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Ultraviolet-curing blends for coating of optical fibres

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An ultraviolet-curable polymeric blend was developed to serve as a coating for optical fibres. The composition of the system was 55.6 wt% urethane acrylate, 44.4 wt% epoxyacrylate, 1.5 wt% benzoin isopropyl ether and 25 wt% 1,3-butanediol diacrylate. Three different silane coupling agents were tested to improve the polymer–glass adhesion. The optical fibres were drawn at 0.45 m sec^{-1} using a CO_2 laser; the ultraviolet curing blend was applied and cured with a xenon flash lamp. Ageing studied in water and in humid environments performed on these coated fibres showed that there was an increase in their strength compared to the silicone-coated fibres. It was possible to triple the fibre's drawing velocity without affecting the percentage conversion of the resin and the mechanical and optical properties of the fibre.

1. Introduction

Optical fibres for light transmission need protection against humidity, abrasion and microbending losses. In Brazil and in almost all the world, this protection has been achieved with silicone [1]. However, its cure limits the velocity of spinning of the fibres. So, a better choice would be a polymeric coating that has its cure accelerated and still maintains good mechanical, adhesive and optical properties.

Ultraviolet-curing polymeric systems represent an excellent industrial alternative, due to the reduction in energy consumption and solvent evaporation, equipment simplicity and low cost [2]. Epoxy acrylate and urethane acrylate oligomers have been the more widely tested of these systems for coating of the fibres [3, 4].

The objective of this work was to develop a new ultraviolet-curing polymeric coating with better mechanical properties than the above-mentioned oligomers. A "blend" of both was explored and tested on the fibres, resulting in an improved material.

2. Experimental techniques: results and discussion

2.1. Ultraviolet curing blend formulation

The epoxyacrylate oligomer used was Epocryl 370 from Shell Chemical Co ($\bar{M}_w = 5000$; $u = 9 \times 10^5$ cP at 25° C). The urethane acrylate was the oligomer 6000 from Thiokol Chemical Division ($\bar{M}_w = 6000$; wax at 25° C). Their chemical structures are shown in Fig. 1.

The epoxyacrylate oligomer gives a coating with high elastic modulus, high impermeability to moisture and high adhesion to the glass, while being hard and brittle after the cure; the urethane acrylate oligomer produces a coating with high abrasion resistance and flexibility, allowing low microbending losses, while being elastomeric after the cure. So, in order to achieve all these properties, "blends" were made of both oligomers. The term "blend" is not strictly correct, because the mixture of both acrylates will form a tridimensional network, with crosslinkings between them. A more appropriate

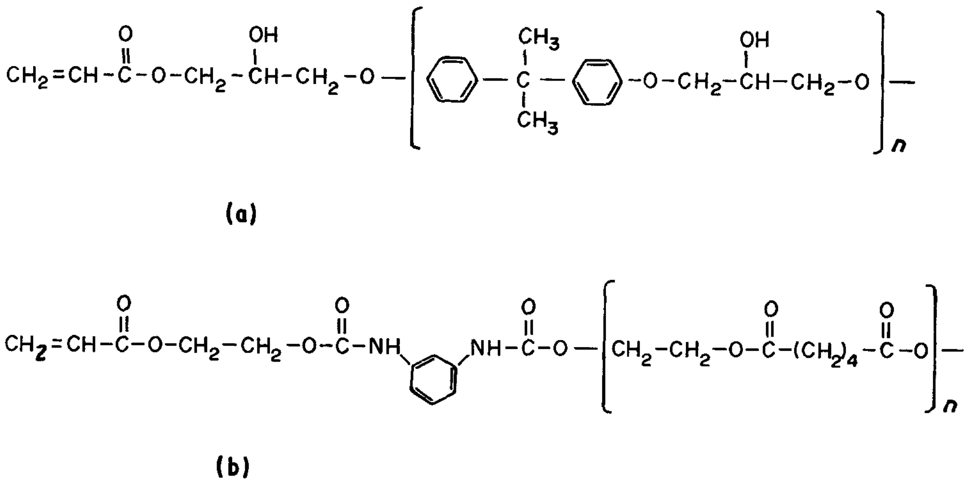

Figure 1 Chemical structure of the oligomers. (a) Epoxy acrylate oligomer; (b) urethane acrlate oligomer.

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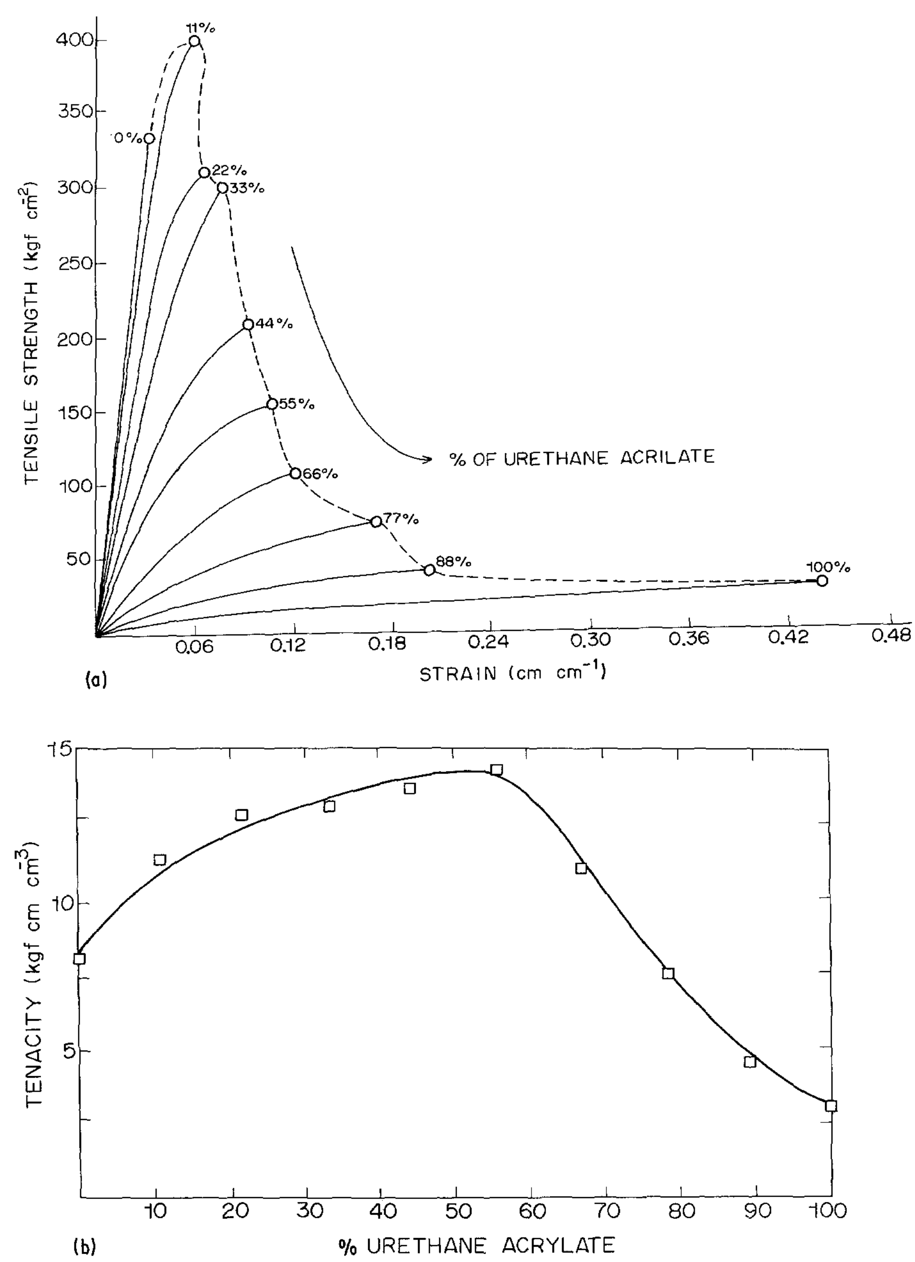

Figure 2 (a) Fracture behaviour of the blends. (b) Tenacity against blend composition.

name would be "simultaneous polymer networks" (SIN) [5]; but for simplification we will retain the term "blend".

The formulations tested varied between 0 and 100 wt % urethane acrylate, with 1.5 wt % photoinitiator benzoin isopropyl ether (Vicure 10, Stauffer Chemical Co) and 25 wt % acrylate functional monometer 1,3-butanediol diacrylate (Polysciences, Inc). Films of these blends (250 μm) were ultraviolet-irradiated for 1.5 sec with a medium pressure mercury lamp (Germetec, 200 W in.$^{-1}$), and their tensile properties measured in a Instron 1127 machine. The results are shown in Fig. 2.

A maximum can be observed at 11 wt % urethane

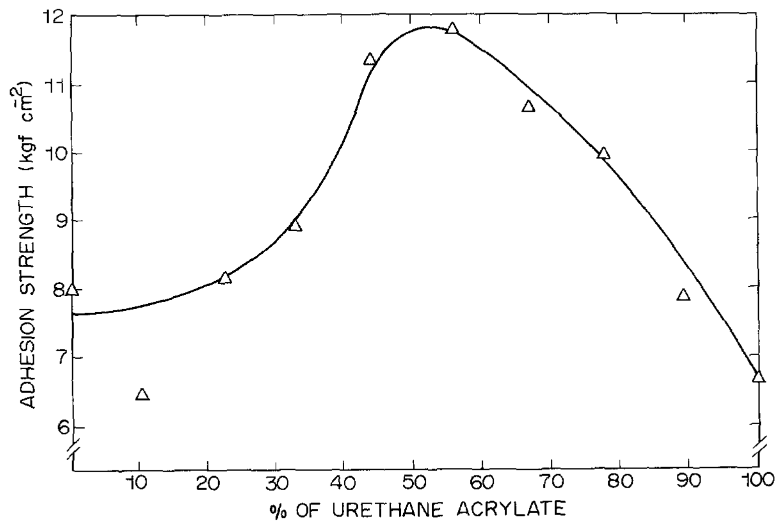

Figure 3 Correlation between adhesive force and blend composition.

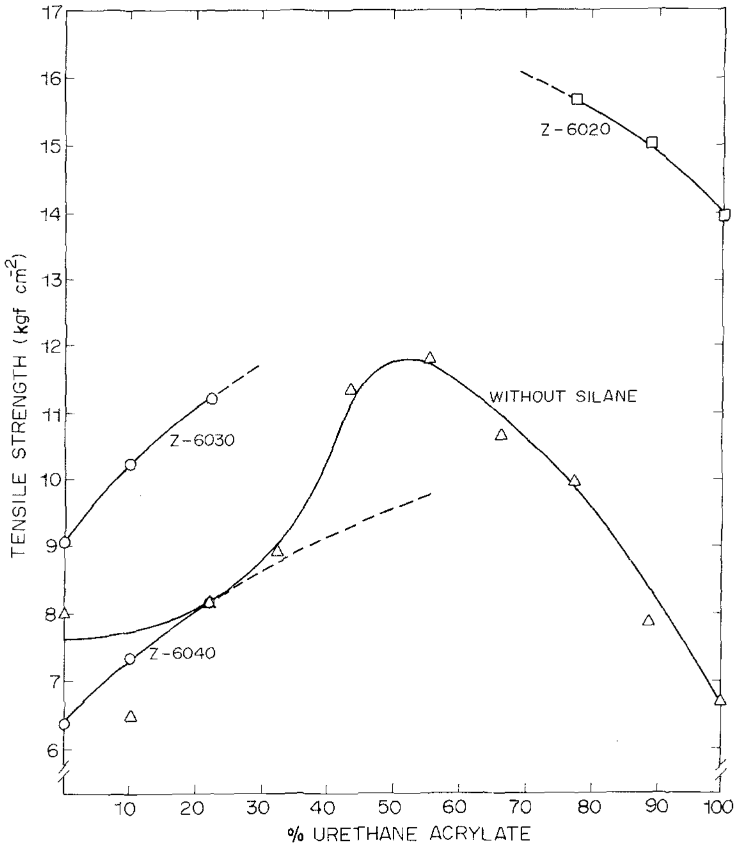

Figure 4 Adhesive force against blend composition, modified with silane coupling agents.

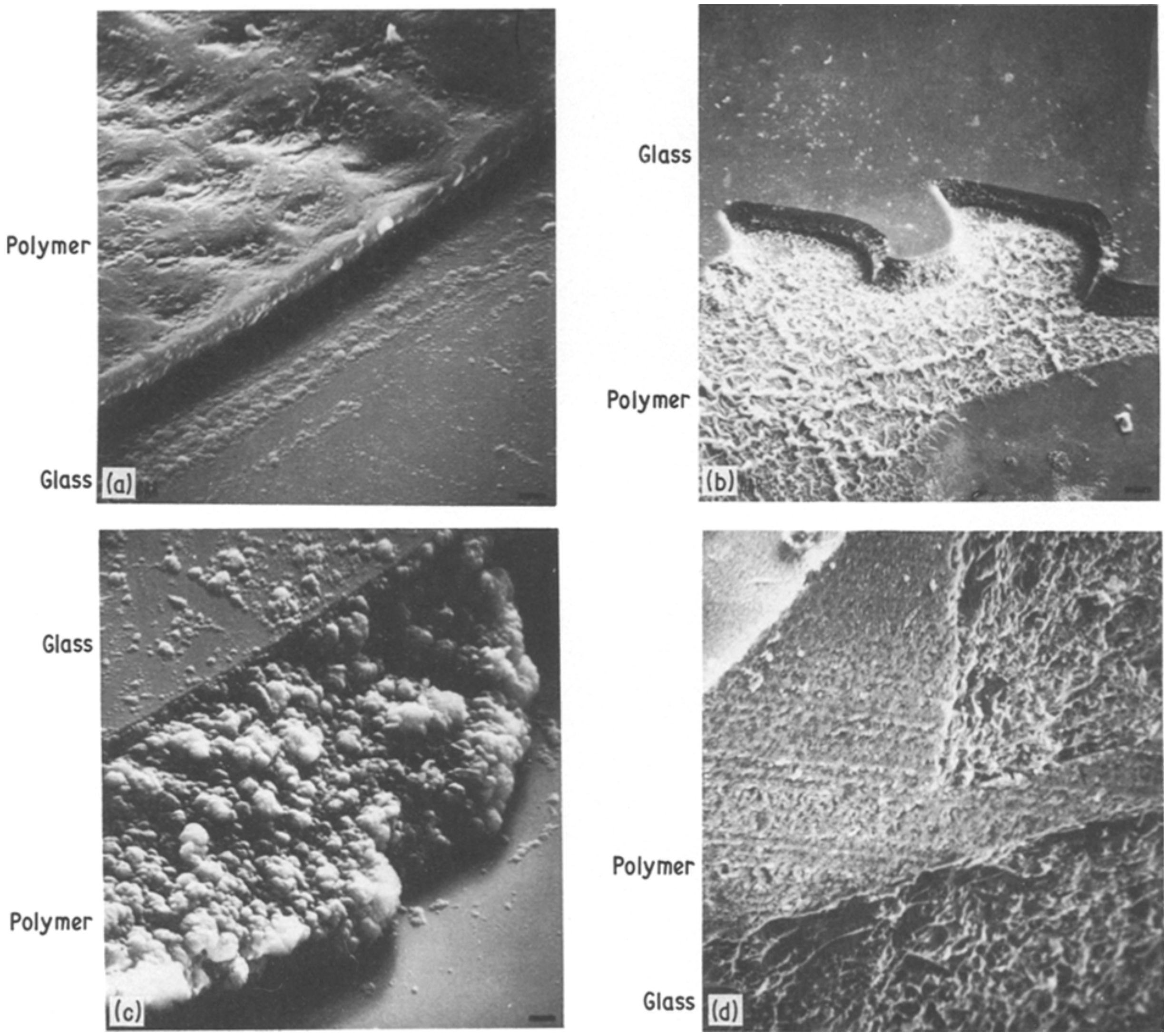

Figure 5 Micrographs of the blend glass interface: (a) without silane (× 1070); (b) with the Z-6030 coupling agent (× 550); (c) with the Z-6040 coupling agent (× 650); (d) with the Z-6020 coupling agent (× 70).

TABLE I Composition of the ultraviolet-curing blend

Component	Parts (g)
Urethane acrylate oligomer	55.6
Epoxyacrylate oligomer	44.4
1,3-butanediol diacrylate	25
Benzoin isopropylether	1.25
Silane coupling agent	2.00

acrylate; this synergism has been observed in polyblends and grafted and block copolymers [6]. The increase of the crosslinking density increases the heterogeneity of the crosslinking length distribution, producing bonds that are smaller than the others, which will break first when under tension. Probably up to 11 wt% urethane acrylate, homogeneization of the length distribution occurs, increasing the tensile strength of the polymer network; but above this concentration, for some reason, the reverse situation is predominant.

Adhesion tests (ASTM D-1002) were performed in "sandwiches" of alkaline glass. The results are shown in Fig. 3. It can be observed that the blends poorer in urethane acrylate have a lower adhesion to the glass than those with 40 to 50 wt%. It seems that, in this system, the polarity of the adhesion is not the determinant factor affecting the adhesion: probably the rheology of the whole set plays a more important role [7].

2.2. Coupling agents

In order to improve the adhesion between the blend and the optical fibre, three silane coupling agents were

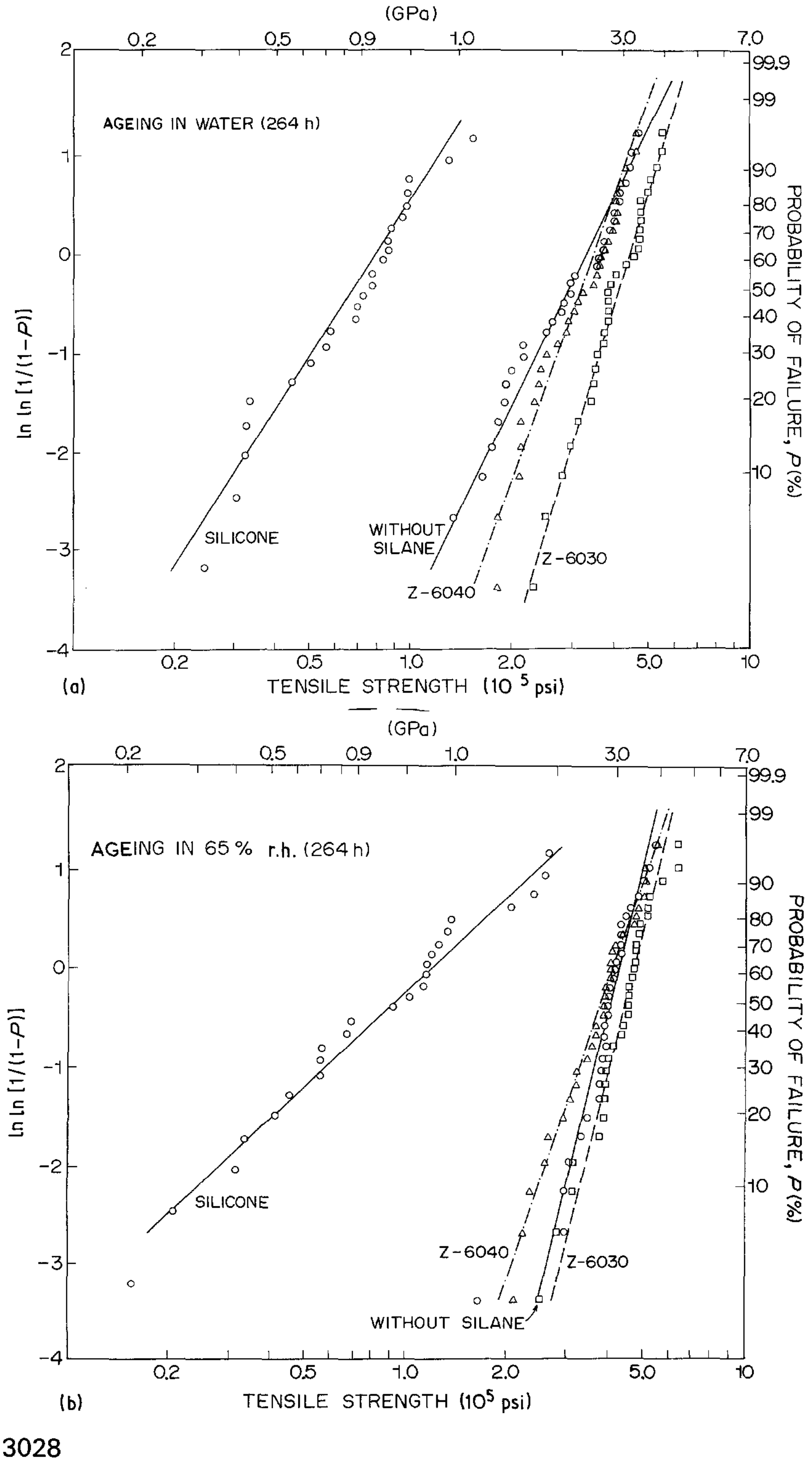

Figure 6 Weibull plots of the fibre tensile strengths: (a) Water-soaked, 264 h, (b) 65% r.h., 264 h.

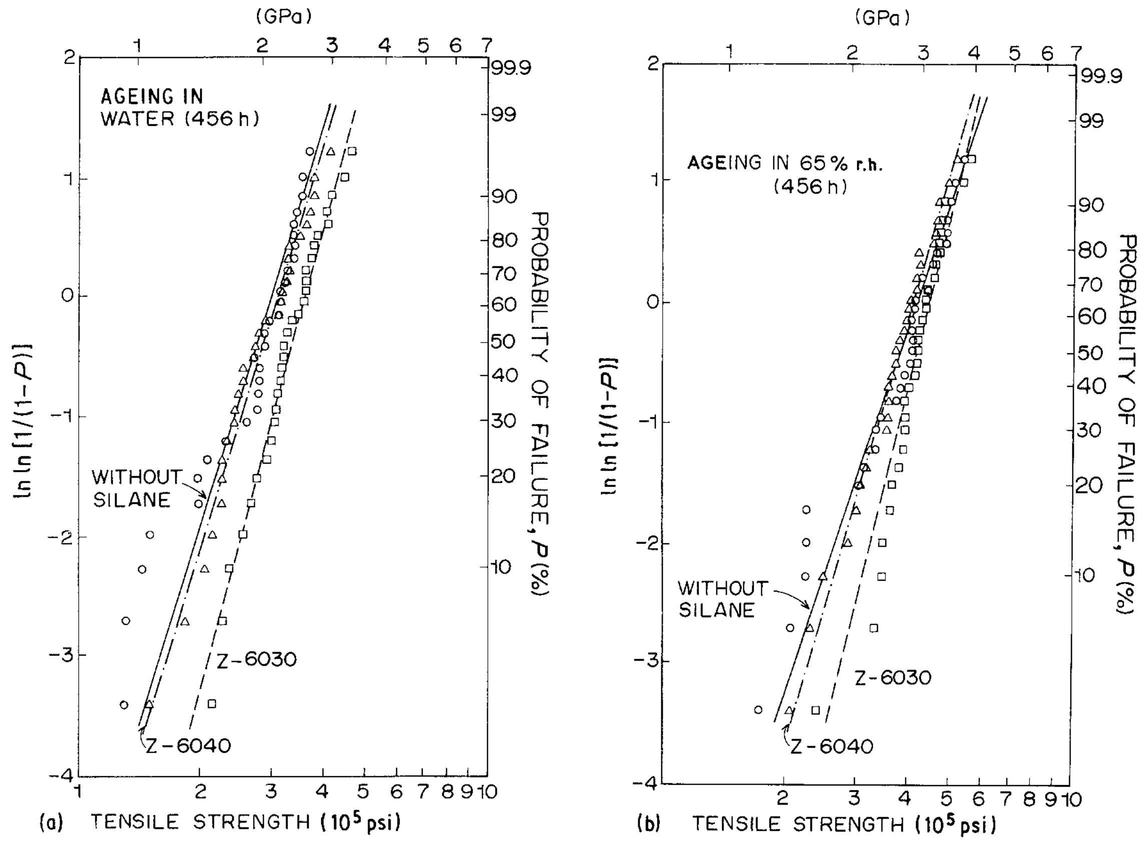

Figure 7 Weibull plots of the fibre tensile strengths: (a) water-soaked, 456 h; (b) 65% r.h., 456 h.

tested. They were the Z-6020 (aminofunctional), the Z-6030 (acrylofunctional) and the Z-6040 (epoxyfunctional), from Dow Corning of Brazil. The results are shown in Fig. 4. The best coupling was obtained with the Z-6020 and Z-6030.

The broken lines represent an extrapolation of the results, because in these samples the glass broke before the interface did. Electron micrographs shown in Fig. 5 illustrate this behaviour.

Table I gives the final blend composition chosen to coat the fibres.

2.3. Ageing studies

The ageing studies consisted of the measurement of the tensile strength upon exposure to two environments: 65% r.h., 18° C and water, 18° C. Tensile tests were performed again in the Instron 1127 machine, at a rate of $10\,\mathrm{mm\,min^{-1}}$, at $20 \pm 2°$ C, $65 \pm 5\%$ r.h.

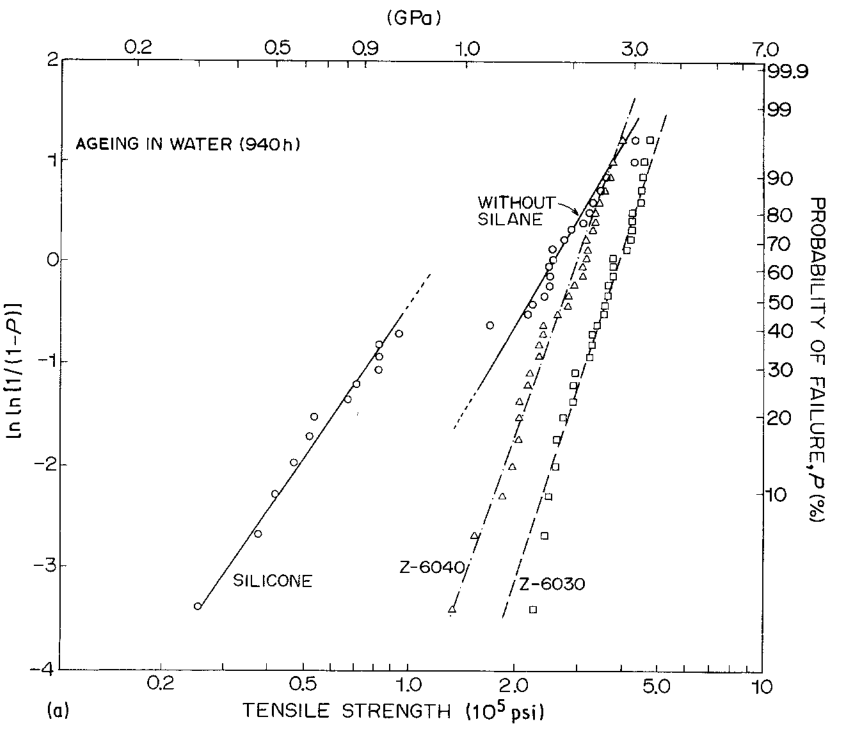

Figure 8 Weibull plots of the fibre tensile strengths: (a) water-soaked, 940 h., (b) 65% r.h., 940 h.

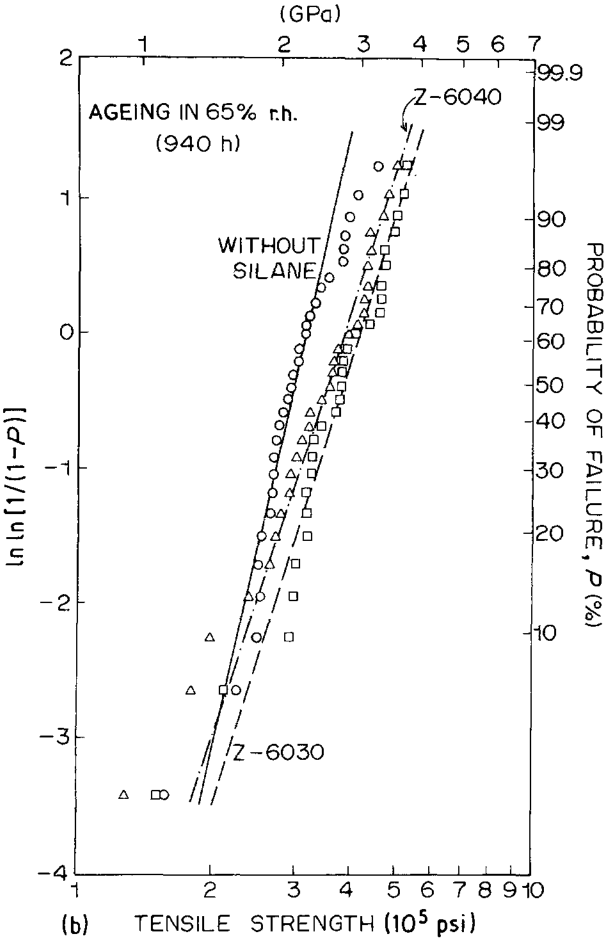

Figure 8 continued.

All samples were conditioned in the test environment for 1 h. A minimum of 30 samples was used in each test. The results are shown in Figs 6 to 8.

The silane Z-6020 was not tested because it reacted with the monomer when heated at 47° C.

Fig. 9 illustrates the correlation between median strengths and ageing time in the two environments. The best performance was obtained with the Z-6030 silane coupling agent. Electron micrographs of some of the coated fibres are shown in Fig. 10.

2.4. Modification of spinning velocity

The cure of the silicone usually limited the velocity of spinning of the optical fibres. With the use of this ultraviolet-curable blend this velocity was increased up to 1.5 m sec^{-1}, without affecting the degree of conversion.

Higher velocities could not be tested owing to mechanical restriction. Figs 11 and 12 show that even increasing the spinning velocity by three times, the degree of conversion and the spectral attenuation remained unaltered.

3. Conclusions

The development of an acrylate functional, ultraviolet-curable blend allowed an increase in the drawing velocity of the optical fibres. These fibres were usually coated with silicone, at 0.45 m sec^{-1}. With the use of the blend, fibres could be drawn at 1.5 m sec^{-1}. This increase in fibre production did not affect the mechanical properties of the coated fibres; on the contrary, the new polymeric coating gave a better protection to the surface glass than the silicone; this can be concluded from the Weibull plots, where it can be seen that even without silanes, the acrylate functional blend is a better barrier against water. In addition, the spectral attenuation of the fibres was almost unaffected by the ultraviolet-curable coating.

The coating applicator was the same as that of the silicone; to apply the blend it was necessary only to increase the heating up to 47° C. Therefore, this polymeric system offers a new option for the coating of optical fibres without having to modify the drawing equipment.

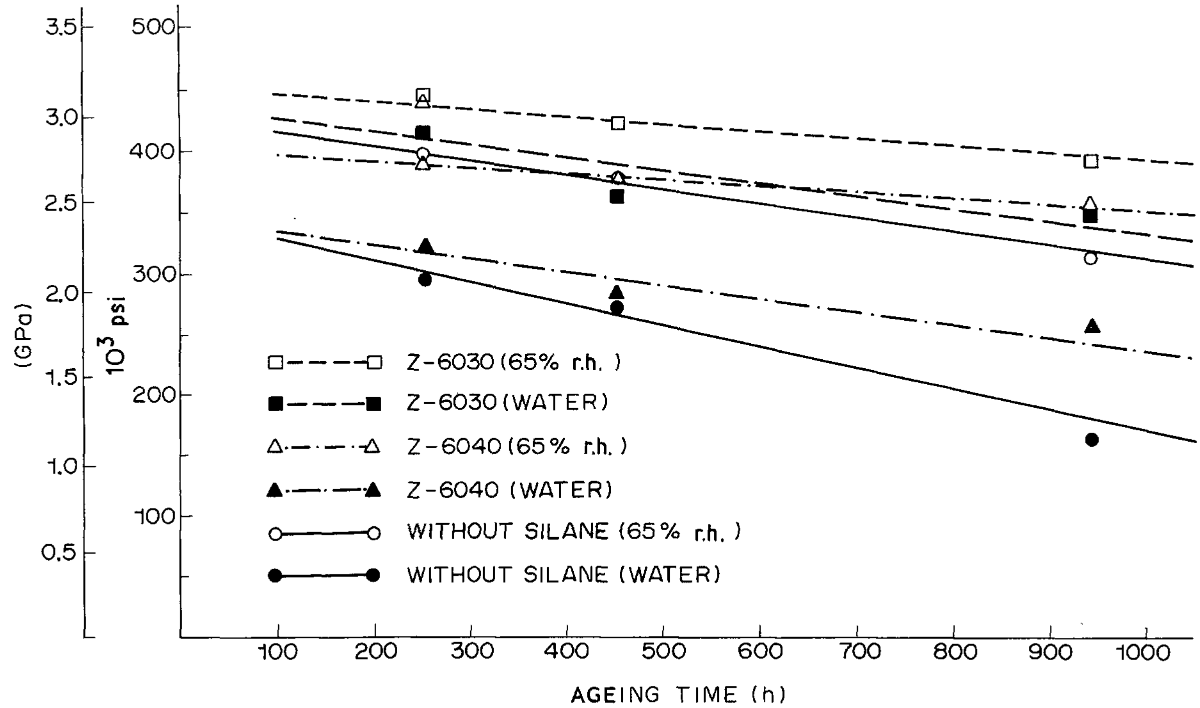

Figure 9 Median strengths against ageing time. Each median was determined from 30 to 40 measurements.

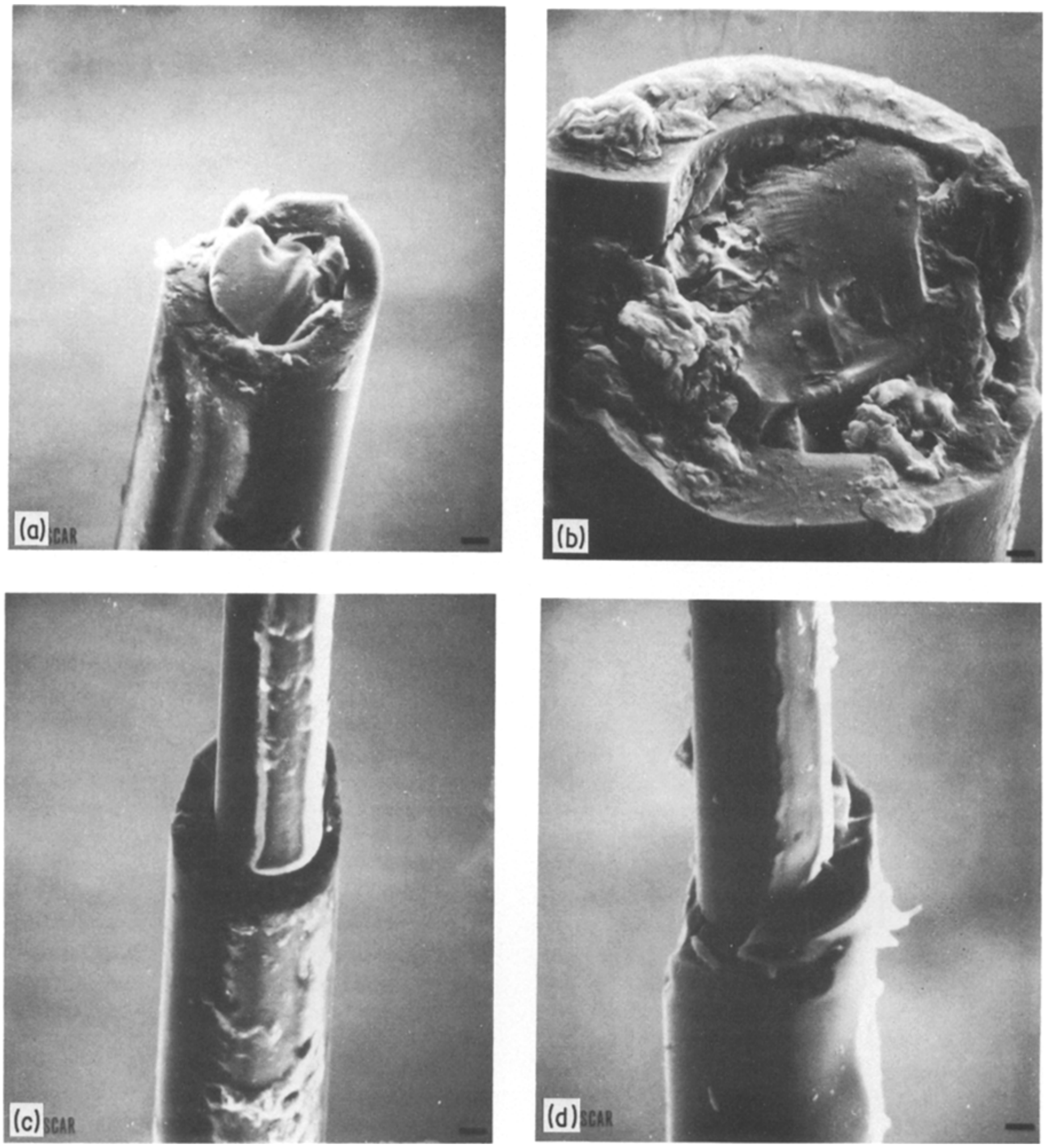

Figure 10 Micrographs of the coated fibres, after fracture: (a) without silane (× 160); (b) with the Z-6030 coupling agent (× 380); (c) with the Z-6040 coupling agent (× 130); (d) with silicone (× 210).

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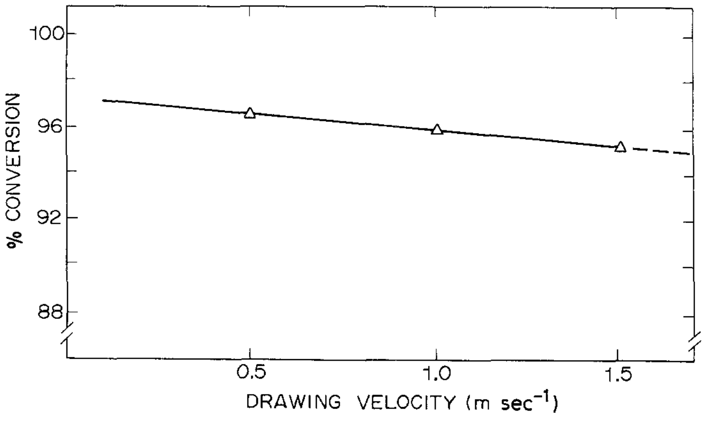

Figure 11 Conversion against spinning velocity.

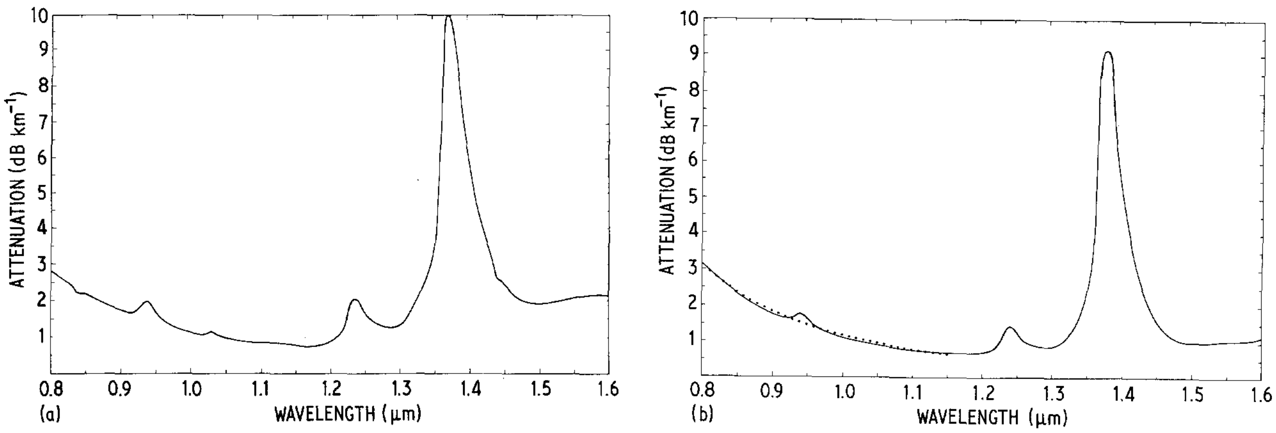

Figure 12 Spectral attenuation against wavelength for: (a) Silicone-coated fibre; (b) ultraviolet-curable blend-coated fibre.

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