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Strengthening and toughening of soda–lime glass by a reinforced coating

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The strength and toughness of soda–lime (container) glass have been enhanced by factors of ~ 2 and ~ 40, respectively, by a 0.1 mm coating of polyurethane containing 6–9 wt % silicon carbide whiskers in random orientation. The strength measurements were made using a standardized procedure and a biaxial ring-on-ring flexure rig. The toughness enhancement has been shown to be due to crack-branching and fibre pull-out mechanisms in the coating, which bridges any strength-limiting flaws in the underlying glass.

1. Introduction

Silica-based glasses, including soda–lime container glass, are isotropic elastic solids in which all the constituent atoms are bonded strongly to one another, but with no long-range or periodic order. It can be estimated from the nature of the interatomic forces in glass that strains of up to 20% should occur before rupture [1, 2]; this is equivalent to strengths in the range 10–20 GPa. For normal samples, however, observed strengths are usually about two to three orders of magnitude smaller than this theoretical level: moreover, samples which have received nominally identical treatment show a wide variation in their individual strengths.

It is well established that the attainable strength of glass is limited by the presence of surface flaws or microcracks which act as sources for fracture. Most glass artefacts possess these flaws as a result of abrasion, indentation, impact, or by differential contraction or chemical corrosion around surface inclusions [3].

Many attempts have been made to increase the strength of real glass. Some procedures are based on the fact that if the glass surface is placed under compression, extra work must be done to overcome this compression before any pre-existing microcrack can be widened and thereby produce catastrophic failure. One such procedure compresses the surface of a glass body by chilling with an air blast at a time when the glass is hot enough to be plastic. Then, under normal cooling, the thermal shrinkage of the bulk compresses the hardened surface layer. This procedure has been used for toughened glass plates.

In another procedure [4], the sodium in the surface layer of glass is exchanged for potassium in a molten salt bath. Because the potassium ions occupy a greater volume than the sodium ions they have replaced, the surface layer is placed under a compressive stress. This procedure works well, but is costly, and cannot be applied reasonably to glass containers that are made in large numbers.

The present paper describes the toughening and strengthening of glass by means of an applied reinforced coating. It was intended that the coating should possess a high tensile strength and adhere strongly to the underlying glass. This coating would lie across any pre-existing strength-limiting flaws in the glass surface, so that under any applied tensile load, the stress across any flaw would be bridged by the coating. Thus, extra work would have to be done before the load-carrying effect of the coating broke down, allowing the microcracks in the glass surface to widen and cause fracture of the glass.

An additional benefit of such a coating would be that the glass surface would be protected against the production of strength-limiting flaws through abrasion or indentation.

2. Experimental procedure

2.1. Glass

Standard glass microscope slides 77 mm × 26 mm × 1 mm were used. The glass had the composition shown in Table I, as determined by X-ray fluorescence spectrometry: this is similar to that of a typical container glass.

It was necessary for the glass specimens to be clean before application of any coating material. The most effective cleaning procedure was found to be a firing in air at 400 °C for 1 h, followed by a slow cool to room temperature.

2.2. Coatings

A simple hand-operated doctor blade spreading device was made in which 11 slides could be clamped with their upper surfaces in the same plane and then coated uniformly with a liquid to a thickness of 0.1 mm.

The most successful coating material (see below) was polyurethane (PU) containing 6–9 wt % silicon

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carbide (SiC) whiskers. The PU was a two-part material (Epiglass Reaction Lacquer) from a retail outlet. When cured thermally, this material provided a tough film that was strongly adherent to clean glass. The SiC whiskers (Tateho Corporation, Japan, $\sim 0.5\ \mu m$ diameter, aspect ratio > 10), handled with appropriate precautions against any ingestion, were added to freshly mixed uncured PU without any prior surface treatment, and dispersed ultrasonically. Entrained air bubbles were removed by degassing the mixture in a vacuum desiccator.

Cleaned, indented slides (see below) were coated with this mixture: the PU was allowed to gel (2 h at room temperature), then cured fully by heating for 2 h at 80 °C. Mixtures containing > 9 wt % whiskers in PU were too viscous to be used in the spreading device.

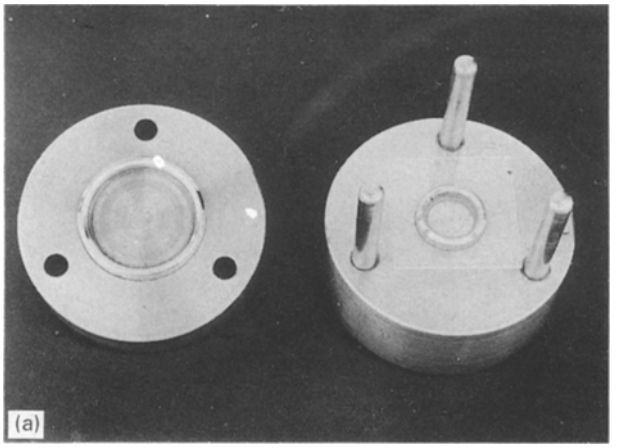
2.3. Strength measurements

The usual three- or four-point bend procedures, when applied to coated or uncoated slides would have been futile because of the extensive arrays of strength-controlling flaws that would have been present around any cut edges of a specimen. Flame polishing such edges could have reduced the effect, but the consequent loss of sodium by evaporation could change the glass composition sufficiently to lead to spurious results.

Strength measurements, therefore, were made with a biaxial bend device to reduce or eliminate the effect of specimen edges [5, 6]. This device (Fig. 1) is effectively a four-point bend rig with outer and inner spans of 23.5 and 12.0 mm, respectively, but with circular symmetry. These spans are smaller than usually accepted, but were the maximum possible for the specimens used here. Provided that the deflection under load was not too great, the wrinkling of the corners which must occur with a rectangular specimen should not have been a serious effect. The device was considered appropriate for comparative strength measurements. It was used in an Instron testing machine, usually with a crosshead speed of $1\ mm\ min^{-1}$.

Normally, two test pieces $\sim 26\ mm \times 26\ mm \times 1\ mm$ were made from a slide by breaking along scratches. All specimens were indented with a Vickers diamond indentor at 1 kg load immediately after the cleaning process, and before any coating or testing, so as to make a single flaw that would control the strength. The flaw was placed centrally on one surface of each half slide, and arranged to be on the tension side of a specimen in the testing rig. The compression side of a specimen was covered with Scotch tape so that all pieces could be retained after a fracture test. In all cases, it was confirmed that fracture originated from the indentation flaw and within the smaller ring of the flexure rig. The purpose of this procedure was to ensure a reasonably constant base value for the strength of untreated glass, so that the effect of any coating would be apparent immediately.

Every specimen from a batch of 22 was tested to provide a mean modulus of rupture (MOR) together with such statistical information as the Weibull modulus. In those cases where the specimens did not show typical brittle behaviour (see below, Fig. 2c) the first major discontinuity in the stress/strain record was deemed to be the condition for rupture, even though the specimen had not failed *per se*. After testing, specimens were examined with an optical microscope or a scanning electron microscope as required.



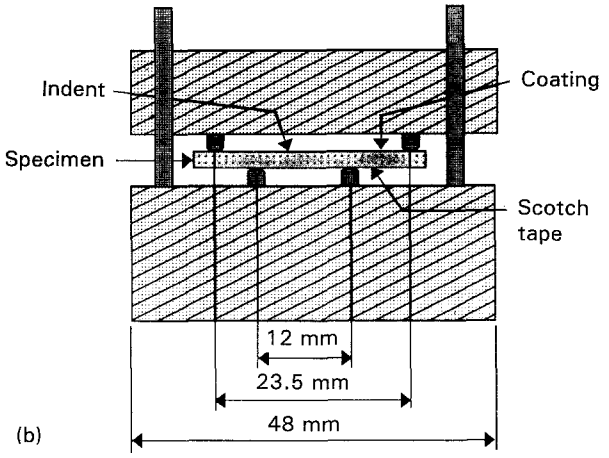


Figure 1 Biaxial strength testing device.

TABLE I Composition (wt %) of microscope slide glass

Na_2O	14.402	Al_2O_3	1.736
K_2O	0.197	Fe_2O_3	0.090
CaO	6.601	TiO_2	0.064
MgO	3.914	Cr_2O_3	0.002
SiO_2 + l.o.i.[a] (by difference) 72.995			

[a] l.o.i. = loss on ignition.

3. Results and discussion

Table II shows typical results of strength measurements on indented glass, both clean and coated. It can be seen from the relatively high value of the Weibull mean for the clean glass (or the relatively small estimated standard deviation of the MOR) that the artificial flaw was particularly effective in providing a base value for the MOR. The MOR was increased by the PU coating, and increased again by SiC whisker

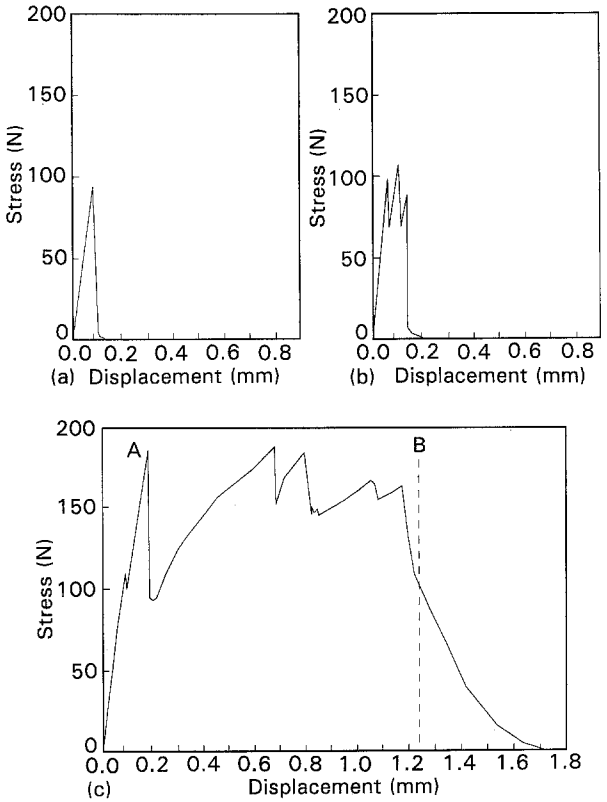


Figure 2 Typical stress/strain records from test specimens: (a) clean indented glass; (b) indented glass coated with 0.1 mm PU only; (c) indented glass coated with 0.1 mm PU–8.8 wt % SiC whiskers. A is the point of nominal rupture. B is the limit of testing: the curve to the right of B is due to unloading of the rig and not to specimen failure.

TABLE II Strength data for indented slides with various coatings

Batch	Mean MOR (MPa)	Weibull mean
Uncoated	55.6 (1.8)[a]	30.3 (0.9)
Coated 0.1 mm PU	70.2 (3.7)	20.1 (1.0)
Coated 0.1 mm PU + 6.2% SiC	114 (24)	4.9 (0.9)
Coated 0.1 mm PU + 7.6% SiC	88 (12)	7.6 (0.8)
Coated 0.1 mm PU + 8.8% SiC	115 (19)	6.3 (0.8)

[a] Estimated standard deviation.

reinforcement of the PU. The reliability of the latter measurements was much reduced for reasons which are given below. These results are relative only, in view of the limitations of the rig, noted above.

The results are more dramatic if the individual stress/strain records are examined. Fig. 2a shows a typical recording from indented uncoated glass. This shows the classical linear stress/strain curve terminating abruptly when catastrophic (brittle) failure occurs. Fig. 2b, typical of indented glass coated with 0.1 mm PU only, is similar to Fig. 2a, but after the first instance of brittle behaviour, some mechanism operates to arrest failure and to extend the region where the applied stress can be supported by the piece. The areas under curves such as Fig. 2b were generally 1.5–2.0 times larger than those for curves such as in Fig. 2a, indicating that the PU conferred a significant toughening to the glass in addition to the small strength increase.

Examination of the fractured test pieces after results such as in Fig. 2a and b showed that the break was simple, most frequently of a cross shape reflecting the pyramidal indentor geometry, or sometimes a single crack (Fig. 3). Such patterns are desirable in terms of reproducibility of results.

As there was no general difference between the crack patterns from clean indented slides and indented slides coated with PU alone (such as more branching, Fig. 3a, b), the increase in toughness must come from the PU coating. Most frequently the coating remained strongly adherent to the glass after fracture, and was macroscopically intact, so that the increase in toughness could be ascribed generally to plastic deformation in the PU. Scanning electron microscopy of the coating after a fracture test often revealed small cracks similar to those expected for clean brittle failure, but with a certain amount of branching (Fig. 4): these also could contribute to the toughening. However, other toughening mechanisms such as delamination of the PU film were not confirmed here.

Fig. 2c shows the dramatic increase in toughness conferred by the whisker-reinforced PU film on indented glass. The applied stress is supported by the test piece for quite large displacements of the rig. Measurement of the areas under the stress/strain curves with a planimeter indicated that the toughness had increased 40- to 50-fold. It is to be noted that the return of the stress/strain curve to zero stress (the region to the right of B, Fig. 2c) is not due to failure of the piece. In every such case the displacement was so large that the rig became inoperable, and had to be unloaded at some point, such as B. Test pieces never failed as such, even though the glass was cracked, i.e. the coating remained macroscopically intact. Even after having been quite seriously cupped in the loaded rig, specimens always returned to a flat condition on unloading. Indeed, some difficulty was experienced in cutting slides into two pieces to make the test specimens.

All indented specimens coated with SiC whisker-reinforced PU showed stress/strain curves of this type, apart from individual differences of detail. In particular, the point of first discontinuity (corresponding to A in Fig. 2c) was sufficiently variable as to make estimates of MOR imprecise.

Examination of specimens after testing revealed a large increase in branched and minor cracking (Fig. 3c and d). However, this effect probably was due to the extreme deformation that these specimens underwent as compared to those of Fig. 3a and b, rather than to any new toughening process exhibited by the coating/glass composite. Pattern variations as in Fig. 3c and d always occurred, and were ascribed to differences in the extent of deformation in each case. It is probable also that the jagged form of Fig. 2c is a consequence of the formation of these extra cracks. Because the reinforced PU film in these cases appeared macroscopically intact, and showed no sign of becoming detached from the glass, the origin of the toughening again must lie in the coating itself.

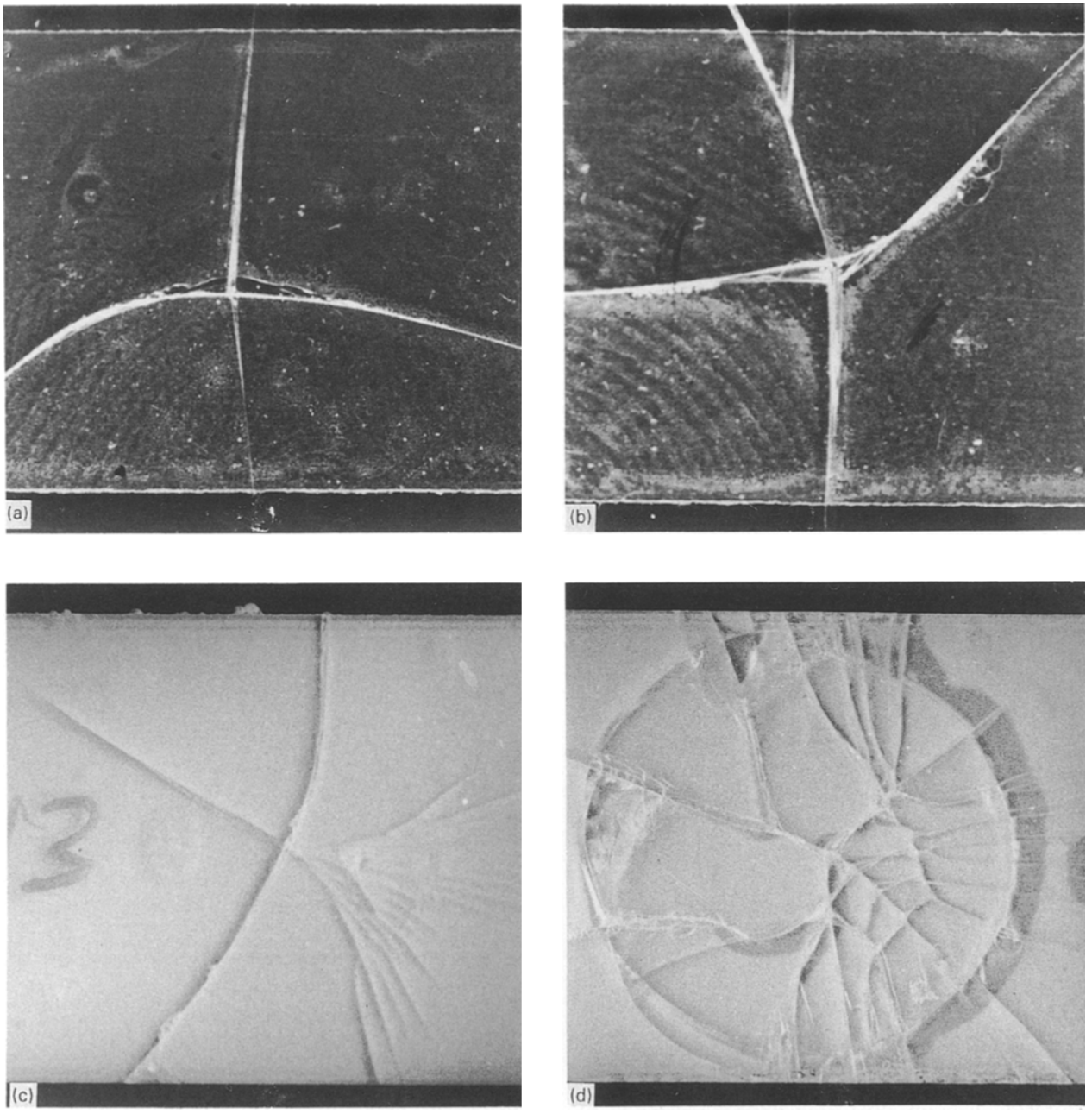


Figure 3 Typical patterns of cracks in glass after flexure testing: (a) clean indented glass; (b) indented glass with 0.1 mm PU only; (c, d) indented glass coated with PU–8.8 wt % SiC whiskers. Each test piece is about 26 mm square. Background detail in (a) and (b) comes from the Scotch tape.

From the evidence of scanning electron micrographs of the film after testing (Fig. 4), at least three toughening mechanisms could be operating if:

(a) any cracks in the coating showed evidence of branching or tearing on a fine scale: this would provide stress dispersion;

(b) the film deformed plastically: this is evident from contrast variations, particularly adjacent to cracks;

(c) the classical fibre pull-out toughening mechanism was operating also.

It would be of interest to study the mechanical properties of the reinforced film alone, but this was not done here.

The SiC-reinforced PU film described here would be entirely compatible with the practice of recycling container glass as cullet: the SiC and PU would oxidize to the benign SiO_2, CO_2 and H_2O. The whiskers are physiologically hazardous, especially if they are free to disperse, so that any commercial process generally would need to use fibre of larger diameter than about 1 μm. The whisker-reinforced films made here were opaque, while fibre–PU films could be distinctly unattractive. This could be reduced if the refractive indices of polymer and filler were matched and if the filler could be made colourless. On the other hand, opacity is of little aesthetical consequence in coloured and decorated glassware.

Numerous attempts were made to produce other reinforced films to strengthen and toughen glass. These included (a) synthetic organic polymers such as alkyd resins, polyacrylates, melamine formaldehyde–alkyd resins and polyvinylbutyral, all with and without appropriate coupling agents, (b) natural proteins,

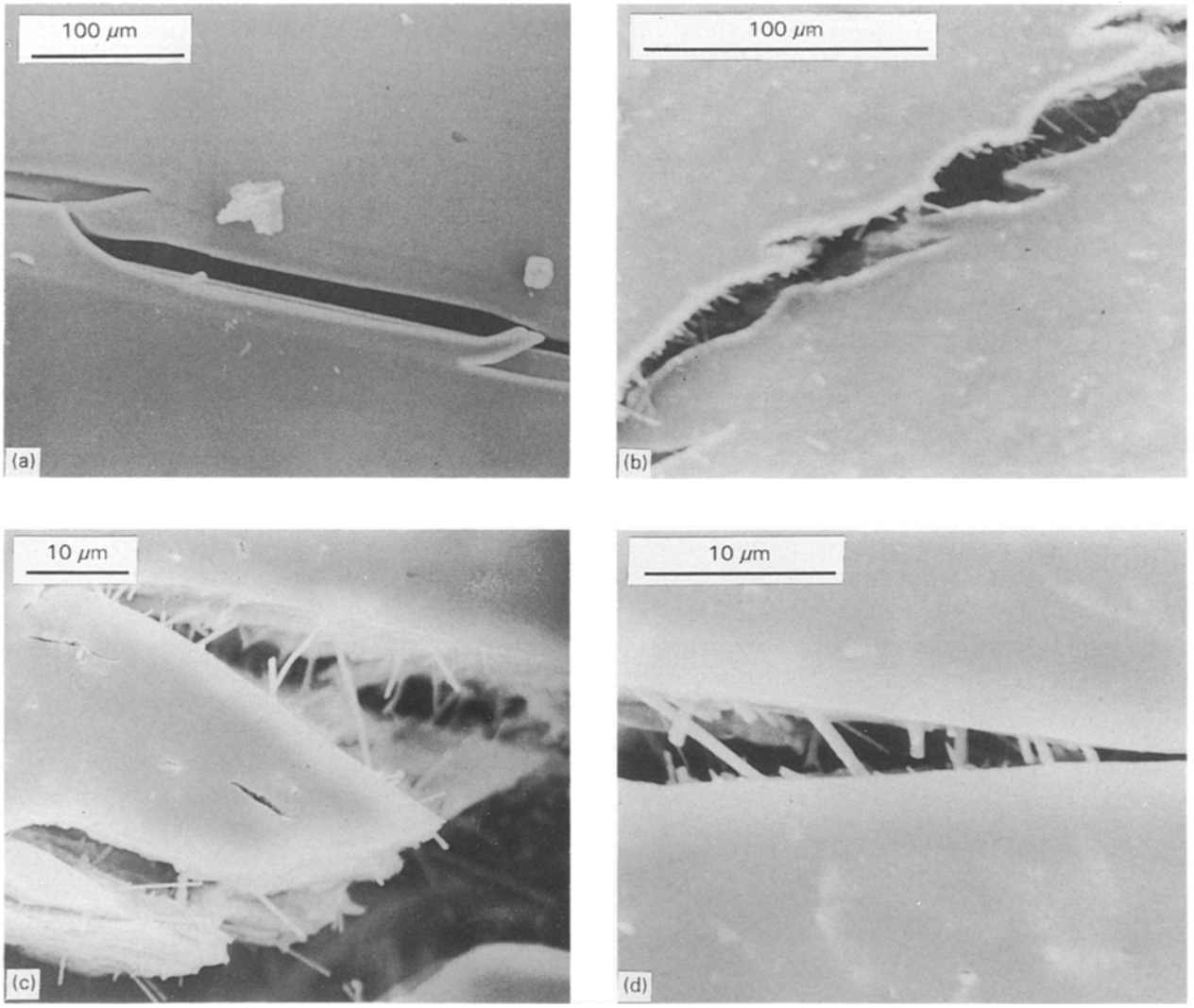


Figure 4 Typical scanning electron micrographs of coatings on glass after flexure testing: (a) PU alone; (b, and d) PU-7.6 wt % SiC whiskers; (c) PU–8.8 wt % SiC whiskers.

and (c) inorganic polymers (glasses and cements) applied by various means, including sol–gel routes. Reinforcing fillers included vermiculite platelets [7], fibrous SiC, Si_3N_4, Al_2O_3 and metals.

None of these produced strengthening or toughening of glass to the extent noted above: indeed, most caused actual degradation of the properties of clean glass. However, the MOR of glass was raised about 50% by a film of polyacrylamide (P-26) containing ~ 20 wt % chemically exfoliated vermiculite platelets and 2% (*N*,*N*-diethyl-3-aminopropyl) trimethoxysilane coupling agent, that had been deposited from aqueous suspension then cross-linked thermally. This coating may be worthy of further development: the platelets lie parallel to the glass surface, so that the resultant film can be more transparent than the SiC whisker/PU film above, whilst toughening analogous to that seen in some mollusc or brachiopod shells (which can have a similar microstructure) [8] could operate.

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