

METHOD FOR THE PRODUCTION OF COMPOSITES

THIS INVENTION relates to a method of producing a composite material. In particular, it relates to a method of producing such composite materials for making structures and/or artifacts wherein a substrate is protected against corrosion and/or permeation of fluids by a surface cladding. It also relates to a method of producing such composite materials wherein one component is strengthened or reinforced by another component. The invention also relates to such composite materials, particularly when produced by means of said method.

According to the invention, there is provided a method of producing a composite material, the method comprising:

subjecting a surface of a polyolefin component comprising a polyolefin material to surface activation thereof; and

adhesively securing together the polyolefin component and a substrate component selected from cementitious components and metal components, at the activated surface of the polyolefin component.

By surface activation is meant that the surface of the polyolefin component is brought into contact with a fluid in a fashion whereby atoms, molecules and/or radicals derived from the fluid are incorporated into the surface of the component.

The polyolefin component may act to protect the substrate component, the polyolefin component forming a surface cladding for the substrate component. The polyolefin surface cladding may protect the substrate component against corrosion. The polyolefin surface cladding may instead or in addition protect the substrate component against permeation of fluids, particularly when the latter is cementitious.

Any suitable surface activation method may be used, such as corona discharge or plasma processes. For large scale applications, the surface activation is preferably surface fluorination. Thus, more particularly, the surface activation may be selected from corona discharge activation, plasma activation and surface fluorination activation, the surface activation providing the activated polyolefin component surface with a surface tension at 20°C of at least 40 mN/m, the polyolefin material being selected from polyethylenes, polypropylenes, copolymers of ethylene and propylene and blends of such polyolefins, such as ethylene-propylene diene monomer elastomers. The polyolefins used include unmodified or modified polyolefins, eg those modified by containing ethyl vinyl acetate as an impact modifier.

Any suitable method can be used to fluorinate the surface of the polyolefin component which is fluorinated before it is adhesively secured to the cementitious or metal substrate component. By fluorinated is meant that the surface of the polyolefin component is treated with a fluorine-containing gas to provide fluorine substituents bound to said surface. Any suitable fluorinating process may be used for this purpose, for example the fluorinating processes described in US Patents Nos. US 3,647,613; US 3,862,284; US 3,865,615; US 4,020,223; US 4,081,574; US 4,142,032; US 4,296,151; US 4,508,781; US 4,536,266; US 4,557,945; US 4,764,405; and US 4,869,859 as well as published European Patent Application EPO 214 635, and South African Patents Nos. 85/9500 and 87/8240, at last some of which describe techniques which can be adapted for the oxyfluorination described hereunder.

Conveniently, the activation is by surface fluorination activation, more particularly surface oxyfluorination, the fluorination being by exposing the polyolefin component to be fluorinated to a fluorine-containing gas at a pressure of 1-500 kPa, preferably 5-150 kPa, at a temperature above 0° C and below the melting point of the polyolefin material of the polyolefin component, typically 20 - 100 ° C. By oxyfluorination is meant that the surface is provided with fluorine and oxygen substituents, eg on -CH₂ and/or -CH₃ groups forming part of the surface. The



fluorine-containing gas may be fluorine itself (F_2), it may be a fluorinated noble gas such as XeF_2 , or it may be a fluorohalogen such as ClF_3 , BrF_5 , IF_7 or the like. The fluorine-containing gas may form part of a mixture with other gases, such as oxides of sulphur, oxides of nitrogen or oxides of carbon, halogens, interhalogens, nitrogen, oxygen, ozone or mixtures thereof, such as air. The proportion of the fluorine-containing gas in such gas mixture can vary within wide limits, the fluorine-containing gas forming eg 0,1-99,9% by volume of said mixture, typically forming 1 - 30% by volume thereof. Particularly preferred gas mixtures include those comprising 5 - 20% by volume of fluorinating gas such as F_2 and 5 - 95% by volume oxygen (O_2 or O_3), so that the surface fluorination is a surface oxyfluorination.

In a particularly preferred version of the method the surface fluorination activation may be by exposing the polyolefin component to the fluorine-containing gas at a pressure of 5 - 150 kPa and at a temperature of 20-100°C, the gas comprising 5 - 20% by volume fluorine and 5 -95% by volume oxygen. As described in more detail hereunder, adhesively securing the activated surface of the polyolefin component to the substrate component may be effected by means of an adhesive composition comprising a thermosetting resin.

The fluorination under the above process conditions will usually take place in a reactor comprising a vacuum chamber with provision for feeding thereto and withdrawal therefrom of gases, pressure control, temperature control and control of the composition of gas mixtures therein, and the process will usually be carried out batchwise.

When the polyolefin cladding component is in the form of a sheet, it may, however, be treated in a roll-to-roll process using a film fluorinator as the reactor, with similar fluorination conditions to those described above with reference to the batch process. The absolute pressure in such reactor will typically be one atmosphere, $\pm$ 20 kPa. The gas mixture composition may be such that the fluorine (F_2) content is 5 to 20 %, the remainder being made up of other reactive gasses,



or inert gasses, eg N_2 . The proportion of said other gases in the mixture may be between 5 and 95 %, the balance being made up by an inert gas such as N_2 .

As indicated above, the surface activation, such as the surface fluorination, may be such as to provide the activated polyolefin component surface with a surface tension at 20° C of at least 40 mN/m, preferably at least 45 mN/m.

The substrate component may be a cementitious component made of a cementitious material such as cement, concrete, cementitious mortar or a related cement-containing material. The cementitious substrate component may be flat, being eg a concrete wall or floor, or tubular, being eg a concrete pipe. The substrate component may instead be a metal component, such as mild steel component, and may be tubular, being eg a pipe, although it may, instead be a box or container-type structure. Accordingly, the material of the substrate component may be selected from cement, concrete, cementitious mortar or mild steel, the thermosetting resin being selected from epoxy resins and polyester resins.

The polyolefin component, when used for cladding, may be of an appropriate shape, depending on the shape of the substrate component. Thus, the polyolefin component may be a flat or curved sheet. When the substrate component is tubular, eg a pipe, the polyolefin component may be a pipe, a polyolefin pipe forming an external and/or internal cladding or lining for the cementitious or metal pipe, as the case may be.

The cladding or other polyolefin component may be of polyethylene, such as high density polyethylene (HDPE), polypropylene (PP), or copolymers of ethylene and propylene, such as ethylene-propylene-diene monomer elastomer (EPDM), modified or unmodified, as indicated above, or blends of such polyolefins.

Adhesively securing the fluorinated surface of the polyolefin cladding component to the cementitious or metal substrate component may be effected by



using a suitable adhesive composition, such as a thermosetting resin as indicated above. The adhesive composition may comprise a curable settable thermosetting resin, eg an epoxy resin or polyester resin. Suitable epoxy resin-based adhesive compositions are those available in South Africa as PRO-STRUCT 121 and PRO-STRUCT 30/71 from Pro-Struct, a division of KayMac Limited. Suitable polyester resin-based adhesive compositions are a polyester resin adhesive paste available in South Africa as FREE FIX 40/6345 from NCS Resins, a division of Sentrachem Ltd, a resilient isophthalic polyester resin adhesive available in South Africa as GELCOAT 65 from said NCS Resins, and an isophthalic, non-accelerated resilient polyester resin adhesive available in South Africa as POLYLITE 8130 from said NCS Resins.

The method may include the step, prior to the adhesive securing, of subjecting the activated surface of the polyolefin component to hydrolysis, to enhance the adhesion of the fluorinated surface to the adhesive composition. The hydrolysis is particularly effective when the activation is by oxyfluorination and the adhesive securing step is by means of an epoxy adhesive composition. The hydrolysis may be effected by contacting the oxyfluorinated surface with water at an elevated temperature for a sufficient period of time, eg by immersing the polyolefin component in water overnight at 50 °C, to hydrolyse any hydrolysable chemical groups on the fluorinated surface of the polyolefin component. Exposure of the fluorinated surface to atmospheric air for extended periods of time should also result in full hydrolysis of the fluorinated surface. In particular, the hydrolysis may be by contacting the activated surface of the polyolefin component with liquid water for a period of 2 - 6 hours.

The surface may be subjected to degreasing prior to fluorination thereof and/or after fluorination and prior to the adhesive securing of the cladding component to the cementitious or metal substrate component. Accordingly, the surface may be subjected to degreasing prior to activation thereof. Furthermore, the surface may, after activation thereof and prior to the adhesive securing, be subjected to degreasing.



Suitable degreasing agents used to degrease the surface may be selected from trichloro-ethylene (TCE), acetone, ethanol, methyl ethyl ketone (MEK) and xylene. Water-soluble detergents can also be used. Naturally routine experimentation will be employed to determine which degreasing agents are compatible with the surface and with the resins employed in the process of the invention.

As indicated above, the polyolefin component may be secured to the substrate component to form a surface cladding of the substrate component. Furthermore, instead, the substrate component may be secured to the polyolefin component to form a surface cladding of the polyolefin component.

Thus, instead of using the polyolefin component to protect the substrate component, the substrate component may be used for strengthening and/or reinforcing the polyolefin component. The polyolefin component in this case may be tubular or hollow cylindrical, eg circular or square in cross-section, suitable for containing and/or transporting a fluid. In particular, the polyolefin component may be a pipe or pipe fitting, or a tank, the metal reinforcing component forming an external cladding or lining for the polyolefin pipe, pipe fitting or tank. Typically in this case, the polyolefin material of the polyolefin substrate component is again polyethylene, such as high density polyethylene (HDPE), polypropylene (PP), or copolymers of ethylene and propylene, such as ethylene-propylene-diene monomer elastomer (EPDM), modified or unmodified, or blends of such polyolefins. The metal strengthening or reinforcing component may be of mild steel. The surface activation method, including the surface fluorination method, for activating the surface of the polyolefin substrate component before it is adhesively encapsulated or clad by the metal reinforcing component, may be similar to that described above for protection of the substrate component by the polyolefin component; and adhesively securing the reinforcing component to the polyolefin component may be effected using a similar adhesive composition as described above for protection of the substrate component by the polyolefin component. A suitable adhesive composition is an epoxy resin-based adhesive such as that available in South Africa as PRO-STRUCT 7907 A and



B from Pro-Struct, a division of KayMac Limited. Typically, the resin may be cured by using a suitable curing agent or catalyst, eg a commercial curing system or package supplied by, and used in the appropriate amount as recommended by, the manufacturer of the particular resin used. This version of the method may also include the further step, prior to the adhesive securing, of subjecting the fluorinated surface of the polyolefin substrate component to hydrolysis, as described above, to enhance the adhesion of the oxyfluorinated surface to the adhesive composition. Plastics pipes are widely used for the transport of fluids and the pressure in such pipes may vary from below atmospheric (vacuum) up to tens of atmospheres. Polyolefin pipes and tanks can be lined or encapsulated by metal reinforcing components in accordance with the method of the invention to increase their pressure rating, and/or to increase their rigidity. Such composite pipes and tanks combine the advantages of the strength (for pressure) and rigidity of eg steel and the relative chemical and abrasion resistance of polyolefin plastics.

The invention extends to a composite material comprising a polyolefin component and a substrate component adhesively secured together, the substrate component being selected from cementitious components and metal components, and the components being secured together at a surface of the polyolefin component which is activated.

The composite material may be made in accordance with the method of the invention.

The invention will now be described, by way of non-limiting illustrative example, with reference to the following Examples and with reference to the accompanying diagrammatic drawings.

Examples 1 - 3 illustrate the method of the invention applied to the protection of cementitious substrates by a polyolefin surface cladding. Example 4 illustrates the method of the invention applied to the strengthening of a polyolefin



component by a metal reinforcing surface cladding. Example 5 illustrates the method of the invention employing various resins. Example 6 illustrates the method of the invention employing various degreasing agents. Example 7 illustrates the method of the invention employing various drying times prior to oxyfluorination. Example 8 illustrates the method of the invention employing various oxyfluorination methods. Examples 9A, 9B and 9C illustrate the method of the invention employing varying activation times. Examples 10A and 10B illustrate the method of the invention in the light of various adhesion tests and kinetics tests. Examples 11A and 11B illustrate the method of the invention employing various hydrolysis media. Example 12 illustrates the method of the invention employing varying drying times after hydrolysis. Example 13 illustrates the method of the invention with regard to degreasing of substrates after activation and prior to adhesion.

In the drawings:

Figure 1 shows a plot of shear strength (MPa) against sample number for polypropylene pipe samples provided with an exterior lining of mild steel, with reference to the required shear strength according to British Standard B.S.6464;

Figure 2 shows a plot of peel strength against time for Prostruct 30/71 with hydrolysis in water; and

Figure 3 shows a plot of mass change against time for activation of HDPE with a F₂/O₂ mixture comprising 10% by volume F₂.

EXAMPLE 1 (Resin Choice)

The following experimental conditions were employed:

Material	:	Black HDPE (PE 300)
Gas Mixture	:	10kPa air, 20kPa F ₂ /N ₂ mixture comprising 20% by volume F ₂ .
Oxy-fluorination Time and Temperature	:	30min at 50°C



Surface Dimensions : length: 200mm, width: 200mm, thickness: 2mm

Resins : a) Pro-Struct 121,
b) Pro-Struct 30/71,
c) Free Fix 40-6345,
d) Gelcoat 65,
e) Polylite 8130.

The HDPE tiles (untreated and activated) were stuck to a concrete wall using the above resins by means of hand pressure. After one week a force was applied to the tiles to endeavour to peel the tiles from the wall.

The results of these adhesion tests are set out in Table 1 below.

Table 1: Results of adhesion tests between PE 300 and concrete using various adhesives

Resin	Manufacturer	Type of Resin	Observation
Pro-Struct 121	Pro-Struct	Multi-purpose Epoxy	Breakline within the Concrete
Pro-Struct 30/71	Pro-Struct	Abrasion Resistant Epoxy	Breakline within the Concrete
FreeFix 40/6345	NCS Resins	Filled Polyester Adhesive Paste	Adhesive Failure between Adhesive and Concrete
Gelcoat 65	NCS Resins	Resilient Isophthalic Polyester Resin	Adhesive Failure between Adhesive and Concrete
Polylite 8130	NCS Resins	Isophthalic, Non-accelerated, Resilient Polyester resin	Adhesive Failure between Adhesive and Concrete

None of the untreated HDPE tiles remained stuck to the concrete wall.



The results in Table 1 indicate that epoxy resins appear to be the most suitable. Pro-Struct 30/71 (polyamido-amine curing agent) appeared to be the most suitable resin due to its cost, ease of mixing, ease of application and it removed less concrete from the wall compared to the other resins when the peel tests were conducted.

EXAMPLE 2

From the results of Example 1 it was clear that further work should be focused on the use of epoxy adhesives. The aim of the further work was to optimise the fluorination conditions for maximum adhesion between the epoxy adhesives listed in Table 1 and fluorinated polyolefin sheet.

Black pigmented HDPE strips (26 x 300 mm) were cut from a PE 300 sheet. The strips were placed in a stainless steel vacuum reaction vessel which was evacuated and then charged with a 10/90 F₂/O₂ mixture. The vessel was kept at 50 °C and the strips were fluorinated for different periods of time to provide a surface fluorine concentration of 55,4 µgF/cm². After the selected period of time, the fluorinating atmosphere was evacuated from the vessel and the strips removed.

The adhesive strength of PRO-STRUCT 30/71 on these strips was evaluated by T-peel tests, according to ASTM D 1876-92. The only changes to the prescribed ASTM procedure were that the pulling rate used was 200 mm/min and that the signal integration interval was 10 cm.

From the T-peel tests, it was clear that the optimum treatment time for maximum adhesion was reached within 30 minutes, using the above treatment conditions. It was also observed that a post-treatment of the fluorinated surface by hydrolysis had a material influence on the adhesion strength. It was found that the maximum adhesion strength (typically 8 N/mm) was obtained when the strips were submerged in water overnight at 50 °C. Strips which were glued immediately after fluorination

without post-treatment by hydrolysis, or which were treated with a basic solution, eg a NaOH solution, showed relatively weak bonding to the epoxy adhesive.

5 The Applicant has found the improved adhesion arising from the hydrolysis to be surprising and cannot account therefor. However, without being bound by theory, the Applicant believes that the fluorination treatment may form acyl fluoride- and carboxylic acid groups on the surface of the polyolefin component. On hydrolysis, the acyl fluoride groups may either be removed or they may be transformed into additional carboxylic acid groups. These carboxylic acid groups possibly act as curing agents for the epoxy resin. A chemical bond may thus actually be formed between
10 the adhesive and the fluorinated surface, which can lead to the high bond strength between the polyolefin component and the epoxy adhesive. This mechanism would explain why basic hydrolysis of the fluorinated surface does not enhance adhesion to the epoxy adhesive, since basic hydrolysis leads to the formation of salts on the polyolefin surface, and not to additional carboxylic acid groups.

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EXAMPLE 3

Tests similar to Example 1 were carried using tiles of EPDM instead of HDPE. In control tests, tiles which were not fluorinated showed no adhesion to the concrete wall using PRO-STRUCT 30/71 as adhesive. When the tiles were fluorinated as in Example 1, adhesion was so strong that breakline within the elastomer was observed.

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EXAMPLE 4

Push out tests were done on a PP pipe which was provided with an external lining/cladding of a mild steel pipe by the method according to the invention. The PP pipe was 90 mm OD class 4 pipe having a wall thickness of 5 mm. The PP was available from Megapipe, a division of Mega Plastics, which is in turn a division of
25 Sentrachem Limited. The outer surface of the PP was fluorinated in a manner to that described in Example 1, using the same fluorination conditions. After



fluorination, the PP pipe was inserted into a pipe of mild steel. The outside diameter of the PP pipe was 1 mm smaller than the inside diameter of the steel pipe. At each end of the steel pipe, a cup flange was bolted, each cup flange incorporating a spacer to keep the steel pipe and the PP pipe apart and also nozzles to allow both adhesive to be injected and air to escape. This technique is known as crack injection. The PP pipe and the steel pipe were then suspended at about $\pm 60^\circ$ and an epoxy-containing adhesive composition, available as PRO-STRUCT 7907 A and B from Pro-Struct, was then injected into the bottom cup flange under pressure, from a pressure pot where the adhesive composition was also premixed. Curing of the epoxy adhesive was by means of a curing agent package supplied by, and used in an amount as recommended by, the manufacturer of PRO-STRUCT 7907 A and B. The epoxy adhesive was allowed to partially cure after which the cups were removed and the composite pipe allowed to stand until full cure was achieved.

The composite pipe was cut into 60 mm lengths to form samples numbered as follows:

1	2	3	4	5	6
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A 15 mm length of the PP was machined out of each end of each 60 mm length for the purposes of push out tests conducted in accordance with B.S. 6464. The push out tests involved the remaining length of the PP pipe of the test pieces being pushed out of the metal cladding and measuring the force required to do so. The shear strength or "push-out" strength was then calculated as follows:

$$\text{Shear strength (MPa)} = \frac{F}{d \cdot \pi \cdot h}$$

where F = maximum force required to shear the PP pipe from the steel pipe cladding [N]

d = PP pipe outer diameter (mm)

h = remaining encapsulated inner plastics liner length (mm)

The push out test results are summarised in Table 2 below. The supporting strength profile of the steel clad PP pipe samples is shown in the accompanying figure. The figure shows for comparison the required shear strength according to the British Standard B.S. 6464. Table 3 shows the average shear forces, taking all the test results, as well as the average when disregarding the highest and lowest values. The standard deviation and variance is also shown, and then finally, whether or not the shear strength of the pipe samples matches or exceeds that specified by B.S. 6464. From Table 3, it can be seen that the pipe samples, though not complying to B.S. 6464, fared well.

Table 2 Steel/PP

SAMPLE NO.	HIGHEST VALUE OF PIPE LENGTH [mm]	PIPE OUTER DIAMETER [mm]	MAXIMUM SHEAR FORCE [N]	SHEAR STRENGTH [MPa]
1	30	111	10.98	1.05
2	30	110	14.56	1.4
3	30	110	14.21	1.3
4	30	110	12.93	1.2
5	30	110	12.22	1.17
6	30	110	13.07	1.26

Table 3

SHEAR STRENGTH (MPa)	
Average	1.23
Average 1	1.23
Std devn	0.11
Varlance	0.01
Acceptable	NO

Average 1 Highest and lowest not included.

Two methods were employed to evaluate adhesion strength, namely a T-peel test and a Lap shear test (ASTM test method)

T-Peel Test (ASTM D 1876-92):

Polymer strips (300mm width x 26mm length and 2mm thickness) were glued along ~ 22cm of the length thereof. After curing the joints were evaluated using an Instron 4465 tensometer with a 5000N load cell and a crosshead speed of 200mm/min. The peel strength was obtained from the average peel force over the central 20cm of peel.

Lap Shear Test (ASTM D 1002-72):

Polymer strips (26mm with x 50mm length) were mounted onto roughened mild steel platforms with Pro-Struct 30/71. The strips were masked with masking tape leaving 10mm available for testing. The physical overlap dimensions were 26mm width x 10mm length. This procedure was used to eliminate any peel forces. The adhesion strength was evaluated using an Instron 4465 tensometer with a 5000N load cell and a crosshead speed of 5mm/min.

MATERIALS USED

The material used was PE 300 HDPE in the form of tiles. PE300 is a GM 5010 based High Density Polyethylene (HDPE) which was obtained from Malzey Plastics, Pretoria, South Africa.

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Example 5**OXYFLUORINATION COMPARED WITH FLUORINATION**

The following experimental conditions were employed:

	Material	: Black HDPE (PE 300)
10	Degreasing Agents Prior to Activation	: TCE
	Surface Area Activated	: 0.0312m ²
	Gas Mixture	: a) 10kPa air, 40kPa F ₂ /N ₂ mixture comprising 11.6% by volume F ₂ b) 40kPa F ₂ /N ₂ mixture comprising 11.6% by 15 volume F ₂
	Oxyfluorination Time and Temperature	: a) 30min at 50°C b) 3hrs at 50°C
	Hydrolysis technique	: Exposure to moisture in air for 1 week
20	Test Method	: Lap Shear
	Dimensions	: length: 26mm, width: 10mm, glue-line thickness: 0.16mm
	Resin	: Pro-Struct 30/71

The results of the lap shear tests conducted are set out in Table 4 below

Table 4: Results of the tests conducted on black PE 300 with oxyfluorination and fluorination

Sample Number	Lap Shear Strength (MPa)	
	Oxyfluorination	Fluorination
1	11.00	1.786
2	15.120	1.392
3	9.788	1.464
4	Poor Glue-line	Poor Glue-line
5	-	-
Average	11.97	1.547

As can be seen in Table 4, oxyfluorination has better adhesive properties than fluorination on PE 300 with Pro-struct 30/71.

DEGREASING PRIOR TO ACTIVATION

Various contaminants that can influence activation as well as the adhesion process may be present on the surface. It is desirable to clean the surface thoroughly prior to activation. Sample surfaces were degreased by wiping each surface with a tissue properly wetted with a degreasing agent.

Example 6: CHOICE OF DEGREASING AGENT

The following experimental conditions were employed:

Material : Black HDPE (PE 300)
Degreasing Agents Prior to Activation : a) Trichloro-ethylene (TCE),

This Sheet Has Been Replaced



- b) Methyl Ethyl Ketone (MEK),
 - c) Ethanol (EtOH),
 - d) Handy Andy (H/A) available from Lever Industrial (Proprietary) Limited.
- 5 Drying Time Prior to Activation : 24hrs
- Surface Area Activated : 0.1248m²
- Gas Mixture : 10kPa air, 40kPa F₂/N₂ mixture comprising 15% by volume F₂
- 10 Oxyfluorination Time and Temperature : 30min at 50°C
- Hydrolysis technique : Immersion in water at room temperature for 18hrs
- Drying Time Prior to Adhesion : 1 week
- 15 Test Method : T-Peel
- Dimensions : length: 300mm, width: 26mm, thickness: 2mm
- Resin : Pro-Struct 30/71

The results of the peel tests conducted are set out in Table 5 below.

Table 5: Peel test results obtained for PE 300 with Pro-Struct 30/71 with various degreasing agents prior to oxy-fluorination

Sample Number	Peel Strength (N/mm)			
	TCE	MEK	Ethanol	Handy Andy
1	5.109	4.310	3.246	3.750
2	4.704	3.210	3.738	4.066
Average	4.906	3.760	3.492	3.908

Degreasing with TCE prior to oxy-fluorination gave the best results. The four particular degreasing agents were chosen as they cover a broad spectrum of chemical groups i.e. an alcohol, a ketone and a soap.

EXAMPLE 7: DRYING TIME PRIOR TO OXY-FLUORINATION

The following experimental conditions were employed:

	Material	: Black HDPE (PE 300)
5	Degreasing Agents Prior to Activation	: TCE
	Drying Time Prior to Activation	: a) ~ 3 months b) 24hrs
	Surface Area Activated	: 0.156m ²
10	Gas Mixture	: 10kPa air, 40kPa F ₂ /N ₂ mixture comprising 15.8% by volume F ₂
	Oxyfluorination Time and Temperature	: 30min at 50°C
	Hydrolysis technique	: Immersion in water at room temperature for 18hrs
15	Drying Time Prior to Adhesion	: 72hrs
	Test Method	: T-Peel
	Dimensions	: length: 300mm; width: 26mm, thickness: 2mm
	Resin	: Pro-Struct 30/71

20 The results of the peel tests conducted are set out in Table 6 below.

Table 6: Peel test results obtained for PE 300 with Pro-Struct 30/71 with a long drying time prior to oxy-fluorination

Sample Number	Peel Strength (N/mm)	
	3 Months	24hrs
1	0.8335	5.109
2	1.608	4.704
3	1.007	-
4	2.887	-
5	1.229	-
Average	1.513	4.906

Table 6 shows that a long drying time prior to activation (after degreasing) caused reduced peel strengths. It is believed that adverse effects arising from additive migration from the bulk of the polymer to the surface are reduced by the degreasing step, the degreasing step thus resulting in more effective oxyfluorination. Without the degreasing, additive on the surface can be fluorinated or oxyfluorinated, instead of the bulk polymer, and this is undesirable.

EXAMPLE 8: CHOICE OF OXYFLUORINATION METHOD

The following experimental conditions were employed:

Material	: Black HDPE (PE 300)
Degreasing Agents Prior to Activation	: MEK
Drying Time Prior to Activation	: 24hrs
Surface Area Activated	: 0.0624m ²
Gas Mixture	: a) F ₂ /O ₂ : 57kPa of a F ₂ /O ₂ mixture comprising 10% by volume F ₂

- b) F_2/N_2 + Air :- 50kPa air, 7kPa F_2/N_2 mixture comprising 15.8% by volume F_2 , the total mixture of air, F_2 and N_2 comprising 10% by volume F_2
- c) 10-40 :- 10kPa air, 40kPa F_2/N_2 mixture comprising 15.8% by volume F_2

Oxyfluorination Time and Temperature

: 30min at 50°C

Hydrolysis technique

: Immersion in 0.48N solution of Hydrochloric Acid (HCl) for 18hrs

Drying Time Prior to Adhesion

: 24hrs after rinsing with distilled water

Test Method

: T-Peel

Dimensions

: length: 300mm, width: 26mm, thickness: 2mm

Resin

: Pro-Struct 30/71

The results of the peel tests conducted are set out in Table 7 below.

Table 7: Peel test results obtained for PE 300 with Pro-Struct 30/71 with various oxyfluorination methods

Oxyfluorination Method	Peel strength (N/mm)		
	1	2	Average
a) F_2/O_2	2.192	1.665	1.929
b) F_2/N_2 + Air	1.543	0.9083	1.226
c) 10-40	4.363	2.954	3.658

The 10-40 condition yielded the best peel strengths when combined with the degreasing, hydrolysis and drying steps described in Example 8.

EXAMPLE 9: ACTIVATION TIME

The following experimental conditions were employed:

Example 9A: Activation Time Study using F₂/O₂

	Material	: Black HDPE (PE 300)
5	Degreasing Agents Prior to Activation	: TCE
	Surface Area Activated	: 0.156m ²
	Gas Mixture	: 50.9kPa F ₂ /O ₂ mixture comprising 10% by volume F ₂
10	Oxyfluorination Time and Temperature	: 2min, 10min, 20min and 30min at 50°C
	Hydrolysis technique	: Immersion in water at 50°C for 18hrs
	Drying Time Prior to Adhesion	: 1hr at 50°C followed by 24hrs at room temperature
15	Test Method	: T-Peel
	Dimensions	: length: 300mm, width: 26mm, thickness: 2mm
	Resin	: Pro-Struct 30/71

The results of the peel tests conducted are set out in Table 8 below:

Table 8: Peel strengths obtained for PE 300 with Pro-Struct 30/71 with various oxyfluorination times

Sample Number	Peel Strength (N/mm)			
	2 min	10 min	20 min	30 min
1	3.7909	6.904	8.7309	6.268
2	1.553	6.123	7.311	7.5597
3	5.413	5.393	7.2613	8.235
4	2.951	8.461	7.3083	9.2347
5	-	6.8838	-	-
Average	3.4063	6.75296	7.6526	7.8248

The data in Table 8 are illustrated in Figure 2.

As can be seen in Figure 2, the peel strength reaches a plateau after about 15min of oxyfluorination. It appears that 20 - 30 min is the preferred oxyfluorination time for PE 300 with Pro-Struct 30/71 under these hydrolysis conditions.

Example 9B: Reaction Time Study using the 10-40 Oxyfluorination Method

Material : Black HDPE (PE 300)

Degreasing Agents Prior to Activation : TCE

Drying Time Prior to Activation : 24hrs

Surface Area Activated : 0.0624m²

Gas Mixture : 10kPa air, 40kPa F₂/N₂ mixture comprising 15.8% by volume F₂

Oxyfluorination Time and Temperature : 1min, 15min and 30min at 50°C

Hydrolysis technique : Immersion in water at room temperature for 18hrs

- Drying Time Prior to Adhesion : 1 week
 Test Method : T-Peel
 Dimensions : length: 300mm, width: 26mm, thickness: 2mm
 5 Resin : Pro-Struct 30/71

The results of the peel tests conducted are set out in Table 9 below.

Table 9: Peel test results of PE 300 with Pro-Struct 30/71 with varying oxyfluorination times

Sample Number	Peel Strength (N/mm)		
	1 min	15 min	30min
1	1.457	4.385	5.109
2	0.9284	4.847	4.704
Average	1.1920	4.616	4.906

Table 9 shows that the longer the oxyfluorination time, the better the adhesion with Pro-Struct 30/71. There is however a cut off time where adhesion decreases due to the formation of a weak boundary layer within the polymer. In such cases, a thin layer of the polymer breaks from the bulk. It appears that it is not the adhesive-polymer interface that falls. This phenomenon is illustrated in Example 9C below.

EXAMPLE 9C: Excessive Reaction Time Investigation

- Material : Black HDPE (PE 300)
 Degreasing Agents Prior to Activation : TCE
 Drying Time Prior to Activation : 1 month
 25 Surface Area Activated : 0.156m²
 Gas Mixture : 50.9kPa F₂/O₂ mixture comprising 10% by volume F₂



Oxyfluorination Time and Temperature : 25hrs at 50°C
Hydrolysis technique : Immersion in water at 50°C for 18hrs
5 Drying Time Prior to Adhesion : 24hrs
Test Method : T-Peel
Dimensions : length: 300mm, width: 26mm, thickness 2mm
Resin : Pro-Struct 30/71

The results of the peel tests conducted are set out in Table 10 below:

10 Table 10: Peel strengths obtained on over activated PE 300

Sample Number	Peel Strength (N/mm)
1	0.5715
2	1.3860
3	-
15 4	-
5	-
Average	0.9788

As can be seen in Table 10, peel strength decreased when the surface was over-activated. The resin within the joints was black after peeling, indicating a weak
20 boundary layer. Only two values are shown since the other three samples gave no peel measurements.

EXAMPLE 10: SUBSTRATE AND SURFACE AREA ACTIVATED

The following experimental conditions were employed:

Example 10A: Adhesion Tests

25 Material : Black and Natural HDPE (PE 300)

	Degreasing Agents Prior to Activation	: TCE
	Surface Area Activated	: 0.0936m^2 and 0.156m^2
	Gas Mixture	: 10kPa air, 40kPa F_2/N_2 mixture comprising 11.6% by volume F_2
5	Oxyfluorination Time and Temperature	: 30min at 50°C
	Hydrolysis technique	: Exposure to moisture in air for 1 week
	Test Method	: T-Peel
	Dimensions	: length: 300mm, width: 26mm, thickness: 2mm
10	Resin	: Pro-Struct 30/71

The results of the peel tests conducted on natural and black PE 300 are set out in Table 11 below.

Table 11: Results of the peel tests on black and natural PE 300 for different activated surface areas

Sample Number	0.0936m^2 Peel Strength(N/mm)		0.156m^2 Peel Strength(N/mm)	
	Black	Natural	Black	Natural
1	3.74	2.808	2.224	1.941
2	4.422	4.104	2.837	1.828
3	2.541	3.665	2.519	2.195
4	-	-	2.604	Poor Glue-line
5	-	-	-	2.195
Average	3.568	3.525	2.546	2.039

From Table 11 it can be seen that black PE 300 gives slightly higher peel strengths than natural PE 300. Higher peel strengths were obtained as the activated surface area decreased. This was expected for fluorination reactions since the same amount

of fluorine was used irrespective of the area treated which reduced activation on larger treated surface areas. With oxyfluorination this was not expected since the reaction did not proceed to completion within 30min as oxyfluorination reactions are usually very slow (and appear to be inhibited by the presence of oxygen)

5 **Example 10B: Kinetics Study**

Material : Black and Natural HDPE (PE 300)
Gas Mixture : F₂/O₂ comprising 10% by volume F₂
Dimensions : length: 5mm, width: 5mm, thickness: 2mm (0.9cm²)

10 Change of mass was monitored using a Perkin Elmer TG2 for a period of 1hr 10min (70min). The sampling frequency was 0.2Hz under isothermal conditions at 50°C.

The results of the kinetic studies on black and natural PE 300 are set out in Figure 3.

15 As can be seen in Figure 3, black PE 300 oxyfluorinates faster than natural PE 300 for times under 60min. At 60min, both substrate surfaces reacted at the same rate. Natural PE 300 reacted faster at times longer than 60min than black PE 300 did. The mass changes were 0.02mg/cm² and 0.013mg/cm² for black and natural PE 300 respectively at typical oxy-fluorination times used in adhesion studies, eg 30min. It is believed that the reason why natural PE 300 has lower adhesion
20 properties than black PE 300 (Table 8) is that natural PE 300 oxyfluorinates far slower at times of 30min and therefore has a lower degree of activation.

HYDROLYSIS OF ACTIVATED POLYMER SURFACE

25 On oxyfluorination of HDPE carboxylic acid, acyl fluoride and fluorocarbon groups are formed on the surface. During hydrolysis the acyl fluoride groups are converted into carboxylic acid groups which it is believed act as a curing agent for epoxy resins, ie a chemical bond is actually formed between the HDPE and the epoxy resin.

EXAMPLE 11: CHOICE OF HYDROLYSIS MEDIUM**Example 11A: Hydrolysis Medium Study on HDPE activated using F₂/O₂:**

	Material	: Black HDPE (PE 300)
5	Degreasing Agents Prior to Activation	: TCE
	Surface Area Activated	: 0.156m ²
	Gas Mixture	: 50.9kPa F ₂ /O ₂ mixture comprising 10% by volume F ₂
10	Oxyfluorination Time and Temperature	: 30min at 50°C
	Hydrolysis technique	: a) No hydrolysis b) Immersion in 0.1M Sodium Hydroxide (NaOH) at 50°C for 5min c) Immersion in water at 50°C for 18hrs
15	Drying Time after Hydrolysis	: 1 hrs at 50°C followed by 24hrs at room temperature
	Test Method	: T-Peel
	Dimensions	: length: 300mm, width: 26mm, thickness: 2mm
	Resin	: Pro-Struct 30/71

20 The results of the peel tests conducted are set out in Table 12 below:

Table 12: Peel strengths obtained on PE 300 with Pro-Struct 30/71 using different hydrolysis mediums

Sample Number	Peel Strength (N/mm)		
	No Hydrolysis	NaOH	Hot Water
1	0.6959	-	6.268
2	0.7800	-	7.5599
3	1.346	-	8.235
4	1.704	-	9.2347
5	-	-	-
Average	1.131	-	7.848

From the results in Table 12, it appears that a hydrolysis step is necessary and that the correct choice of hydrolysis medium is very important. It can be concluded from the above results that acyl fluoride groups on the polymer surface do not enhance the adhesion but actually decrease the adhesion properties with Pro-Struct 30/71.

No values for the samples hydrolysed in NaOH could be measured thus indicating that the NaOH treatment weakened the bond dramatically. With the NaOH treatment, hydrolysis did initially occur but due to a large excess of base in the system, deprotonation of the carboxylic acid group followed yielding an ionic salt on the surface.

Example 11B: Hydrolysis Medium Study on HDPE Activated using the 10-40 Oxyfluorination Method

Material : Black HDPE (PE 300)

Degreasing Agents Prior to Activation : TCE

Drying Time Prior to Activation : 24hrs

	Surface Area Activated	: 0.156m ²
	Gas Mixture	: 10kPa air, 40kPa F ₂ /N ₂ mixture comprising 11.6% by volume F ₂
5	Oxyfluorination Time and Temperature	: 30min at 50°C
	Hydrolysis technique	: a) Exposure to moisture in air for 1 week b) Immersion in 0.48N HCl for 18hrs
	Drying Time after Hydrolysis	: 24hrs
10	Test Method	: T-Peel
	Dimensions	: length: 300mm, width: 26mm, thickness: 2mm
	Resin	: Pro-Struct 30/71

The results of the peel tests conducted are set out in Table 13 below.

15 **Table 13: Peel strengths obtained on PE 300 with Pro-Struct 30/71 using different hydrolysis media**

Sample Number	Peel Strength (N/mm)	
	Air	HCl
1	2.224	4.67
2	2.837	2.674
20 3	2.519	2.5420
4	2.604	3.584
5	-	3.047
Average	2.546	3.299

25 Similar increases in peel strength as for the HCl hydrolysis had been previously witnessed with water. It appeared to be better to hydrolyse the surface with a wet process than with air for adhesion with Pro-Struct 30/71. Water gave the best results.

Example 12: DRYING TIME AFTER HYDROLYSIS

The following experimental conditions were employed:

	Material	: Black HDPE (PE 300)
5	Degreasing Agents Prior to Activation	: TCE
	Drying Time Prior to Activation	: 24hrs
	Surface Area Activated	: 0.156m ²
10	Gas Mixture	: 50.9kPa F ₂ /O ₂ mixture comprising 10% by volume F ₂
	Oxyfluorination Time and Temperature	: 30min at 50°C
	Hydrolysis technique	: Immersion in water at 50°C for 18hrs
15	Drying Time after Hydrolysis	: 1hr
	Test Method	: T-Peel
	Dimensions	: length: 300mm, width: 26mm, thickness 2mm
	Resin	: Pro-Struct 30/71

The results of the peel tests conducted are set out in Table 14 below.

20 **Table 14: Peel strengths obtained on PE 300 with Pro-Struct 30/71 after a
drying time of 1hr**

	Sample Number	Peel Strength (N/mm)
	1	0.8950
	2	1.340
25	3	2.057
	4	1.224
	5	-
	Average	1.379

On comparison between the results in Example 11A (peel strengths of 7.8 N/mm were obtained on dry samples) it can be seen that it is undesirable to use Pro-Struct 30/71 on a wet substrate. It is important that the polymer is properly dried prior to adhesion.

5 DEGREASING AFTER ACTIVATION PRIOR TO ADHESION

Once the surface of a polyolefin component has been activated, subsequent handling can contaminate the surface rendering it relatively inactive towards adhesion. A further cleaning step can therefore be an important step to promote the adhesion properties of the activated surface.

- 10 During transportation of activated HDPE sheets to a user, the sheets may become contaminated. The contamination may be due to dust as well as fats and oils as a result of handling of the sheets. Since dirt on the surface of the HDPE sheet will interfere with the adhesion it is important to clean the sheet prior to glueing.

EXAMPLE 13:

- 15 The following experimental conditions were employed:

	Material	: Black HDPE (PE 300)
	Degreasing Agents Prior to Activation	: TCE
20	Drying Time Prior to Activation	: 24hrs
	Gas Mixture	: 10kPa air, 40kPa F ₂ /N ₂ mixture comprising 11.6% by volume F ₂
	Oxyfluorination Time and Temperature	: 30min at 50°C
	Hydrolysis technique	: Exposure to moisture in air for 1 week
25	Degreasing Agents Prior to Adhesion	: a) TCE b) Acetone

This Sheet Has Been Replaced



c) Ethanol

d) MEK

e) Xylene

5 **Drying Time Prior to Adhesion** : 3hrs

Test Method : Lap Shear

Dimensions : length: 26mm, width: 10mm, glue-line thickness: 0.16mm

Resin : Pro-Struct 30/71

10 The results of the lap shear tests are set out in Table 15 below.

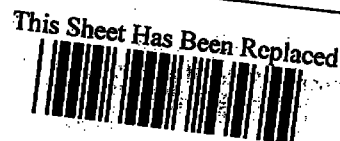
Table 15: Lap shear values obtained for PE 300 degreased with various degreasing agents prior to adhesion

Sample Number	Lap Shear Strength (MPa)					
	Control	TCE	Acetone	Ethanol	MEK	Xylene
1	11.21	6.331	10.42	4.673	4.950	5.346
2	10.14	10.71	10.62	6.481	6.054	8.796
3	10.9	8.438	Platform Failure	5.585	6.068	4.262
4	Poor Glue-line	8.188	Platform Failure	8.669	5.012	9.385
5	Poor Glue-line	Poor Glue-line	Platform Failure	4.946	7.792	Platform Failure
Average	10.75	8.416	10.52	6.071	6.083	6.947

As can be seen from Table 15, degreasing of the surface prior to gluing made a difference to adhesion strength. Acetone appeared to be the best degreasing agent for this particular system, i.e. black PE 300 and Pro-Struct 30/71, as the shear strength was practically the same as the control samples.

It must be stressed that these results showed only an interaction with the surface and the resin and do not necessarily give similar results when used together with peel tests. However, it can be seen that degreasing prior to adhesion with Pro-Struct 30/71 is not recommended.

- 5 It is an advantage of the invention that it provides a method of protecting a cementitious or metal substrate component, eg against corrosion, corrosive or aggressive chemicals or the like, using a polyolefin cladding, which does not involve mechanical securing methods. It is a further advantage that the invention provides a method of strengthening a polyolefin substrate component, using a metal cladding,
10 which similarly does not involve mechanical securing methods.

C L A I M S

1. A method of producing a composite material, the method comprising:
subjecting a surface of a polyolefin component comprising a polyolefin material
to surface activation thereof; and
5 adhesively securing together the polyolefin component and a substrate
component selected from cementitious components and metal components, at the
activated surface of the polyolefin component.
2. A method as claimed in claim 1, in which the surface activation is selected from
corona discharge activation, plasma activation and surface fluorination activation, the
10 surface activation providing the activated polyolefin component surface with a
surface tension at 20°C of at least 40 mN/m, the polyolefin material being selected
from polyethylenes, polypropylenes and copolymers of ethylene and propylene
and blends of such polyolefins.
3. A method as claimed in claim 2, in which the activation is by surface
15 fluorination activation, the fluorination being by exposing the polyolefin component
to a fluorine-containing gas at a pressure of 1-500 kPa, at a temperature above 0°C
and below the melting point of the polyolefin material of the polyolefin component.
4. A method as claimed in claim 3, in which the surface fluorination activation is
by exposing the polyolefin component to the fluorine-containing gas at a pressure of
20 5 - 150 kPa and at a temperature of 20-100°C, the gas comprising 5 - 20% by
volume fluorine and 5 -95% by volume oxygen, so that the surface fluorination is
a surface oxyfluorination.
5. A method as claimed in any one of the preceding claims, in which adhesively
securing the activated surface of the polyolefin component to the substrate
25 component is effected by means of an adhesive composition comprising a
thermosetting resin.





THIS SHEET HAS BEEN
REPLACED

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6. A method as claimed in claim 5, in which the material of the substrate component is selected from cement, concrete, cementitious mortar or mild steel, the thermosetting resin being selected from epoxy resins and polyester resins.
- 5 7. A method as claimed in any one of the preceding claims, which includes the step, prior to the adhesive securing, of subjecting the activated surface of the polyolefin component to hydrolysis.
8. A method as claimed in claim 7, in which the hydrolysis is by contacting the activated surface of the polyolefin component with liquid water for a period of 2 - 6 hours.
- 10 9. A method as claimed in any one of the preceding claims, in which the surface is subjected to degreasing prior to activation thereof.
10. A method as claimed in any one of the preceding claims, in which the surface, after activation thereof and prior to the securing, is subjected to degreasing.
- 15 11. A method as claimed in any one of the preceding claims, in which the polyolefin component is secured to the substrate component to form a surface cladding of the substrate component.
12. A method as claimed in any one of claims 1 - 10 inclusive, in which the substrate component is secured to the polyolefin component to form a surface cladding of the polyolefin component.
- 20 13. A composite material comprising a polyolefin component and a substrate component adhesively secured together, the substrate component being selected from cementitious components and metal components, and the components being secured together at a surface of the polyolefin component which is activated.
- 25 14. A composite material as claimed in claim 13, whenever produced in accordance with the method of any one of claims 1 - 12.

