The paper already sent to MP, USA. The acceptan will come in 6 month ABK

ENVIRONMENTALLY INFLUENCED DEGRADATION OF FIBER REINFORCED COMPOSITES

PRIYA SAMPATH, A.S. KHANNA and *S.S. GANTI
CORROSION SCIENCE AND ENGINEERING,
IIT, BOMBAY - 400 076, INDIA
***NMRL, BOMBAY**

ABSTRACT

Two fiber reinforced polymer composites were examined for susceptibility to degradation due to exposure to aggressive environments. Composites and fibers were exposed to a mixed inoculum of aerobic bacteria and also to an anaerobic sulfate reducing bacteria. Glass fiber reinforced vinyl ester and isophthalic ester composites as well as the individual glass fibers were extensively degraded due to the bacterial attack. Degradation due to exposure to water at elevated temperatures as well as exposure to 1N sulfuric acid were studied and it was found that in both the cases the composite samples underwent degradation which were in the form of fiber pullout as well as matrix cracking , leading to subsequent reduction in the mechanical properties.

INTRODUCTION

Fiber glass reinforced vinyl ester and isophthalic ester composite materials are used extensively in marine environments especially in the construction of hulls. These materials, with their high strength - to - weight ratio, improved corrosion resistance and better mechanical properties are replacing conventional metals and alloys as structural materials. However, the myth that these materials do not undergo corrosion is fast exploding, due to the various degradation mechanisms that have come to light.

Wagner et al [1] have studied the microbiologically influenced degradation of epoxy and vinyl ester resins and glass fibers due to different kinds of bacterial attack. Wagner et al [2] have also studied the effect of microbial degradation under stressed conditions. Thorp et al [3] have studied the effect of fungi like Aspergillus on composites. Possible mechanisms for microbiological degradation of polymeric composites include: direct attack of the resin by the acids or enzymes, blistering due to gas evolution, polymer destabilization due to sulfides and blistering due to gas evolution [4] . Besides, the degradation due to microbial attack, polymer composites also degrade due to moisture absorption and also exposure to chemical environments. Extensive studies have been

Published in Materials Performance, 1997 36(5): 65-69
(Prepublication drafts.

carried out to understand the degradation's in polymer composites due to absorption of water [5, 6, 7]. Barkatt et al [8] have studied the degradation caused to FRP materials in acidic, aqueous and neutral solutions. Tucker et al [9] showed that carbon / polymer composites galvanically coupled to metals are degraded by cathodic reactions in sea water.

EXPERIMENTAL PROCEDURE

Maintenance of bacterial cultures

The microbial attack on glass fiber reinforced vinyl ester composites and isophthalic ester composites were studied using ODB, SBC and the Sulfate reducing bacterial (SRB) cultures. The cultures were obtained from NMRL, Bombay.

The culture medium for the ODB and SBC strains of bacteria was maintained by making use of the following substances Ammonium nitrate [NH_4NO_3] - 1g , Potassium hydrogen phosphate [K_2HPO_4] -1.0g, hydrated Magnesium sulfate [$MgSO_4.7H_2O$]-0.20 g , Potassium dihydrogen phosphate [KH_2PO_4] - 1.0 g, Calcium chloride [$CaCl_2$] - 0.20 g , Sodium chloride - 35g. The above substances were dissolved in 1000ml distilled water. The salt solution as sterilized by autoclaving at 15 lb / in^2 for 20 minutes. The above organisms were isolated from sea water.

Sulfate reducing bacteria were maintained in a Postgate medium- B. The medium was prepared by making use of Potassium hydrogen phosphate [K_2HPO_4] - 0.25g , Ammonium chloride[NH_4Cl] - 0.50g, Calcium sulfate [$CaSO_4$] - 0.50g, hydrated Magnesium sulfate [$MgSO_4.7H_2O$] -1.0g, Sodium lactate -1.75g, Ascorbic acid -0.05g, Thio glycollic acid - 0.05g, hydrated Ferrous sulfate- 0.25 g.

The microbial attack on glass fiber reinforced isophthalic ester composites were studied using an anaerobic sulfate reducing bacteria (SRB). The culture medium was maintained by making use of the following substances . Sodium lactate - 4ml of 70%, Yeast extract - 1.0g, Ascorbic acid - 0.10g, Potassium hydrogen phosphate - 0.01g, Magnesium sulfate hepta hydrate - 0.20 g , Sodium chloride - 10.0g, Mohr's salt -0.20g. The above substances were dissolved in 250ml distilled water and the salt solution was autoclaved at 15 lb /in^2 for 30 minutes.

Exposure Conditions

Composite samples of glass fiber reinforced vinyl ester resins (weight -3.8g, diameter-26.3 mm, thickness-5mm) were exposed to the above mentioned microbial cultures for a period of 21 days. The samples were cured and autoclaved at 15 lb /in^2. The samples were introduced individually into the conical flasks containing the different bacterial cultures.

All cultures were maintained at room temperature and were left in a mechanical shaker for a period of 21 days.

Composite samples of glass fiber reinforced isophthalic ester resins were exposed to the above culture medium for 21 days. Individual glass fibers alone were also exposed to the above culture medium. All cultures were kept in a thermostat and a temperature of 37°C was maintained. In order to maintain complete anaerobic conditions the conical flasks containing samples were completely sealed with wax thus preventing the entry of oxygen. Uninoculated controls were maintained under the same exposure conditions.

EFFECTS OF WATER ABSORPTION

Glass fiber reinforced composites are being used extensively in various capacities in different environments. The environmental effects of moisture on these materials is of great significance. In this study, the moisture absorption behaviour of glass fiber reinforced vinyl ester and isophthalic ester composites were investigated. Specimens were immersed in distilled water after conditioning for a period of 6 hours. The following tests were performed.

Boiling water immersion

Vinyl ester composites were immersed in distilled water containers maintained at different temperature of 40°C, 80°C and 100° C till cracks were detected visually. Isophthalic ester composites were also immersed under similar conditions in order to determine the effect of absorption of water. However, the experiment in this case was extended for more number of days to observe the changes caused to this material in contrast to the vinyl ester composites.

Effect of absorption of acids

Glass fiber reinforced composites are sensitive to attack by acids. The effect of 1N sulfuric acid on glass fiber reinforced vinyl ester and isophthalic ester composites at room temperature were studied by the following method. Composite samples were immersed in 1N sulfuric acid at room temperature. Glass fibers alone were also immersed in the acid to find out the extent of damage caused to the fibers.

Weight and dimension changes

The effect of bacterial attack, absorption of water and acids on the composites were studied by monitoring the changes caused to the materials in terms of weight and dimensions which were measured at regular intervals of time during the entire course of

the experiment. Specimens were weighed periodically in case of water and acid absorption tests, for determining changes in weight, after removing the surface water by using a dry tissue paper, in an analytical balance with a resolution of 0.01 mg. Water and acid induced expansion and corresponding dimensional changes were measured at regular intervals of time. Plots of weight and dimension changes versus time were made to determine the effect of absorption of water on the composites at different temperatures. Plots of weight and dimension changes versus time of immersion in acid medium were also made.

Evaluation of mechanical properties

Absorption of water and acid brings about a reduction in mechanical properties of the materials in terms of reduction in tensile strength, Young's modulus etc. Often, it is found that the stress required for the failure of the specimen also decreases with absorption of water and other chemical media. These properties were evaluated using standard (ASTM D 638) testing methods in an 810 MTS testing machine at 2mm/min and 72°F as a mean value of three determinations.

Optical density measurements

Optical density measurements were made to determine the extent of bacterial growth using a Spectronic-20 instrument. The spectronic 20 meter was adjusted to show zero absorbance before the sample was placed in it. A few ml of the culture medium was transferred into the cuvettes and OD measurements were made.

RESULTS AND DISCUSSION

In all cases, composites and the glass fibers were colonized by the bacteria. SEM micrographs revealed distinct fiber pullout and matrix cracking due to bacterial attack. All surfaces exposed to SRB cultures were black due to sulfide deposition. Figure 1 shows the effect of ODB, SBC culture on the matrix. The vinyl matrix after exposure for 21 days shows cracks, pores and surface roughness. Figure 2 (a) shows deposits on the surface of isophthalic ester composite after exposure to ODB, SBC culture, while vinyl eater composite shows much drastic damage in SRB bacteria in the same exposure time Fig. 2(b). Other kinds of damage due to bacterial attack were, fiber pullout and debris formation as depicted in Fig.3. Figure 4 shows a very nice example of the damage of glass fibber itself when exposed to bacteria. Well woven glass fibers were extensively attacked by SRB. In a short duration of 10 days the whole fiber pattern is completely shattered. Optical density measurements made, were in the range of 0.20 to 0.50 nm, confirming the bacterial growth.

Polymer composites, both vinyl ester and isophthalic ester, were extensively degraded due to absorption of water. Composite samples exposed to a temperature of 80°C, exhibited an increased rate of water absorption in comparison to specimens maintained at 40°C. However, composites exposed to temperatures of 100°C showed an initial increase in weight followed by a subsequent decrease. This has been shown in the Fig. 5 for both vinyl eater and isothalic ester composites. At lower temperatures, the absorption of water is predominantly by Fickian diffusion leading to a continuous increase in weight but at higher temperatures, the formation of cracks leads to soluble resin materials leaching out resulting in a decrease in weight. Figure 6 shows the degradation caused to the composite materials due to absorption of water. Composite samples also show a reduction in mechanical properties due to absorption of water. Table I shows the reduction in tensile strength and modulus due to absorption of water for the vinyl ester composite.

The effect of exposure to acids was also investigated. Composite samples exposed to 1N sulfuric acid at room temperature, degraded due to absorption of acid. The mechanism of absorption of acid was found to be the same as that of water, an initial increase in weight due to absorption of acid, followed by a subsequent decrease, after prolonged exposure, due to soluble matrix materials getting leached out. Degradation's in the form of fiber breaking and pullout were observed due to absorption of acid (Fig 7).

The hygrothermal environmental effects and the behaviour of resin-matrix composites are quite complex and it is difficult to explain the observed changes in a composite by a generalized mechanism. Irrespective of the environment, water, acid or bacterial, the main cause of degradation appears to occur by moisture absorption. The overall weight changes encompasses the combined effect of water diffusion into the matrix which promotes weight gain initially, followed by weight loss which could be due to surface peeling, leaching out of additives etc. All these factors are enhanced by increasing temperature or severity of the environment such as acid instead of water. Once, the moisture diffuses into the resin, it attacks the fiber resulting in fiber pull out breaking or its dislocation. In the presence of bacteria, the there is disruption of fiber-matrix bonding, resulting in fiber pull out and breaking. It is however, still not clear whether the bacteria attacks and colonizes the resin, resulting in crack development or moisture absorption led to crack development, followed by bacterial attack. More work is needed to ascertain the exact mechanism.

CONCLUSIONS

Vinyl ester and isophthalic ester composites are susceptible to attack by bacteria. Individual glass fibers exposed to sulfate reducing bacteria showed loss of rigidity and the interwoven pattern was completely destroyed. Degradation due to absorption of water was pronounced at higher temperatures which was also characterized by reduction in

tensile strength and modulus. Absorption of acids also led to degradation and a reduction in tensile strength but to a lesser extent.

REFERENCES

1. **Patricia Wagner, Wayne. C. Tucker,** " Microbiologically influenced degradation of fiber reinforced polymeric composites," Materials Performance, 33 (1994) 46-48.
2. **Patricia Wagner, Richard Ray, Kevin Hart ,Brenda Little, Walter Bradley and Pin - Lin Chou ,** " Microbial degradation of stressed fiber reinforced polymeric composites", Corrosion -95, Paper 200.
3. **Thorp, R.Mitchell, T. E. Ford,** " Microbial deterioration of fiber reinforced composite materials" - To be published.
4. **Jones,** "Moisture absorption - Anomalous effects, " Handbook of reinforced composites", Ed. F. R. Jones (1994) 371-373.
5. **Dewimiller and A.R. Bunsell,** " Accelerated aging of glass fiber reinforced epoxy resins in water," Composites, 14 (1983) 35-40.
6. **R. Loader,** " Water absorption by polyester resins ", The 14th Reinforced Plastics Cong, (1984) 161-164.
7. **Tohru Morii and Hiroyoki Hamada,** "Weight changes of fiber / matrix interface in GRP panels immersed in hot water", Composites Science and Technology 50 (1994) 373-379.
8. **Aaron Barkatt, Lawrence C.Bank, T. Russel Gentry, Luca Prian, Rongamin Shan,**"Environmental degradation of FRP materials in neutral, acidic and basic aqueous solutions". - To be published.
9. **Wayne. C. Tucker and Richard Brown,** " Blister formation in galvanically coupled graphite / steel in sea water", Journal of composite materials, 23 (1989) 107- 115.

Table .1. Effect of absorption of water on the mechanical properties of vinyl ester composites

TEST	LOAD AT BREAK (KN)	DISPLACEMENT AT BREAK (mm)	% STRAIN AT BREAK	STRESS AT BREAK (MPa)	YOUNG'S MODULUS (MPa)
Unexposed	12.87	3.2	2.10	97.87	7092
Water -40 °C	11.6	2.30	1.53	91.33	7059
Water- 80°C	10.86	2.15	1.43	85.51	7029
Water -100°C	9.86	2.05	1.37	77.67	6950

Fig. 1. SEM micrographs showing vinyl ester matrix, a) before exposure and b) after exposure to bacterial culture for 21 days.

Fig. 2. SEM micrographs, showing the degradation of a) glass fibre-isophthalic ester composite in SRB bacteria and b) glass fibre-vinyl ester composite in ODB, SBC bacteria culture, exposed for 21 days.

Fig. 3. SEM micrographs, showing a) fibre pull out and b) matrix debris on glass fibre-vinyl ester composite due to exposure to ODB, SRB culture for 21 days.

Fig.4. SEM micrographs showing a) galss fibre without any exposure, b) glass fibre, exposed to culture medium alone, and with SRB bacteria after c) 10 days and d) 21 days.

Fig. 5. SEM micrographs, showing the degradation of glass-vinyl ester composite due to water adsorption at 100°C for 10 days immersion, a) fibre pull out in in the vinyl ester composite and b) broken fibres in the isothalic ester composite.

Fig. 6. Weight change plots of a) isophthalic ester composite and b) vinyl ester composite, tested in immersion water at various temperatures.

Fig. 7. SEM micrograph showing the degradation due to absorption of acid. broken fibre and fibre pull out is seen for 24h exposue in 1N HCl.

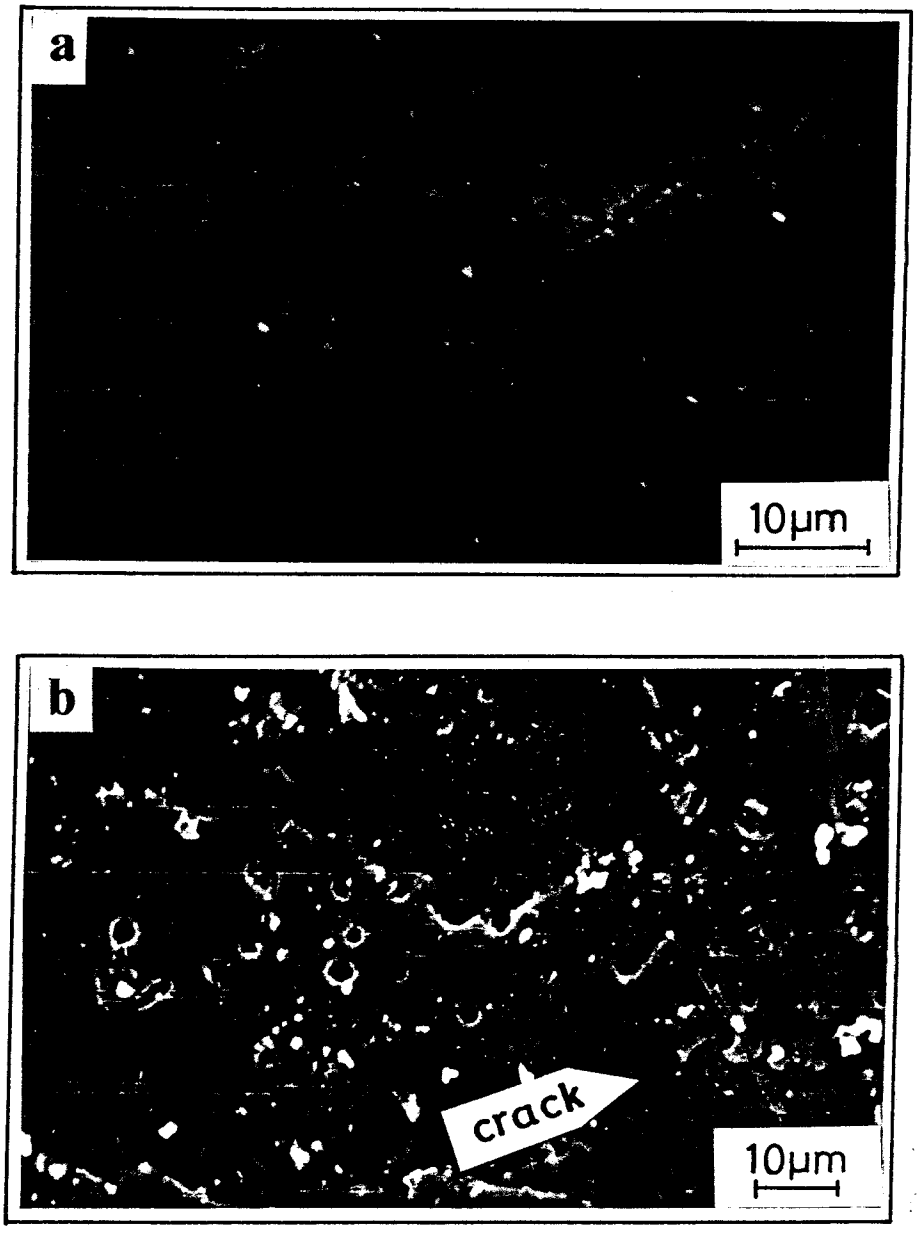

Fig. 1. SEM micrographs showing vinyl ester matrix, a) before exposure and b) after exposure to bacterial culture for 21 days.

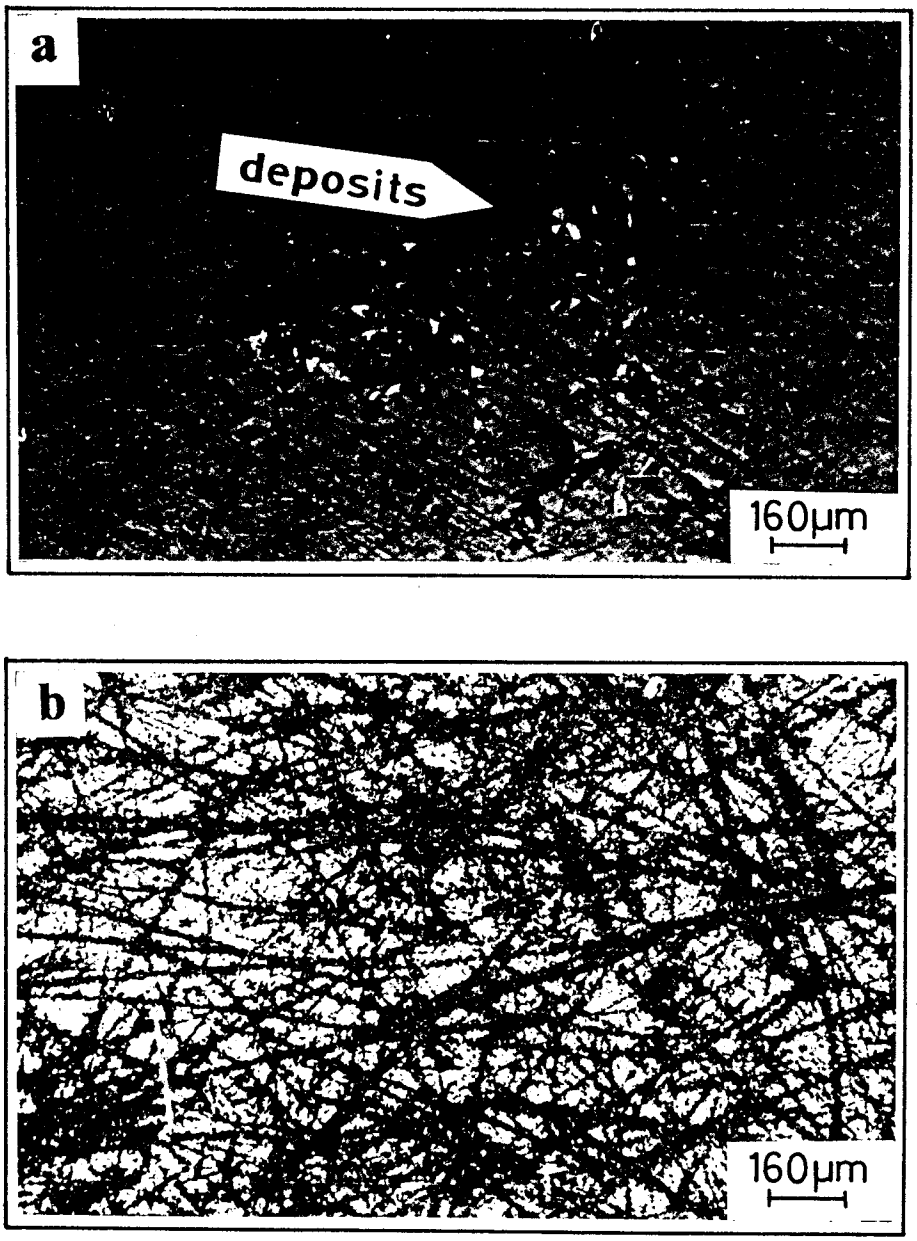

Fig. 2. SEM micrographs, showing the degradation of a) glass fibre-isophthalic ester composite in SRB bacteria and b) glass fibre-vinyl ester composite in ODB, SBC bacteria culture, exposed for 21 days.

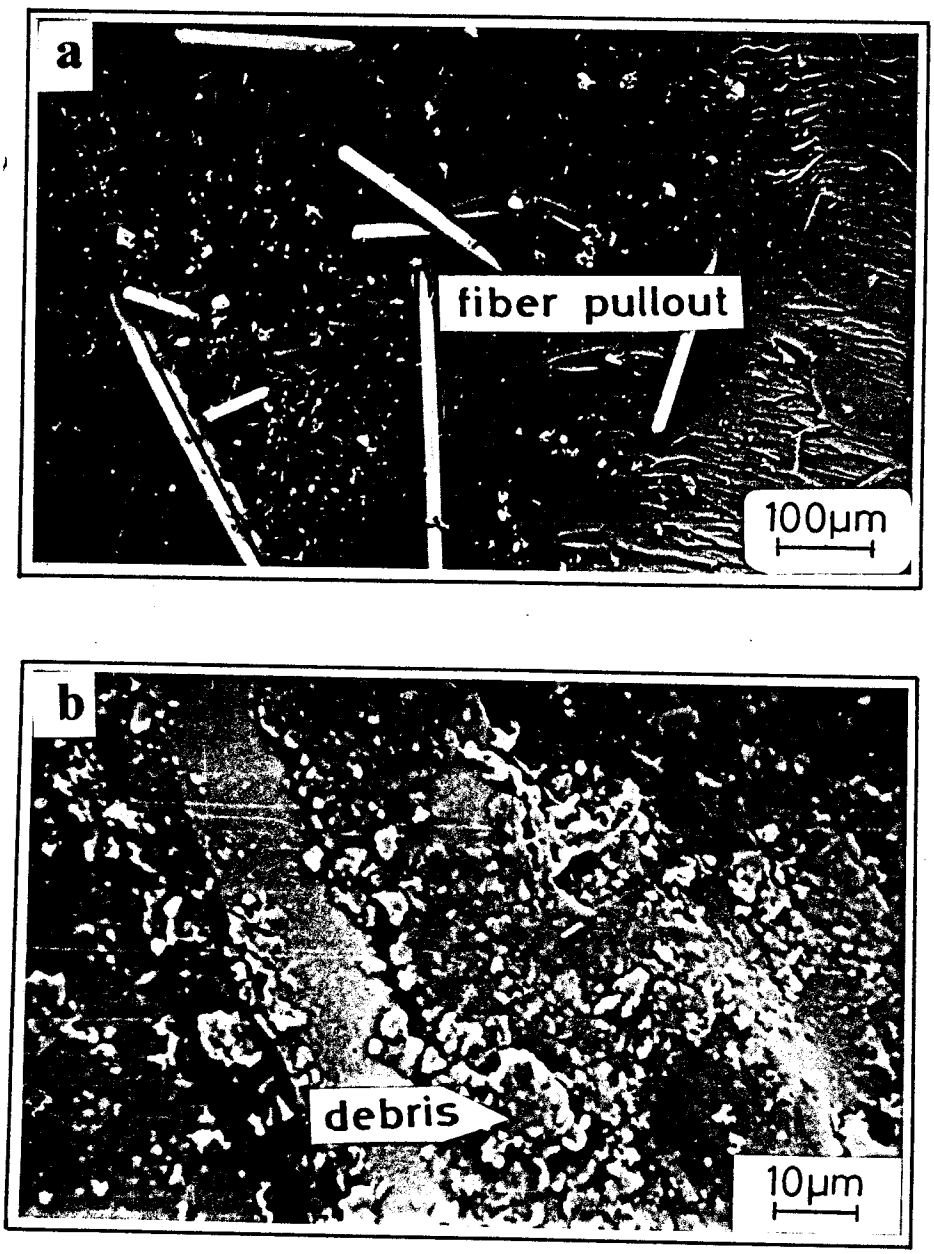

Fig. 3. SEM micrographs, showing a) fibre pull out and b) matrix debris on glass fibre-vinyl ester composite due to exposure to ODB, SRB culture for 21 days.

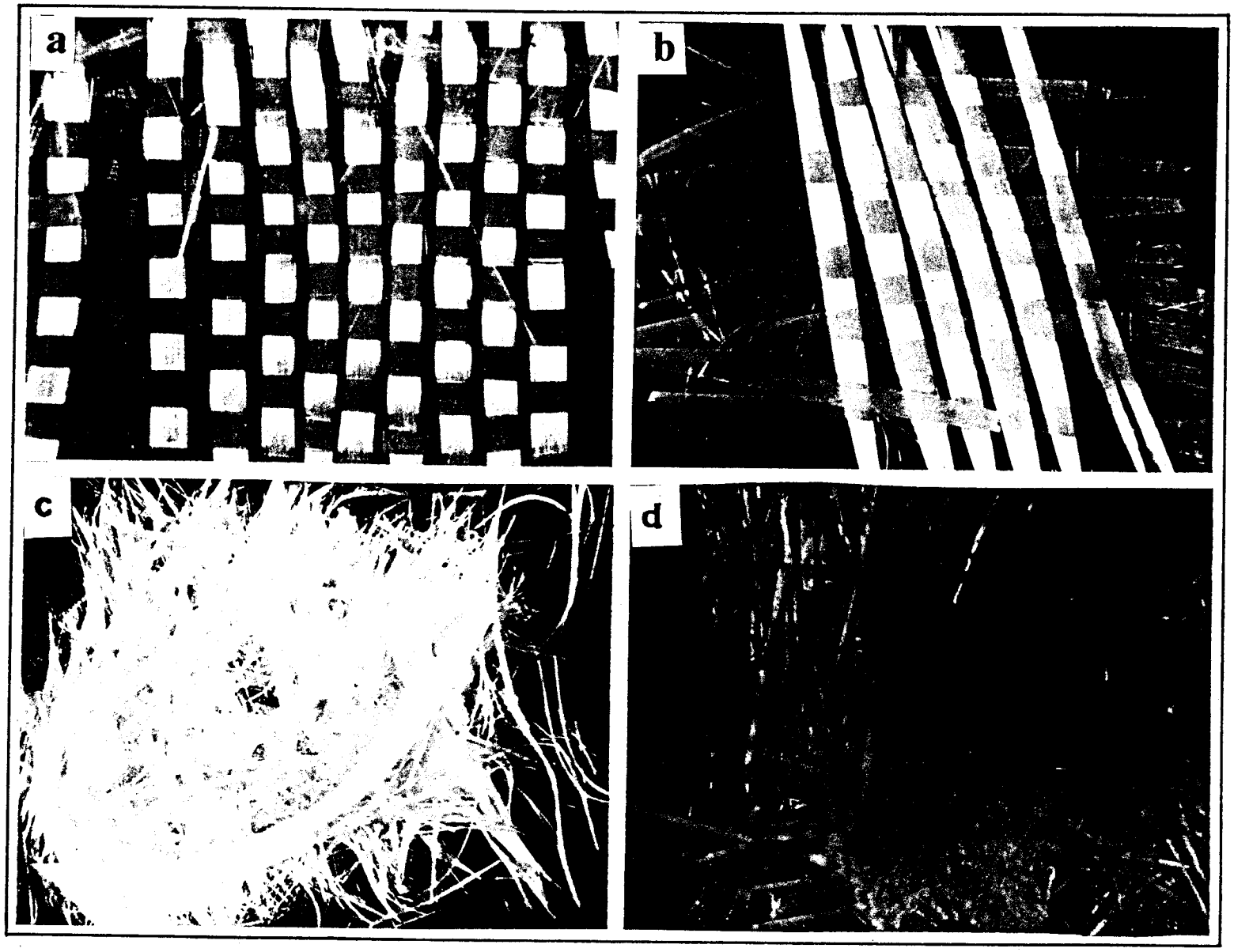

Fig.4. SEM micrographs showing a) galss fibre without any exposure, b) glass fibre, exposed to culture medium alone, and with SRB bacteria after c) 10 days and d) 21 days.

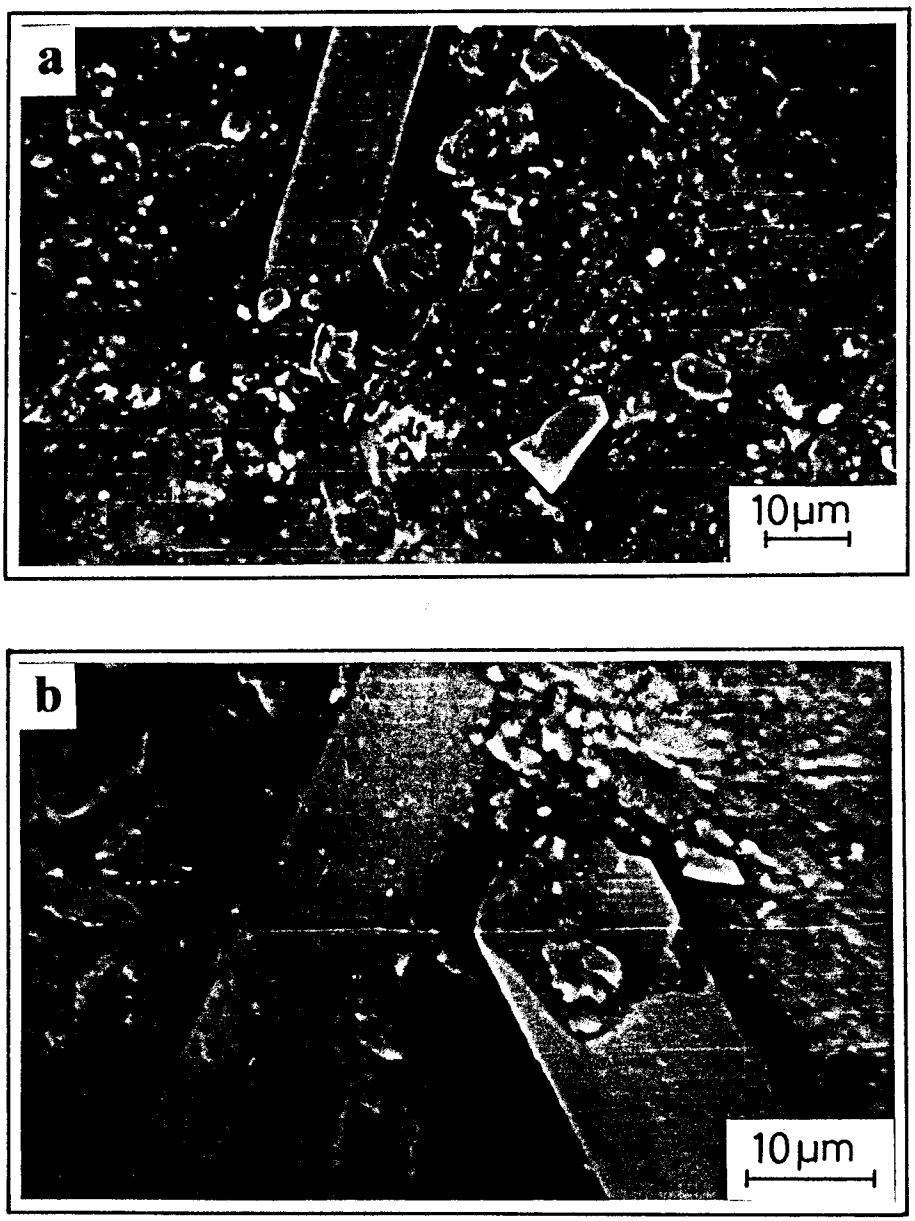

Fig. 5. SEM micrographs, showing the degradation of glass-vinyl ester composite due to water adsorption at 100°C for 10 days immersion, a) fibre pull out in in the vinyl ester composite and b) broken fibres in the isothalic ester composite.

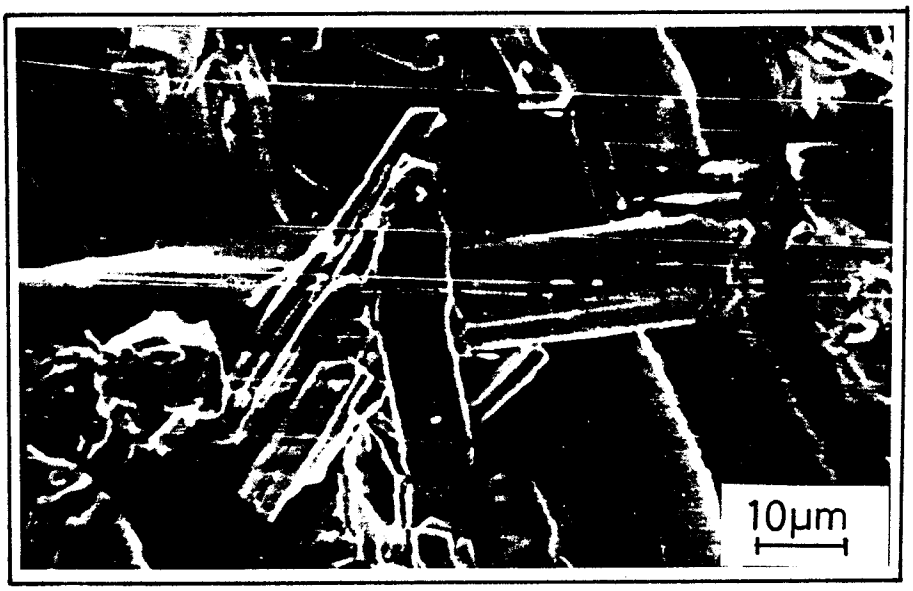

Fig. 7. SEM micrograph showing the degradation due to absorption of acid. broken fibre and fibre pull out is seen for 24h exposue in 1N HCl.