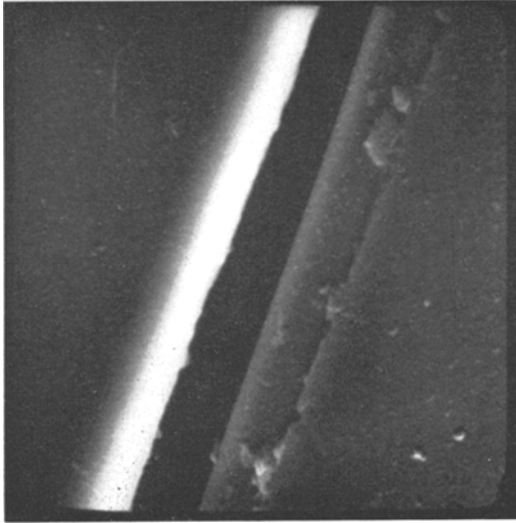


Figure 14 GRP sheet aged for 270 cycles in the Climate Lab ($\times 1300$).

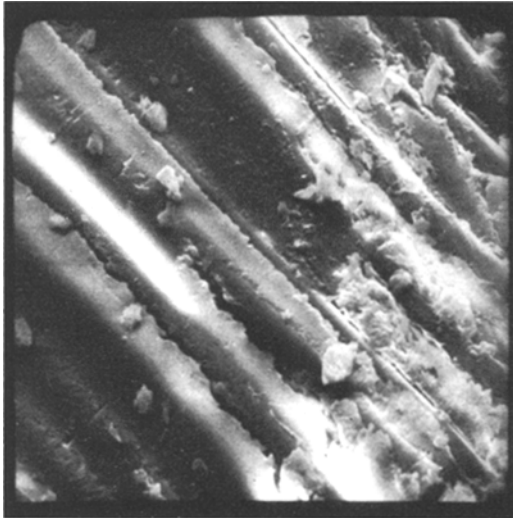


Figure 15 GRP sheet aged for 40 cycles in the Climate Lab ($\times 680$).

and accelerate weathering of GRP composites in the absence of radiation in environments where humidity and temperature variations exist. It demonstrates that breakdown in the interface region can be produced by physically-induced stresses and the chemical action of water, and that radiation is not necessary.

3.3. Ageing under constant humidity at constant temperature and in the absence of moisture at variable temperature

SEM examination did not reveal any surface breakdown in GRP sheets subjected to either of these two treatments. In the first case (Table I, treatment 3), water is present but there are no physically-induced cyclic stresses (Table II). In the other (Table I, treatment 4), there are thermally-induced cyclic stresses, but the action of water is completely absent (Table II). The results of these two treatments, and those previously described indicate that to produce surface breakdown in the interface region, cyclic stresses are necessary in addition to moisture.

3.4. Breakdown under variable humidity at constant temperature and constant humidity at variable temperature

Both of these treatments (Table I, treatments 5 and 6), resulted in breakdown similar to that observed in the Weather-Ometer or in the Climate Lab, but the deterioration proceeded at a much slower rate. The driving forces for the breakdown may be attributed to the physically-induced cyclic stresses produced either thermally or by moisture. This confirms previous observations that breakdown may be produced by the action of water in conjunction with cyclic stresses induced thermally and/or by moisture.

3.5. Artificial versus outdoor weathering

Observations show that breakdown features in artificial weathering were qualitatively similar to those found in the GRP sheets weathered outdoors [1]. For example, rupture at a ridging filament of a GRP sheet weathered outdoors for 880 days (Fig. 16) showed features similar to those observed in the Weather-Ometer after 4 days' exposure (Fig. 5). Fig. 17 displays a site at a single filament of an outdoor-weathered surface where the failure appears to have been produced by predominantly axial shear stresses, thus showing similarity to a corresponding failure produced by artificial weathering (Fig. 8). Furthermore, the micrograph shown in Fig. 18 shows fracture features in a multi-filament region (880 days outdoor weathering) that are almost identical with those present in Fig. 9 (150 days in the Weather-Ometer). Similarity in breakdown can be demonstrated for all the other artificial weathering treatments that produced deterioration in the interface region in GRP sheets. However, there are differences



Figure 16 GFRP sheet weathered outdoors at Ottawa for 880 days ($\times 1300$).

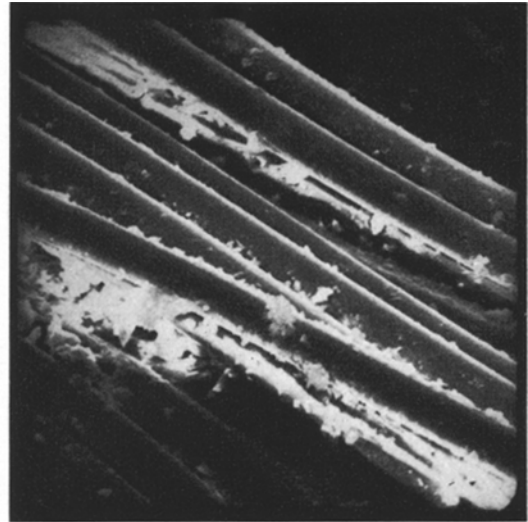


Figure 18 GFRP sheet weathered outdoors at Ottawa for 880 days ($\times 680$).

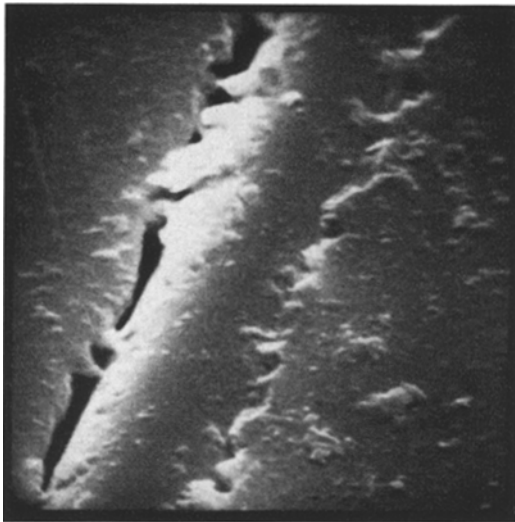


Figure 17 GFRP sheet weathered outdoors at Ottawa for 880 days ($\times 2900$).

in the rate and extent of breakdown. Although the rate of breakdown is comparable for the different treatments during the initial stages, it varies considerably during subsequent stages. The rate of breakdown is faster in the Weather-Ometer than in the Climate Lab, because the sheet (front side) is exposed to thermal shock and actinic action of the radiation. The thermal shock exerts an accelerating effect on the fracture process, whereas the actinic radiation

induces extra cross-linking of the resin and renders it more brittle. The factors involved in outdoor weathering are similar to those in the Weather-Ometer, but the breakdown rate is considerably slower presumably because these factors are milder, e.g., the intensity and frequency of thermal shock as well as the average level of radiation are lower. Results of the breakdown of GFRP sheets during artificial and outdoor weathering are summarized in Table III.

In conclusion, breakdown in the interface region of GFRP sheets during environmental ageing occurs at the surface and proceeds inwards. The breakdown may be attributed to both moisture- and physically-induced stresses. The cyclic stresses may be produced by moisture or by temperature cycling or by a combination of both and have a gradient decreasing from the surface toward the bulk.

4. Mechanism of breakdown in the interface region of GFRP composites

The interface region of a GFRP composite is more susceptible to environmental breakdown than the bulk of the matrix, because its main components, glass and resin, have very different properties. Dissimilarity in such properties as rate of water absorption, equilibrium water of absorption, coefficient of thermal expansion, hydrolytic stability and strain response, cause these components to interact differently with

TABLE III Nature and time of initial occurrence* of breakdown features during environmental ageing of GRP sheets

Description of deterioration feature	Time when deterioration feature was first detected (cycles)						
	Treat-ment 1	Treat-ment 2	Treat-ment 3	Treat-ment 4	Treat-ment 5	Treat-ment 6	Outdoor weathering†
Ridgings above filaments.	3-4	3-5	No break-down	No break-down	4-5	5-6	450-480‡ days
Rupture of resin above filaments.	4-5	4-6	„	„	4-6	6-7	—
Littering of surface with resin debris.	4-5	4-6	„	„	4-6	6-7	850-880 days
Formation of long cavity parallel to the filaments (partial delamination).	15-18	12-14	„	„	16	18-20	850-880 days
Fibre prominence.	450	650-700	„	„	—	—	850-880 days

*These observations refer to the initial stages only, i.e., when the feature was first detected. They do not necessarily reflect breakdown rate during the subsequent stages for the various treatments.

†The samples were exposed on standard racks (ASTMD1435-56) inclined at 45° to the horizontal facing south with no backing.

‡Weathering time could not be converted into cycles.

environmental factors such as moisture and temperature.

Because most of the GRP composites are cured well above room temperature, there are large residual stresses concentrated in the glass-resin interface region as a result of differential thermal shrinkage on cooling during fabrication [5-10]. These stresses, and those induced by moisture and/or temperature, play an important role in the environmental breakdown of GRP composites. The nature of the residual stresses depends on the ratio of glass to resin, and the geometry of the local composite system.

4.1. Breakdown at single filaments

To illustrate the breakdown mechanism of GRP composites, the deterioration in resin-rich regions will be discussed in greater detail. Fig. 19 shows a schematic drawing of a single filament surrounded by a resin sleeve many times its diameter. At the curing temperature, the composite is stress-free (Fig. 19a), because the isothermal volume change during solidification does not result in stress [10]. Since the coefficient of thermal expansion of a typical polyester resin is greater than that of E-glass (70 to $100 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ versus $5.0 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$), the resin

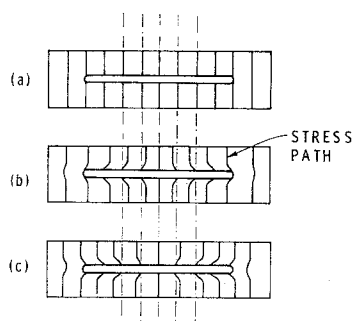


Figure 19 Schematic drawing of deformational stresses in a resin-rich region (single filament): (a) at the curing temperature; (b) after cooling to ambient temperature; (c) at high humidity and/or increased temperature.

contracts more than the glass. In the direction parallel to the filament (Fig. 19b) this differential contraction produces axial compression in the filament and axial tension in the resin [9]. This results in large axial and tangential shear stresses. Similarly, in the direction perpendicular to the filament, cooling results in large radial compressive stresses [9] as illustrated in Fig. 20a.

During environmental ageing, water penetrates into the composite by diffusion through the resin or by filtering through voids and micro-

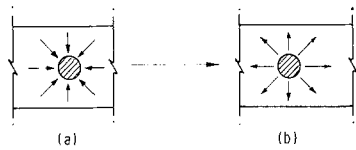


Figure 20 Schematic drawing of radial stresses in a resin-rich region (cross-section perpendicular to the glass filament): (a) radial compressive stresses at ambient temperature; (b) radial tensile stresses at high humidity and/or increased temperature.

cavities; the amount of water absorbed increases with humidity. The absorbed moisture, and/or a rise in temperature, induces much greater expansion in the resin than in the glass. Hence, the resin is severely restrained by the glass. This produces compression in the resin and tension in the glass, resulting in stresses that oppose the original residual stresses in the interface region. Consequently, during periods of high humidity or increased temperature, or both, the residual stresses may be gradually reduced, cancelled or exceeded. If the magnitude of the environmentally-induced stresses is large the residual stresses are reversed. The state of stresses in this situation may be represented schematically as in Figs. 19c and 20b. It is noteworthy that the residual radial stresses have changed from compressive (Fig. 20a) to tensile (Fig. 20b).

During the cycle period of low humidity or temperature, or the two combined, the differential shrinkage due to water desorption and/or thermal contraction results in stresses opposing those produced in the high level period, i.e., operating in the same direction as the residual stresses. Therefore, during environmental ageing, the interface region of the composite is subjected to physically-induced alternating stresses that exert a type of stress-fatigue.

It is believed that, initially, the resin layer in the interface region can undergo reversible deformation without rupture. In fact, Erickson and co-workers [11] have presented evidence for the presence of such an elastic transitional layer consisting of under-cured resin located between the coupling agent and the more completely cured matrix. Environmental ageing, however, may have caused the transitional resin layer to undergo chemical changes that rendered it less able to withstand the stress-fatigue produced by the alternating stresses. The resin may undergo cross-linking and hydrolytic scission reactions. Cross-linking is known to occur under the

influence of the actinic action of the radiation when polymeric materials are exposed in the Weather-Ometer or in outdoor weathering. In the absence of radiation, such as ageing in the Climate Lab, cross-linking may also take place by the reaction of residual ethylenic bonds under the influence of free radicals still present in the network of molecules [12]. Hydrolytic scission of the polyester chains by the absorbed water would allow more freedom of movement to the molecular segments involved. Consequently, free radicals until now inaccessible, might be reached by the reactive groups. This would result in additional cross-linking. Obviously, this alternate process of cross-linking may also take place in the presence of radiation. The extra cross-linking produces shrinkage and thus tensile stress. The hydrolysis reaction may be catalysed either by hydroxyl ions produced by the action of water on the glass or by hydrogen ions from the acid components of the resin. Furthermore, during ageing the ester bonds are stress-activated for hydrolytic attack by the physically-induced stresses. Hydrolytic scission of ester chain produces hydroxyl and carboxyl end groups; an accumulation of these in certain microregions constitutes weak points that function as stress concentrators. The hydroxyl and carboxyl end-groups also render the resin more hydrophilic, thereby increasing its capacity for water absorption. The cracking or fracture in the interface region under the effect of stress-fatigue in conjunction with chemical action may be described as a process of environmental stress cracking (or stress corrosion cracking). It is known that in stress-fatigue, cracking will occur after a number of cycles at stress levels much smaller than those that would be required under direct stress loading. Mechanically-induced stress-fatigue is known to involve the creation and incremental propagation of flaws or cracks until they reach macroscopic proportions. Thus, initiation of failure in the interface region may start from flaws created during ageing (by stress-fatigue or chemical action) or from pre-existing flaws or defects that act as stress concentrators, e.g., microvoids, occlusions, microbubbles, microcavities, microregions of low molecular density or low cross-link density [13]. Some of the microflaws and microdefects are abundant in the interface region [14].

As mentioned previously, fracture in the interface region during environmental ageing occurs under the effect of multi-axial complex

stresses. However, the observed cracks or fractures display features that are indicative of a particular set of predominant stresses. The most frequently observed features were those of fractures produced by predominantly axial shear stresses (Figs. 6 to 8, 15 and 17). Another frequent failure occurring in resin-rich regions is rupture of the resin above the ridging superficial fibre produced by predominantly radial tensile stresses (Fig. 5).

4.2. Failure at multi-filaments

Glass-rich composite systems (multi-filament regions) undergo breakdown by an environmental stress cracking process analogous to that operating at single filaments (resin-rich systems). The nature and distribution of the residual stresses are, however, different from those prevailing in resin-rich systems. In multi-filament regions, the axial stresses diminish as the filament spacings decrease [9]. The radial stresses may be either tensile or compressive, depending again upon the filament spacings [9]. Within the core of the multi-filament where the matrix forms approximately triangular columns of resin surrounded by filaments, the resin shrinks away from the glass when cooling from curing to service temperature. This results in residual, radial stresses that are tensile and of considerable magnitude [9]. Like the resin-rich systems, the glass-rich systems are subjected, during environmental ageing, to alternating stresses induced either by variations in moisture or temperature or both. Observations show that failure at multi-filaments is more severe (Figs. 9 to 11, 15 and 18) than at superficial single filaments. This is in agreement with the fact that tensile residual stresses have a harmful effect on stress-fatigue, while compressive residual stresses have a favourable influence [15]. These residual stresses are further influenced by those resulting from the unilateral shrinkage of the resin due to additional cross-linking. The characteristic features of fractures at multi-filaments indicate that the predominant stresses causing failure are radial tensile and tangential shear stresses.

5. Conclusions

Composites such as GRP sheets subjected to environmental ageing undergo surface breakdown in the glass-resin interface region long before any signs of deterioration in the bulk of the matrix may be noticeable. The fracture

occurs mostly within the resin adjacent to the interface. The overall deterioration in the interface region proceeds by a process of environmental stress cracking, consisting of the concerted action of physically-induced stress-fatigue and the gradual embrittlement and hydrolytic degradation of the resin phase. The stress-fatigue is caused by alternating stresses induced by moisture and/or temperature. Water is believed to be the most detrimental environmental factor.

There is a great similarity between the characteristic features of breakdown in the interface region induced by artificial weathering and those occurring in outdoor weathering. It may be concluded, therefore, that breakdown in the interface region in outdoor weathering proceeds by the same mechanism.

Our observations suggest that to produce GRP with improved resistance for long-term outdoor performance, the resin used should be not only resistant to hydrolysis but also as impermeable as possible to water. Furthermore, the properties of the reinforcement and the matrix should be as closely matched as possible.

Results also suggest that an accelerated method based on mechanically-induced (instead of physically-induced) cyclic stress-fatigue in the presence of moisture may be devised to evaluate the durability of the resin without reinforcement.

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