OUTDOOR WEATHERING OF GLASS FIBRE REINFORCED POLYESTER AND VINYL ESTER COMPOSITES: FIRST RESULTS AFTER ONE YEAR EXPOSURE

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ABSTRACT

In the current paper, first results of a long-term outdoor exposure tests of glass fibre reinforced polyester and vinyl ester composites, conducted at seven European sites, are reported. Aged specimens from the first three exposure periods were tested for their colour, gloss, hardness and flexural strength. Relative changes in the properties tested were examined as functions of accumulated UV exposures. Ageing environments were ranked according to the severity of the UV exposure and other major environmental stress factors: temperature, precipitation, humidity and tropospheric ozone concentration. Spearman rank correlation analysis was applied on the relative property changes in the specimens and the severity of environmental agents. Statistically significant correlation coefficients were considered indicators for factors mainly responsible for the observed property change.

Evolution in all properties and especially in hardness and flexural strength was found resin dependent. The stress factors most severely degrading the materials were found both resin and property specific. The most significant results in the performed Spearman rank correlation test were obtained for UV exposure causing the yellowing (in GFR polyester), heat stress contributing both to the yellowing (in GFR polyester and vinyl ester) and decrease of flexural strength (in GFR polyester), and precipitation also promoting the yellowing (in GFR vinyl ester). In general, GFR polyester appeared slightly more susceptible to weathering than GFR vinyl ester over the first year of the experiment. Differences in the performance might be traced to higher resistance of GFR vinyl ester to two phenomena: Norrish II types photochemical processes and hydrolytic degradation.

1. INTRODUCTION

In spring 2005, a material research project funded by the Finnish Meteorological Institute and the Finnish Funding Agency for Technology and Innovation was launched. The project was named UVEMA (UV radiation Effects on MAterials). Within the framework of the project, a weathering network of seven European sites (Fig. 1) was established. The network extends from the Canary Islands of Spain (latitude 28.5°N) to the Lapland of Finland (latitude 67.4°N), covering a wide range of weathering conditions. Since autumn 2005, the sites of the network have been maintaining weathering platforms of specimens of different kinds of polymeric materials, including glass-fibre-reinforced polyester and vinyl ester composites. Tests of the weathered samples are to provide unbiased information on the degradation of the materials in their real outdoor service environments. Environmental data collected from the test sites over the weathering experiment will also make it possible to estimate the correlation between accelerated test environments and the natural service environments.

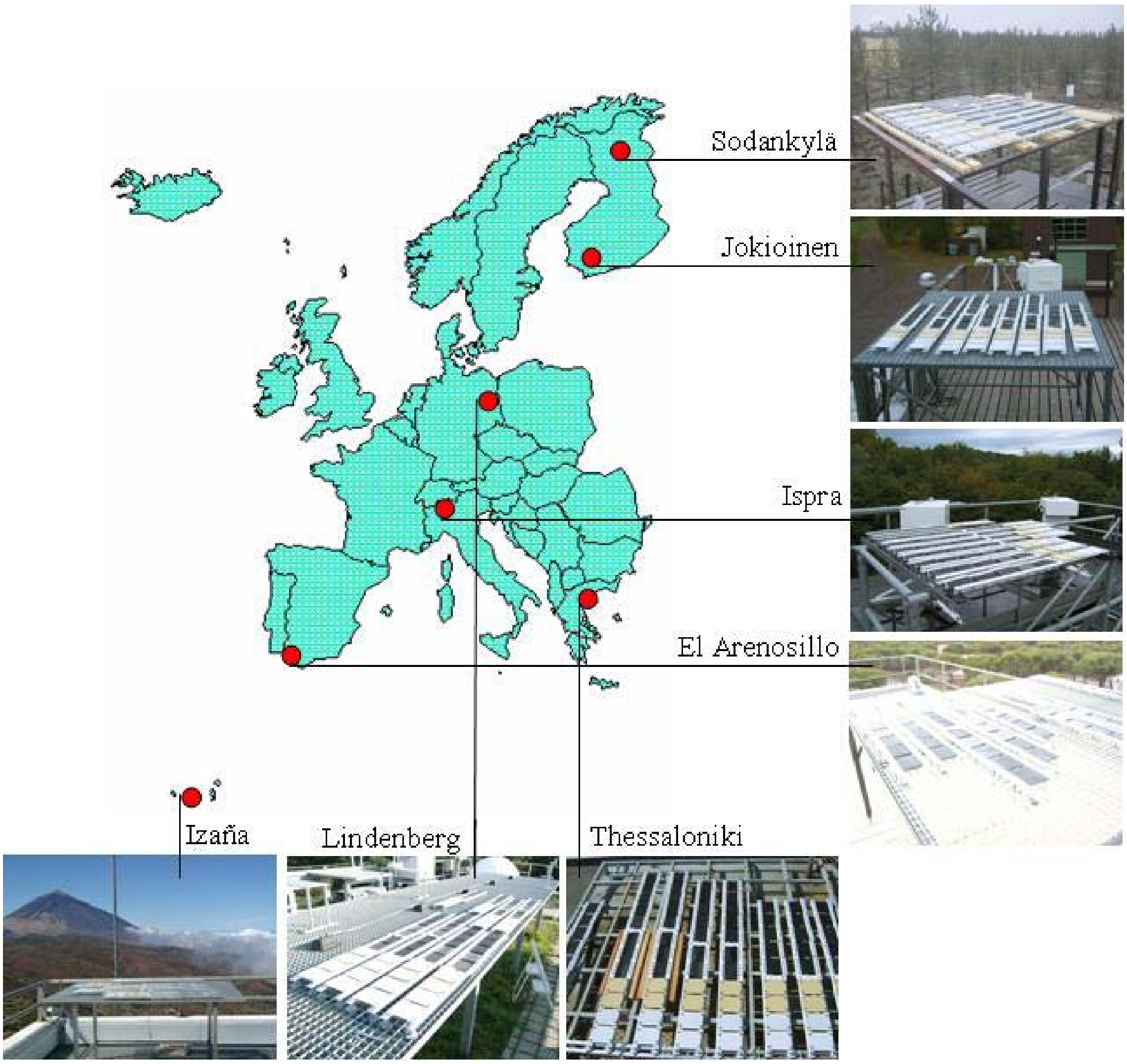


Figure 1. Outdoor weathering network established within the UVEMA project. Whitish plates in the racks are the GFR polyester and vinyl ester samples.

In this paper, we will for the first time report on the results of our four-year outdoor exposure tests of GFR polyester and vinyl ester composites. Results from the first three epxosure periods of lengths 44-292 days are presented. Weathering characteristics of the test sites is depicted and changes in material properties as regards to colour, gloss, hardness and tensile strength are examined. Main stress factors attributable to the observed property changes are distinguished through the use of Spearman's rank correlation analysis. Differences between the ageing behaviour of GFR polyester and vinyl ester are discussed.

2. EXPERIMENTAL

2.1 Test sites

The test sites were selected from the sites regularly submitting spectral UV irradiance data to the European UV database hosted by the Finnish Meteorological Institute (http://uvdb.fmi.fi/uvdb). In addition to the high quality of the UV measurements, the selection criteria included regular on-site measurements of the major meteorological parameters and nearby monitoring of tropospheric ozone concentration. The sites were selected in such a way that a representative European scale of the weathering parameters would be covered. The main characteristics of the sites are listed in Table 1.

Table 1. Characteristics of the sites forming the UVEMA network.

Type	Site	Country	Lat° (N)	Lon° (E)	Alt (m)	UV-I (max)	Level of pollution	Relative humidity
northern	Sodankylä	Finland	67.4	26.6	179	5	low	moderate
	Jokioinen	Finland	60.8	23.5	104	6	low	moderate
central	Lindenberg	Germany	52.2	14.1	100	8	moderate	moderate
southern	Ispra	Italy	45.8	8.6	214	9	moderate	moderate
	El Arenosillo	Spain	37.1	-6.7	41	10	low	high
	Thessaloniki	Greece	40.6	23.0	20	10	high	high
extreme	Izaña	Spain	28.5	-16.5	2367	13	low	low

2.2 Exposures

The weathering of the GFR polyester and vinyl ester composites started in autumn 2005. Until autumn 2007, five specimen batches have been removed from exposure by following a pre-defined schedule [1] for post-exposure material testing. The schedule was based on predicted accumulation of UV dose. Start and end dates for the first three exposure periods, together with the length of the periods, are listed in Table 2.

Table 2. Start dates, end dates and lengths of the first three exposure periods within the outdoor exosure programme.

Site	Start date	Period #1		Period #2		Period #3	
	(ddmmyy)	End date	Length (d)	End date	Length (d)	End date	Length (d)
Sodankylä	090905	240306	197	070506	241	270606	292
Jokioinen	210906	220306	183	100506	232	020706	285
Lindenberg	270905	130206	140	010506	217	290606	276
Ispra	041005	210106	110	210406	200	270606	267
El Arenosillo	220905	071105	47	100406	201	250606	277
Thessaloniki	170905	221005	36	210306	186	180606	275
Izaña	111005	231105	44	130306	154	190606	252

Measurements of spectral UV irradiance, temperature, humidity, precipitation and tropospheric ozone concentration were conducted by each test site along the weathering experiment (Fig. 2). Measured data were collected from the test sites and stored into a database.

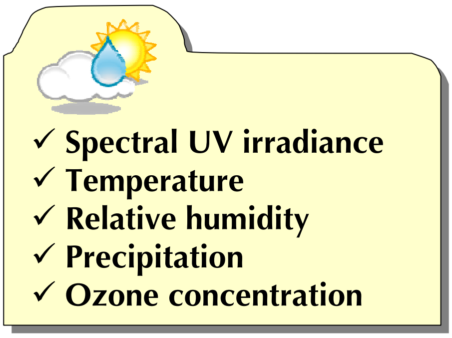


Figure 2. Environmental data collected from the test sites.

2.3 Composite materials

The composites are short glass fibre reinforced polyester and vinyl ester. The materials only differed from each other in respect of the matrix resin. No stabilizers were used in manufacturing of the samples.

2.4 Test methods

Surface and bulk property changes of the weathered samples were characterized by measurements of colour, gloss, hardness and strength. A summary of the test methods is given in Table 3.

Table 3. Methods used in testing the properties of the exposed samples.

Property tested	Equipment	Quantity measured
Colour	Minolta Chroma Meter CR-200	Colour in Yxy notation (Y = lightness in %; xy = colour tones)
Gloss	Zehnter Glossmeter 2 GM 75°	Gloss angle in degrees
Hardness	AFFRI Hardness Tester	Hardness in Shore D scale
Strength	Messphysik MIDI 10-20/4x11	Flexural strength in MPa

2.5 Data analysis methods

The temporal resolution of the primary environmental data varies from 10 minutes to 3 hours and daily means or sums. For coherent data analysis, suitable secondary quantities have to be derived from the collected data. For temperature, relative humidity and ozone concentration, this is performed in two steps. First, daily means are computed from the primary data series for each site. Next, medians of the daily means are computed for each exposure period and for each site. To make the figures computed for periods of different lengths commensurable, the medians are further multiplied with the lengths of the periods. For precipitation, accumulations over the periods are computed. For UV exposure, predicted accumulation of CIE erythemally weighted UV dose is used as in exposure timetable planning. The figures computed and passed to further analysis are summarized in Table 4.

Table 4. Environmental stress factors and the quantities assumed to represent the stress on the materials over the exposure periods of varying lengths.

Stress factor	Quantity describing the stress over the period	Unit
UV radiation	Sum of the daily sums	kJ m^{-2}
Temperature	Median of the daily means × length of the period	K days
Precipitation	Sum of the daily sums	mm
Relative humidity	Median of the daily means × length of the period	% days
Ozone concentration	Median of the daily means × length of the period	μg m^{-3} days

From the test results of the exposed samples, averages of the five measurements are computed. Averages for gloss, hardness, and flexural strength are used as such in the following analysis. From the colour measurements, none of the measured values Yxy appeared suitable for describing the white colour of the unexposed samples turning into yellowish. Therefore, the yellowness index YI, defined by formula

$$YI = \left[(1.28X - 1.06Z)/Y\right] \times 100 \qquad (1)$$

and earlier used by, e.g., Cho et al. [2], was computed and used as a measure of colour change. In formula (1), symbols XYZ denote tristimulus values that can be computed from the Yxy-coordinates by using equations

$$X = \frac{xY}{y}\ ,\ Y = Y \text{, and } Z = \frac{(1-x-y)Y}{y}. \qquad (2)$$

Spearman rank correlation analysis is employed to find out the stress factors attributable to the property changes observed in the exposed samples. The exposure treatments (N=21) are ranked according to the values of the quantities given in Table 4, i.e., the severity of each stress factor. Relative property changes, as compared to the unexposed samples, are ranked similarly. Correlation between the variables (X_1,X_2) = (rank number of exposure, rank number of relative property change) is examined by computing the Spearman rank correlation coefficient ρ_S. If the null hypothesis is formulated as H_0: "X_1 and X_2 are independent of each other, $\rho_S = 0$", the obvious formulation of the alternative hypotheses is either H_1: "X_1 and X_2 are positively correlated with each other, $\rho_S > 0$" or "X_1 and X_2 are negatively correlated with each other, $\rho_S < 0$". By performing one-tailed tests of H_0 at confidence levels $\alpha = 0.01$ and $\alpha = 0.05$, statistically very significant and significant rank correlations, respectively, are distinguished.

3. RESULTS AND DISCUSSION

3.1 Exposure environments

Values computed for the quantities listed in Table 4, describing the strength of each environmental stress factor over each exposure period, were first examined separately from the data obtained from the tests of the exposed samples. To quantify the average harshness of the weathering microclimates prevailing by each test site over the exposure periods, the rank numbers obtained by each site during the three exposure periods were defined. The resulting numbers were used to arrange the sites from the mildest to the hardest weathering environments as shown in Table 5.

Table 5. Sites ranked according the severity of the different stresses, number 1(7) in each column indicating the mildest(hardest) exposure. UV = UV stress; T = heat stress; P = stress caused by rain; RH = stress caused by moisture; O_3 = stress caused by ozone concentration of the air.

Site	Period #1					Period #2					Period #3				
	UV	T	P	RH	O_3	UV	T	P	RH	O_3	UV	T	P	RH	O_3
Sodankylä	1	7	7	7	7	1	7	4	6	6	1	6	3	6	4
Jokioinen	2	6	6	6	5	2	6	3	7	4	2	4	2	7	3
Lindenberg	3	5	5	5	6	3	5	5	5	7	3	3	5	5	6
Ispra	4	4	3	4	1	4	3	6	4	1	4	2	6	3	1
El Arenosillo	5	3	2	1	2	5	4	2	2	2	5	7	4	2	2
Thessaloniki	6	2	4	3	3	6	2	7	3	3	6	5	7	4	5
Izaña	7	1	1	2	4	7	1	1	1	5	7	1	1	1	7

The ranks for UV stress is exactly the same for every period, as the timing of the exposure was adjusted to the accumulation of UV. For the other factors, the ranks differ from period to period, as expected. The result obtained for heat stresses, especially during the first period, may appear peculiar at first sight. However, it is explained by the start of exposure taken place in the autumn and the varying lengths of the periods.

3.2 Property changes in GFRPs

The property changes were first viewed in terms of medians of the relative changes occurred over the exposure periods. The bar charts are shown in Fig. 3.

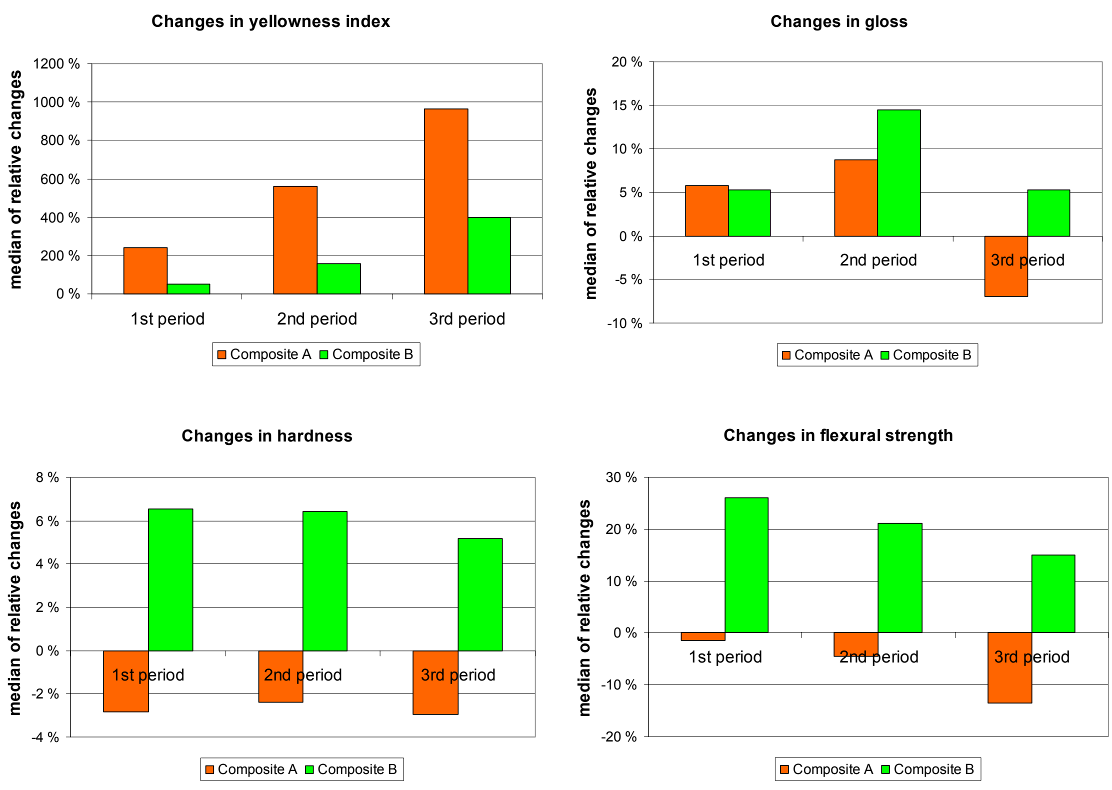
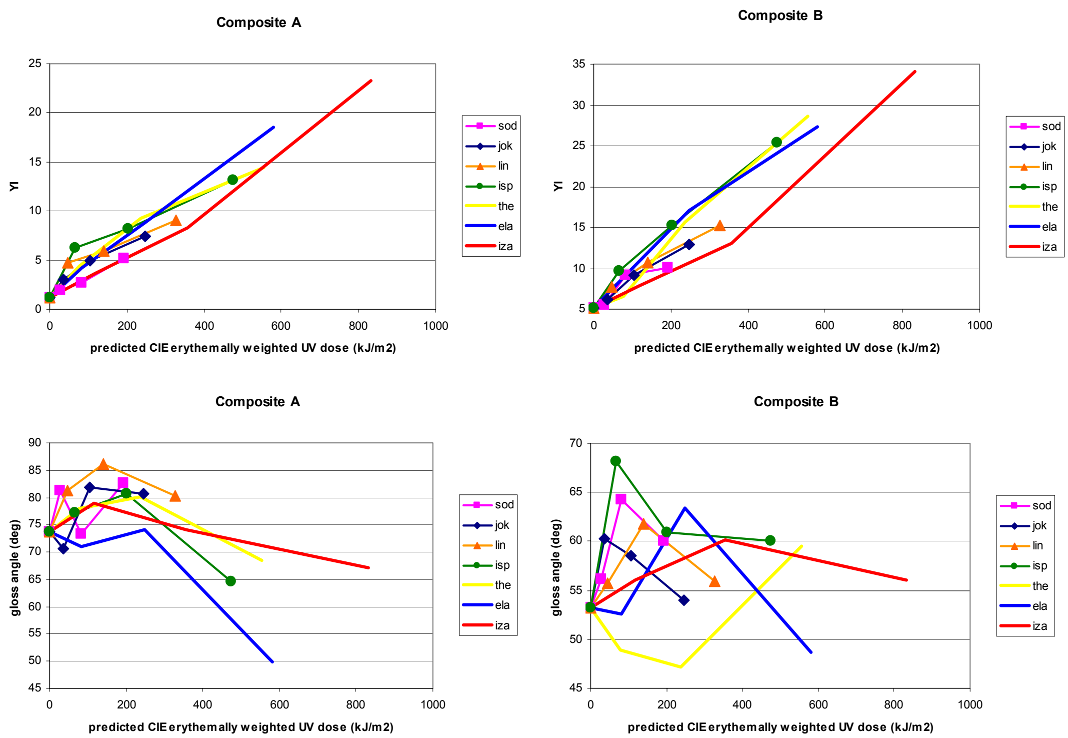


Figure 3. Medians of the relative property changes of the exposed composite samples over the first three exposure periods, with Composite A denoting the GFR polyester and Composite B denoting the GFR vinyl ester.

The change in the yellowness index is remarkable and in the same direction for both GFR composites. GFR polyester seems to turn yellow more rapidly than GFR vinyl ester. Changes in gloss include an initial increase of gloss, followed by a decrease as the weathering proceeds. Again, GFR polyester looses its gloss more rapidly than GFR vinyl ester. Changes in hardness are not high in percentages, but occur in the opposite directions for the two types of composites. While the hardness of GFR polyester increases, the hardness of GFR vinyl ester decreases. Changes in flexural strength repeat the same feature: GFR vinyl ester gets stronger, but GFR polyester weaker.
The temporal evolution of the properties were next viewed by plotting the observed changes as functions of predicted accumulation of UV dose. The results are shown in Fig. 4.



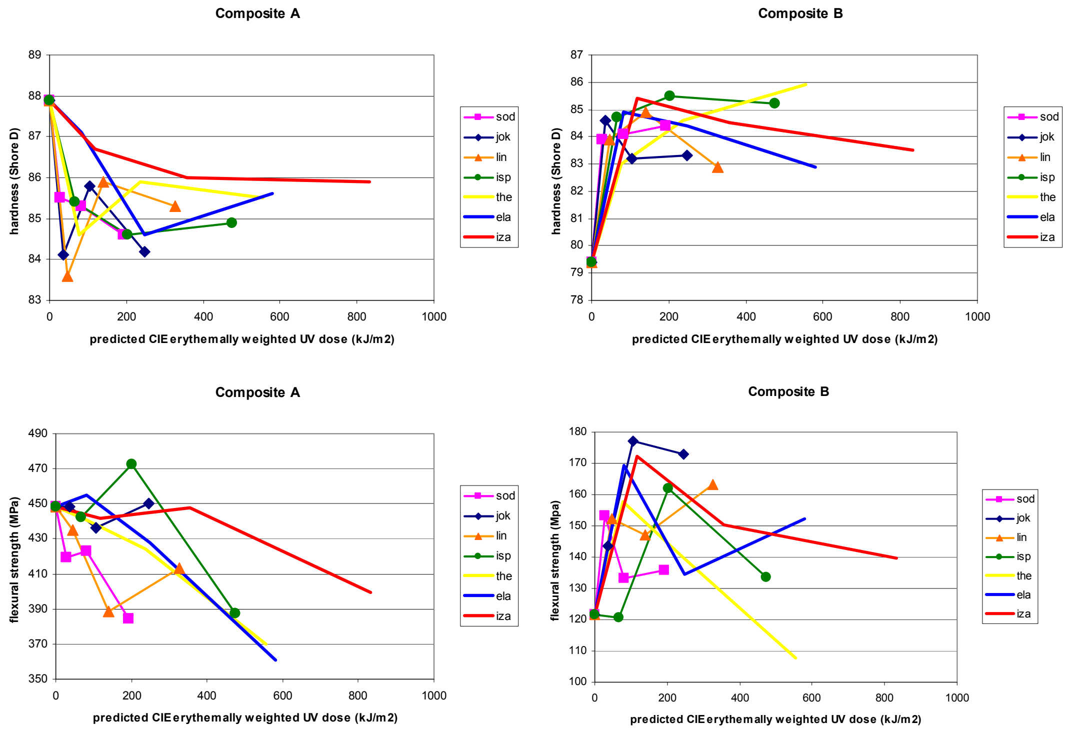


Figure 4. Property changes observed in the exposed samples over the first three exposure periods as functions of predicted accumulation of UV dose.

The same features as revealed by the medians studied above may be detected in the graphs of Fig. 4 as well. On the basis of the graphs, UV stress could be expected to explain most of the yellowing. For the other property changes, UV is clearly not the only factor attributing to the changes.

3.3 Spearman rank correlation analysis

To proceed towards the estimation of the most important agents, Spearman rank correlation analysis is next performed as described in section 2.5. The correlation coefficients are shown in Table 6. The statistically very significant ($\alpha = 0.05$) coefficients are surrounded with a thick-line rectangular and the statistically significant ($\alpha = 0.01$) coefficients with a thin-line rectangular.

Table 6. Spearman rank correlation coefficients computed for the ranks of the exposures and the relative property changes; a) for GFR polyester (Composite A) and b) for GFR vinyl ester (Composite B).

a)	UV	T	P	RH	O_3
Yellowness index	0.905	0.566	0.474	0.087	0.465
Gloss	-0.430	-0.074	-0.044	0.299	0.003
Hardness	0.282	-0.175	-0.340	-0.399	0.049

Flexural strength	-0.443	-0.679	-0.488	-0.377	-0.601
b)	UV	T	P	RH	O_3
Yellowness index	0.934	0.606	0.557	0.121	0.491
Gloss	-0.138	-0.021	0.144	0.116	-0.095
Hardness	0.004	-0.222	-0.060	-0.384	-0.465
Flexural strength	-0.195	-0.274	-0.203	0.060	-0.097

According to the Spearman rank correlation test, UV stress indeed is the major cause for yellowing of the both composites. However, stress caused by heat, rain and ozone concentration of the air may also explain some of the observed color change. Changes in gloss seem to be explained by the UV stress for GFR polyester. Decrease in flexural strength of GFR polyester might be mainly attributed to the heat stress, and in some extent to ozone, rain and UV. Moisture seems to be significant only in respect of changes in hardness. Tropospheric ozone partly explains the changes in hardness of GFR vinyl ester but not GFR polyester. For changes in gloss and flexural strength of GFR vinyl ester, no particular agents can be found through this analysis.

3.4 Questions left open

A question arises as to whether the computed statistical figures as such adequately well describe the prevailing weathering conditions or not. In the current figures, temporal variations are not taken into account in any way. Yet especially for composite materials, these kinds of features in the ageing environment may play an important role in the ageing behaviour of the material.

The performed Spearman rank correlation analysis fails to catch the most effective stress factors for changes in hardness and flexural strength of GFR vinyl ester. This might indicate that these changes could be attributed to a synergistic effect of two or several agents, which cannot be detected by the analysis method used.

4. CONCLUSIONS

Polyester and vinyl ester composites differ from each other in their response to environmental exposure. Only changes in gloss seem to be similar for the both types of composites. An initial increase, followed by a decrease in gloss, is observed. Polyester composite shows more severe yellowing than vinyl ester. Polyester composite also shows decrease both in surface hardness and flexural strength. Hardness and flexural strength of vinyl ester composite increases first but then starts to decrease. The results are mainly in line with the previous findings (e.g., [3,4]). Polyester resin matrix appears to be slightly more susceptible to all significant environmental stress factors (UV radiation, precipitation, humidity, temperature and ozone concentration) than vinyl ester. This is probably due to the fact that the lack of non-terminal ester groups makes vinyl ester less vulnerable to hydrolytic degradation [5]. Furthermore, vinyl ester has a higher glass transition temperature *Tg* than polyester [5] and hence exhibits a higher resistance to certain (Norrish II) types of photochemical processes [6].

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