Coupling of Polystyrene to a Silane-Treated Mica

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Synopsis

This paper deals with the coupling of polystyrene to a closely packed and highly ordered cationic vinylbenzyl silane (CVBS) on mica. It is shown that a thermal treatment is required for maximum retention of polystyrene on treated mica. Moreover, a thermal treatment at 250°C is much more effective than one at 170°C. The effect of the number of silane monolayers on mica was investigated. In general, one monolayer of CVBS gave optimum retention of polystyrene. The addition of peroxides further improved this retention and at the same time allowed the use of lower treatment temperatures. Some data are presented which consider the importance of the silane solution concentration and silane functional groups.

INTRODUCTION

A silane treatment applied at the interface of a polymer resin and a particulate mineral filler is known to improve the mechanical properties of the composite material that these substances form particularly after exposure to moisture.

The mechanism of adhesion between silane and thermoset resins or reactive thermoplastics is fairly simple to understand. These materials can readily undergo chemical reaction with the organic portion of the coupling agent and form covalent bonds.[1] However, the adhesion process of silane-treated materials to nonreactive thermoplastics is not well understood, and various theories have been proposed in an effort to explain this phenomenon.[2] The Van der Waals forces and hydrogen bonding theories predict that a silane surface treatment is desirable if it leads to a surface polarity similar to that of the polymer. The surface energy theory suggests that any surface of a higher critical surface tension than the polymer results in good adhesion. The diffusion theory of adhesion emphasizes the importance of the mutual diffusion of the two phases in question. A charge transfer theory has also been suggested[3] which envisages the formation of radicals; this in turn results in the copolymerization of silane and resin. None of the above proposals, however, supplies a comprehensive explanation of the silane–resin interaction.

Recently, Plueddemann and Stark proposed that the adhesion of nonreactive thermoplastics to silane-treated surfaces is the result of the formation of an interpenetrating polymer network.[4] They suggested that at the high temperatures required for molding, a thermoplastic is normally soluble in the siloxane phase. As cooling occurs, its solubility is lost, but the two phases are held together by chain entrapment, which takes place at the higher temperatures. This theory has not yet been proved, but it seems to be more comprehensive than the previous ones.

In recent publications, the results of a study on the interaction of coupling agents with mica surfaces were reported.[5,6] Mica flakes, a silicate material like glass, are known to be capable of imparting high degrees of reinforcement when suitably delaminated and oriented in a polymer matrix.[7-9] This material is very abundant, and it is cheaper than glass fiber. In previous studies, we have shown that by controlling the treatment time and the concentration of the silane solution, individual and complete silane monolayers can be deposited on mica flakes. Quantitative analysis of these layers showed them to be highly oriented and closely packed with the silane chains oriented normal to the surface.

In this paper, the study has been extended to include the resin, specifically polystyrene, a nonreactive thermoplastic. Mica flakes were treated in the same fashion as before, and samples were obtained containing one, two, and three monolayers of a cationic vinylbenzyl silane (CVBS) coupling agent. It was therefore possible to study the effect of the number of monolayers on polystyrene retention with respect to parameters such as temperature, dwell time at various temperatures, and the effect of peroxides. The effect of the concentration of the silane-treating solution was also studied.

The purpose of this paper is to report on the importance of parameters such as silane-surface coverage, temperature, and peroxide addition on the retention of polystyrene by mica and to shed some light on the possible mechanism of adhesion between a nonreactive thermoplastic and a silane-treated mica.
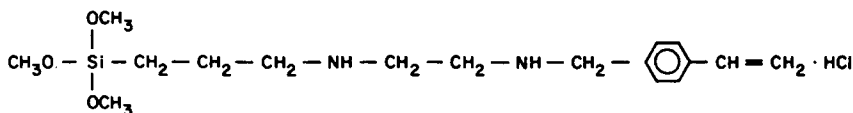
EXPERIMENTAL

Starting Materials

The mica used in this study was obtained from Marietta Resources International, Ltd. and is of the Phlogopite variety (trade name Suzorite mica). In these experiments, the 60HK mica was used, a designation whereby the value 60 corresponds to the average mesh size of the flakes and HK refers to its classification as being highly delaminated. Data for the characterization of this mica were presented in an earlier work.[5] A 60NP Suzorite mica from Marietta was also studied. This particular mica differs from the 60HK type in that it was surface-treated by Marietta and is somewhat less delaminated.
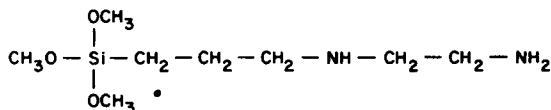
Most of the surface treatments reported in this publication involved a cationic vinylbenzyl silane (CVBS) obtained from Dow Corning Inc. (trade name Z-6032). Its molecular formula is shown in Figure 1 (molecular weight = 332 g·mol^{-1}), and it is designated as N-β-(N-vinylbenzylamino)-ethyl-γ-amino-propyltrimethoxy silane monohydrogen chloride.[10]

In order to determine the importance of the benzyl and vinyl groups in CVBS to the coupling of polystyrene, an alternate silane surface treatment with N-(2-aminoethyl)-3-amino-propyltrimethoxy silane (APS), also obtained from Dow Corning (trade name Z-6020), was undertaken. Its molecular formula is shown in Figure 1 (molecular weight = 180 g·mol^{-1}).

A commercial polystyrene obtained from Haven Chemicals was used. Its molecular weight was determined by gel permeation chromatography and by viscosity measurements. Its number-average molecular weight is 70,000, its weight-average molecular weight is 216,000, and its viscosity-average molecular weight is 219,000 g·mol^{-1}.

$$CH_3O - \underset{\underset{OCH_3}{|}}{\overset{\overset{OCH_3}{|}}{Si}} - CH_2 - CH_2 - CH_2 - NH - CH_2 - CH_2 - NH - CH_2 - \langle\bigcirc\rangle - CH = CH_2 \cdot HCl$$

CVBS

$$CH_3O - \underset{\underset{OCH_3}{|}}{\overset{\overset{OCH_3}{|}}{Si}} - CH_2 - CH_2 - CH_2 - NH - CH_2 - CH_2 - NH_2$$

APS

Fig. 1. Molecular formulas of the coupling agents studied.

Preparation

Mica flakes were treated with a very dilute CVBS solution (0.025 g silane/100 mH H_2O at a pH of 3.5. The time of treatment was controlled in such a way that mica samples prepared with one, two, and three monolayers of the coupling agent were obtained as described in the previous work.[5] The treated mica flakes were filtered on a Büchner filter, washed with distilled water, dried in air, and heated briefly for approximately 15 min at 140°C in order to complete the condensation process. The quantity of silane adsorbed on the mica was verified by carbon analysis. The one, two, and three monolayer silane-treated mica samples were labeled M-1, M-2, and M-3: they contain, respectively, 0.1, 0.2, and 0.3 g of silane per 100 g of mica.

These mica samples, M-1, M-2, and M-3, were subjected to a 2-h water boil desorption experiment. In all three cases, as shown in Table I, only the first silane monolayer is retained on the mica surface. These data indicate that the interactions between multilayers are much weaker than those of the first monolayer with the mica surface and support similar conclusions which were made earlier with respect to the time dependence of silane adsorption.[5,6]

In preparing treated mica–polystyrene films, the mica was dispersed in a 20% polystyrene–toluene solution. The dispersion was poured onto an evaporating dish and left at atmospheric pressure in order to evaporate the solvent. Constant weight of the films was generally obtained after 4 days. The dried films contained 40% mica and 60% polystyrene (by weight) in all cases. In the peroxide experiments, benzoyl peroxide was used and was simply added to the dispersion before evaporation of the solvent.

Once the dried film had been submitted to the appropriate thermal treatment, it was placed in a Soxhlet extraction apparatus and the polystyrene was subse-

TABLE I
Desorption of CVBS-Treated Mica after Exposure to Boiling Water for 2 h

Sample	Initial silane content (no. of monolayers)	CVBS retained after desorption (no. of monolayers)
M-1	1	0.8
M-2	2	0.9
M-3	3	1.3

quently extracted with benzene for approximately 20 h. Extractions carried out for 40 h gave the same results. The extracted material was left to dry, and later analyzed by carbon analysis òn an F and M Model 185 Carbon, Hydrogen, and Nitrogen Analyzer. The quantity of carbon due to the mica and to the silane treatment was subtracted from the total percent carbon in order to determine the carbon increase due to polystyrene coupling

A series of extraction blanks were carried out in order to verify that the benzene extraction step did not alter the carbon content of a particular sample. In each case, untreated mica flakes and mica flakes prepared with approximately two monolayers of CVBS gave, within experimental error, the same carbon content before and after a 20-h extraction with benzene.

RESULTS AND DISCUSSION

Figure 2 shows the quantity of polystyrene coupled to mica at room temperature, after extraction, as a function of the number of silane monolayers deposited on the surface. It is interesting to note that there is significant adhesion of polystyrene to mica in the absence of any surface treatment and that this value decreases with silane surface coverage. With three silane monolayers on mica (0.3 g silane/100 g mica), essentially no polystyrene couples to the treated mica surface at room temperature. These results may be understood on the basis of surface energetics. Untreated mica, which is a high energy surface, rapidly interacts with polystyrene, a low energy material, in order to achieve a lower energy state. Surface treatment of the mica creates a lower energy surface, and, in the absence of any other driving force, the tendency for interaction of polystyrene will be low.

Figure 3 illustrates the effect of thermal treatment at 170°C on the quantity of polystyrene which remains on mica after extraction. It can be seen that samples M-1 and M-2 retain more polystyrene after thermal treatment. The results indicate further that this improvement is obtained within 5 min of treatment and that no additional difference in the quantity of polystyrene cou-
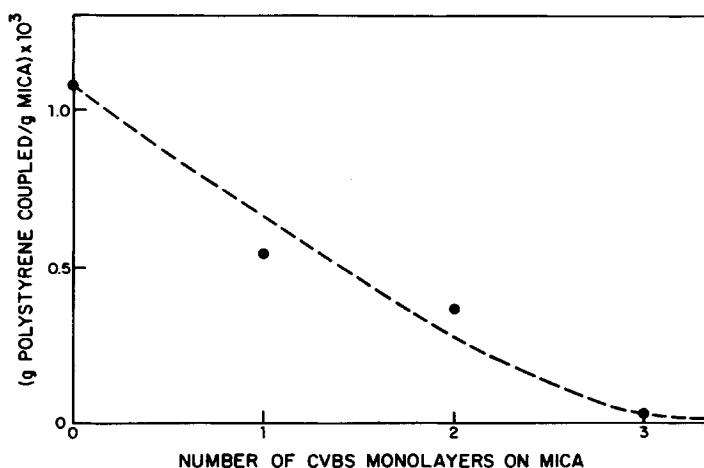

Fig. 2. Dependence of polystyrene retention at ambient temperature conditions on the number of CVBS monolayers on mica.
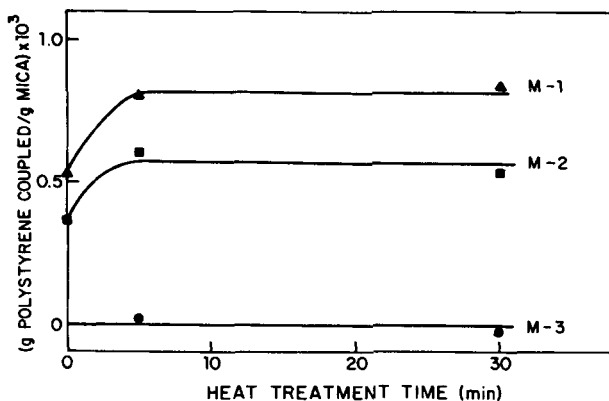
Fig. 3. The dependence of polystyrene retention on CVBS-treated mica with heat treatment time at 170°C.   M-1, M-2, and M-3 correspond to one, two, and three monolayers of CVBS on mica, respectively.

pled is observed after 30 min of treatment time.   Thermal treatment of sample M-3 at 170°C does not improve the retention of polystyrene after extraction over that retained when the sample is exposed only at ambient conditions.   Exposure of a mica–polystyrene composite, with no silane treatment, to 170°C for 30 min also resulted in the same polystyrene adhesion, as was observed under ambient conditions.

Figure 4 shows the effect of thermal treatment at 250°C.   All of the treated samples retain significantly more polystyrene after treatment at this temperature than at 170°C.   Samples M-1 and M-2 again obtain their maximum retention of polystyrene within approximately 5 min.   Sample M-3 only begins to retain polystyrene after 5 min of thermal treatment, and there is then a continual increase in polystyrene retention with time of heat exposure.

These studies indicate that in most cases the maximum retention of polysty-
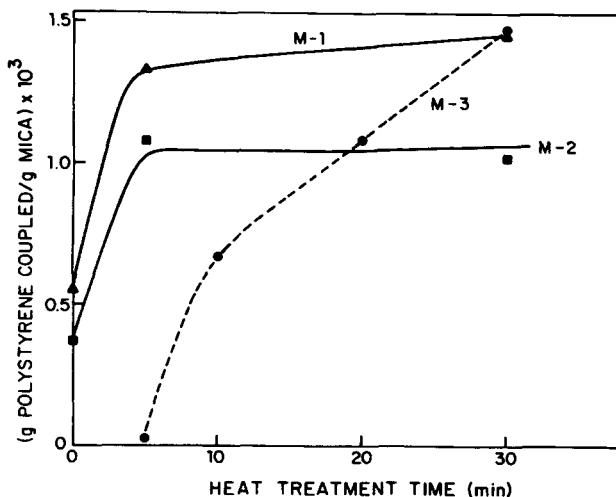

Fig. 4. The dependence of polystyrene retention on CVBS-treated mica with heat treatment time at 250°C.   M-1, M-2, and M-3 correspond to one, two, and three monolayers of CVBS on mica, respectively.
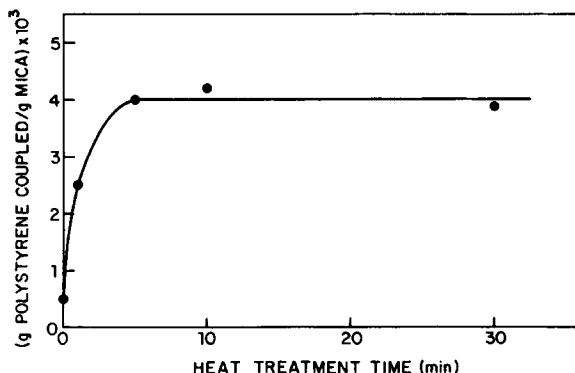
Fig. 5. The dependence of polystyrene retention on a commercially silane-treated mica (60NP Suzorite mica) with treatment time at 170°C.

rene onto treated mica is obtained with one monolayer of silane, and in general this retention drops off with increasing silane content on the mica. The differences in the quantity of polystyrene coupled to samples M-1, M-2, and M-3 suggest that although the molecular orientation within each layer is normal to the surface,[5] the proportion of head-to-head, or head-to-tail, arrangements may differ from one layer to another. The first monolayer of CVBS treated mica should consist almost exclusively of vinyl groups extending away from the surface since there is a specific reaction of the silanol functionality of CVBS with the hydrated inorganic surface. The direction of orientation of the two following monolayers may be more disordered.

Figure 5 shows the effect of thermal treatment at 170°C on a commercially silane-treated sample (60NP Suzorite mica). The general form of this curve is similar to that of samples M-1 and M-2 in Figure 3. As for these latter curves, the maximum retention of polystyrene when the samples are treated at 170°C is obtained within a 5-min exposure time. It should be noted that the quantity
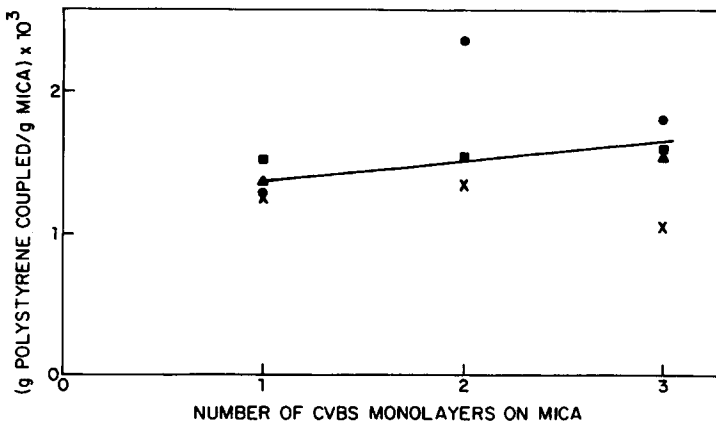

Fig. 6. The effct of CVBS monolayer coverage on the polystyrene retention on mica for various peroxide contents. The peroxide content was based on the total weight of the film. One silane monolayer is approximately 0.1×10^{-3} g silane/g mica. All samples were treated for 5 min before extraction. (X) 0.2% peroxide, 170°C; (●) 0.4% peroxide, 170°C; (■) 1% peroxide, 170°C; (▲) 1% peroxide, 250°C.

of polystyrene adsorbed onto the 60NP mica, under ambient temperature treatment conditions (intercept value on the y-axis), is less than that for the untreated mica. This reemphasizes the predominant role of surface energetics at room temperature as mentioned in reference to Figure 2. The high retention of polystyrene in these experiments may be the result of additives used to en-hance the adhesion process. Unfortunately, the chemical structure of the silane adsorbed on the 60NP mica is not known, excluding the possibility of a more complete interpretation.

Figure 6 illustrates the effect of peroxides on the retention of polystyrene at 170°C. The results show that, under the same conditions of time and temper-ature (see Figs. 3 and 4), the addition of peroxides increases the quantity of polystyrene coupled to the treated mica surface. In fact, it tends to normalize all of the data to the same region and except for one of the M-2 treated samples, the differences in polystyrene retention as a function of silane surface coverage are much less apparent than those observed when the films are subjected solely to thermal treatment. Figure 6 also illustrates that there is relatively little difference in the results obtained at 170°C or 250°C for peroxide-treated samples. It is evident that the addition of peroxides facilitates the coupling of polystyrene at lower temperatures and shorter heat exposure times. Changes in the con-centration of peroxide from 0.2% to 1.0% (based on the total weight of the film) did not, in general, result in any significant differences.

The effect of the thermal treatment and the addition of peroxides is likely to induce the formation of free radicals, which may result in one or more of the following: (1) the production of crosslinking in the CVBS phase; (2) the co-polymerization of the silane with the resin; (3) further polymerization of the polystyrene itself. The first two processes are expected to take place through the vinyl group of the CVBS which would most readily form radicals.

In order to examine the importance of the vinyl and benzyl groups of CVBS on the retention of polystyrene, an experiment was carried out using APS instead of CVBS on the surface of mica (see Fig. 1). Table II compares the results ob-tained when the mica was treated with a solution of APS to those obtained with a CVBS treatment. These results show that the APS-treated mica samples re-tain more polystyrene than do CVBS samples treated under similar conditions. They emphasize that the rates of homopolymerization and/or copolymerization which are expected to be enhanced by the presence of vinyl groups are not the sole criterion in the overall coupling mechanism.

Table II also illustrates that, with a CVBS treatment, the mica treated with

TABLE II
Effect of Silane Type and Concentration on the Retention of Polystyrene on Treated Mica

Silane	Silane solution concn (g silane/100 mL H_2O)	Quantity of silane molecule adsorbed [(silane/g mica) $\times 10^{-18}$]	No. of monolayers adsorbed	Quantity of polystyrene coupled[a] [(g PS/g mica) $\times 10^3$]
CVBS	0.025	3.8	2.1	0.6
CVBS	0.5	4.4	2.4	1.4
APS	0.5	3.0	1.7	2.4

[a] Each composite was treated at 170°C for 5 min before polystyrene extraction.

a concentrated solution retains much more polystyrene than treated with a dilute solution. The assumption that a loosely packed silane phase is obtained from a concentrated solution and that a dense and closely packed one is obtained from a more dilute solution would lead to the conclusion that the rate of penetration of the polymer into the silane phase is an important factor for polystyrene retention.

More work needs to be undertaken in this area. However, it is possible that two requirements optimize coupling: the ability to form bonds, as is shown by the results with peroxides, and the diffusion or penetration of the polymer into the silane phase. The bond formation may take the form of homopolymerization which would result in an interpenetrating polymer network or copolymerization through a charge transfer mechanism. It should be noted that these two requirements are closely related. For example, it is conceivable that a rapid silane–silane crosslinking reaction through the vinyl groups of CVBS would reduce the capability of the polymer to penetrate the silane phase.

CONCLUSIONS

A thermal treatment was found to be necessary in order to obtain maximum coupling of polystyrene to a silane-treated mica. The retention of polystyrene was sensitive to the temperature of this treatment, to the silane coverage, and to the presence of peroxides. In general, it was found that the number of monolayers on the surface of mica influenced greatly the retention of polystyrene. The best results were normally obtained with a single monolayer, the treated mica surface being then composed of a large number of accessible and reactive vinyl groups. However, the addition of peroxides tended to eliminate this factor, making all surfaces equally effective for coupling with polystyrene.

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