Effect of interface on the mechanical behaviour of glass bead-filled PVC

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The surface of glass beads of average particle size 100 μm was modified (a) by incorporating extra hydroxyl groups by chemcial treatment, and (b) by applying a thin coating of polymethacrylic acid (PMA) on the glass surface. The corresponding chemical changes were investigated using infrared spectroscopy. The tensile behaviour of a glass bead-filled PVC composite prepared with surface-modified glass beads, showed the following effects: (a) hydroxyl groups incorporated on to the glass surface did not affect the glass–PVC interface and hence did not change the tensile behaviour of the composite; (b) PMA coating on the glass surface caused improvement in the tensile behaviour in the low strain region and deterioration in the high region. An SEM study of the fractured surface suggested debonding at the glass–PVC interface in the first case, and failure of the PVC–PMA interface in the second case.

1. Introduction

Development of silane coupling agents has revived interest in the chemical bonding theory of GRP in recent years [1]. Extensive work has been reported on the effect of chemical adhesion on the properties of the interface in multiphase systems [2–5]. However, mechanisms through which chemical adhesion affects mechanical properties of bulk composite material are not yet fully understood.

An attempt has been made in this work to make a preliminary study of the tensile properties of glass bead-filled PVC by incorporating different chemical groups on to the surface of the glass. It may be mentioned here that glass bead–PVC composite has been chosen essentially as a simple model system. Use of spherical filler helps in eliminating fibre-length-distribution and fibre-orientation-distribution parameters and the use of a polar matrix such as PVC is expected to increase the probability of chemical bonding at the interface.

2. Materials, characterization and sample preparation

A commercial grade plasticized PVC (NOCIL WB 85) supplied by National Organic Chemical Industries Ltd, Bombay was used as the matrix material. Spherical glass beads of average particle size 100 μm supplied by Light and Co., Azamgarh, were used as fillers. All samples were injection moulded into dumb-bell-shaped tensile specimens with different filler loadings.

Prior to composite processing, the following treatments were given to the spherical glass filler:

(a) extra hydroxyl groups were incorporated by chemical treatment of the glass surface;

(b) a thin coating of polymethacrylic acid

$$[(CH_2 = C - OOH)_n]$$
$$|$$
$$CH_3$$
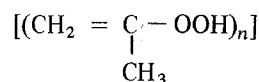
was applied to the glass surface. The chemical effects of above treatments were investigated separately by infrared spectroscopy.

2.1. Incorporation of extra hydroxyl on the glass surface

In order to incorporate different amounts of hydroxyl groups on the glass surface, the following treatments were attempted:

1. glass beads were boiled in an aqueous solution of 1N HCl for 1 h;

2. glass beads were boiled in an aqueous solution of pH 10 for 1 h.

3. glass beads were heated in vacuum at $400°C$ for 1 h.

These three samples, and untreated glass beads, were studied using an infrared spectrophotometer. For the sake of comparison, exactly the same amount of samples was taken in each case.

2.2. Results of infrared spectroscopic measurements

2.2.1. Incorporation of extra hydroxyl groups

Fig. 1 shows infrared spectra of glass beads subjected to different chemical treatments. The corresponding variations of optical density with wave number are presented in Fig. 2 where two absorption bands centred around 2700 and $3300\,cm^{-1}$ due to hydrogen-bonded hydroxyl groups and free hydroxyl groups, respectively, are clearly visible. Comparison of the infrared spectra of the chemically treated glass beads with untreated glass beads shows that (a) heating in vacuum at $400°C$ has reduced the number of hydroxyl groups of both types, as is expected. Optical density at $2700\,cm^{-1}$ is reduced to 59.5% and that of $3300\,cm^{-1}$ is reduced to 38.9%. This is expected, because free hydroxyl groups are likely to be released more easily than hydrogen-bonded hydroxyl groups which are bonded to sodium ions on the glass surface through hydrogen bonding. (b) A slight increase in hydrogen-bonded hydroxyl
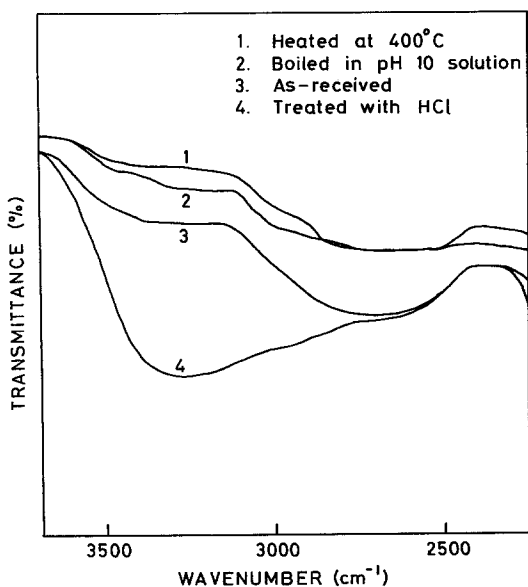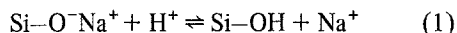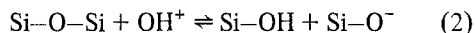
groups and a considerable increase in free hydroxyl groups was effected by acid treatment. (c) Alkali treatment caused reduction in both free hydroxyl groups and hydrogen-bonded hydroxyl groups.

Observations (b) and (c) can be explained in the following manner. Corrosion of glass in an aqueous medium may be represented by

$$Si{-}O^-Na^+ + H^+ \rightleftharpoons Si{-}OH + Na^+ \qquad (1)$$

and

$$Si{-}O{-}Si + OH^+ \rightleftharpoons Si{-}OH + Si{-}O^- \qquad (2)$$

Equation 1 gives the predominant reaction of glass in an acidic medium, and Equation 2 gives that in an alkaline medium. Thus it is clear that in an acidic medium (1 N HCl) extra hydroxyl groups are incorporated into the glass due to ion exchange. This, however, is not the case in an alkaline medium, as is evident from infrared data. Silicic acid on the glass surface dissociates in the following way:

$$H_2SiO_3 + OH^- = HSiO_3^- + H_2O \qquad (3)$$

$$H_2SiO_3 + 2OH^- = SiO_3^{2-} + 2H_2O \qquad (4)$$
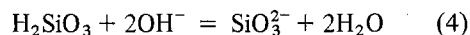
Equation 3 gives the predominant mode in an alkaline medium having a pH of about 9 to 10 and Equation 4 gives the predominant reaction mode when the pH is greater than about 10 to 12. Therefore, glass boiled in an aqueous solution of pH 10 leads to the formation of a soluble silicate ion and this is likely to produce fewer hydroxyl groups on the surface than the acid-treated glass.

Consequently, acid-treated glass beads containing extra hydroxyl groups have been used as fillers in subsequent composite preparation.

2.2.2. Glass beads coated with polymethacrylic acid (PMA)

The infrared spectrum for glass beads coated with a thin layer of polymethacrylic acid is given in Fig. 3. Comparison of this spectrum with that of polymethacrylic acid is also made in the same figure. The presence of peaks due to C—O and C—OH stretching vibrations indicate the presence of additional COOH groups due to PMA coating.

3. Tensile test data

Standard ASTM tensile specimens of glass bead-filled PVC were tested at about $20°C$ in an Instron testing machine. The initial strain rate was kept to $0.5\,cm\,min^{-1}$ (minimum strain rate available in that Instron) until a load of 15 kg was attained.

1. Heated at $400°C$
2. Boiled in pH 10 solution
3. As–received
4. Treated with HCl

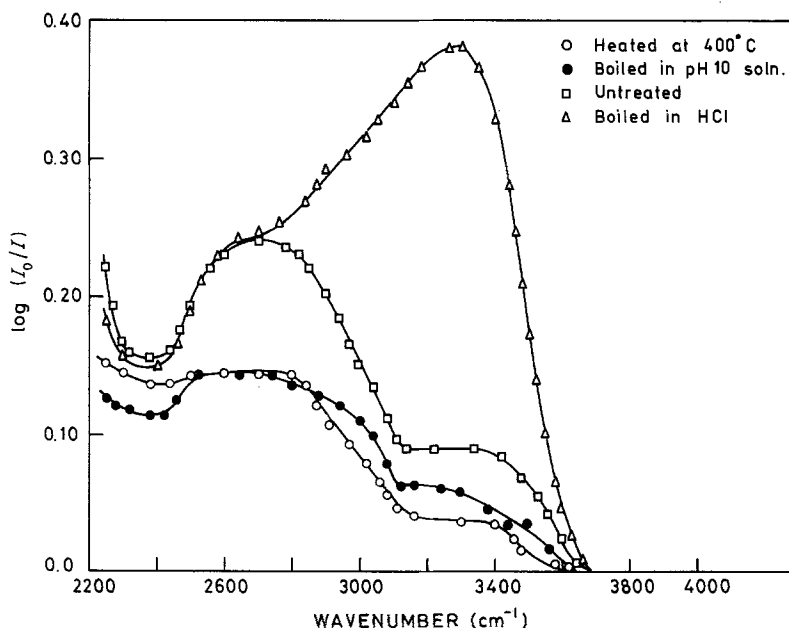*Figure 1* Infrared spectra for glass beads after chemical treatment.

Figure 2 Optical density of chemically treated glass beads as a function of wave number.

This 15 kg limit was arbitrarily chosen, so that it fell much above the linear elastic limit for all samples. After that, the strain rate was increased and maintained at 20 cm min^{-1} until failure. It may be mentioned here that the strain in each case has been calculated using grip-to-grip distance as the gauge length, which is larger than the parallel portion of the specimen. However, it was checked earlier that error due to such simplification is not large [6]. Although strain calculated in this way is always lower than the actual strain, for a comparative study of tensile property this procedure does yield meaningful results.

Typical stress–strain curves for unfilled and glass bead-filled PVC are presented in Figs. 4 and 5. Lower and higher strain regions have been shown separately in these figures, because strain rates in the two cases are different. Samples with lower loadings of glass beads tended to slip away from the grip when strain was large; for such samples often the failure point could not be reached.

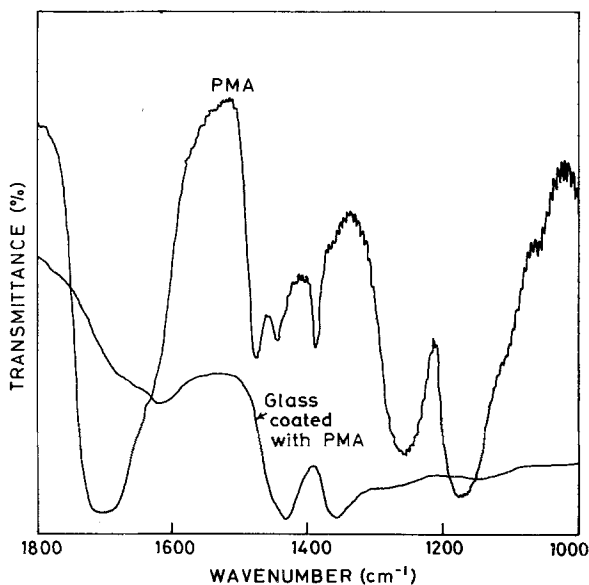Tensile moduli for untreated, HCl-treated and

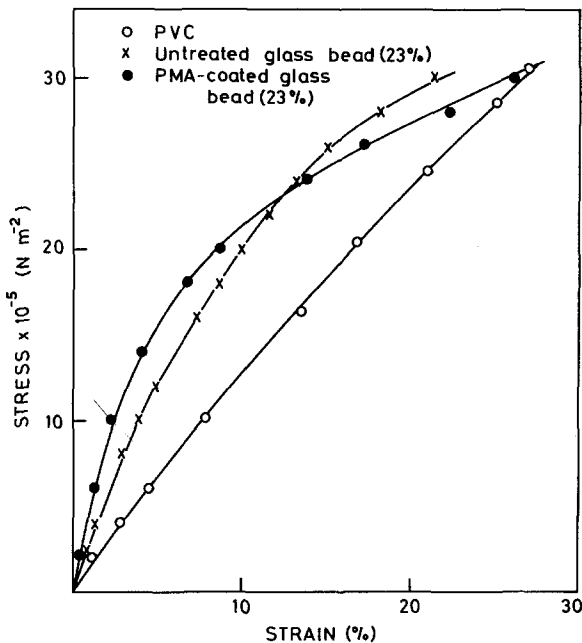*Figure 3* Infrared spectra for glass beads with PMA coating.

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Figure 4 Typical stress–strain curves for glass bead-filled PVC (small strain region).

PMA-coated glass bead-filled PVC are calculated from the linear portion of the stress–strain curve. Moduli at different glass loadings as a function of volume fractions of filler are presented in Fig. 6. It may be noted that points corresponding to untreated and HCl-treated fillers fall on a single smooth curve, whereas PMA-coated glass-bead-filled PVC consistently shows higher modulus. Attempts were made to fit the modulus data with the existing theories. It can be seen in Table I that

modular ratios for untreated and HCl-treated glass bead-filled composites showed a better fit with the Guth–Smalwood equation than with Kerner's equation [7] (assuming a Poisson ratio of matrix $\nu_1 = 0.5$). On the other hand modular ratios of PMA-coated glass bead-filled composites were much higher than corresponding theoretical predictions.

Variations of stress at failure and strain at failure with volume fraction of filler are shown in
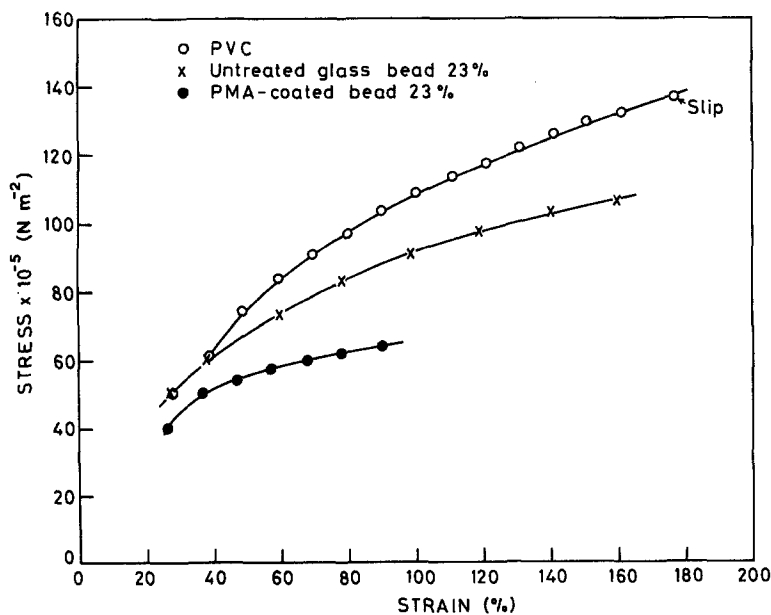

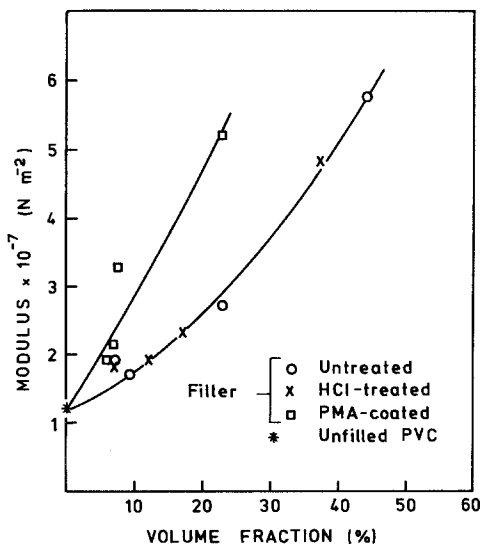*Figure 5* Typical stress–strain curves for glass bead-filled PVC (large strain region).

Figure 6 Tensile modulus as a function of filler volume fraction.
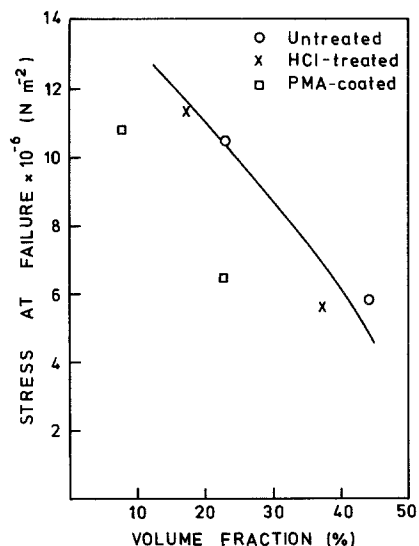

Figure 7 Stress at failure, as a function of filler volume fraction.

Figs. 7 and 8, respectively. It can be seen that points corresponding to untreated and HCl-treated glass bead-filled PVC fall again on a single smooth curve, whereas both stress and strain at failure are lower for PMA-coated glass bead-filled PVC at comparable glass loadings.

Thus examination of tensile test data leads to the following conclusions:

1. HCl-treated glass bead-filled PVC shows no change in tensile behaviour as compared to untreated glass bead-filled PVC samples;

2. PMA-coated glass bead-filled PVC shows improvement in tensile properties in the lower strain region and deterioration in the higher strain region.

4. SEM study

Scanning electron micrographs of fractured surfaces of tensile specimens are presented in Fig. 9 which shows that (a) for both untreated and HCl-treated glass bead-filled PVC, matrix–filler adhesion is rather poor. Debonding of fillers has taken place along the interface, without any PVC sticking to the debonded glass surface. The extent of plastic deformation of the matrix material appears to be small in both cases. (b) In PMA-coated glass bead-filled PVC, even after "debonding", the coating adheres to the filler surface and the extent of plastic deformation of the matrix material is relatively large.

5. Discussion

From the above results it seems that hydroxyl groups incorporated on to the glass surface do not affect tensile properties of the composite. From the data of optical density, density and average size of glass-bead particles, the total hydroxyl content per unit surface area has been calculated with the reported specific absorption coefficient data of Scholze *et al.* [8]. On a rough estimation,

TABLE I

Filler volume fraction ϕ_2	Modular ratio (E composite/E matrix)		
	Experimental	$1 + \dfrac{\phi_2}{\phi_1}\left\{\dfrac{15(1-\nu_1)}{8-10\nu_1}\right\}$ (Kerner equation)	$1 + 2.5\phi_2 + 141\phi_2^2$ (Guth–Smallwood equation)
0.100	1.417	1.278	1.391
0.200	2.142	1.625	2.064
0.300	3.125	2.071	3.019
0.400	4.292	2.667	4.256
0.450	4.917	3.045	4.980
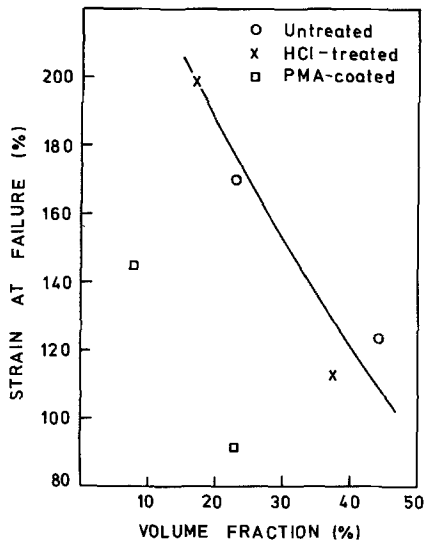
Figure 8 Strain at failure, as a function of filler volume fraction.

technique might have been too few to affect the mechanical properties of the interface.

On the other hand, PMA coating adheres strongly to the glass surface as is evident from SEM and infrared data. However, despite good adhesion at the PMA–glass interface, "debonding" takes place and the material fails not only at low strain, but also at low stress level. This appears to indicate that neither a sharp boundary with strong chemical bonding nor a diffused interphase containing molecules of both the components has been formed at the PMA–PVC interface ([5], p. 380). If this is true, then only weak Van der Waals' forces are likely to be operative. Such a weak interface is expected to lead to failure at low stress and low strain levels, as has happened in this case.

6. Conclusions

1. Hydroxyl groups incorporated on to the surface do not affect the glass–PVC interface and hence do not change the tensile behaviour of the composite.

2. PMA coating on the glass surface causes

hydroxyl groups occupy only about 1% of the total glass surface sites even on glass beads boiled in 1N HCl. This implies that hydroxyl groups incorporated on to the glass surface by this
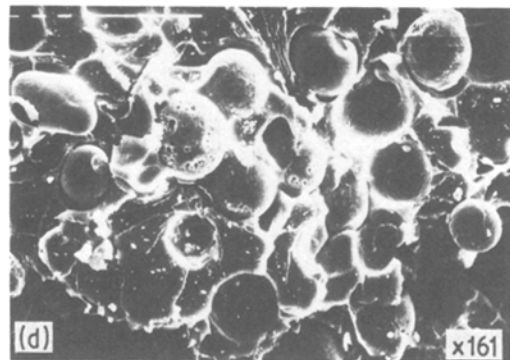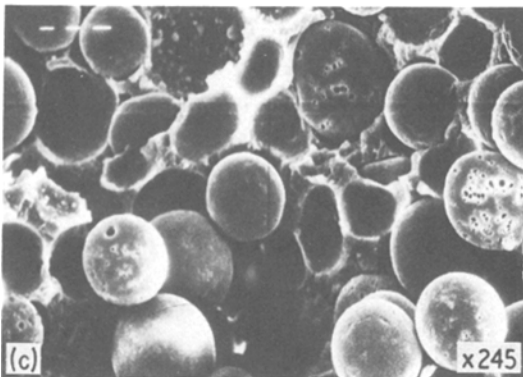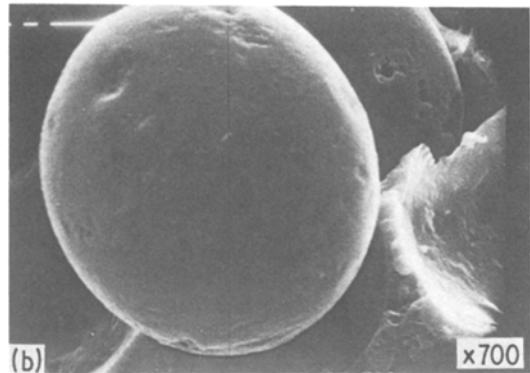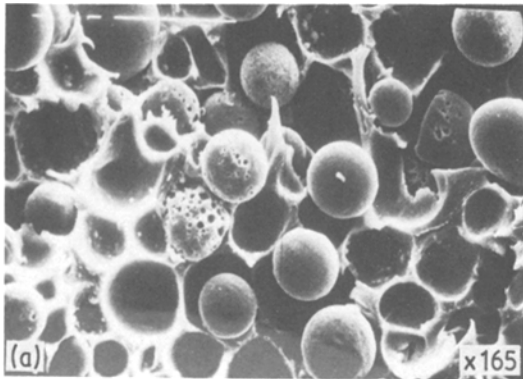

Figure 9 Fracture surface of the composite containing (a) and (b) untreated glass beads, (c) treated with HCl, (d) and (e) treated with PMA.

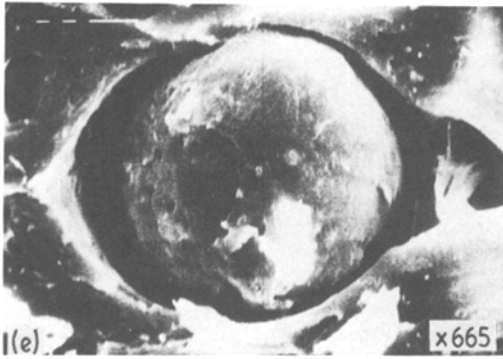*Figure 9* Continued.

improvement in tensile behaviour in the low strain region and deterioration in the high strain region.

7. Acknowledgements

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