Scratch resistance of different silica filled resins for obturation materials

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The authors have synthesised new silica filled polymeric resins for use as dental obturation materials. In contrast to earlier materials prepared for similar purposes, the present ones contain up to 80% silica nanoparticles providing the materials with improved mechanical properties. Scratch testing results show low values of the penetration depths. The ceramic concentrations used exceed a threshold concentration needed to change the mechanical properties from a soft polymer to a rigid ceramic. Further addition of silica has only insignificant effects on tribology. The penetration depths vary more or less linearly with the load, while viscoelastic recovery has a more complicated dependence on the load. These new materials have scratch resistance values in the range appropriate for applications as obturation materials.

Keywords: Obturation materials, Polymer + silica, Hybrids, Polymer tribology, Scratch resistance

Introduction and scope

Polymer based materials (PBMs) constitute an important class of biomaterials.[1,2] As noted by Deng and Shalaby,[2] advantages of PBMs include diverse physical and chemical properties, a wide range of rigidity from hard to soft elastomers, and ease of fabrication in different forms.

On the other hand, the incidence of dental caries is widespread in practically all countries in the world[3] including the US and Mexico. With an increasing demand for aesthetic obturation materials with high durability, the need for better obturation materials persists. Since teeth are constantly subjected to scratching by hard food items, eating utensils, toothbrushes, and even other teeth during mastication, both the natural tooth and materials used to repair tooth damages must have the capacity to recover from repetitive scratching.

Previously the authors have synthesised and tested different polymer based obturation materials, comparing their performance to that of commercially available resins.[4,5] The naturally occurring dentin that exists in teeth is a composite of organic (collagen, etc.) and mineral [hydroxyapatite (HAp)] phases. The outer enamel layer is mainly crystallised mineral but contains very small concentrations of specialised proteins that bind together the HAp crystals. A synthetic counterpart to the natural tooth materials is a hybrid organic–inorganic material. Therefore, organic–inorganic hybrids are becoming more and more important, particularly due to the possibility of reproducing the morphology of the real tooth and thereby allowing the potential for tooth ingrowth.[6] It was demonstrated previously[4] that nanohybrids consisting of a polyurethane matrix and nanoparticles of either silica or alumina dispersed into the polymer performed nearly as well as several commercial obturation resins in tests of scratch resistance.

Hardness and size of the inorganic filler particles strongly affect the final mechanical and tribological properties of the hybrid material. The chemical properties of the particles determine compatibility with the polymer matrix and strongly influence the morphology (through the control of interfaces) and the performance of the material. Now the authors have developed new materials comprised of a majority mineral phase with a smaller amount of polymer resin that acts mainly as agglutination agent but also exhibits by itself intrinsic high abrasion resistance. Whereas the previous materials consisted of 60% or more polymer phase,[5] the new materials contain from 20 to 30% polymer resin, with ceramic nanoparticles comprising the rest of the material. Such hybrids are also more representative of the ratio of organic to inorganic material found in natural enamel and dentin.

Scratch testing with a diamond indenter is one way to assess the durability of obturation materials. Such testing is important since the mastication process produces scratching and high shear and compression stresses that can lead to a premature wear of the fill-in

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material. As discussed by Rabinowicz, stresses have harmful effects on tribological properties of materials.[7] Moreover, cracks and fissures caused by poor scratch resistance offer host sites for bacterial growth. Measurements of scratch resistance under various loads have been used before to compare the behaviour of thermoplastics[8] including polymer liquid crystals,[9] thermosets,[10] polymer blends[11] and dental materials.[5] The penetration depth of the groove formed by scratching is generally deeper for soft materials and shallower for hard ones. The residual depth measured after allowing some time for recovery is indicative of the viscoelastic nature of polymer based materials. Thus, rigid materials tend to have smaller penetration depths but less recovery while the opposite is generally true for softer materials. From the user standpoint, the residual depth is the most important value since it represents the final scratch depth in the material. Note that tooth bone alone exhibits scratch healing, and thus constitutes a viscoelastic material.[12]

In the present study, scratch testing was applied to a set of hybrid materials produced by synthesising a polyurethane based on an hydroxylated alkyd resin. Alkyd resins are commonly used in commercial 'oil based' coatings, mainly in outdoor applications due to their high resistance to those environments; these are essentially polyester resins functionalised with hydroxyl (OH) groups. A second component is added to form a polyurethane network; here polyisocyanate is used as the curing agent. Precise control of the molecular weight of the resin is required because the amount of OH groups depends on the size of the polymer molecules. A low molecular weight resin produces materials with poor properties; on the other hand, a very high molecular weight resin increases too much the viscosity – making difficult the homogenisation. Thus, a moderate molecular weight (between 100 000 and 300 000 daltons) is recommended. The concentration of the curing agent depends not only on the number of OH groups of the alkyd resin, but also on the OH groups of the HAp $[Ca_{10}(PO_4)_6(OH)_2]$. The reaction between the crosslinking agent and HAp assures a chemical link between the obturation material and the substrate (dentin). Reducing the risk of microfiltration (through the tooth into the body) is a desired result of the crosslinking reaction.

Polyurethane (PU) resins are good candidates for dental applications based on their good mechanical properties and good tailorability, which comes from their wide range of chemical structures and the resulting ability to achieve a wide range of flexibilities.[13,14] Important also is biocompatibility of PUs.[15] The authors have synthesised an aromatic polyurethane which has intrinsically flexibility in the desired range. Such a balance of rigidity and flexibility is important because very rigid and tough materials may prematurely wear down the natural teeth.[16] The hybrids were prepared providing the synthesised polyurethane with varying amounts of silica nanoparticles. The methods of synthesis and the scratch resistance of the prepared nanohybrid materials are reported here.

Experimental

Materials

The polymer matrixes were synthesised from commercial reagents: a hydroxylated polyester resin of alkyd type 300M and the crosslinking agent di-cyclo-hexyl-methane-di-isocyanate (DCHMDI) are from Bayer, Leverkusen, Germany; dimethyllol propionic acid (DMPA), N-methyl-2 pyrrolidone and the ethanol diamine from Aldrich, USA; and silica nanoparticles of 16 nm diameter from Degussa, Hanau, Germany.

Polymer synthesis

The polyester resin was mixed with DMPA in the proportion resin: DMPA=10 : 1 by volume. The solvent (pyrrolidone) was used at 20% by volume; the solvent concentration can be changed to adjust the material viscosity for better handling. The resin with the DMPA and the solvent were heated at reflux conditions (85°C). Then the isocyanate was added dropwise in the volume ratio resin: isocyanate=4 : 1. The mixture was kept at this temperature for 4 h with medium agitation; after that the PU system was cooled down to the room temperature.

Synthesis of hybrid materials

Samples designated as A70, A72, A75 and A80 were prepared by slowly adding silica nanoparticles of 16 nm to the PU at different concentrations (70, 72, 75 and 80% by weight with respect to PU), under strong agitation during 10 min to achieve dispersion of the particles into the polymer. The catalyst (ethanol diamine) was added at 0·03 wt-% with respect to PU and under strong agitation; when one half of the ceramic particles had been added, the catalyst was incorporated into the mixture. At this moment the viscosity of the system is not very high, allowing the catalyst to be well mixed. After addition of the ceramic particles, the mixture, now close to a solid, was poured into Teflon moulds of $1·5 \times 1·0 \times 0·3$ cm and was kept there for 10 min. It is pertinent to mention that the catalyst accelerates the curing to such an extent that the reaction is completed in <10 min. In the case of the samples PU3 and PU3S where a catalyst was not used, the preparation went as follows: PU3 was prepared adding the nanoparticles to the resin + isocyanate + solvent mixture; while PU3S was prepared dispersing first the nanoparticles in the alkyd resin and, when a homogeneous dispersion was obtained, the crosslinking agent and the solvent were incorporated to form the hybrid material. In both cases 70% of nanoparticles were used and the crosslinking reaction took ~30 min. Sample names and compositions are listed in Table 1.

Single scratch tests

Single scratch tests were conducted on a microscratch tester (CSEM Instruments, Neuchatel, Switzerland) equipped with a Rockwell diamond tip of 200 μm radius. Scratch resistance is measured as the instantaneous penetration depth R_p and 5 min later as the residual or healing depth R_h along grooves 5 mm long at

Table 1 Characteristics of all samples

Sample name	Composition
A70	30% alkyd resin + 70% silica + 0·03% catalyst
A72	28% alkyd resin + 72% silica + 0·03% catalyst
A75	25% alkyd resin + 75% silica + 0·03% catalyst
A80	20% alkyd resin + 80% silica + 0·03% catalyst
PU3	30% alkyd resin + 70% silica (no catalyst)
PU3S	30% alkyd resin + 70% silica (no catalyst)
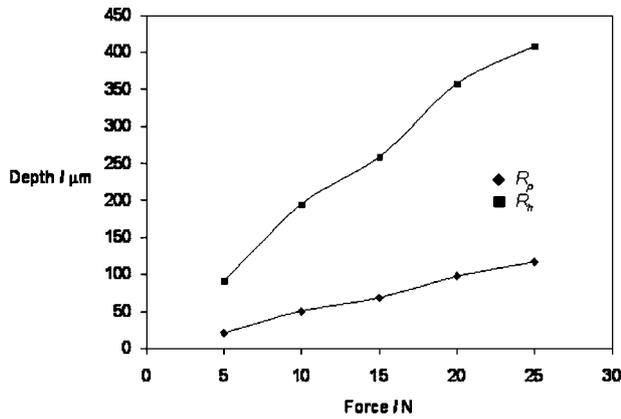
1 Penetration R_p and residual R_h depth as function of increasing load for sample A75
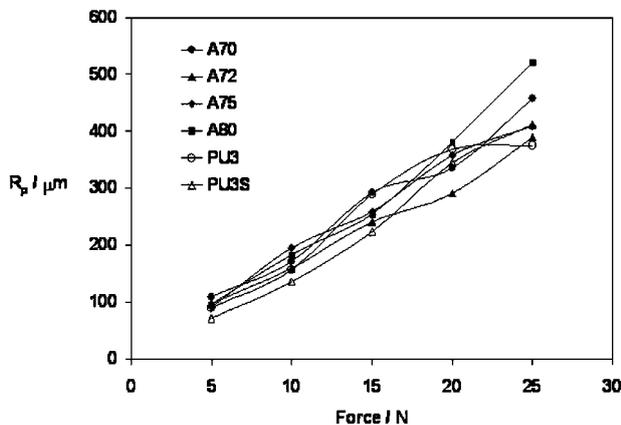

3 Residual depth versus force of indenter

a scratching speed of 5 mm min^{-1}. Results were obtained for scratching under applied loads between 5·0 and 25·0 N in 5 N increments. Under these conditions the pressures applied to the samples vary from 9·95 to 49·7 MPa. Experimental points represent averages of values obtained for four specimens of each sample type. The percentage of viscoelastic recovery f is calculated according to the equation defined previously in Ref. 10 (*see* also Ref. 17)

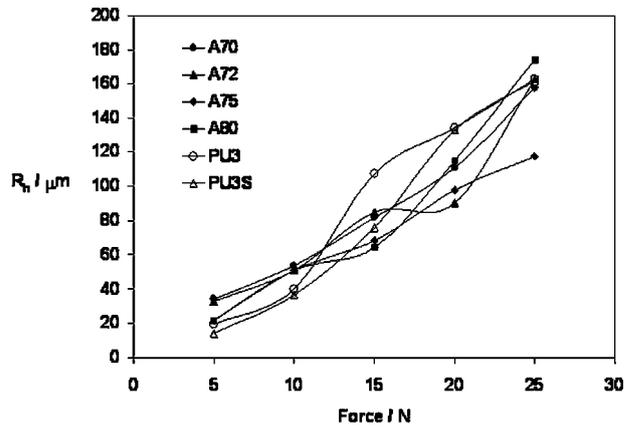$$f = \left(1 - \frac{R_h}{R_p}\right) \times 100\% \qquad (1)$$

Results and discussion

Figure 1 shows a plot of both the penetration and residual depths as a function of the load for the A75 sample. As expected, R_p increases with the applied force; a slightly convex shape of the curve is seen. The residual depth R_h increases practically linearly with the load, but its values are significantly smaller than those of R_p. Since $R_p \approx 410$ μm while $R_h \approx 100$ μm, a significant recovery takes place. According to equation (1), f exceeds 75%. The hard ceramic particles offer strong resistance against the indenter 'attack' while the soft polymer matrix makes possible a good recovery.

Figure 2 shows the plot of the penetration depth as a function of load for all samples. For low loads (5·0 N) the penetration depths are nearly the same for all samples. Apparently the concentration of the dispersed silica phase is such that comparable resistance to the

indenter action is provided; the respective matrixes play lesser roles than the filler.

At the ceramic concentrations used by the authors, the particles are practically touching each other. Therefore, the samples are well above the filler threshold concentration value and the scratch resistance is now practically independent of the filler concentration. When the applied load is increased, the diamond tip penetration increases, digging more deeply into the material and consequently interacting with more of the ceramic/polymer interfaces. This is the reason why the data spread wider and wider with an increasing load. At 5 N the range of R_p spans only 20 μm while at 25 N the difference in R_p between A75 and A80 is 45 μm. Actually for all samples the penetration increases with the load at a rate of ~17 μm N^{-1}.

The healing depths for all samples can be seen in Fig. 3. The R_h values are much lower than the R_p values in Fig. 2. However, there are certain similarities. For low loads R_h varies approximately linearly with the load, but this is not the case for higher loads. Again, wider spread is seen at higher loads, for reasons similar to those for R_p (Fig. 2) diagrams. The recovery depths start at very low values (~20 μm) for 5 N load, reaching values up to 170 μm for 25 N.

Since the obturation materials exhibit good recovery, quantitative results are presented as the percentage f from equation (1) as a function of the force of the indenter in Fig. 4. Values of f vary between 60% (A72 at 25 N) and 78% (A80 at 5 N), and between 54% (PU3 at 25 N) and 81% (PU3S at 5 N) with an average about

2 Penetration depth versus force of indenter
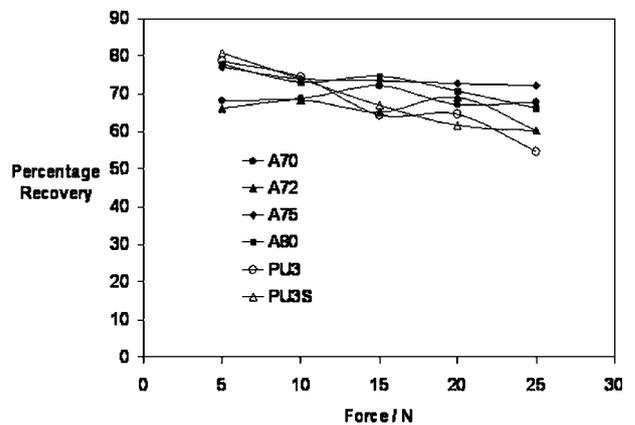
4 Percentage recovery versus force of indenter

70% for all samples at all forces. The percentage recovery is approximately constant or slightly decreasing (at most a 12% reduction from 5 to 25 N for A80) for samples A70, A72, A75 and A80. That decrease is greater for samples PU3 and PU3S, which drop 24 and 20% respectively, between 5 and 25 N. It is interesting to note that absence of the catalyst during sample preparation seems to result in greater variability of properties in the final product. As already evident comparing R_p and R_h curves for just one material in Fig. 1, high ceramic filler loads result in lower recovery. The authors recall how similarly multiwall carbon nanotubes hamper the recovery of polyamide 6.[18]

The authors have mentioned above biocompatibility only once. A mandatory requirement for materials used in medicine and dentistry is the lack of toxicity. For instance, in LAPOM, there have been extensive investigations on epoxies[10,19–21] but epoxy based materials are typically toxic. The polyurethane used is non-toxic, and the same applies of course to silica. Thus, the materials that were developed are viable candidates for obturation materials.

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