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Reinforcement of acrylic polymers with radiopaque cellulose fibres

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The incorporation of $BaSO_4$ containing cotton threads into acrylic matrices was studied, as a means of reinforcing the polymer and producing radiopacity at the same time. Coating the threads with a thin poly(vinyl acetate) film containing $BaSO_4$ was defined as the most suitable method, providing strength and wettability to the fibres. A percentage of about 10 p.h.r. fibres can be characterized as satisfactory for both objectives, i.e. radiopacity and reinforcement.

1. Introduction

Poly(methyl methacrylate) (PMMA) is a well established material in dental prosthetics because of the combination of properties such as biocompatibility, versatility in preparation and repair as well as excellent appearance. A recognized disadvantage of the acrylics used for the construction of dentures, is their brittleness leading to breaks during service as a result of fatigue failure in the mouth or impact failure out of the mouth.

Many attempts have been made to overcome this problem by the introduction of new materials or the modification of existing acrylics. Stafford and Smith [1] investigated polycarbonates and pointed out that this polymer is superior to acrylic resins in deflection, impact strength and thermal expansion. Grant and Greener [2] attempted to reinforce acrylic resins using sapphire whiskers and reported an improvement of physical properties such as flexural strength.

The development of new, high-strength and high-modulus reinforcing fibres has, of course, attracted the interest of many scientists. Schreiber [3, 4] investigated the reinforcing effect of carbon fibres and reported considerable improvement. The same reinforcing medium was also used by Manley *et al.* [5, 6], whereas other researchers studied the effect of carbon fibres on the fatigue resistance and bending properties of denture resins, the modification of flexural strength and modulus of carbon fibre–acrylic resin composites [8]. Apart from carbon fibres, many other reinforcements have been tested, such as carbon black [9], aramid fibres [10], or combinations of carbon and glass fibres leading to hybrid composites [11]. On the other hand, the strengthening of acrylic resins has also been attempted by the incorporation of shock absorbers such as small rubber particles [12, 13].

An additional problem of the acrylics as well as other polymers used as prosthetic materials is that they are radiolucent, i.e. transparent to X-rays. There is, therefore, a danger in their use in dentistry, medicine and surgery. Dentures or parts of dentures may be aspirated or swallowed and it is also possible that in case of traumatic injuries to the face (as in road traffic accidents) dentures or fractured portions of dentures may become impacted into the tissues. The radiolucency of the material causes problems in the detection of such foreign bodies. Many attempts were made therefore to modify acrylics and other prosthetic polymers to radiopaque materials, including the dispersion of finely divided inorganic salts, such as bismuth halides [14], subcarbonate [15] or subnitrate [16]. Most of the above salts have proved inadequate although they satisfactorily promote the radiopacity. Problems arising from the incorporation of these salts are concerned with mechanical properties deterioration, solubility, hydrolysis or even toxicity.

On the other hand, barium sulphate is a medium that has found approval for incorporation into acrylics, at a maximum level of about 8%. This concentration does not seriously affect the mechanical properties but its radiopaque effect is also insufficient. Further solutions were proposed, such as the copolymerization of monomer with metal salts of unsaturated organic acids. Simons [17] prepared methyl methacrylate–zinc acrylate copolymers, whereas Combe [18] used barium acrylate as comonomer. These products have good X-ray opacity, but a reduction of mechanical strength, higher water absorption and hydrolysis are reported as disadvantages.

Another attempt includes the incorporation of bismuth [19] or barium [20] containing glasses. Nevertheless, the increase in specific gravity and the

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embrittlement induced prohibit their application. Aliphatic or aromatic halides with low volatility were also added to PMMA polymers but because this incorporation is not accompanied by chemical bonding, a migration and leaching of the additive is possible, leading to the loss of radiopacity and causing health hazards, as in the case of 1,1,2,2 tetrabromoethane and 1,2 dibromoethane [21]. More sophisticated but effective procedures are reported by Davy and Causton [22], who polymerized methyl methacrylate with a halogenated methacrylate derivative and produced radiopaque polymers defining the limits that ensure the retention of an acceptable level of mechanical and physical properties.

It should also be noted that some attempts to produce radiopaque materials have been reported in the field of surgical dressings and related products [23–25]. These attempts include the preparation of radiopaque tracer threads and then the incorporation of these threads in the surgical dressings. Such materials are described in the related patent literature [23–26]. According to these works, filaments composed of a thermoplastic are loaded with X-ray-detectable materials. Typical thermoplastics are polyolefins, vinyl polymers, polyamides or cellulose derivatives. As radiopaque fillers, the non-toxic barium compounds, chromium dioxide or bismuth trioxide can be used. Similar materials with improved strength and dimensional stability can be produced by the incorporation of reinforcing thread-like metal strands or textile yarns such as fine cotton filaments and polyester or polyamide fibres [24, 25].

2. Experimental procedure

X-ray-detectable threads were prepared by two methods, as described in detail elsewhere [27]. The first method includes the precipitation of $BaSO_4$ in the cotton thread, at room temperature, after the immersion into 0.1 N sulphuric acid and barium hydroxide baths. The threads were then washed with 0.02 N sulphuric acid and water.

The second method follows a coating of the thread with an alcoholic solution of poly(vinyl acetate) containing barium sulphate. Treated and untreated threads were cut into short sections and mixed with acrylate dough in weight ratios varying from 3–25 p.h.r. The acrylic powder (ICI, DA 100) was mixed with freshly distilled methyl methacrylate in weight ratio 2/1 and the produced dough was compression moulded into plaques 2 mm thick. Moulding conditions were 20 min at 100 °C.

Tensile specimens were cut from the moulded plaques and measured, using a JJ Instrument tensile machine working at a grip separation speed of 20 mm min^{-1}.

3. Results and discussion

The typical characteristics and properties of treated and untreated threads are shown in Table I. It is evident that both methods of treatment allow the retention of essentially the same $BaSO_4$ percentage. A decrease in the tensile strength is clear in the case of chemical treatment whereas an increase is shown for the coated threads, in comparison with the strength of the untreated threads. On the other hand, elongation seems to be unaffected by either method of treatment. A possible explanation for the strength reduction of the acid-processed thread could be the beginning of hydrolysis of the cellulosic material.

TABLE I Characteristics and properties of untreated and treated threads

	Untreated	Chemically treated	Coated
$BaSO_4$ content (%)	0	41.5	43.3
Tensile strength (cN/tex)	37.4	27.5	49.7
Elongation (%)	12.1	9.4	13.7

The tensile properties of specimens reinforced with untreated or treated threads are shown in Fig. 1. In all cases, an increase in the tensile strength with the concentration of reinforcement is clear, but above 10 p.h.r. a limiting effect or even a decrease is displayed. This is due to the difficulty of wetting and dispersion of higher amounts of threads resulting in defects that statistically lead to failure at relatively low stress levels.

The weakened threads have, as expected, the least effect on the tensile characteristics of the specimens. On the other hand, the reinforcing result produced by the coated and untreated fibres is disproportionate to their initial strength. The better performance of the coated reinforcement could be explained by the fact that the poly(vinyl acetate) film formed on the surface of treated thread facilitates wetting and thus the interfacial bonding between matrix and fibre.

The X-rays for treated threads and reinforced specimens are shown in Figs 2–5. It is evident from the contrast that coating is a procedure that leads to more radiopaque materials, as a consequence of the retention of the $BaSO_4$ on the surface of the thread, whereas the same percentage of $BaSO_4$ precipitated by the chemical method is distributed more uniformly within the thread.

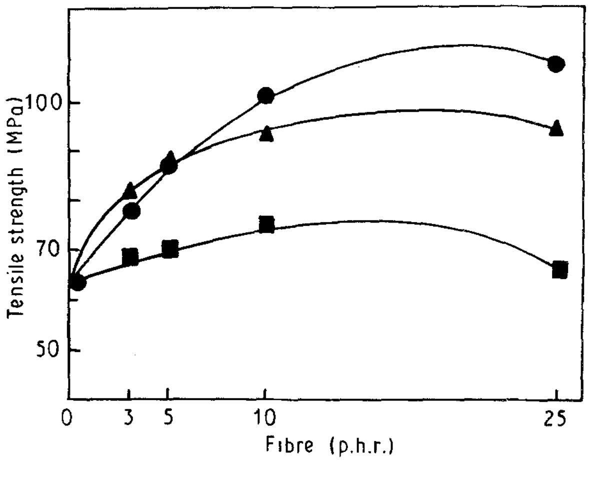

Figure 1 Effect of reinforcement on the tensile properties of acrylic samples: (■) untreated, (▲) chemically treated, (●) coated.

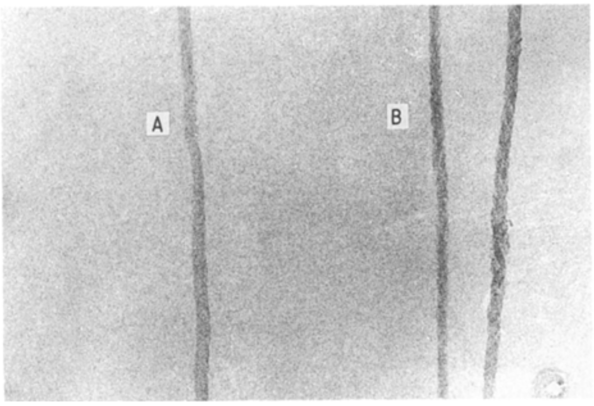

Figure 2 Radiopacity of threads: (A) chemically treated, (B) coated.

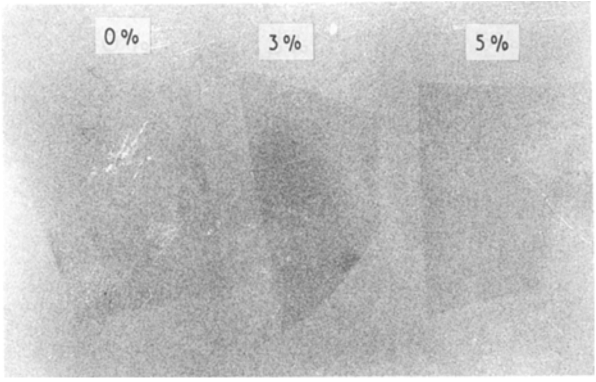

Figure 3 Radiopacity of specimens reinforced with chemically treated threads.

The effect of the two kinds of thread on the radiopacity of the reinforced acrylic specimens is of the order expected according to their initial differences. The increase in concentration enhances, of course, radiopacity. Finally, it should be noted that some aggregates are present at higher thread concentrations, as already mentioned when the tensile data were evaluated and discussed.

4. Conclusions

The evaluation of the above results can lead to the following conclusions.

1. The coating method prevents fibres from losing their strength and facilitates dispersion in polymer matrices.

2. Incorporation of treated cotton threads at a percentage of 10 p.h.r. is efficient as a reinforcement and in producing a radiopaque agent for biomedical acrylic resins.

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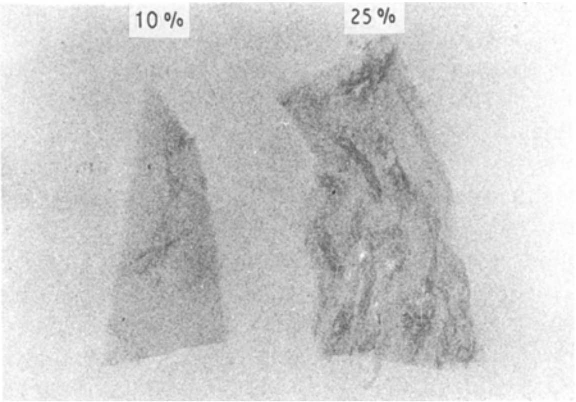

Figure 4 Radiopacity of highly loaded samples.

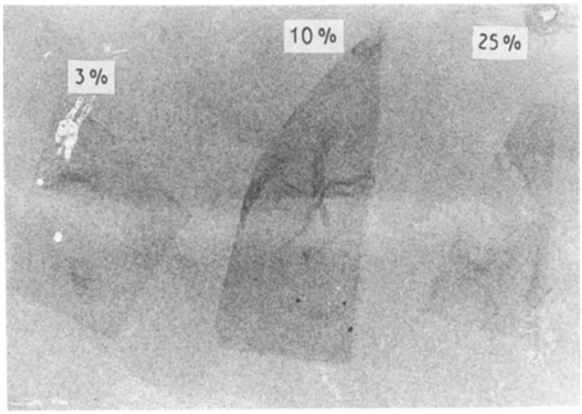

Figure 5 Radiopacity of specimens reinforced with coated threads.

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