Chemical resistance of E-glass reinforced polyester composites made by pultrusion

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Abstract

As pultruded composites can be used in different chemical environments, a good understanding of their corrosion behaviour is necessary.
In this work, the chemical resistance of pultruded E-glass fibre reinforced polyesters with different filler types is studied. The mechanical, physical, optical and structural properties of the pultruded flat profiles before and after immersion in different chemicals, e.g., sea water, demineralised water, sulfuric acid (10%) and sodiumhydroxide (5%) are analysed.

1 Introduction

Pultruded composites can be used as structures, handrails, ladders, gratings, vessels and tanks in various industrial environments (e.g. chemical industry, nutrition industry, paper industry, waste water treatment). (Lubin[1], Trevor Starr[2], Martin[3])

Compared to traditional materials, e.g. metal, wood and concrete, composites are appreciated for their lower weight, good mechanical properties, electrical and thermal insulation characteristics, lower demand for painting and maintenance and better wear, weathering and corrosion resistance. The last mentioned characteristic is one of the main reasons for the use of composites in chemically aggressive environments.

Although fibre reinforced plastics cannot corrode in the strict meaning of the word, they do however degrade in other manners when exposed to

chemical environments. Corrosion data and corrosion design data of pultruded glass fibre reinforced plastics are sparsely available (e.g. Sonawala[4], Sonawala[5], Harris[6], Haarsma[7]) since corrosion studies are mainly restricted to compression moulded laminates containing 30 w% glass and based on an unfilled clear resin.

A good understanding of the corrosion behaviour of the pultruded composites is necessary in order to guarantee the lifetime and the safety of the structural components in service.

In this work, the chemical resistance of pultruded E-glass fibre reinforced polyesters with different filler types is studied. The mechanical, physical, optical and structural properties of the pultruded flat profiles before and after immersion in different chemicals, e.g., sea water, demineralised water, sulfuric acid (10%) and sodiumhydroxide (5%) are analysed.

2 Experimental procedure

Flat profiles (l x t, 80x3 (mm)) of E-glass reinforced isopolyester were pultruded.

The polyester resin used for the pultrusions is isophtalic polyester, a polyester of isophtalic acid, maleïc acid anhydride and propylene glycol cross-linked with styrene monomer. Rovings (4800 tex) and continuous strand mats (450 g/m^2) of E-glass are used as reinforcement material. Calciumcarbonate or clay serves as a filler. Pultruded composites without filler are also made. Curing of the thermoset polyester is initiated and enhanced by peroxy catalysts. A phosphatic lubricant serves as a release agent. A polyethylene terephtalate veil (40 g/m^2) is used to cover the glass fibre reinforced plastic with a protective resin rich layer. The pultruded composite contains 50 w% and 60 w% glass. The dimensions of the strip are 100*3 mm.

The pultruded composites were examined on their mechanical, physical, optical and structural properties.

Strips of the pultruded composites (200*100*3 (mm)) were exposed to seawater (in unstressed and stressed state), demineralised water, sulfuric acid 10% and sodiumhydroxide 5%. The samples are examined on their mechanical, physical, optical and structural properties after 30, 90, 180 and 360 days of immersion. (cfr. ASTM C581-83) (As the corrosion tests are still going on, some test results are not available at this moment.)

All immersed samples are weighted on an analytical balance, the dimensions are measured with a micrometer.

The visual defects are classified according to ASTM D4385-84a.

The flexural properties are measured with a Monsanto T10 tensile testing machine according to ASTM D790-86. The support span to depth ratio is 32 (L/d=32/1).

The tensile properties are measured with a Zwick 1485 tensile testing machine according to ASTM D638-89.

Barcol hardness is measured with a Barcol-Colman impressor according to ASTM D2583-87.

The structure of the composite and the fracture surfaces are analysed with a scanning electron microscope (SEM) Philips 501. The samples were glued on a sample holder and coated with a gold layer of approximately 150 Å. The accelerating voltage of the instrument is 30 kV.

The failure mode is also analysed with optical microscopy (OM).

The colour and the gloss of the sample is measured with an ICS-Texicon colorimeter. Measurements were made with the specular component included and excluded. A D65 illuminant is chosen and the reflectance is measured between 400 nm and 700 nm at 20 nm intervals under 2° and 10° observation.

3 Results and discussion

3.1 Test samples

The pultruded composites under study are:
UP50z: unsaturated iso-polyester, 50% E-glass, no filler
UP50c: unsaturated iso-polyester, 50% E-glass, chalk as filler
UP50k: unsaturated iso-polyester, 50% E-glass, kaolin clay as filler
UP60z: unsaturated iso-polyester, 60% E-glass, no filler
UP60c: unsaturated iso-polyester, 60% E-glass, chalk as filler
UP60k: unsaturated iso-polyester, 60% E-glass, kaolin clay as filler

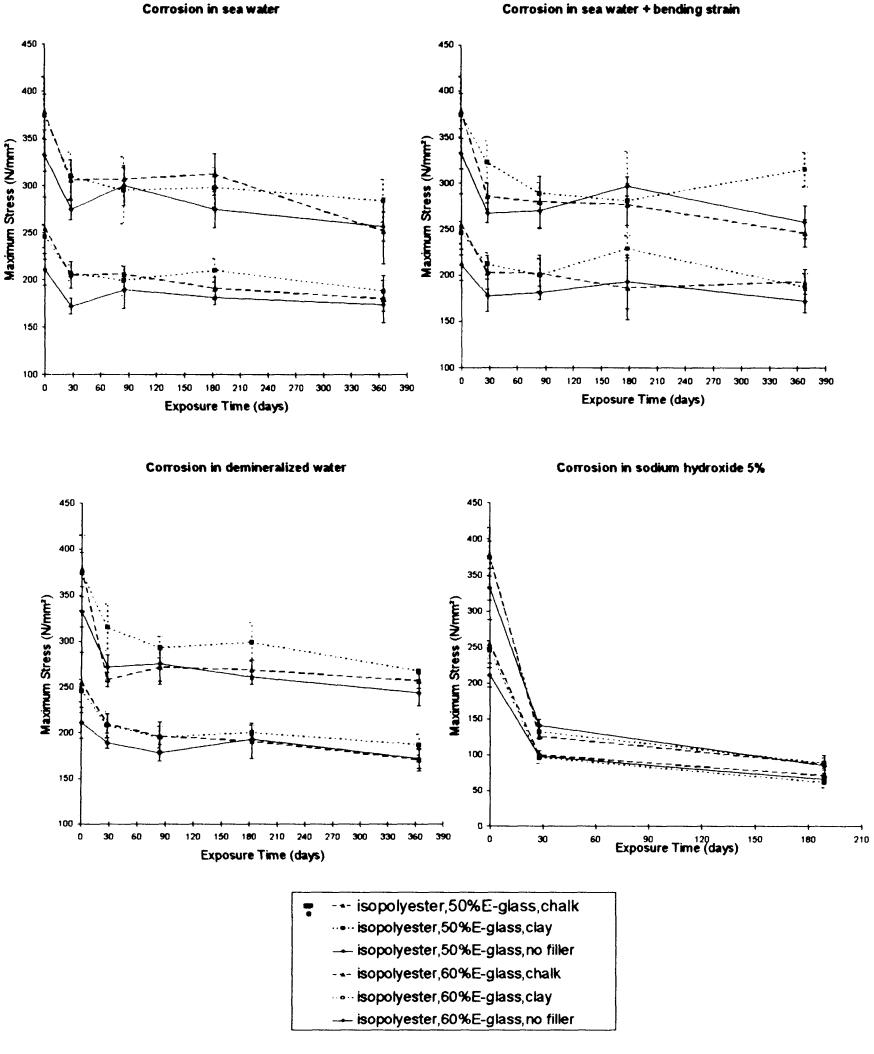
3.2 Dimensions and weights

In general, the weights of the pultruded composites increase after immersion due to absorption of the fluid. Variations in the dimensions of the samples are recorded.

3.3 Flexural tests

The maximum load (F_m), the maximum stress (S_m), the strain at maximum stress (r_m), and the modulus of elasticity in bending (E_b) are measured with 3-point loading test. The mean values of the testing results, the standard deviations and the coefficients of variation are calculated.

The flexural strength (maximum stress in outer fibre at moment of break) against the test periods for the various samples and per type of chemical are given in the following charts.



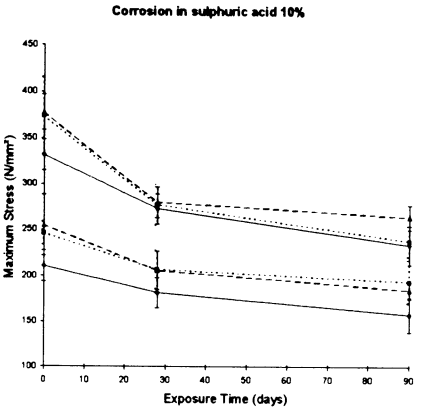


Figure 1: Maximum stress vs. exposure time for pultruded composites in different chemical environments.

Six kinds of pultruded composites are under study. They all consist of an isopolyester matrix reinforced with 50% or 60% E-glass. The composites are either unfilled or filled with chalk or kaolin clay.
As expected the mechanical properties of the pultruded composites with the highest reinforcement level are the best. Considering the fillers, the composites filled with clay or chalk are stronger than the unfilled composites.

A deterioration of the mechanical properties of the pultruded composites in flexure after exposure is observed. The reduction in strength and moduli is most obvious after one month exposure. Thereafter, considering the standard deviations, the mechanical properties are roughly maintained.
The same kind of observations are made for the hardness of the samples.(see further)
The absorption of the chemicals by the matrix (higher weights and higher thicknesses are determined) results in a drop of the mechanical properties after one month of exposure. Due to a saturation of the system, no real deterioration of the mechanical and physical properties after three and six months of exposure is seen.
A further and real drop in the mechanical properties is expected when the glass fibres will be attacked by the chemicals.

The results point out that demineralised water has a stronger corrosive effect than sea water. Due to the osmotic effect of demineralised water, low molecular components are leached out of the matrix resulting in a deterioration of the properties. The extra voids in the samples are seen on the electron microscopy photographs.

The corrosive effect of sulphuric acid is mostly seen on the pultruded composites filled with chalk or clay, due to chemical reaction with the fillers. Visual inspections and SEM also show the corrosive effect of sulphuric acid.

For sodium hydroxide, an abrupt drop in the mechanical properties after one month of exposure is observed. Sodium hydroxide attacks the polyester matrix, causing a saponification of the matrix. The E-glass fibre is also attacked, a leaching out of some ions and ion exchange took place.

The fracture mechanics in flexure of the composites is a delamination between the mat reinforcement and the rovings due to the accumulation of stress between these layers.

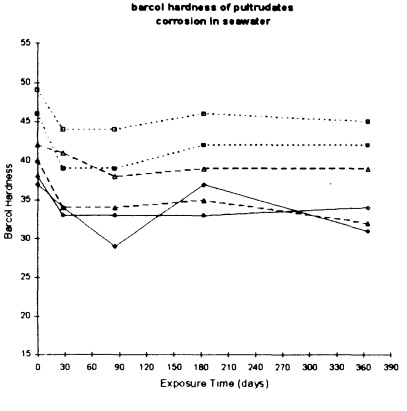
3.4 Tensile tests

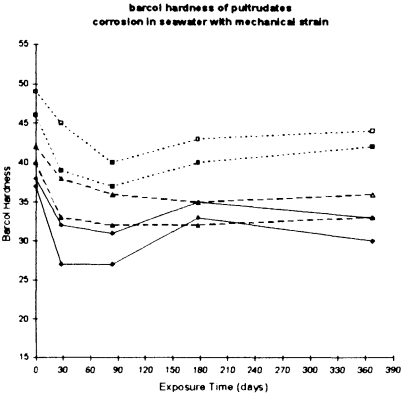
Exposure of the different pultruded composites to sea water, demineralised water, sulphuric acid (10%) and sodiumhydroxide (5%) results in a diminution of the tensile strength. This is most obvious for the environments sodium hydroxide and sulphuric acid. Attack of the glass fibres by sodiumhydroxide results, after one month exposure, in a drop of the tensile strength of 50%, and even more. After three months exposure to sulphuric acid, a 70-80% retention of the tensile strength is observed.

Variations in the elastic moduli are also mostly expressed for the samples exposed to sulphuric acid and sodium hydroxide.

3.5 Barcol hardness

The Barcol hardness of the pultruded composites before and after exposure are given in following charts.





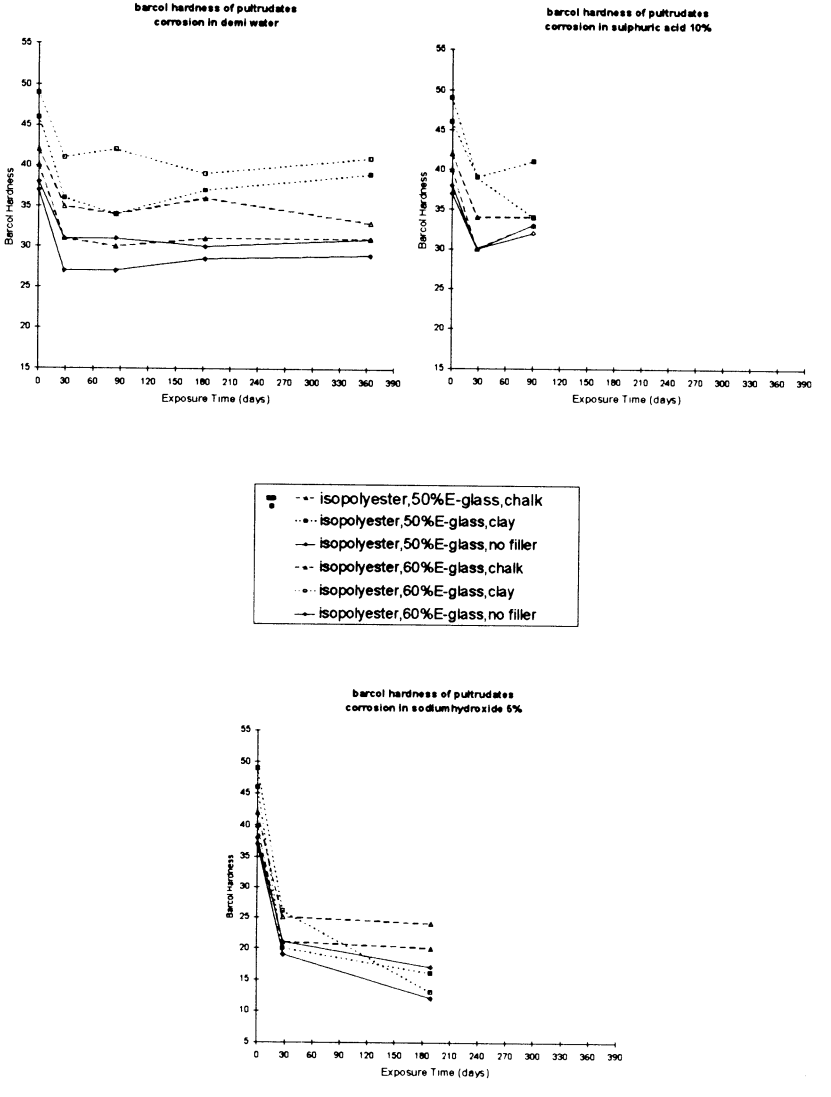


Figure 2: Barcol hardness vs. exposure time for pultruded composites in different chemical environments.

The Barcol hardness of the composites filled with clay are higher than those with chalk as a filler. The unfilled composites have the lowest hardness. The higher the glass content, the higher the Barcol hardness is valid for each of them.

A reduction of the Barcol hardness after exposure to the different environments is seen. The highest decreases are seen after one month of exposure. The corrosive effect of sodium hydroxide and sulphuric acid is most obvious.
Remarkable is the increasing hardness of the composites after longer times of exposure to sulphuric acid due to the higher expression and visibility of the glass mats on the surface and the erosion of the polymers.

3.6 Visual observations

The visual defects are in agreement with the other techniques.

3.7 Scanning Electron Microscopy

With the electron microscope little cracks on the surface and the cross sections of the composites are seen. Those cracks are the results of crimp and bad impregnation during the pultrusion process. In these weak points a migration of the exposure fluid can take place.

After exposure and depending on the type of environment, more cracks on the surface just beside a glass fibre and deeper cracks in the cross section as a result of dissolvation of matrix material and debonding between the glass fibres and the matrix material were seen.

The results of SEM are in agreement with the mechanical observations.

3.8 Colour Matching System

The percentage reflectance at different wavelengths and the tristimulus values L, a, b, the hue h, chroma C and white index are measured.

Exposure of the samples to the corrosive environment results in yellowing and diminution of the lightness L of the surfaces.
The effects are mostly expressed after exposure to sodium hydroxide.

4 Conclusions

The chemical resistance -against sea water, demineralised water, sulphuric acid (10%) and sodiumhydroxide (5%)- of pultruded E-glass fibre reinforced polyesters with different filler types is studied.

The results point out that sodium hydroxide is the most corrosive environment, followed by sulphuric acid. Sea water is less corrosive than demineralised water.

References

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