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Mechanism of surface microcracking of matrix in glass-reinforced polyester by artificial weathering

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The first stage in the deterioration of glass-fibre reinforced polyester (GRP) composites, fibre prominence, has been reported. The mechanism of the second stage, surface microcracking, is now described. Under controlled conditions GRP sheets were subjected to cyclic variation of moisture and temperature and to radiation. It is proposed that surface microcracking takes place under the combined action of radiation-induced tensile stresses in the surface region and physically-induced stress-fatigue. Tensile stresses in the surface region are caused by shrinkage of the matrix that results from cross-linking induced by the ultra-violet portion of radiation. Stress fatigue is imposed on the composite system by physically-induced alternating stresses produced by cyclic variation of temperature and, probably, moisture resulting from thermal and moisture gradients and inhomogeneities. Stress-fatigue probably plays a dominant role in microcracking induced by artificial weathering, whereas radiation-induced stresses in the surface region are more important in microcracking occurring in outdoor weathering.

1. Introduction

A study of environmental breakdown of GRP sheeting carried out by means of scanning electron microscopy (SEM) has been reported in two previous papers [1, 2]. The first describes the deterioration of GRP sheets on outdoor weathering in a temperate northern climate; the second reports results and discusses the mechanism of environmental breakdown in the interface region. Discussion in these papers and results now reported establish that there are two chronologically different stages in the environmental breakdown of GRP sheeting, resulting in two main types of failure*.

The first stage of environmental breakdown [2] produces failure associated with the region of the glass-resin interface, where cracks form along the filaments (fibres) and delamination or debonding takes place, giving rise to fibre prominence. The second stage consists of the formation of a network of surface microcracks that divide the matrix surface into small polygons [1].

Surface microcracking has now been reproduced indoors by subjecting GRP sheets to ageing under variable temperature and humidity in the presence of light radiation. The present paper reports such a study of the second stage and discusses the role of environmental factors and proposes a mechanism of deterioration. This will permit the development of an accelerated method for assessing the resistance of GRP sheets to microcracking.

2. Experimental

GRP samples were subjected to artificial weathering treatments as described in Table I, which includes outdoor weathering conditions for comparison. Additional details are given in Figs. 1 and 2. Table II describes stress conditions employed in the various ageing treatments.

Cycling of temperature and/or moisture induces alternating stresses that exert a stress-fatigue believed to be involved in the breakdown of the GRP sheet. The thermally-induced alternating stresses were estimated and expressed as % change in volume, that is increase (+) and decrease (−) of volume at median temperature

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

TABLE I Methods of environmental ageing of GRP sheets

Treatment no.	Description of ageing conditions: General	Details
1	Cyclic variation of humidity and temperature in the presence of radiation (Atlas Xenon Arc Weather-Ometer)*	4 h at 100% r.h. and 12°C, 4 h at 50% r.h. and 55°C; 3 cycles per day.
2	Cyclic variation of temperature between − 34 and 22°C†	10 min cooling to − 34°C and 10 min warm-up to + 22°C; 72 cycles per day.
3	Cyclic variation of humidity and temperature (Aminco Climate Lab)*	7 h at 100% r.h. and 56°C, and 5 h at 25 to 100% r.h. and 11 to 56°C; 2 cycles per day.
4	Outdoor weathering at Ottawa (temperate northern climate)	Sample exposed at 45° facing south, with no backing in accordance with ASTM D1435-56.

*Additional details are given in Figs. 1 and 2.
†This treatment was used to subject the samples to more severe stress-fatigue conditions than in 1, i.e. greater temperature interval (ΔT), lower ageing temperatures and higher rate of application of alternating physically-induced stresses.

TABLE II Stress conditions used in environmental ageing of GRP sheet

Sample no.	Over-all treatment*		Number of cycles	Duration of radiation (h)	Estimated temperature-induced stresses by means of thermal volume changes†			Estimated moisture-induced stresses by means of sorbed water (wt %)	
	1st	2nd			Alternating stresses (%)	Extreme rate of change (% min^{-1})	Thermal shocks (no.)	Median moisture content	Alternating stresses (ΔSD)
1	$1F_2$	—	900‡	3600	± 0.5	− 0.5	900	0.43	± 0.06
3	$1B_4$	—	1300	None	± 0.5	< − 0.5	—	0.43	± 0.06
4§	$1F_1$	$2F_5$	100‡	3100	± 0.7	± 0.9	200	0.35	± 0.0
6§	$1B_1$	$2B_6$	600	None	± 0.7	± 0.9	1200	0.35	± 0.0
7	3	—	1250	None	± 0.5	− 0.2	—	0.94	± 0.12
8	$4F_7$	—	1440 days	9000¶	± 0.3	± 0.3	—	0.6	± 0.1
9	$4B_7$	—	1440 days	None	± 0.3	< ± 0.3	—	0.6	± 0.1

*F = irradiated (front) side; B = non-irradiated (back) side. Subscripts 1-7 = different periods of exposure.
†Explanation and details are given in Section 2.
‡When single cracks were first detected in the matrix surface.
§Samples were subjected to 3100 h of Weather-Ometer radiation (780 cycles) and then to temperature cycling.
¶Bright sunshine hours.

using 25×10^{-5} °C^{-1} as thermal coefficient of cubic expansion of polyester resin. The rate of change of the thermally-induced alternating stresses may also play a role in surface microcracking. This was calculated for the period of the most rapid temperature change and is expressed as % volume change (increase and decrease) per minute. It is a measure of the thermal shock the GRP sheet undergoes during treatment. A thermal shock is considered significant only when the rate of change is $\geq 0.5\%$ min^{-1}. Weather-Ometer ageing involved only one thermal shock, that with temperature decrease (Table II, sample 1), whereas temperature cycling imposes two thermal shocks during both increase and decrease of temperature (Table II, samples 4 and 6).

As the % water absorbed is only slightly larger than % swelling [2], change in % water content may be considered a good measure of volume change (swelling and shrinking) and thus of changes in stress. Moisture-induced alternating stresses were, therefore, expressed in terms of % weight (ΔSD) increase or decrease with respect to median water content. The moisture content values for outdoor weathering were

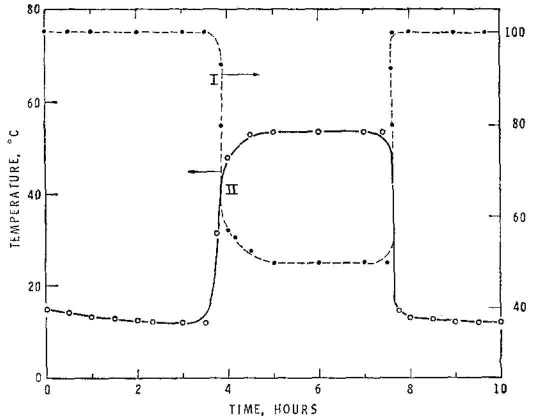

Figure 1 Humidity-temperature cycle (8 h) in the Atlas Xenon Arc Weather-Ometer. I Humidity, II temperature of colourless GRP panel (exposed side).

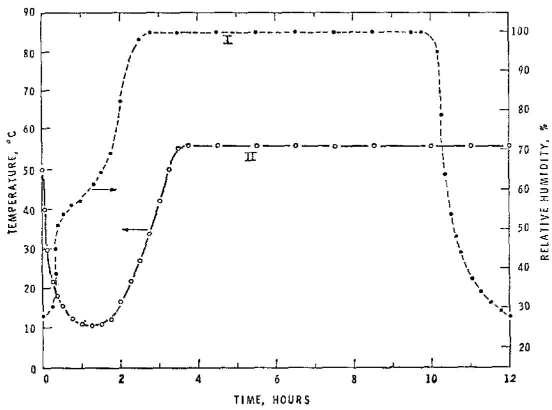

Figure 2 Humidity-temperature cycle (12 h) in the Aminco Climate Lab. I Humidity, II temperature.

obtained twice daily (08.30 and 16.00 h) during September and October 1972.

2.1. Materials

The GRP test samples (0.12 to 0.13 cm thick) 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 ultra-violet-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. Examination by scanning electron microscopy

The surface deterioration of GRP sheets subjected to environmental ageing was assessed with a Stereoscan scanning electron microscope operated at 20 kV and a tilt angle of 45°. The GRP specimens were sampled at appropriate intervals and coated with carbon and gold to render them conductive for examination by SEM.

3. Results and discussion

The results of the study on surface microcracking of matrix in GRP sheets during environmental ageing are summarized in Table III. The formation and characteristic features of surface microcracking in GRP sheets are illustrated by SEM micrographs presented in Figs. 3 to 16. (Figs. 3 and 4 show the surface and cross-section of the control GRP sheet.)

3.1. Surface microcracking under conditions of cyclic variation of humidity and temperature in the presence of radiation

The matrix surface of the irradiated (front) side of GRP sheets subjected to ageing in the Xenon Arc Weather-Ometer developed fine microscopic cracks after 900 cycles (300 days) of exposure (Table III, sample 1). Some distance from the surface filaments the cracks are randomly oriented, but closer to them they are unidirectional and parallel to the filaments. As ageing is

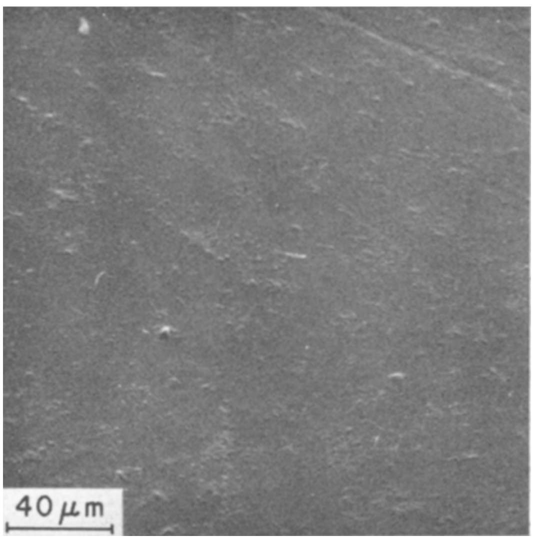

Figure 3 GRP sheet. Control.

TABLE III Effect of radiation- and physically-induced stresses on the formation of surface microcracking of matrix in GRP sheets.

Sample no.	Over-all treatment		Assessment of stresses contributed by			First occurrence of cracks in cycles. Single cracks (network of cracks)	Nature of fracture	Conclusions
	1st	2nd	Radiation	Temperature	Moisture*			
1	$1F_2$	—	Moderately severe	Moderately severe	Mild	900	Brittle	Brittle fracture indicates that cracks are formed under the influence of stresses produced at a rapid rate.
2	$1F_3$	—	> 1	> 1	> 1	(1000)	Brittle	As above.
3	$1B_4$	—	None	< 1	< 1	No cracks	—	Shows that radiation is necessary to produce cracking.
4	$1F_1$	$2F_5$	< 1	Very severe	Negligible	100 + 780†	Brittle	As in sample 1, fracture propagates rapidly. The stress-fatigue being more severe, than in 1, cracking occurs at a lower amount of radiation.
5	$1F_1$	$2F_6$	< 1	Extremely severe	Negligible	(600 + 780)†	Brittle	As above.
6	$1B_1$	$2B_6$	None	Extremely severe	Negligible	No cracks	—	Confirms conclusion of sample 3.
7	3	—	None	Mild	Very severe	No cracks	—	Even severe moisture-induced stresses cannot produce cracking in the absence of radiation.
8	$4F_7$	—	Very severe	Mild	Mild	1440 days‡	Ductile	If the amount of radiation is relatively high, cracking occurs under relatively less severe stress-fatigue.
9	$4B_7$	—	None	Mild	Mild	No cracks	—	As in artificial ageing, radiation is necessary to produce cracking on outdoor weathering.

*This is the over-all contribution of moisture to stress.
†These samples were aged for 780 cycles in the Weather-Ometer prior to subjecting them to temperature cycling.
‡Outdoor weathering time could not be converted into cycles.

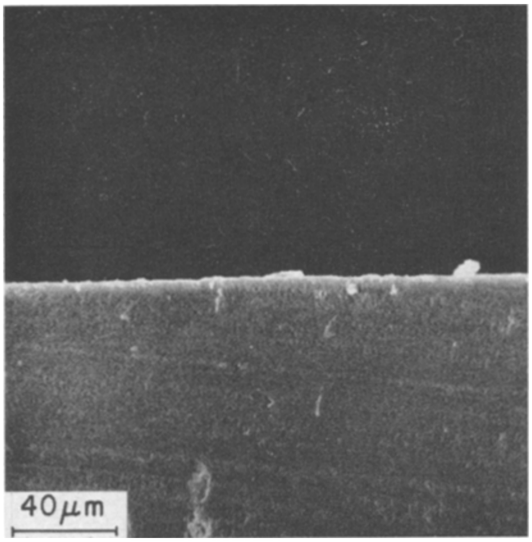

Figure 4 Cross-section of GRP sheet. Control.

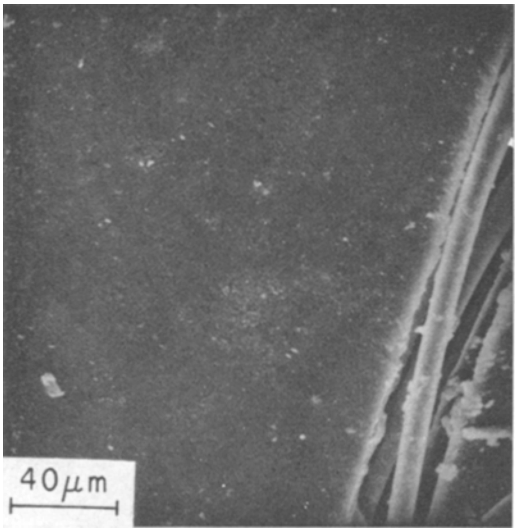

Figure 5 GRP sheet aged in the Climate Lab for 1060 cycles.

continued, the cracks propagate and intersect each other to form a network (Table III, sample 2). In the glass-rich region, but not close to the glass-resin interface, additional cracks propagate in a direction perpendicular to the existing ones, dividing the surface into (mostly) four-sided, fairly regular polygons. The cracks are generally empty, containing only occasional particles of matter and have none of the characteristics of crazes, as the latter term is currently understood [3, 4]. The different stages in the formation of surface microcracks during artificial weathering are illustrated in Figs. 6 to 10. In general, the cracks are very narrow (0.3 to 0.8 μm) and appear as bright lines at low magnification (Fig. 6) because of electric charging associated with the SEM technique. Observed under higher magnification, they exhibit characteristics of distinct cracks (Fig. 7).

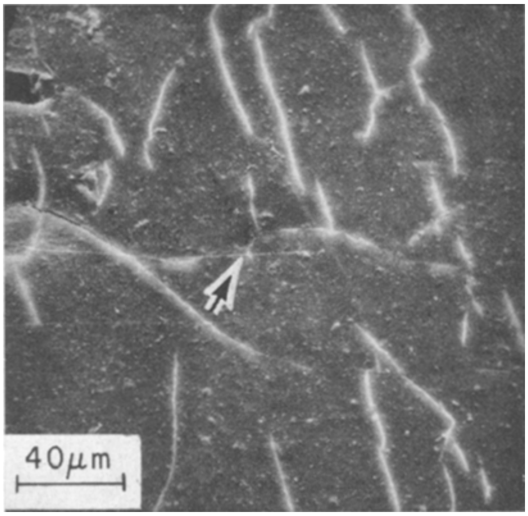

Figure 6 GRP sheet aged in the Weather-Ometer for 900 cycles.

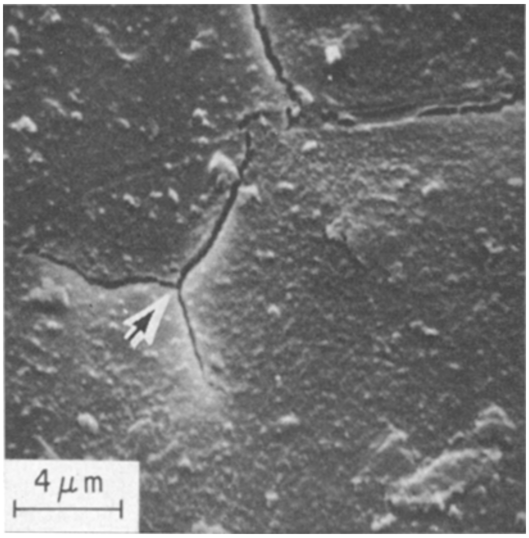

Figure 7 GRP sheet aged in the Weather-Ometer for 900 cycles.

Examination of the non-irradiated (back) side of the GRP sheet revealed no microcracks in the matrix. Thus, radiation is necessary to produce microcracking in the Weather-Ometer.

3.2. Microcracking in pre-irradiated GRP sheet under conditions of temperature cycling

When GRP sheets exposed for 780 cycles (260 days) in the Weather-Ometer and free of microcracks were subjected to cyclic temperature variation between -34 and $22°C$, surface microcracks were produced on the pre-irradiated side (Table III, sample 4). The non-irradiated side of the sheets did not show surface cracks at the end of this treatment. Similarly, microcracks could not be induced by this procedure in sheets aged for 650 cycles (315 days) in the Climate Lab or in control (unaged) samples subjected to 600 temperature cycles.

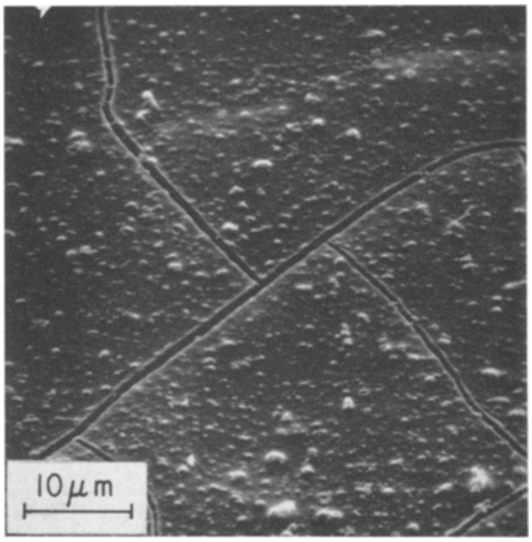

Figure 10 GRP sheet aged in the Weather-Ometer for 1100 cycles.

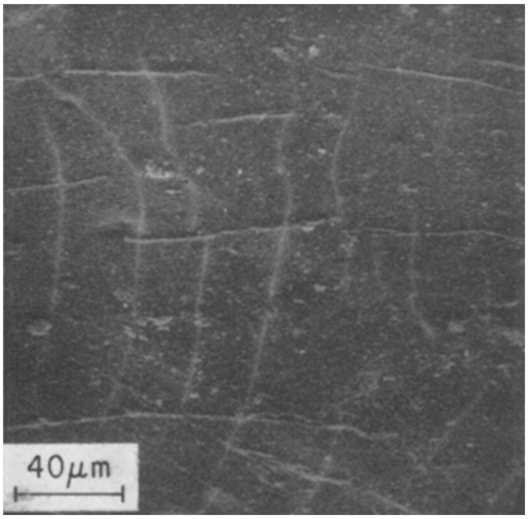

Figure 8 GRP sheet aged in the Weather-Ometer for 1000 cycles.

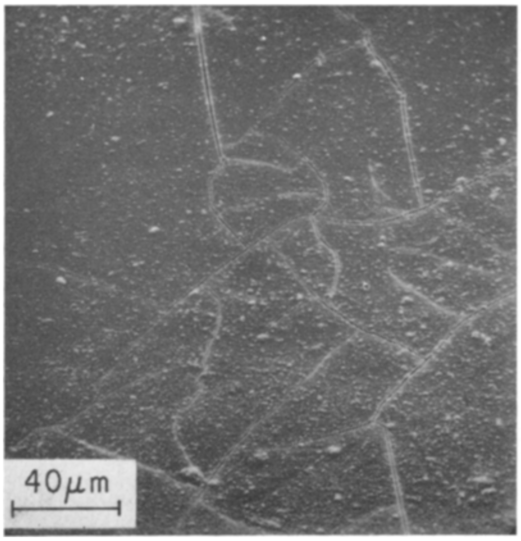

Figure 9 GRP sheet aged in the Weather-Ometer for 1100 cycles.

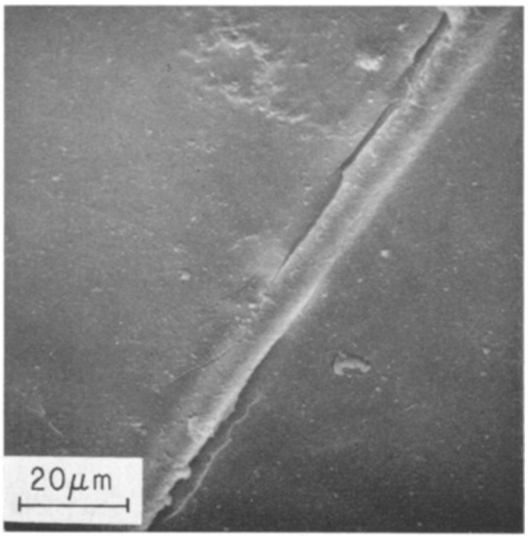

Figure 11 GRP sheet subjected to 3100 h of Weather-Ometer radiation.

The pre-irradiated surfaces of GRP sheets showed a large number of very narrow cracks, mostly parallel to each other, after 100 temperature cycles (Table III). The concentration of cracks became very large after 300 cycles. After 600 temperature cycles, the surface showed an extensive network of very narrow cracks (0.2 to 0.4 μm). The topography of the pre-irradiated GRP surface before and after 600 temperature cycles is shown in Figs. 11 and 12, respectively. As in Weather-Ometer ageing, the cracks produced by temperature cycling are empty. Characteristic features of cracks indicate that they are formed as a result of brittle fracture (without any plastic deformation) and by a process of very rapid propagation.

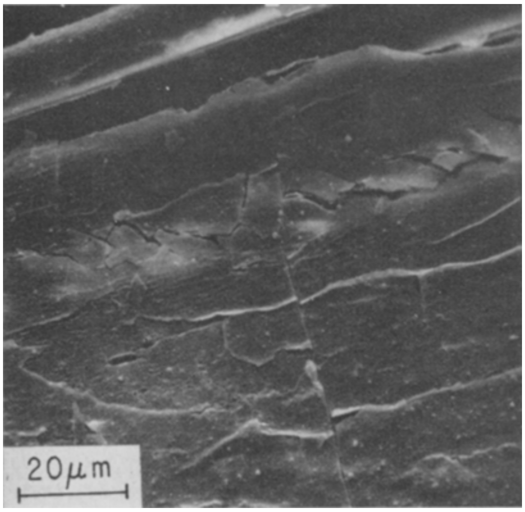

Figure 12 GRP sheet subjected to 3100 h of Weather-Ometer radiation and then to temperature cycling for 600 cycles.

3.3. Outdoor induced surface microcracking

Figs. 14 to 16 show surface microcracking of GRP sheets exposed outdoors for 47 and 80 months. As in Weather-Ometer ageing, the microcracks intersect each other to form a network dividing the surface into predominantly four-sided polygonal areas. The microcracks formed during outdoor weathering are relatively wide (2.5 to 6.0 μm), whereas those induced by Weather-Ometer ageing are relatively narrow (0.3 to 0.8 μm). Initially, the edges of the cracks produced in outdoor weathering are sharp, then gradually become rounded off. As weathering continues, the edges ridge up gradually and the cracks become wider, indicating that the matrix continues to shrink as a result of continued cross-linking (Fig. 15). Furthermore, the areas confined by the intersecting cracks are relatively large in the early stages (Fig. 14), but diminish with weathering because the surface splits to form secondary cracks as the resin continues to shrink (Fig. 15).

As in Weather-Ometer ageing, the non-

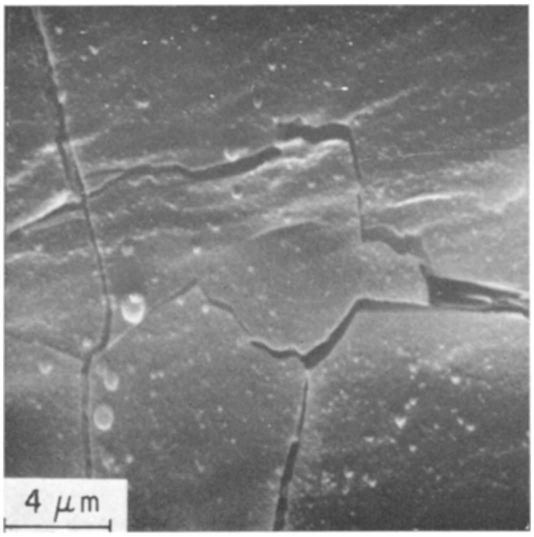

Figure 13 GRP sheet subjected to 3100 h of Weather-Ometer radiation and then to temperature cycling for 600 cycles.

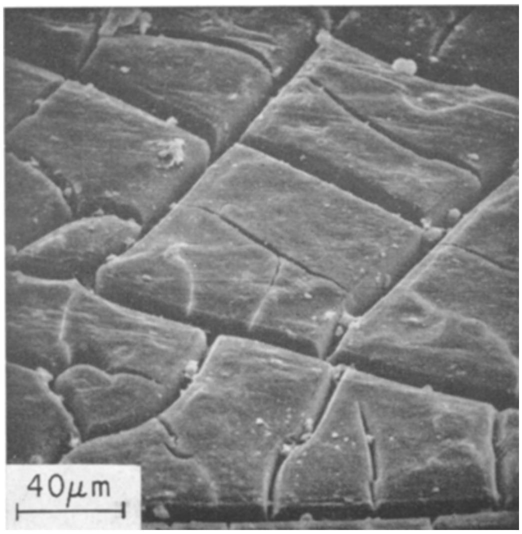

Figure 14 GRP sheet weathered outdoors at Ottawa for 47 months.

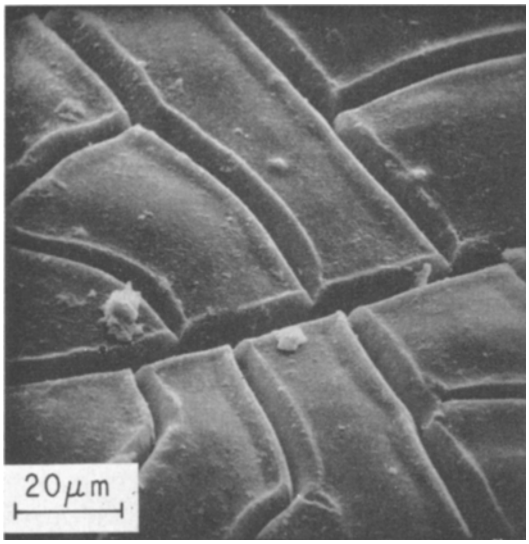

Figure 15 GRP sheet weathered outdoors at Ottawa for 80 months.

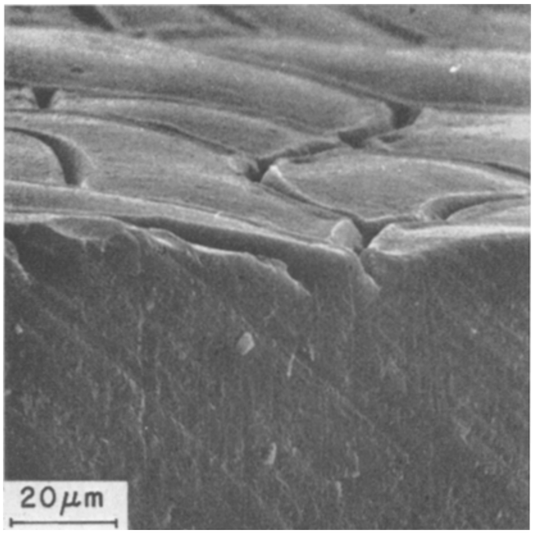

Figure 16 Cross-section of GRP sheet weathered outdoors at Ottawa for 80 months.

irradiated (back) side of the weathered sheet does not undergo surface microcracking. This is in agreement with previous observations indicating that radiation is necessary to produce surface microcracking.

4. Mechanism of surface microcracking

Under the influence of ultra-violet radiation the surface resin of the GRP sheets undergoes gradual cross-linking, resulting in shrinkage that produces permanent tensile stresses. Some cross-linking, producing additional tensile stresses, may also take place by an alternate process involving the reaction of residual ethylene bonds under the influence of free radicals still present in the network. This process is promoted by the hydrolytic action of absorbed water on the polyester chain, causing scission that imparts a greater freedom of movement to the molecular segments involved; thus the free radicals heretofore inaccessible can be reached by the reactive groups [2]. As cross-linking is greatest at the surface, the resulting permanent tensile stresses have a gradient from the surface inwards.

Cyclic variation of temperature, and probably moisture, during weathering induces alternating tensile and compressive stresses in the surface region because of thermal and moisture gradients existing from the surface inwards. In addition, physically-induced alternating stresses are produced by the cyclic variation of temperature and moisture at the boundaries of inhomogeneities such as the glass-resin interface, micro-inclusions and other microflaws as a result of dissimilarities in thermal and moisture absorption properties. The combined effects of all these physically-induced stresses exert a stress-fatigue on the system. When the surface resin reaches a certain degree of rigidity as a result of cross-linking, it can no longer deform reversibly under the action of stress-fatigue and undergoes fracture. As both radiation- and physically-induced stresses have a gradient, the fracture produces microcracks that propagate from the surface towards the bulk. The cracks are confined to the surface resin layers of the exposed side; none were detected in the bulk of the sheet (Fig. 16).

The initiation of cracking is believed to occur at the inhomogeneities and flaws, which function as local stress concentrators. In a polyester-based matrix, fracture could also be initiated in microregions of low molecular and cross-link densities [5] and at submicroscopic defects resulting from the accumulation of hydroxyl and carboxyl end groups in certain microregions. These groups are produced by the hydrolytic action of water on the ester linkage.

Microcracks induced by artificial weathering (Weather-Ometer) have the characteristics of brittle fracture, indicating that they are produced under the influence of a set of stresses changing at a fast rate (Table II, sample 1). Because the tensile stresses induced by cross-linking in the surface region are formed gradually, the physically-induced alternating stresses (stress-fatigue), which change at a fast rate, must thus play the predominant role in producing the cracks. When the physically-induced stress-fatigue is very severe (Table II, sample 6) the microcracks are even more irregular and fracture shows greater brittle characteristics (Fig. 12). This also demonstrates that microcracking may be induced at lower radiation levels when the applied stress-fatigue is adequately increased.

Observations indicate that there is a significant similarity between the features of surface microcracking produced during artificial and outdoor weathering. In both types of weathering the microcracks require radiation for their formation, they occur only after extensive fibre prominence has taken place, and they do not display craze characteristics.

In outdoor weathering, however, the cracks have ductile characteristics, for example, crack boundaries are generally smooth and straight and show plastic deformation. With weathering, the boundaries of the areas confined within the cracks ridge up and become more V-shaped (Fig. 15) indicating that the matrix continues to undergo slow shrinkage with a gradient decreasing from the external surface towards the bulk. These features suggest that the cracks occur under the influence of tensile stresses (Fig. 15) operating at a slow rate.

Observations show that in the absence of radiation microcracking does not take place, even under severe moisture conditions and relatively high stress-fatigue (Tables II and III, sample 7). This indicates that cross-linking taking place in the presence of moisture probably does not produce sufficient shrinkage and corresponding, adequate permanent tensile stresses in the surface region.

Thus, in microcracking produced by artificial weathering, physically-induced stress-fatigue is predominant; in microcracking induced by outdoor weathering, tensile stresses resulting from shrinkage in the surface region are more important. A summarized analysis of the results is presented in Table III.

5. Conclusions

During environmental ageing of GRP composites the matrix resin undergoes fracture at the surface and becomes covered with a network of microcracks. Surface microcracking takes place only after the surface has developed extensive fibre prominence and thus constitutes the second stage in the over-all deterioration of GRP during environmental ageing.

Microcracking takes place under the combined action of radiation-induced tensile stresses in the surface region and physically-induced stress-fatigue. Tensile stresses operating in the surface region are produced by shrinkage of the matrix that results from cross-linking induced by the ultra-violet portion of radiation. Stress-fatigue is produced by physically-induced alternating stresses. These, in turn, are induced by cyclic variation of temperature and, probably, moisture as a result of thermal and moisture gradients and the presence of inhomogeneities. In microcracking produced by artificial weathering, stress-fatigue plays a dominant role; whereas in that produced by outdoor weathering, radiation-induced stresses in the surface region are more important.

To minimize or retard this type of failure in GRP composites the resin used should have very good resistance to ultra-violet light because radiation has been found to be a necessary factor in surface microcracking. Artificial weathering using the SEM technique and the methods here described may be developed into an accelerated method to evaluate the resistance of GRP sheets to surface microcracking.

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