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Highly filled particulate composites enhancement of performances by using compound coupling agents

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The compressive and bending strength of epoxy and unsaturated polyester resins composites containing high volume of particulate silicas have been studied. Different coupling agents were tested, whose formulation was tailored to allow the creation of chemical bonding between filler and matrix. Fracture surfaces were analysed by scanning electron microscopy, and a qualitative correlation was found between increasing strength and interfacial adhesion.

1. Introduction

Growing interest in composites is mainly due to their excellent performances, especially high specific modulus, high specific strength and also their capability to be shaped as complex parts in one operation with lower manufacturing costs compared to more traditional materials: metals and ceramics.

Epoxy and polyester based composites reinforced with fibres are the most widely used composites [1, 2]. More recently, highly filled particulate composites, such as, polyester concrete [3] (based on unsaturated polyester and calcium carbonate) and magnetic polymeric composites [4] have been developed.

Although the performance of polyester concrete is better than general cement concrete in compressive strength, bending strength and corrosion resistance, it has not been used more widely as it possesses high deformability and low abrasion resistance [3].

High performance composites based on hybrid reaction which set up a chemical bond between organic and inorganic molecules are being developed at present [2]. A variety of methods may be used to create the hybrid bond between organic and inorganic molecules. In our work the method based on the addition of suitable coupling agents was followed. Thomas [5] and Han *et al.* [6] have reported that coupling agents can improve the interfacial adhesion between filler and polymer matrix and some mechanical properties of these composites were improved even though the coupling agent did not connect the filler and matrix by a true chemical bond. Chiang and Yang [7] reported a method for grafting acrylic acid onto polypropylene to be used as matrix in composites. As PP is a nonpolar hydrophobic material, a coupling agent should improve the performance of composites.

Some recent studies [8–11] support the idea that highly filled particulate composites based on thermoset resins such as epoxies and polyesters have a bright future.

The SiO_2 powders are some of the most abundant, naturally occurring fillers with high strength and hardness without cleavage, good corrosion resistance activated surface and lowest cost. Some results on the addition of silane coupling agents to SiO_2-epoxy composites have been reported [10, 11], but the analysis was not carried up to a very high content of filler. In order to increase the hardness, the abrasion resistance and reduce the cost of hybrid composites, the SiO_2 must be added in a large percentage.

The present paper deals with preliminary results in the field of the improvement of mechanical performances of epoxy and polyester composites with as high as 90 wt % of SiO_2 filler content. Moreover a compound coupling agent able to form molecular chains between SiO_2 and polyester resin has been used.

The properties of such highly filled particulate composites are related to the kind of morphology and structure after the cure reaction with particular attention to the capability of the coupling agent in generating adhesion between particle and resins.

2. Experimental details

In this work, natural glass beads (SiO_2 content $> 98\%$) were used as basis and percentages of up to 90 wt % were adopted to make composite specimens. Unsaturated polyester resin (UPE) was supplied by Alusuisse (Italy) with trade name of SNIATRON H 35. The base resin is usually available as solution containing about 68 wt % of prepolymer dissolved in a styrene monomer. Methyl ethyl ketone peroxide (Butanox, 1 wt %) and co-octoate (0.25 wt %) were used as catalyst and accelerator, respectively. CTBN (carboxyl-terminated copolymer of butadiene and acrylonitrile, trade mark: Hycar 1300 × 8 produced by BF Goodrich) is used in

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some samples as a plasticizer. The selected coupling agents for polyester were γ-aminopropyltriethoxysilane (A-1100, Union Carbide product) with the formula:

$$H_2N\text{-}CH_2CH_2CH_2\text{-}Si(OCH_2CH_3)_3$$

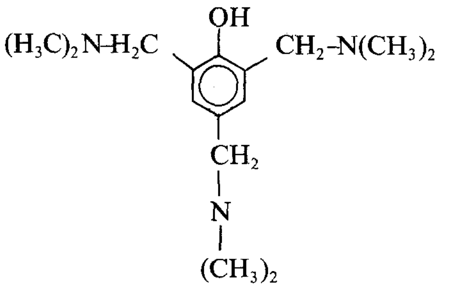
and hexamethylendiisocyanate (HMDI) with the formula:

$$O{=}C{=}N\text{-}CH_2CH_2CH_2CH_2CH_2CH_2N{=}C{=}O$$

which was a Fluka reagent grade product.

The epoxy resin used was a diglycidil ether of Bisphenol A (DGEBA) (trade mark EPIKOTE 828 supplied by Shell Chemical Co.) with an epoxy equivalent weight of 187 g mol^{-1} epoxy.

The 2, 4, 6-tris-(dimethylamino-methyl)-phenol (DMP-30) produced by Fluka A.G. with the formula:



is used as curing agent for epoxy. DOP (dioctyl phthalate) produced by Carlo Erba was selected as plasticizer in epoxy. Meanwhile, A-1100 is still used as coupling agent for epoxy composite.

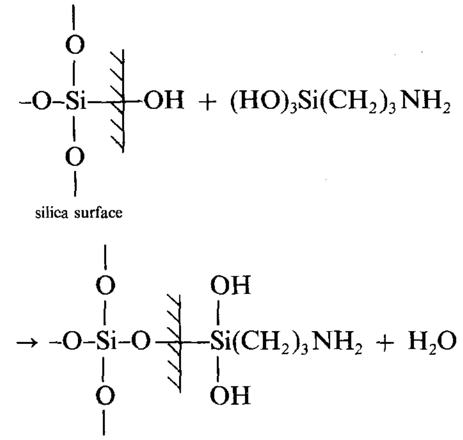
Teflon spray was used as demould agent for all the samples.

3. Sample preparation

Two kinds of glass beads with different granulometrics (the average diameters were 0.1 mm for the crude and 0.01 mm for the fine powders) were intimately mixed after washing with water and dried. In this mixture, the crude beads were 80 wt % and fine powder 20 wt %, this latter being used for filling the vacancies between the crude particles. For most specimens, the mixture will be treated with 1 % aqueous solution of A-1100 in which the coupling agent is hydrolysed immediately according to the following scheme of reaction:

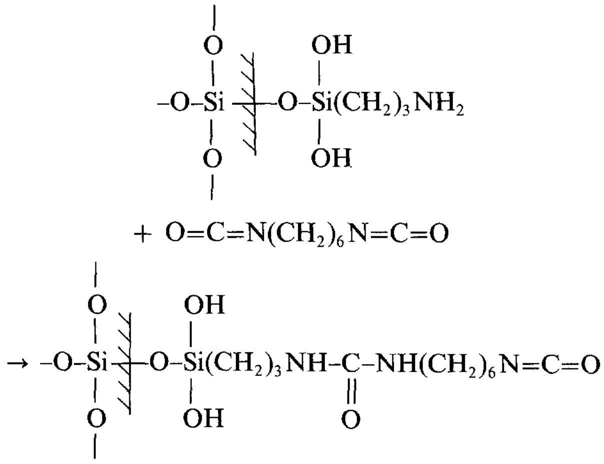
$$H_2N(CH_2)_3Si(OC_2H_5)_3 + 3H_2O$$
$$\rightarrow H_2N(CH_2)_3Si(OH)_3 + 3C_2H_5OH \qquad (1)$$

Then the aminosilane reacts with silica surface upon mixing at 80° C.



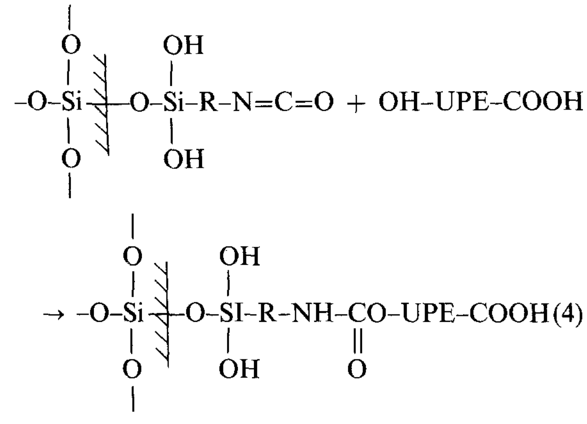
$$\text{-O-}\underset{\text{O}}{\overset{\text{O}}{\text{Si}}}\text{-OH} + (HO)_3Si(CH_2)_3NH_2 \rightarrow \text{-O-}\underset{\text{O}}{\overset{\text{O}}{\text{Si}}}\text{-O-}\underset{\text{OH}}{\overset{\text{OH}}{\text{Si}}}(CH_2)_3NH_2 + H_2O \qquad (2)$$

After reaction the treated beads are dried again at 80° C. SiO$_2$-grafted A-1100 alone cannot create a chemical bond between SiO$_2$ and polyester. This can be obtained however, if A-1100 is reacted with HMDI to build up bonded polyester chains onto SiO$_2$ which are likely to impart strength to the composite. For this reason in some specimens the glass beads treated by A-1100 will be wet through with 1% solution of HMDI in chloroform for one day and then dried again at 80° C. A reaction between SiO$_2$ hydrolysed A-1100 and HMDI occurred immediately, already at room temperature according to the following scheme of reaction:



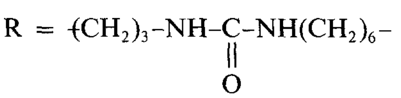
$$\text{-O-}\underset{\text{O}}{\overset{\text{O}}{\text{Si}}}\text{-O-}\underset{\text{OH}}{\overset{\text{OH}}{\text{Si}}}(CH_2)_3NH_2 + O{=}C{=}N(CH_2)_6N{=}C{=}O \rightarrow \text{-O-}\underset{\text{O}}{\overset{\text{O}}{\text{Si}}}\text{-O-}\underset{\text{OH}}{\overset{\text{OH}}{\text{Si}}}(CH_2)_3NH\text{-}\underset{\text{O}}{\underset{\Vert}{\text{C}}}\text{-}NH(CH_2)_6N{=}C{=}O \qquad (3)$$

The SiO$_2$-A100-HMDI compound was called a "compound coupling agent" and it might be effective to increase the strength of the composite. When this compound is mixed with the polyester resin solution in styrene (together with catalyst and accelerator) the following reaction occurs and a chemical bond between glass beads and polyester will be created



$$\text{-O-}\underset{\text{O}}{\overset{\text{O}}{\text{Si}}}\text{-O-}\underset{\text{OH}}{\overset{\text{OH}}{\text{Si}}}\text{-R-}N{=}C{=}O + OH\text{-}UPE\text{-}COOH \rightarrow \text{-O-}\underset{\text{O}}{\overset{\text{O}}{\text{Si}}}\text{-O-}\underset{\text{OH}}{\overset{\text{OH}}{\text{SI}}}\text{-R-NH-}\underset{\text{O}}{\underset{\Vert}{\text{CO}}}\text{-UPE-COOH} \qquad (4)$$

where



$$R = \text{-(}CH_2)_3\text{-NH-}\underset{\text{O}}{\underset{\Vert}{\text{C}}}\text{-NH}(CH_2)_6\text{-}$$

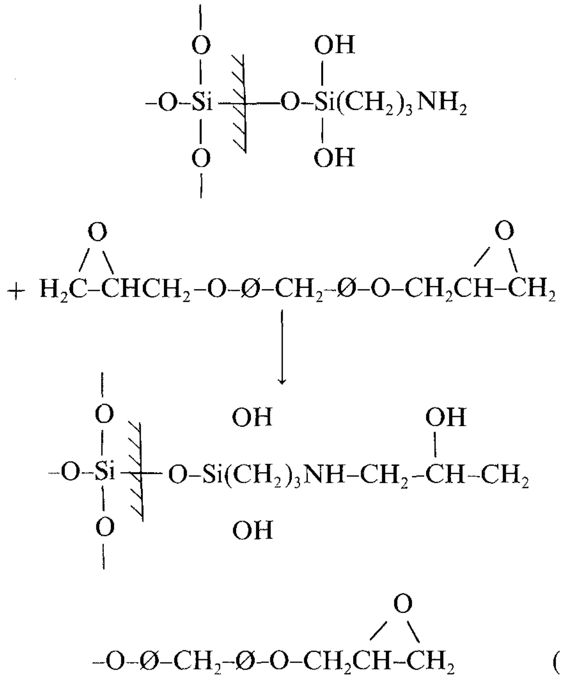
Finally, the composite is cured in a stainless steel mould sprayed by demould agent at a pressure of 100 kg cm^{-2}, and at a temperature of about 100° C for 3 h. During this time, styrene bridges set up between the polyester chains leading to the final thermoset material. The cured samples are demoulded after cooling at room temperature.

More details of mentioned reactions and characterization of the products have been researched by infrared spectroscopy and will be reported on a forthcoming paper [13].

For epoxy resin, the procedure of making samples is similar except that 15 wt % of DOP is added as plasticizer and 2.5 wt % 2, 4, 6-tris-(dimethylaminomethyl)-phenol (DMP-30) as a curing agent is used. The following procedure was used: Epon 828 is first mixed with DOP and DMP-30 at 60° in order to have a uniform mixture, then this latter is blended with particulate SiO_2 previously coated with hydrolized A1100 (see reactions 1 and 2).

A precuring step is effected under mixing at 80° C for 2 h. After pressing in the mould the specimens are placed in oven for the final curing step (4 h at 80° C).

The compound responsible of interfacial effect would have the following formula:



$$\mathrm{-O-\overset{\overset{|}{O}}{\underset{\underset{|}{O}}{Si}}-O-\overset{OH}{\underset{OH}{Si}}(CH_2)_3NH_2} + \mathrm{H_2\overbrace{C-CH}^{O}CH_2-O-\text{Ø}-CH_2-\text{Ø}-O-CH_2\overbrace{CH-CH_2}^{O}}$$

$$\downarrow$$

$$\mathrm{-O-\overset{\overset{|}{O}}{\underset{\underset{|}{O}}{Si}}-O-\overset{OH}{\underset{OH}{Si}}(CH_2)_3NH-CH_2-\overset{OH}{CH}-CH_2}$$

$$\mathrm{-O-\text{Ø}-CH_2-\text{Ø}-O-CH_2\overbrace{CH-CH_2}^{O}} \qquad (5)$$

where Ø = phenyl ring.

4. Results and discussion

4.1. Mechanical properties

Bending strength was measured by using the three points method (see Fig. 1 and [9]). The shape and dimensions of specimens are shown in Fig. 1. All of the specimens were notched with a diamond saw which is 1 mm thick. The distance between support points (d) is 50 mm. The measurements were made by using an INSTRON-10000. An X–Y plotter was used during testing to record the loads versus deflection. The critical load was obtained from the peak measured on the load–deflection curve (Fig. 2). The fracture toughness was calculated by using the following relation [9]:

$$K_{IC} = 6\, M_c a^{0.5}\, Y/(bw^2) \qquad (6)$$

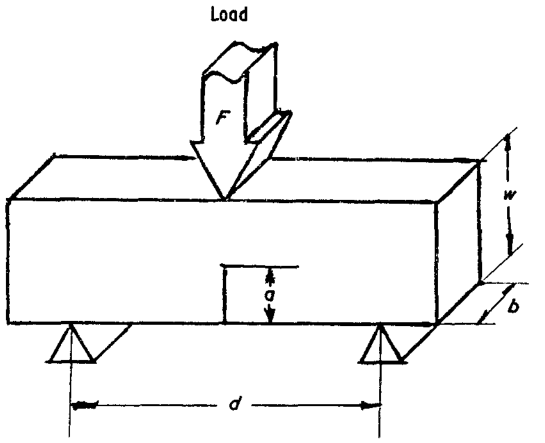


Figure 1 Sketch and dimension of specimens for bending testing: w = 20 mm, a = 10 mm, b = 10 mm, d = 50 mm, d is fixed distance of supports, F = load.

where M_c is the applied critical bending moment at the centre of the specimen (calculated as the product of the applied critical load times $d/2$)a is the size of notch and w, b are width and thickness of the specimen, respectively. The term Y is a dimensionless parameter which depends on the a/w ratio and is given by

$$Y = 1.93 - 3.07(a/w) + 14.53(a/w)^2 - 25.11(a/w)^3 + 25.8(a/w)^4 \qquad (7)$$

The specimens for testing the compressive strength were small cylinders with diameter of 1.6 cm, height 2 cm. A typical curve of a test is shown in Fig. 3. The results are listed in Table I and II.

When considering the results of bending strength and compressive strength of UPE based composites, it is evident that without coupling agent or with the A-1100 coupling agent only, both tests gave rather poor results. Evenmore, the addition of A-1100 causes a significant decrease in these properties. K_{IC} values of those samples were around 2 which are similar with literature data [9, 10]. On the contrary, when A-1100 and HMDI were used as compound coupling agents the K_{IC} significantly increases. Moreover, when the polyester content is 15% the bending strength results are higher. The addition of 10% CTBN of the total polyester (i.e. 1% of total composite), give rise to composites characterized by values of the bending strength still higher and by enhanced values of compressive strength (3.49 kg cm^{-2} and 1580 kg cm^{-2}, respectively).

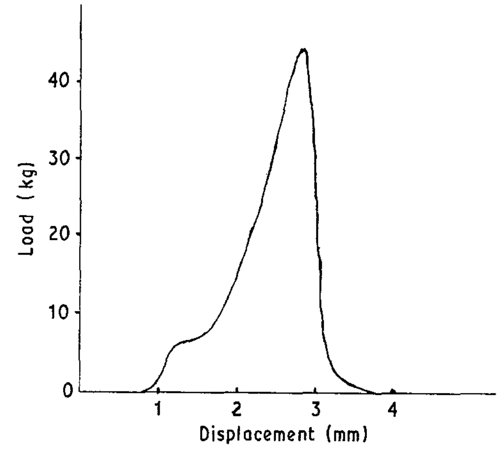


Figure 2 A typical curve of bending testing: load speed is 5 mm min^{-1}, record speed is 10 mm min^{-1}.

TABLE I Performance of composite based on SiO$_2$ and unsaturated polyester

No.	SiO$_2$		Polyester†		K_{IC} (MPa m$^{1/2}$)	Compressive strength (kg cm^{-2})
	(wt %)	Treated with*	(wt %)	Plasticizer		
1	90	no	10	no	2.23	963
2	90	A-1000	10	no	1.98	725
3	90	A-1100 +HMDI	10	no	2.63	889
4	90	A-1100 +HMDI	10	CTBN (1%)	3.49	1580
5	85	A-1100 +HMDI	15	no	3.32	–

*1% aqueous solution of A-1100 and /or 1% chloroform solution of HMDI.
†Used as solution of a prepolymer in styrene.

In the case of epoxy resin composites, the behaviour is somewhat different. In fact, the addition of A-1100 alone causes an enhancement both in the values of K_{IC} and compressive strength. The epoxy content, however, has a negative influence on both when it was over 10 wt %.

The different behaviour of the two systems can be explained as follows: upon hydrolysis, the A-1100 molecules can be bonded to the surface of SiO$_2$, but they cannot react with polyester resin. In our opinion, the polar surface of SiO$_2$ exhibits a better adhesion to polyester than the same surface upon coating with A-1100. This is an important phenomenon as in general the silane is used alone as coupling agent to increase the performance of polyester composites, but in fact the silane coupling agent only acts as a lubricant but it cannot set up any effective chemical bond between polyester and SiO$_2$. Thus in the case of a composite based on SiO$_2$ and polyester, the addition of A-1100 alone has no positive effect on the compressive and bending strength, similarly with ordinary lubricant. This is not the case of epoxy matrixes, where the silane can bond itself to both the components of the composite structure, so assuring a good stress transfer between the phases.

4.2. Morphology of composite by SEM analysis

The fracture surfaces of specimens after bending test were observed by a scanning electron microscope after coating with gold–palladium.

There are some clear differences between specimens with and without compound coupling agent for polyester composites. As reference, the known brittle fracture surfaces of polyester and epoxy are presented in Figs 4 and 5.

Figs 6 and 7 show fracture micrographs of the composite based on polyester and SiO$_2$ not treated with any coupling agent. It is easy seen especially from Fig. 7 that the polyester resin coats but does not stick on the surface of silica particles. Figs 8 and 9 correspond to sample No 2 in which the sands were treated with A-1100 alone. It is clear that the crack creates at the boundary between sand and polyester so that on the Fig. 8 (magnification × 160) all of sands particles are exposed on the fracture surface. At higher magnification (see Fig. 9) the surface of sand appears very clean and the crack is created on the boundary of grain of SiO$_2$ and polyester, with complete debonding. Figures 10 and 11, corresponding to sample No 3, show that there is a strong boundary between sand particles and polyester resin in the presence of A-1100+HMDI, so that it is easy to find the crack front passing inside the polyester resin or inside the particles of sand but not on the boundary between them. Similar features can be seen in Figs. 12 and 13, where more can be found in the polyester resin dispersed rubbery particles of very small dimensions ($< 1\,\mu$m).

Figs 14 to 17 refer to samples No 6 and 7, i.e. epoxy matrices without and with A-1000. Fig. 14 looks very similar to Fig. 9 which confirms that while the absence of A-1000 in epoxy composite gives a material with a weak boundary between resin and sand, its presence with no additional reactive component gives a weak interphase in the case of polyester. On the contrary, Figs 16 and 17 show a very strong adhesion between epoxy and SiO$_2$ when the silane coupling agent is present. In fact (see Fig. 16) most of the sand particles are broken when fracture happens and show a smooth surface. It is very clear in Fig. 17 that SiO$_2$ grains and epoxy stick very firmly to each other.

5. Concluding remarks

Our preliminary studies on the preparation of com-

TABLE II Performances of composite based on SiO$_2$ and epoxy

No.	SiO$_2$		Epoxy 828		K_{IC} (MPa m$^{1/2}$)	Compressive strength (kg cm^{-2})
	(wt %)	Treated with*	(wt %)	Plasticizer		
6	90	no	10	DoP (1%)	3.64	1413
7	90	A-1100	10	DoP (1%)	4.89	1663
8	85	A-1100	15	DoP (1%)	4.89	1581
9	80	A-1100	20	DoP (1%)	4.35	1050
10	91	A-1100	9	DoP (1%)	4.19	1563

*1% aqueous solution of A-1100

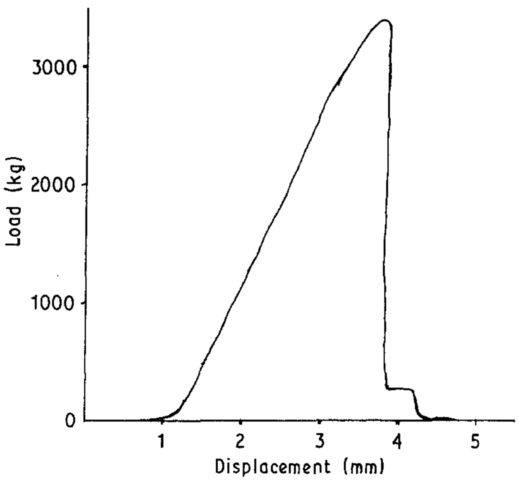


Figure 3 A typical curve of compressive testing: load speed is 5 mm min^{-1}, record speed is 10 mm min^{-1}.

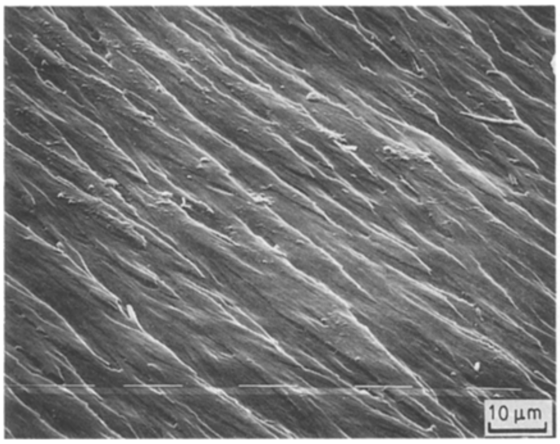


Figure 4 SEM micrograph of fracture surface after bending of unsaturated polyester resin. Magnification 1250 ×

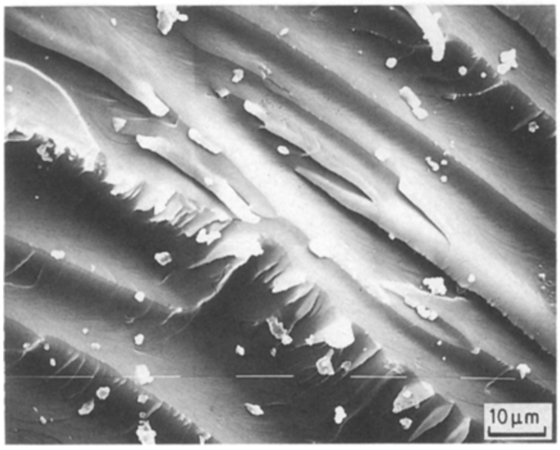


Figure 5 SEM micrograph of fracture surface after bending of pure epoxy resin. Magnification 1250 ×

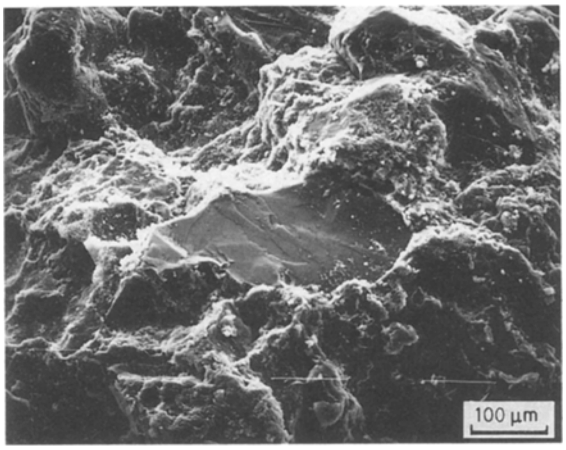


Figure 6 SEM micrograph of fracture surface after bending test of sample No. 1. (10 wt % polyester and 90 wt % of untreated glass beads). Magnification 160 ×

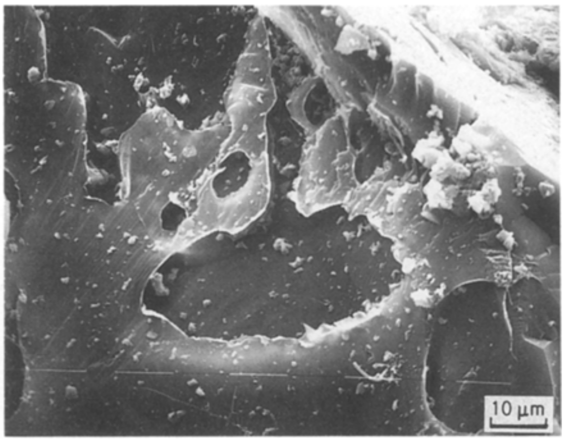


Figure 7 SEM micrograph of fracture surface after bending test of sample No 1 (10 wt % of polyester and 90 wt % of untreated glass beads). Magnification 1250 ×

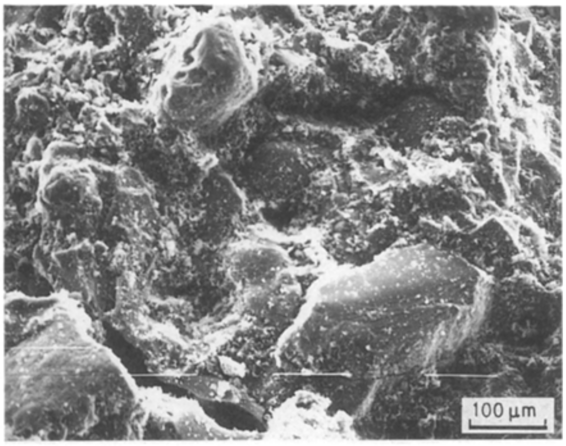


Figure 8 SEM micrograph of fracture surface after bending test of sample No 2 (10 wt % of polyester and 90 wt % of glass beads, which are treated with A-1100 only). Magnification 160 ×

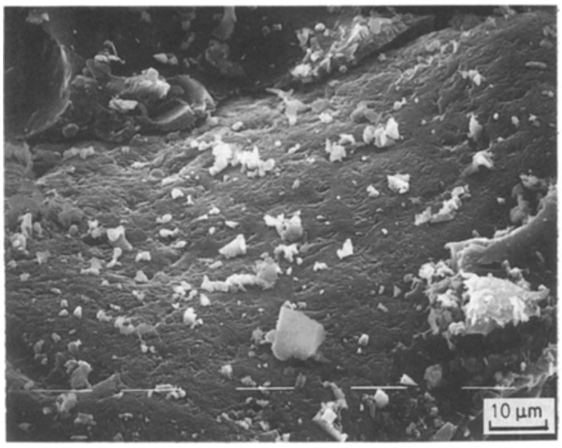


Figure 9 SEM micrograph of fracture surface after bending test of sample No 2 (10 wt % and 90 wt % of glass beads, which were treated with A-1100 only). Magnification 1250 ×

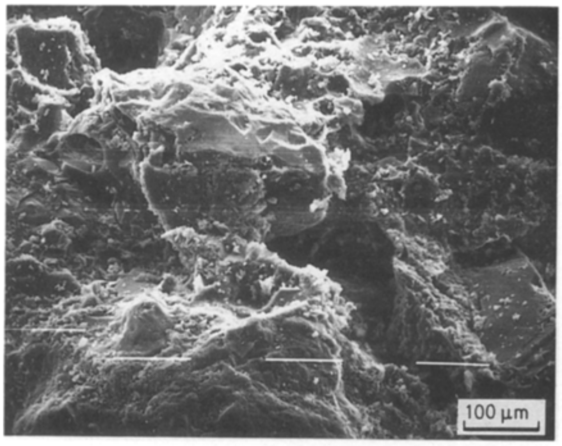


Figure 10 SEM micrograph of fracture surface after bending test of sample No 3 (10 wt % of polyester and 90 wt % of glass beads, which were treated with A-1100 and HMDI). Magnification 160 ×

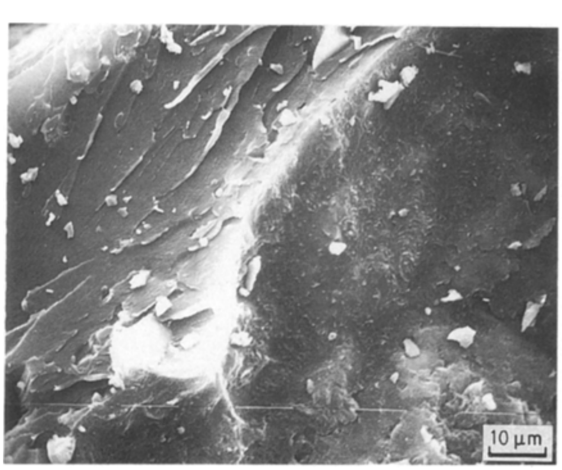


Figure 11 SEM micrograph of fracture surface after bending test of sample No 3 (10 wt % of polyester and 90 wt % of glass beads, which were treated with A-1100 and HMDI). Magnification 1250 ×

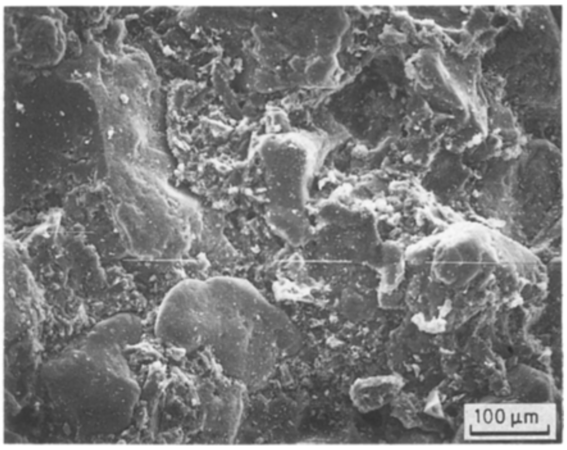


Figure 12 SEM micrograph of fracture surface after bending test of sample No 4 (10 wt % of polyester was mixed and 90 wt % of glass beads which were treated with A-1100 and HMDI). Magnification 160 ×

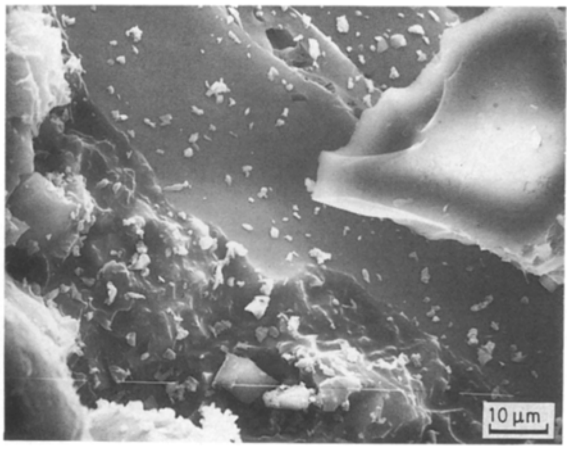


Figure 13 SEM micrograph of fracture surface after bending test of sample No 4 (10 wt % of polyester in which 1 wt % CTBN was mixed and 90 wt % of glass beads which were treated with A-1100 and HMDI). Magnification 1250 × .

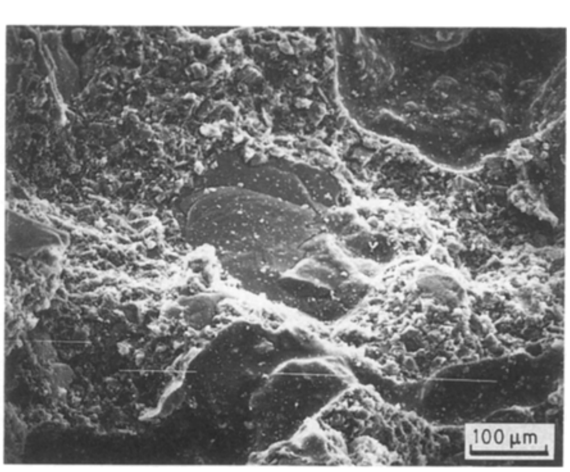


Figure 14 SEM micrograph of fracture surface after bending test of sample No 6 (10 wt % of epoxy and 90 wt % of glass beads which were untreated with any coupling agent). Magnification 160 ×

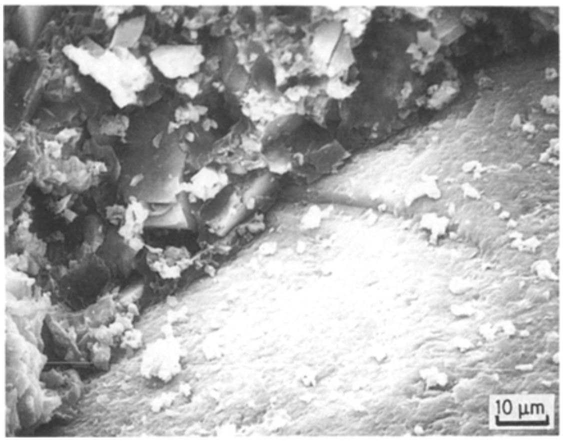


Figure 15 SEM micrograph of fracture surface after bending test of sample No 6 (10 wt % of epoxy and 90 wt % of glass beads which were untreated with any coupling agent). Magnification 1250 ×

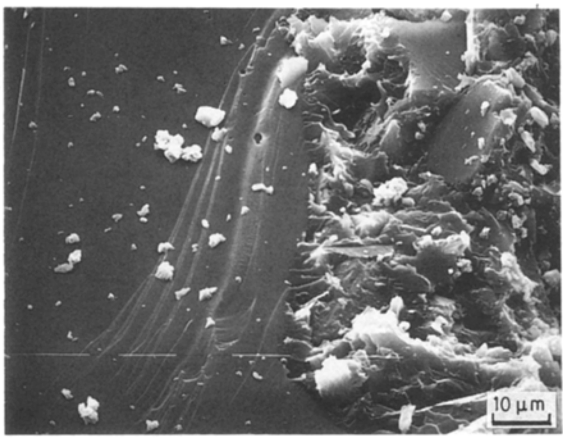


Figure 17 SEM micrograph of fracture surface after bending test of sample No. 7 (10 wt % of epoxy and 90 wt % of glass beads treated with A-1100). Magnification 1250 ×

posite materials with very high content of inorganic filler to be used in structural applications brought us to the following considerations

1. Coupling agent may improve effectively the bending and compressive strength of highly filled particulate composite based on SiO_2 and epoxy. The K_{IC} values are increased about 30% and this kind of composite has high strength and low cost.

2. For the composite based on epoxy resin, the addition of the only silane coupling agent really increases the strength, as an effective chemical bond can be created among epoxy and treated sand particles.

3. For the composite based on polyester and SiO_2, it is observed that the addition of the only silane coupling agent used alone will cause a lowering of the strength, as a molecular chain between matrix and particles of SiO_2 could not be created. When HMDI is used to build a bridge between A-1100 and polyester, the strength of composite is increased, and even more when a reactive rubbery phase is included.

4. Morphologies of fracture surfaces greatly support the above mentioned conclusions.

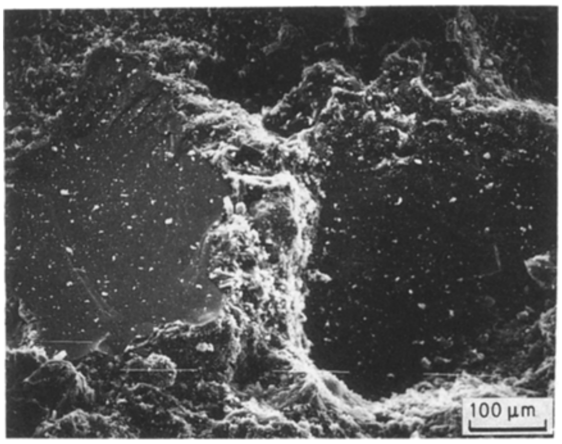


Figure 16 SEM micrograph of fracture surface after bending test of sample No 7 (10 wt % of epoxy and 90 wt % of glass beads which were treated with A-1100). Magnification 160 ×

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