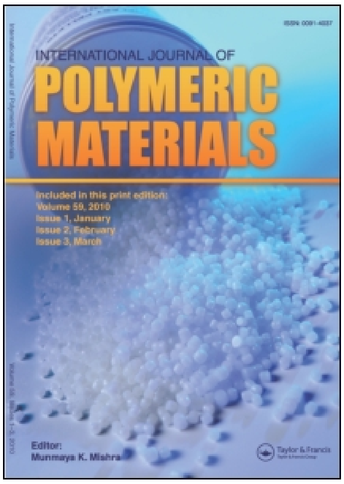

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Modification of Solid Surfaces, Pigments and Fibres through Chemical Attack or through Polymer Grafting

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Modification of Solid Surfaces, Pigments and Fibres through Chemical Attack or through Polymer Grafting

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The aim of this paper is to evidence the influence of strong filler-elastomer or fibre-matrix interactions upon the mechanical performance of the corresponding composite materials. The methods of modification of the surface properties such as polymer grafting are described. Recent efforts on surface energy characterization calling on molecular probes adsorption are indicated. Finally, the case of an epoxy resin-carbon fibre composite is examined using monofibre adhesion tests on initial or highly oxidized samples.

1. INTRODUCTION

Polymers and solid surfaces are associated in many practical systems as for example in composite materials. Certain mechanical properties of these materials are influenced by the behaviour, under stress, of the polymer-solid interface and interphase; the interface is a region of molecular dimension in the close vicinity of the surface whereas the interphase is a much more deeper zone where the polymer matrix still experiences the influence of the solid surface.

Most theories of reinforcement of elastomers, or of composites, state that the filler has to be wetted by the polymer in order to achieve optimum performances. Wetting results from interactions which may be physical, if they are reversible, or chemical, if they are irreversible in nature. Hence the question of the relative significance of physical or chemical interactions is raised. Now some experimental evidence exists which sometimes call for physical and sometimes for chemical interactions. However, the choice of the relevant macroscopic property which is believed to trace the influence of the nature of the interface is indeed a difficult task since no direct experimental proof is so far available.

It seems obvious however, that depending on the deformation conditions, static or dynamic, of large or low amplitude... the physical forces may present advantages over the strong, relatively immobile chemical link. For instance, on the one hand if chains can easily slip over the filler surface, thus relieving or distributing more uniformly the stress, it is clear that adsorption energy will be released, a phenomenon which will take over part of the mechanical energy applied on the chains. This mechanism was initially proposed by Dannenberg[1] as a contribution to the reinforcement of elastomers.

On the other hand, if a repeated, of low amplitude deformation or a dynamic strain is applied to the composite, a fatigue phenomenon may intervene at the polymer-filler interface causing dewetting, void formation and premature rupture of the material: Chemical linking would thus be more appropriate.

A tremendous amount of work has been devoted to solving the problem of reinforcement or more specifically to the elucidation of the role assumed by the interface. The aim of this paper is not to review the literature, but rather to concentrate on some of the work performed in this domain, in our Laboratory and to point to the future evolution of our investigations. Three points will be discussed:

1) The methods used for the modification of solid substrates: the guiding idea was to graft a polymer on the filler, thus realising the chemical interaction under well defined conditions and considering the modified substance as a model filler for elastomers.

2) Looking at the mechanical properties of a composite containing these model fillers will lead to information about the interest of having a tightly chemically bound surface layer. Now, this will provide only an indirect proof which will hardly define the optimum surface properties a filler should process. Therefore, the nature of the research, in progress, relative to the measurement of the surface energy of a filler in conjunction with its modification will be mentioned.

3) Finally, the results obtained with a glassy material, namely an epoxy resin reinforced with carbon fibres, will be described. Such a study highlights the role of another parameter, which is the surface roughness where polymer chains become anchored.

2. THE GRAFTING METHODS

A series of grafting methods have been developed[2] and it would certainly be tedious to make an exhaustive review. Two situations can be distinguished:

1) the grafting onto a solid substrate.
2) the grafting starting from the solid surface.

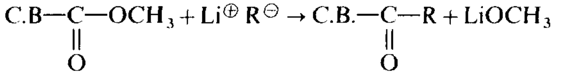
What is meant by these obvious situations will be clarified with the help of a few examples. An intermediate procedure is provided by the use of coupling agents. These are bifunctional molecules: one of the reactive end enables the fixation onto the solid surface whereas the other is liable, at least theoretically to form a chemical link with the polymeric matrix. Much work has been devoted to coupling agents, but it is not still clear why only a limited number of functionalities is efficient.

The methods of *grafting starting from the solid surface respond to the following principle:*

A polymer chain grows from an initiating site previously introduced on the solid surface, the initiating site being of a free radical or of an ionic nature. For instance, a peroxide group can be fixed on carbon black. During thermal decomposition, and in the presence of a monomer, it will initiate the free radical polymerization of say styrene or isoprene. The carbon black thus becomes part of the growing chain. Similarly, carbon black can become initiator of an anionic polymerization when some of the hydrogen atoms of the graphitic surface layers are substituted by lithium atoms.

With a pigment, having 100 m^2/g, about 20% in weight of polymer can be irreversibly fixed by these methods. *Grafting onto the surface* corresponds to the formation of chemical links consecutive to a termination step of a polymer carrying either a free radical or an anionic or cationic active site. Free radicals are readily formed on polymers, using mechanical or chemical procedures. These methods generally lead to the desired practical result, but the pertaining reaction schemes remain often obscure.

For a fundamental study, the following scheme is more suitable:



$$\mathrm{C.B{-}\underset{\underset{O}{\|}}{C}{-}OCH_3 + Li^{\oplus}\, R^{\ominus} \rightarrow C.B.{-}\underset{\underset{O}{\|}}{C}{-}R + LiOCH_3}$$

Here, the surface acidic groups of a carbon black are blocked after methylation. Then, an anionic polymer (R^-Li^+) is prepared separately; since anionic polymerization does not show spontaneous termination reactions, it is possible to obtain macromolecules of a given chain length, keeping their reactive extremity until a deactivating species, such as the methylated carbon black, is added.

Now, this reaction medium is well defined since:

1) the number of grafting sites is known
2) the number of grafted chains can be measured knowing the weight loss under pyrolysis and the molecular weight of the anionic polymer (measured on the homopolymer).

Hence, the yield of the grafting reaction can be followed as a function of numerous experimental factors such as the molecular weight of the grafts, the extent of the solid surface area.

The main results are the following:

1) Grafting is limited. As soon as a monolayer of partly interpenetrated coils is established, grafting stops.

2) The important factors which affect the grafting ratios are: the extent of available solid surface area and all these variables which alter the morphology of the polymeric coils in solution (before grafting).

Perhaps, the surface coverage model is best illustrated by electron micrographic observations.[3] Silica has been grafted with polybutadiene which was then stained with osmium tetroxide so as to increase the contrast for electron micrographic examination.

The electronmicrograph (Figure 1) illustrates the morphology of the silica (treated with OsO_4). Particles have about 100–150 Å in diameter. Care must be taken during prolonged observation, because silica may undergo severe thermal deformation. The electron micrograph (Figure 2) pertains to the silica carrying polybutadiene grafts stained with OsO_4: Clearly, the polymeric coils

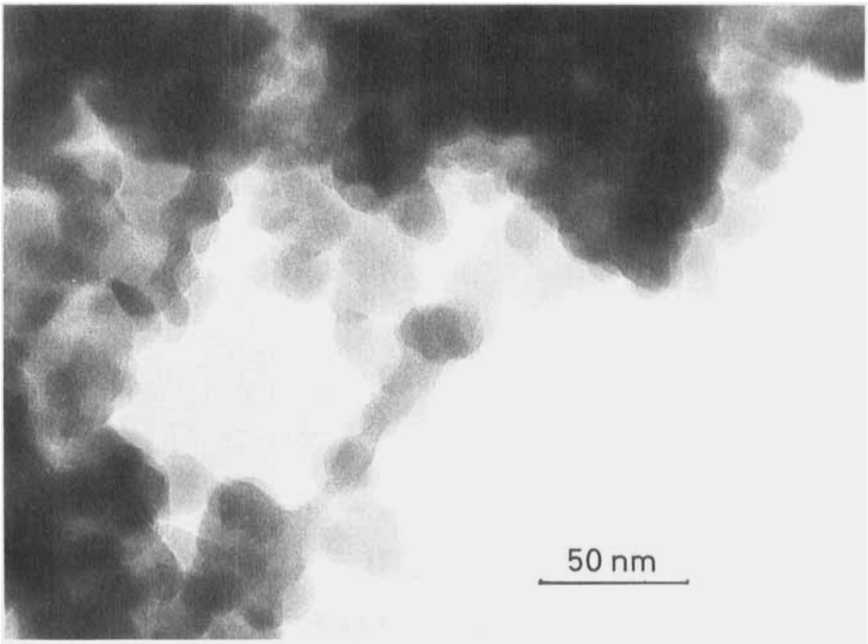


FIGURE 1 Electron micrograph of silica (Aerosil 130, from Degussa) treated with $OsO_4 - G = 800\,000$.

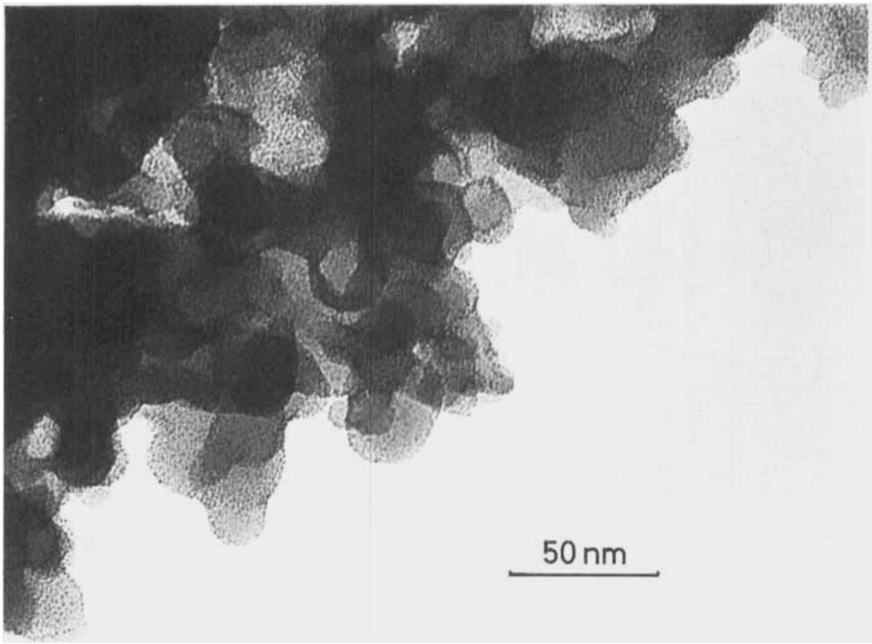


FIGURE 2 Electron micrograph of polybutadiene grafted silica, stained with $OsO_4 - G = 800000$.

form a very regular array around the silica particles: a picture which substantiates the model of the surface coverage we proposed earlier.

Such a filler, with its monolayer of chemically fixed polymer appears, at least at first sight, as a model for a study of the influence of chemical linkages on mechanical characteristics.

Carbon blacks were therefore modified either with polyisoprene or polystyrene grafts using the anionic method. Masterbatches were prepared, according to a solution procedure, so as to avoid the common milling step of the ingredients, where chemical interactions between filler and matrix are believed to occur. After classical vulcanization, the dynamic mechanical properties of the vulcanizates were established using a (Rheovibron) visco-elasticimeter which yields the storage modulus and the loss modulus. Three vulcanizates are compared (Figure 3):

1) the vulcanizate containing the initial non modified carbon black

2) the previous vulcanizate, having received an additional milling, so as to be comparable to vulcanizates prepared in the classical way

3) the vulcanizate containing the grafted sample, prepared by a solution mixing technique.

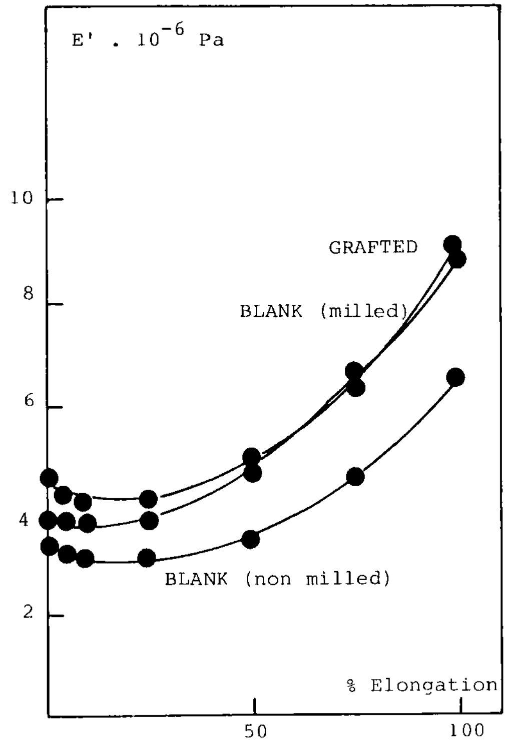


FIGURE 3 Storage moduli of polyisoprene-carbon black vulcanizates (33 phr carbon black) measured at room temperature, (35 Hz), with a double amplitude of deformation equal to 0.00316 cm.

The variations of the storage moduli with the degree of deformation differentiate the behaviour of the 3 samples. Obviously, the vulcanizate prepared from the initial unmilled black has the lowest performance.

The property of the milled sample (containing the initial black) to exhibit properties close to the grafted filler sample, points out that, during milling, strong interactions, comparable to those obtained by grafting, are indeed occurring. Moreover, it can be added[4] that chemical interactions are beneficial, as far as low dynamic deformation is concerned.

3. THE SURFACE ENERGY OF MODIFIED FILLERS

However, a curious observation was the fact that grafted polystyrene and grafted polyisoprene samples behave in a very similar manner when incorporated into a polyisoprene matrix. Indeed the same improvement in dynamic mechanical properties is recorded. The molecular compatibility of the grafts with the matrix is not therefore the determining factor. Apparently, the two modified carbon blacks must have very close surface energies or potentials of interaction.

Unfortunately, there is no easy method for the measure of the surface energy of finely divided pigments. The technique of liquid contact angle determination, on compressed powder, is not applicable without special precautions and even so, the results are often doubtful. A different technique which appears more promising is the measurement and exploitation of adsorption isotherms of selected molecular probes. This work is in progress and only a few indicate results will be given in this instance.

A study[5] has been made on silicas modified systematically by esterification with alcohols, having 1 to 20 carbon atoms.

The grafted silicas were then taken as stationary phases for gas chromatography. The adsorption characteristics of hexane, a model apolar substance for many of the important elastomer molecules, were measured. Typical adsorption isotherms are shown on Figure 4.

Initial silica, or silica carrying short grafts is still able to exchange strong and specific interactions through their polar surface groups which are not yet shielded: the type II isotherm is indicative of this behaviour. With increasing grafted chain length, the shape of the isotherm is simplified, becoming linear,

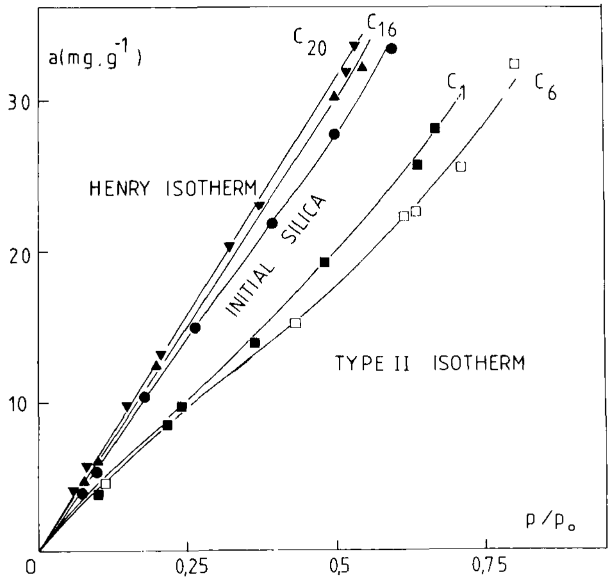


FIGURE 4 Adsorption isotherms of hexane on esterified silicas (spherosil XOB 075, Rhône Poulenc) (temperature: 47°C).

following Henry's law. It can also be noted that up to a given grafted chain length, no further significant change in the shape of the isotherms is recorded.

A series of informations can be drawn from the adsorption isotherms. Firstly, it is possible to measure the decrease in specific surface energy resulting from the adsorption of a vapour. A strong decrease of this quantity is indicate of a high energy surface. Gibbs equation was used:

$$\Delta G = \frac{RT}{MS} \int_0^p \frac{a}{p} \cdot dp$$

In this expression S is the specific surface area
M is the molecular weight of the probe
a is the adsorbed amount
p is the equilibrium pressure

ΔG can be calculated knowing the adsorption isotherm.

The entropy of adsorption becomes available if the enthalpies of adsorption are known. Adsorption enthalpies can be directly determined by calorimetric methods, but they can also be calculated by applying Clausius–Clapeyron equation. For two isotherms measured at two close temperatures (T_1 and T_2).

$$(\Delta H)_a = -R \frac{T_1 T_2}{T_1 - T_2} \left(\ln \frac{P_2}{P_1} \right)$$

where $(\Delta H)_a$ is the isosteric heat of adsorption, P_2 and P_1 the values of the equilibrium pressures, for a given value of adsorption (a), corresponding to temperatures T_2 and T_1 respectively.

The actual results are gathered on Figure 5. It is seen that, for untreated silica, the heat of adsorption decreases sharply as the surface coverage, consecutive to the adsorption of hexane, increases: this variation is due to the progressive elimination of the high energy surface sites. These high energy surface sites, in the case of the esterified silicas, are shielded: hence the heat of adsorption becomes constant, at a value close to the heat of condensation of hexane.

Figure 6 shows the variation of the enthalpies of adsorption, for a given fixed value of the surface coverage, and the corresponding values of the entropies of hexane adsorption on silicas carrying grafts of increasing chain length. Clearly, a chain length exceeding about 16 atoms of carbon will not give further advantages as far as only dispersive forces are concerned.

Thus it is understandable that polymeric grafts will behave similarly, whatever the chain length, if they are hydrocarbons: that is, substances able to exchange only dispersive forces.

As mentioned earlier, work is in progress: the goal being now to match the surface properties of the fillers and those of the polymers on the basis of the molecular interactions which can be detected by these techniques. Up to now,

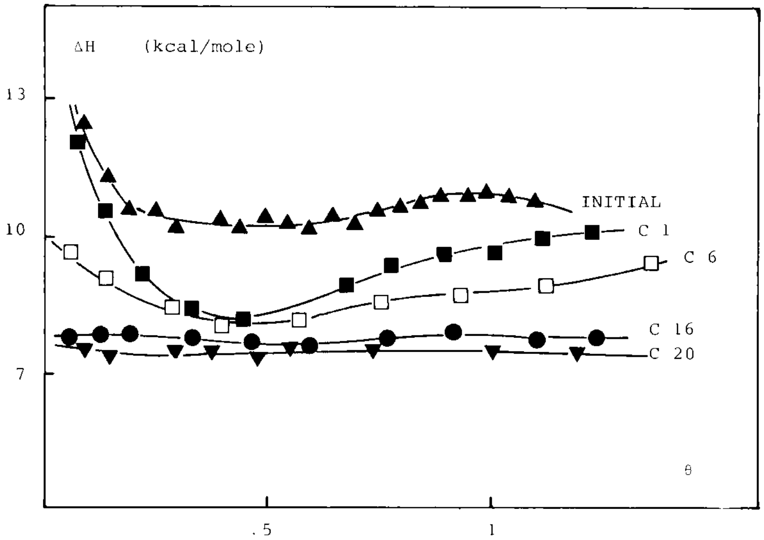


FIGURE 5 Isosteric heats of adsorption of hexane onto esterified silicas as a function of the hexane surface coverage.

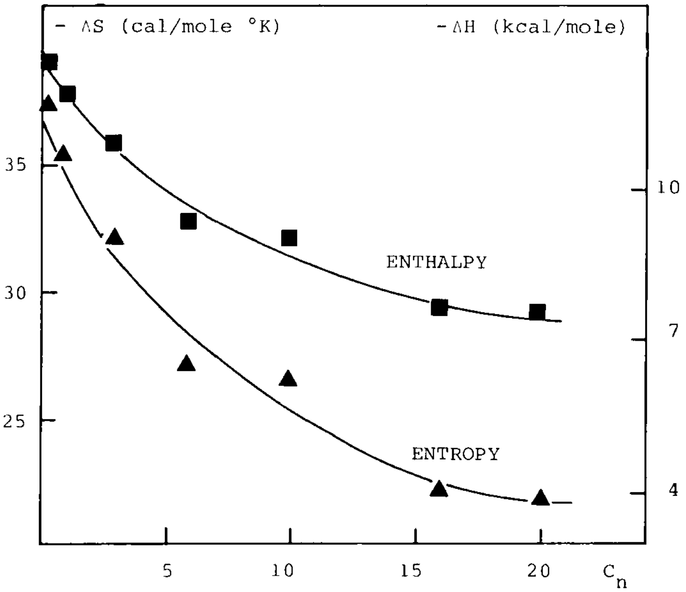


FIGURE 6 Enthalpies and entropies of hexane adsorption on esterified silicas, as a function of chain length (C_n) of the modified silicas.

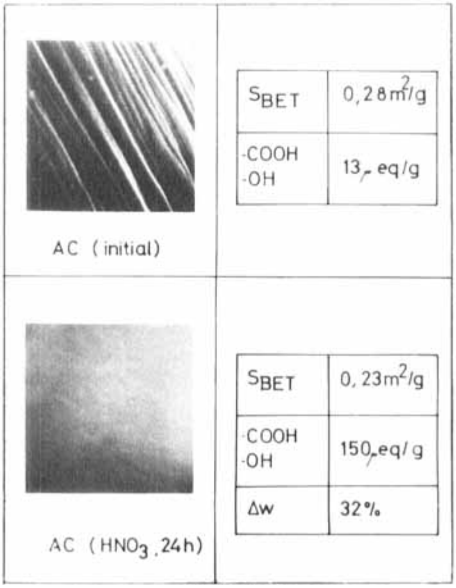
only elastomeric materials have been considered. To finish, we shall take the example of a transparent glassy composite for which it is easier to observe in some cases the behaviour of the interface, at least from a macroscopic point of view.

4. THE CARBON FIBRE-EPOXY INTERFACE[6]

The composite is made from a resin compounded from epichlorhydrin and bisphenol A and contains two types of carbon fibres: the AC and AG fibres, both issued from an acrylic precursor. AC fibres have received a heat treatment of only 1100°C whereas AG fibres were treated at 2700°C and have a more pronounced graphitic type of structure. Thus, they will be less sensitive towards nitric acid attack and will give derivatives typical of graphite.

Without a surface treatment, these fibres do not satisfactorily reinforce the epoxy resin which shows low shear strength accounted by the poor adherence of the matrix to the fibre, resulting in poor stress transmission.

Figure 7 summarizes the main results of the nitric acid oxidation of the less structured AC fibres. Initial AC fibres present irregularities or scratches which are eliminated upon oxidation. The area of the interface slightly decreases which is detrimental for adhesion. But, at the same time, the content of



S_{BET}	0,28 m^2/g
-COOH -OH	13 μeq/g

S_{BET}	0, 23m^2/g
-COOH -OH	150 μeq/g
Δw	32 %

FIGURE 7 Characteristics of AC fibres before and after nitric acid treatment.

oxygenated groups is significantly augmented, producing an increase in the surface energy especially of the polar component, thus favouring interactions with the polar matrix. The two opposite trends however, make the situation confusing. Indeed, when the shear resistance of an aligned fibre composite is measured, according to a standard Cantilever test, no real difference between the behaviour of the initial and the oxidized fibre is evidenced. It follows that the apparition of oxygenated surface groups compensates the loss in surface roughness which plays the role of allowing the anchorage of polymeric chains or offers, to the polymer, a volume where it will escape stress.

With graphitized fibres, the results of Figure 8 are obtained. In opposition to AC fibres, AG fibres show after treatment a higher surface roughness, and consequently a higher specific surface area, though not an appreciable increase in the number of surface chemical groups. Nevertheless, as seen in Table I the value of the shear resistance (*hb*) has almost doubled after a 48 h treatment with nitric acid.

TABLE I

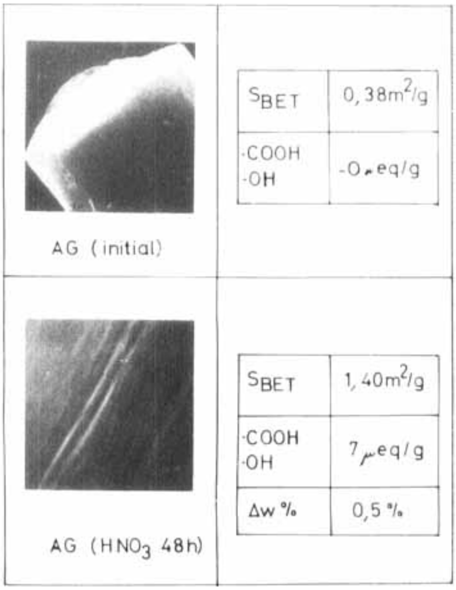
Shear resistance of modified carbon fibre-epoxy composites

	shear resistance (*hb*)
Initial AC fibre	5.5
AC + HNO_3 (24 h)	5.6
Initial AG fibre	2.2
AG + HNO_3 (48 h)	4.3
A. G. (Hummers) (40°C, 10 min)	6

The value of the shear resistance of the composites containing the AG fibres has almost doubled after a 48 h treatment with nitric acid. One can however notice that the initial value is already very low, much smaller than that relative to AC fibre.

Table I shows the important increase of the shear resistance after treatment of the graphitic carbon fibre with Hummers reagent. As indicated earlier, since AG fibres show much of the reactivity of graphite, it was possible to form on their surface a controlled amount of graphitic oxide, a highly oxygenated compound, transforming the low energy surface of the fibre to a very high energy surface capable of polar interactions and chemical bonding. The good adherence is also illustrated by the morphology of the composite surface, after rupture, as shown on Figure 9. Treated AG fibres readily stick to the matrix.

The improvements of the shear resistance results, as seen, from the formation of surface roughness and from increased interactions possibilities



S_{BET}	0,38 m^2/g
·COOH ·OH	-0 μeq/g

S_{BET}	1,40 m^2/g
·COOH ·OH	7 μeq/g
Δw %	0,5 %

FIGURE 8 Characteristics of AG fibres before and after treatment with nitric acid.

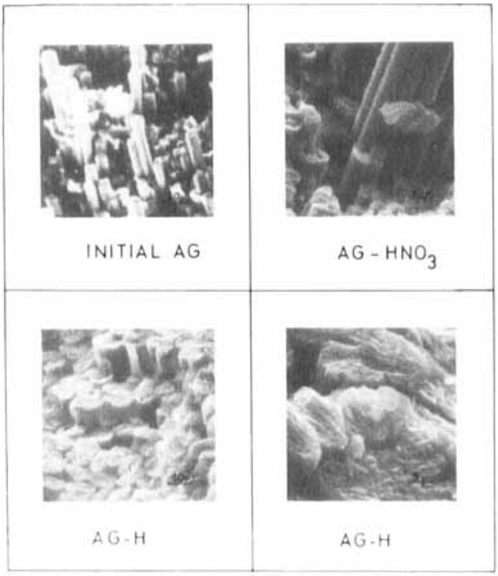


FIGURE 9 Scanning electron microscopic observation of the composites, after rupture.

and it would be of value to distinguish the respective contributions of these two factors.

Chemical or strong interactions between the fibre and the matrix will keep their influence whatever the direction of the stress. Hence the composite is reinforced equally in all directions. This, of course, is not the case when surface roughness is the only possibility of anchorage of the macromolecules on the fibre surface.

Tests have been designed to characterize the adhesion parallel or perpendicular to the axis of the fibre.

In McGarry's[7] procedure, the filament is placed in the centre of a specially shaped test piece (Figure 10). This piece is compressed. Owing to the differences in Poisson's coefficients between fibre and resin, a stress perpendicular to the fibre axis is created at the fibre-resin interface. Its intensity is a maximum where the section is a minimum. With increasing stress a rupture occurs at the interface, as indicated by bright spots when the fibre is illuminated.

In Shiriajeva's[8] test, a filament is encapsulated in resin and the force necessary to separate the filament from the resin is recorded. The length of the adhesion joint is chosen sufficiently small to avoid rupture of the fibre. Adhesion is estimated by dividing the force required for rupture at the interface by the area of the interface: the value of the adhesion parallel to the

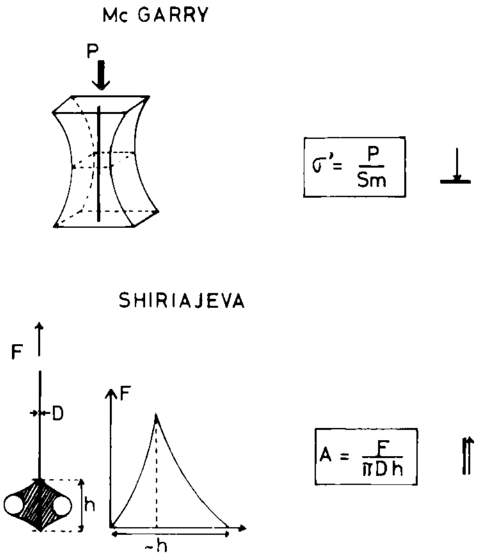


FIGURE 10 Schematic representation of the mono-filament tests.

axis of the fibre is thus determined. In summary, McGarry's test gives an estimate of the adhesion perpendicular to the fibre axis while Shiriajeva's test gives the adhesion parallel to the axis. Experimental results are shown in Table II.

TABLE II

Estimate of adhesion (*hb*)

	McGarry	Shiriajeva
Initial AG Fibres	115–150	1.28–1.70
AG + HNO_3 (48 h)	160–190	3.00–3.80
AG Hummers (40°C, 10 min)	≈500	»

These results clearly indicate that, in the case of AG fibres treated with nitric acid, the adhesion is preferentially increased when a force is applied to the fibre parallel to its axis. This fact points to adhesion by mechanical immobilization of the resin in the asperities of the surface. With AG fibres adhesion increased in both parallel and perpendicular directions. It was not even possible to determine a value in the parallel direction, since the fibre itself broke before the end of the run: an observation which suggests chemical bonding.

5. CONCLUSION

In conclusion, we are aware that we have selected only some examples of studies on fillers or composite materials which highlight the relation between the quality of the interface and its influence on the composites mechanical behaviour. But clearly, a more quantitative relationship is needed to predict theoretically and hence to design the filler surface properties so as to achieve optimum performance of the composite. This will be possible with a better knowledge of the surface characteristics of the filler.

References

1. E. M. Dannenberg, *Trans. I.R.I.*, **42,** T26 (1966).
2. J. B. Donnet, E. Papirer and A. Vidal, Grafting of macromolecules onto carbon black. *Chemistry and Physics of Carbon*, **12** 171 (1975), M. Dekker, Ed.
3. A. Vidal, E. Papirer and J. B. Donnet, *Europ. Polym. J.* **15,** 895 (1979).
4. J. Le Bras and E. Papirer, *Appl. Polym. Sci.* **22,** 525 (1978).
5. Z. Kessaissia and E. Papirer, *J. Chim. Phys.*, **75,** 709 (1978); Z. Kessaissia, *Ph D thesis*, Mulhouse (France), 1979.
6. J. B. Donnet, E. Papirer and H. Dauksch; *Proc. International Conf. Carbon Fibres* (London), 1974.
7. F. J. McGarry and J. J. Bikerman, *Glass Ind.* 525 (1959).
8. G. W. Shiriajeva, G. D. Andrejewskaya, *Plast. Massy* **4,** 43 (1962).