

Abrasive wear of particle-filled polymers

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The abrasive wear rates of quartz and glass particle-reinforced PMMA have been measured as a function of filler volume fraction for silicon carbide, quartz and calcite abrasives. The wear rates were found to exceed those predicted by a simple series model. Abraded surfaces were studied by surface profile measurement and SEM. The excess wear is attributed to rapid wear of the filler at the matrix interface and to particle pulls-outs.

1. Introduction

Reinforcement of polymers by high-modulus fibres results in composite materials of high modulus with tensile strength and toughness which can be greater than those of the component materials. Hard-particle reinforcement of glassy or crystalline polymers gives an increase in modulus but no improvement or a reduction in tensile strength and impact strength [1-3]. Particle-filled polymer composites are thus suited to uses where a high modulus is needed, where loads are mainly compressive or where high-temperature creep resistance is important.

Dental filling materials are one such application. The requirements for a suitable material are that it can be inserted into a cavity as a viscous liquid or paste and will rapidly set. It should provide a good match to natural tooth in modulus, thermal diffusivity and thermal expansion. Also the material should be wear resistant and dimensionally stable so that it fits tightly into the cavity without leakage. Amalgam is generally used to fill cavities in the occlusal (grinding) surfaces of posterior molar teeth but has the disadvantage of being unaesthetic in front teeth. Silicate cements are used for filling front teeth but these have poor mechanical properties and slowly dissolve so that the filling lifetime varies between 1 and 10 years but typically is only about 5 years. In the 1950s polymeric filling materials were tried but were unsatisfactory as they wore rapidly, showed excessive polymerization shrinkage and had a coefficient of thermal expansion which was much greater than that of teeth. Subsequently, particle-filled polymer com-

posites were developed with much improved properties. Current dental composites are mostly based on BIS-GMA, a condensate of bisphenol A and glycidyl methacrylate developed by Bowen [4]. This dimethacrylate monomer which has a viscosity of 1.4 N s m^{-2} is mixed with other methacrylates such as glycol dimethacrylate to reduce the viscosity, together with quartz or a glass filler and with a peroxide initiator and amine accelerator. Typically, the inorganic phase is 75% by weight or 50% by volume. Table I compares the properties of composites with other materials.

The wear properties of composite filling materials are of concern for two reasons. Firstly, it is preferable that a filling should have a smooth surface so that deposits and bacteria do not easily collect. To achieve this the filling may be initially moulded against a smooth surface or polished with a fine abrasive, in either case subsequent abrasion may lead to a surface roughening. Secondly, composites have not yet proved satisfactory for use in the occlusal surfaces of molars and premolars (class I and II restorations) as they wear too

TABLE I Properties of dental materials

	Tensile strength (MN m^{-2})	Compressive strength (MN m^{-2})	Modulus (GN m^{-2})
Enamel	10	100-400	50
Dentin	50	200-350	12
Amalgam	60	400	
Silicate cement	3-7	150-200	20
Unfilled resin	2-3	75	2
Composite	2-3	150-250	5-12

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rapidly. Craig and Powers [5] have reviewed clinical observations of the relative wear rates of filling materials and compared these with the results of laboratory wear tests. In general, laboratory tests correlate with clinical experience within any group of materials but are misleading when comparing different classes, for instance composites, unfilled resins and amalgams.

Wear processes take many forms [6] but the processes most important for dental fillings presumably involve combinations of indentations and ploughing. Here we will be concerned with abrasive wear in which a hard particle ploughs or cuts a surface. In two-body abrasion the abrasive is in the form of a grit bonded into a matrix. Rabinowicz [6] models two-body abrasion of ductile materials as a ploughing process which gives rise to an expression for the wear rate, R , volume removed per unit length of movement as:

$$R = KP/H, \quad (1)$$

where H is the indentation hardness, P is the applied load and K depends on the particle shape and on the proportion of the material displaced from the ploughed furrow which is actually removed. K thus depends on the toughness and work hardening of the material abraded. Brittle materials apparently wear as a result of surface cracking [7]. This process has been treated by Lawn [8] and gives a final equation similar to Equation 1.

In three-body abrasion the abrasive is in the form of loose particles between the sample and a backing plate. Wear rates also follow Equation 1 but the K values for metals are found to be one to two orders of magnitude lower [6]. Three-body abrasion is experimentally simpler in that the abrasive can be continually replenished and so is less subject to blunting and clogging which can reduce wear rates in two-body abrasion tests. Three-body abrasion of brittle materials has been extensively studied in this laboratory by Wilshaw and co-workers [9]. In this present work a simple equation is developed to describe abrasive wear of composite materials in terms of the wear properties of the individual components and this is compared with experiment.

2. Model

A full understanding of the abrasive wear of composites would require a full understanding of abrasive wear of homogeneous materials. In the

absence of this we will formulate a rule of mixtures which can be expected to give approximate values for composite wear rates in terms of the wear rates of the separate phases.

The volume of material removed, V , on abrasion of a composite should be the sum of the wear of the filler and matrix components:

$$V = V_f + V_m. \quad (2)$$

Wear studies on many systems have shown that the volume lost is proportional to the load and, after an initial stage, to the distance moved by the sample [6, 8, 9].

Given a load P on a sample moved over a sweep distance L with wear rates per unit load, R_f , R_m the volume losses will be:

$$V_f = R_f L P A_f \quad (3)$$

$$V_m = R_m L P A_m \quad (4)$$

where A_f and A_m are the exposed areas of filler and matrix as a fraction of the total area, which will vary depending on the relative wear rates. At steady state the ratio of loss rates from the filler and matrix must be equal to the ratio of volume fractions $x/(1-x)$

$$\frac{x}{1-x} = \frac{R_f A_f}{R_m A_m} = \frac{R_f A_f}{R_m (1 - A_f)} \quad (5)$$

$$A_f = x R_m / [(1-x)R_f + x R_m]. \quad (6)$$

Putting this into Equations 3 and 4, we get an expression for V and hence for R_c , the wear rate of the composite per unit load and per unit sweep length.

$$1/R_c = (1-x)/R_m + x/R_f. \quad (7)$$

This expression is equivalent to a series model for wear in which the two components are exposed successively to abrasion. This expression is not expected to be a complete description of composite wear. In particular we will interpret our observations in terms of particle pull-out and enhanced interfacial wear. However, Equation 7 does provide a base-line with which to compare experimental results, it is an "ideal" wear rate.

3. Sample preparation

Our aim was to produce samples which were as reproducible as possible, rather than to mimic the conditions under which dental composites are usually prepared.

The fillers used in this study were quartz and glass beads (Garoquartz S12 and Ballotini GP.00 supplied by Plastichem Ltd, Esher, Surrey). The quartz was sedimented in acetone to remove the fines ($< 5 \mu\text{m}$) then sieved to produce a 45 to 75 μm fraction. The glass beads were used as supplied with a 4 to 44 μm particle size range. When required the particles were silane treated from a 1% solution of γ -methacryloxy propyl trimethoxy silane (A174, Union Carbide Corp.) in toluene for 24h. The particles were then washed with toluene and dried at 120° C for 12h. An infra-red analysis of the reaction of this silane with fumed silica under the same conditions found 1.4 silane groups to be bonded per 1 nm² [10]. Treatment with γ -aminopropyl triethoxy silane (A1100) was also tried but this was found to be less effective in enhancing the compressive and flexural strengths of the composites over the values obtained with untreated particles. Samples were prepared using methylmethacrylate with 1 wt % benzoyl peroxide (initiator) and 0.03 vol% *N,N*-dimethyl *p*-toluidine (accelerator). The polymerizing system was immediately mixed with the filler, then rotated at 5 rpm about a horizontal axis for 2 h until the viscosity increased sufficiently to prevent the filler subsequently settling. The mixture was then poured into 2.2 cm diameter glass sample tubes which were left to stand in cold water to prevent excessive heating during polymerization. Samples were then heated to 110° C for 1 h to complete polymerization and slowly cooled to eliminate internal stresses. Resin burn off tests showed no filler sedimentation had occurred during preparation. Density measurements gave an estimated porosity of less than 2 vol % up to 30 vol % filler but 4 vol % at 40 vol % filler. Modulus and compressive strength were found to increase with unsilanated filler content whilst flexural strength was unchanged. Silanation increased compressive and flexural strengths by about 40% [10].

4. Wear tests

Wear tests were carried out using an Engis-Kent lapping machine in which a sample rests on a rotating turntable whilst reciprocating along a roughly radial path. The load on the sample could be varied from 800 to 2700 g. For silicon carbide and quartz abrasion the turntable surface was a slightly roughened glass plate and fresh slurry of abrasive in water was fed by hand continually onto the surface. For calcium carbonate abrasive, a drip feed

mechanism was used to replenish the abrasive slurry and a soft polyurethane sheet was used on the turntable. Wear rates were determined by weighing the sample after washing in water, ultrasonic cleaning in alcohol, and drying at 60° C. Several successive measurements were made on each sample to ensure that a constant wear rate was reached. A significantly high initial rate was seen only with the calcium carbonate abrasive. Otherwise the weight loss was found to be proportional to the time of abrasion and to the applied load. Weight loss was independent of sample diameter at constant load. Filler particle size had little effect over the range 20 to 200 μm but the wear rate decreased with decreasing abrasive particle size below 20 μm . This abrasive size effect has also been seen in other systems [6, 9].

The abrasives used were silicon carbide supplied by the Carborundum Company with mean particle sizes from 4.5 to 105 μm , unfractionated Garoquartz S12 with a mean size of 10 μm and precipitated calcium carbonate, calcite (BDH Ltd) with a mean size of 3 μm . The silicon carbide mainly used was F1000 with a mean particle size of 4.5 μm . Surface profile measurements were made using a Rank Taylor Hobson Talysurf fitted with a 2.5 μm tip diamond stylus.

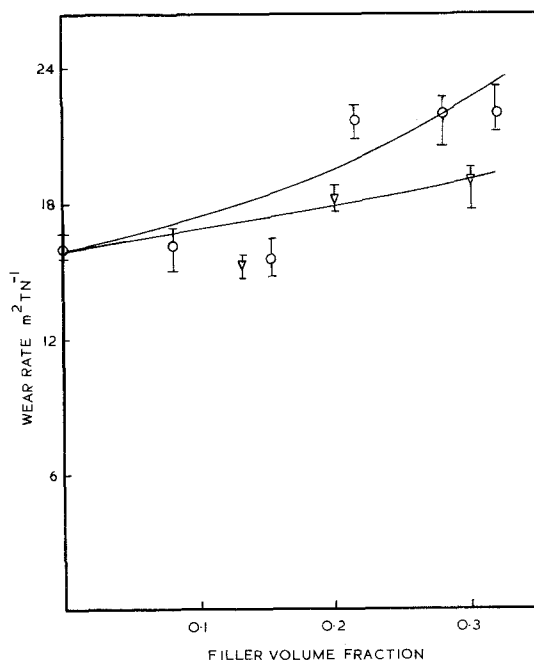


Figure 1 Wear rates of quartz-PMMA composites by loose 4.5 μm silicon carbide abrasive. (∇) Silane-treated quartz filler, (\circ) untreated filler. Full lines - fitted using Equation 7.

5. Results

The wear rate of quartz-filled polymethylmethacrylate (PMMA) against $4.5\ \mu\text{m}$ silicon carbide abrasive increases with filler volume fraction as shown in Fig. 1. If the particles are silane treated the increase is less marked. Crimes [11] and Hartley [12] found that the wear rate of quartz plates against $5\ \mu\text{m}$ silicon carbide under similar circumstances was 5 to $9\ \text{m}^2\text{TN}^{-1}$ ($\mu\text{m}(\text{MN}\ \text{m}^{-2})^{-1}\ \text{m}^{-1}$). Under the same conditions the wear rate of PMMA is $16\ \text{m}^2\text{TN}^{-1}$. Thus according to Equation 7 a decrease in wear rate with filler content would be expected. Equation 7 can be fitted to the data

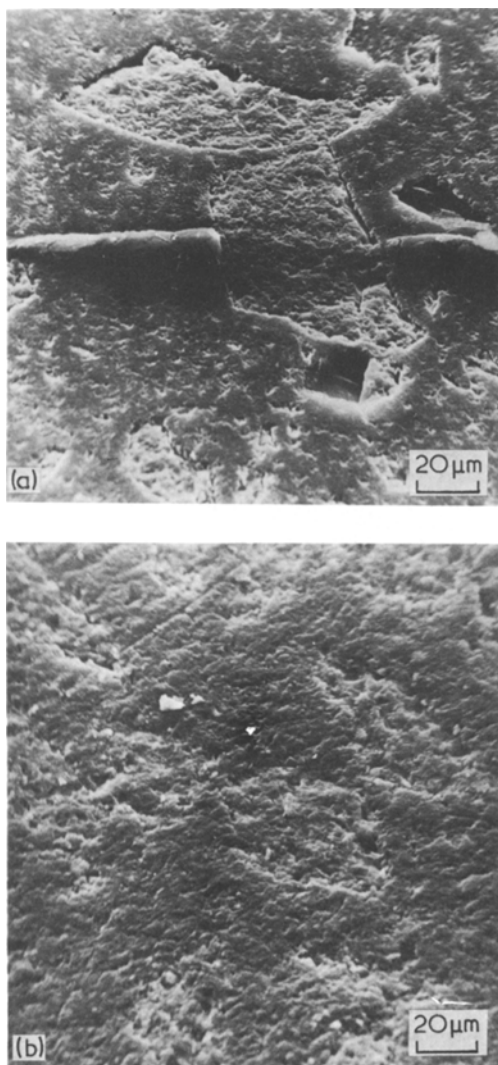


Figure 2 Scanning electron micrographs of 30 vol% quartz-filled PMMA abraded by $4.5\ \mu\text{m}$ silicon carbide. (a) Untreated filler particles. Central ridge is due to beam damage. (b) Silane-treated filler particles.

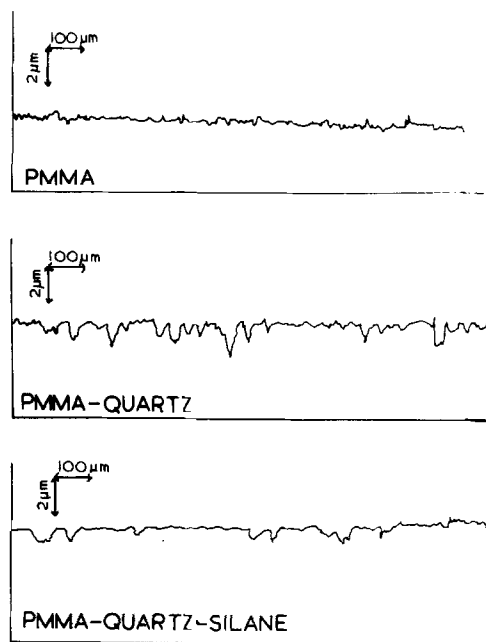


Figure 3 Talysurf traces of quartz-PMMA composites abraded by $4.5\ \mu\text{m}$ silicon carbide.

using an apparent filler wear rate as shown in Fig. 1 which is five times the measured rate for treated fillers and sixteen times for untreated fillers.

Scanning electron micrographs (Fig. 2) suggest that the components are both wearing by chipping since both are covered with small pits. The silica particles are somewhat recessed with respect to the surface as if they were wearing faster. The non-silanated particles also show more gaps between the particles and the matrix and more places where particles have pulled out. Thus silane treatment does seem to improve the particle-matrix bond.

Surface profiles of the abraded surfaces (Fig. 3) show numerous holes about $50\ \mu\text{m}$ wide and $1\ \mu\text{m}$ deep. These are not sites of pulled-out particles, which appear infrequently and only in the unsilanated samples. Rather it confirms that the quartz particles are recessed below the resin surface. This effect is less in the silanated samples, the holes being half as frequent and half as deep. Composites filled with non-silanated glass beads show numerous fractured and pulled-out beads (Fig. 4).

Wear rates for composites against quartz abrasive are shown in Fig. 5. In this case the wear rate drops markedly as silane-treated quartz particles are introduced into the resin. Wear rates of PMMA and quartz against the same quartz abrasive were 19.9 and $1.6\ \text{m}^2\text{TN}^{-1}$, respectively. Using these

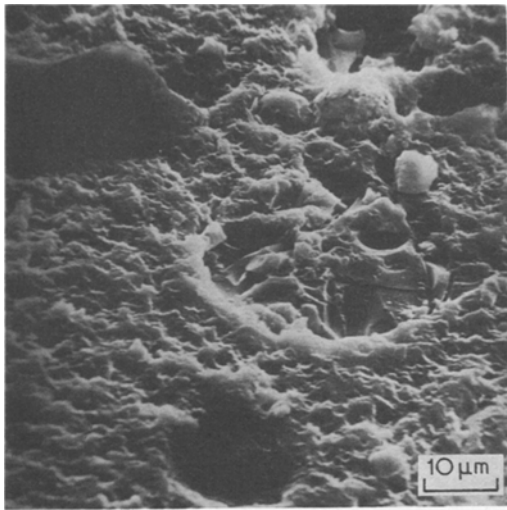


Figure 4 Surface of glass bead-PMMA composite abraded by 4.5 μm silicon carbide.

values and Equation 7 we predict an even more marked decrease in wear rate. Non-silanated quartz fillers give little improvement in wear rate and glass beads give an increased rate. The wear rate for glass sheet against abrasive was $25 \text{ m}^2 \text{ TN}^{-1}$ so that Equation 7 predicts a slight increase in wear rate with filler content but not as great as is observed. Micrographs of the silane-treated composites show that the particles stick out above the

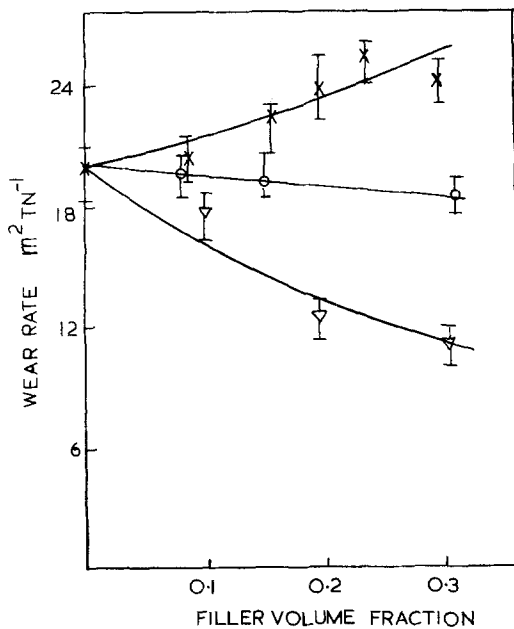


Figure 5 Wear rates of composites by $10 \mu\text{m}$ quartz abrasive. (∇) Silane-treated quartz filler, (\circ) untreated quartz, (\times) untreated glass-bead filler. Full lines fitted using Equation 7.

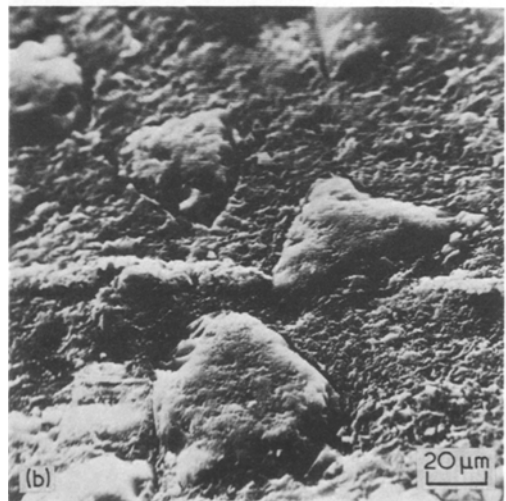
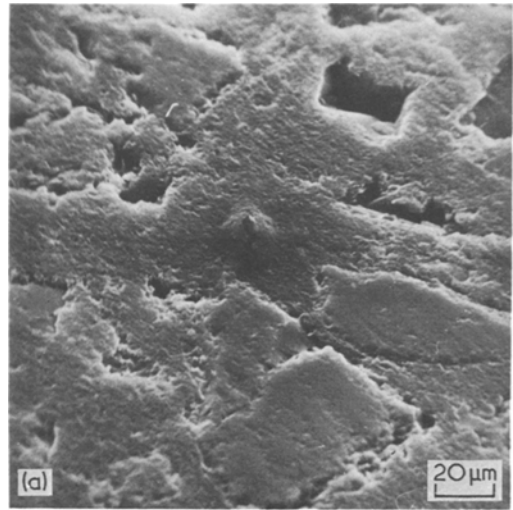


Figure 6 30 vol% quartz-filled PMMA abraded by $10 \mu\text{m}$ quartz particles. (a) Untreated filler (b) Silane treated filler.

matrix by a few μm whilst in the untreated composites the particles tend to be flush with the surface and occasionally pull out (Fig. 6). The particle surfaces appear smoother than the matrix except close to the edge of the particle (Fig. 7). The Talysurf results (Fig. 8) confirm this. Glass bead composites again showed numerous fractures and pull-outs.

With calcium carbonate abrasive the wear rates decrease markedly with filler content and the effect is again greatest with the silanated quartz filler and least with the glass beads (Fig. 9). Particles stand out clear of the matrix as seen in the micrographs (Fig. 10). The Talysurf traces also show large bumps on the surface. In this case, since the filler is essentially unworn by the

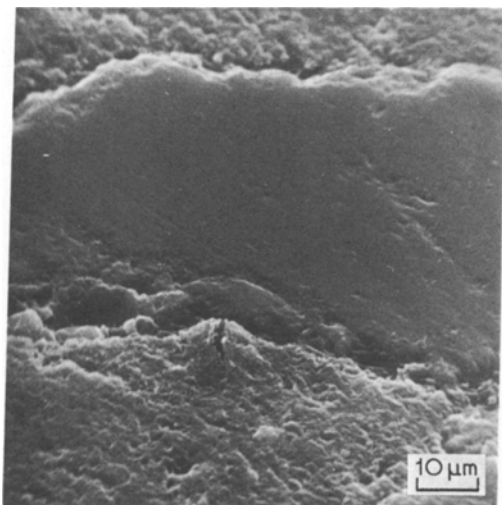


Figure 7 Interface in quartz filled PMMA abraded by 10 μm quartz particles.

abrasive, the predicted composite wear rate by Equation 7 is zero.

6. Discussion

The wear results presented here show two regions of behaviour. With silicon carbide and silica

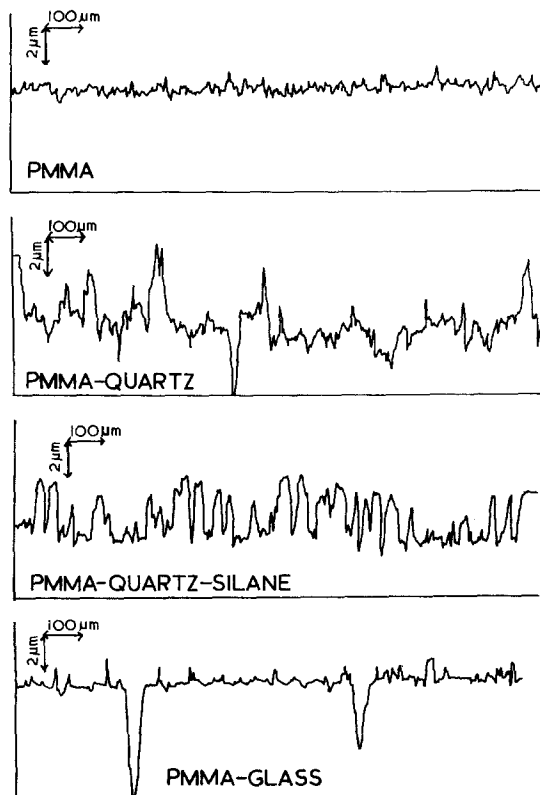


Figure 8 Talysurf traces of composites after quartz abrasion.

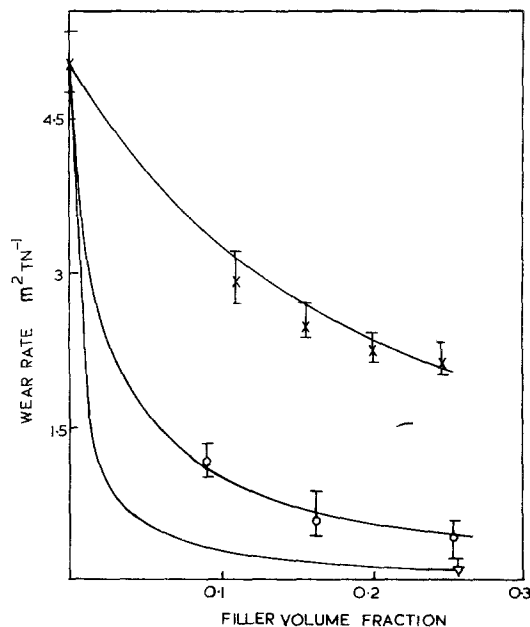


Figure 9 Wear rates of composites abraded by loose 3 μm calcite particles. (▽) Silane-treated quartz filler, (○) untreated quartz filler, (×) untreated glass filler. Full lines fitted using Equation 7.

abrasives the wear rate of the filler material is comparable to that of the matrix and the predominant wear process is chipping. With the relatively soft calcium carbonate abrasive the filler wear rate is very small and composites wear by matrix loss and particle pull-out.

Using Equation 7 with the measured matrix wear rate it is possible to obtain an apparent filler wear rate. Values obtained for this apparent wear rate from the fitted curves shown in Figs. 1, 5 and 9 are given in Table II. The form of Equation 7 is in reasonable agreement with the filler-volume-fraction dependence of the composite wear rate but the apparent filler wear rates are greater than the rates measured on silica plates by a factor of about 4 for silane-treated silica fillers and 10 or more for untreated silica. Glass-bead fillers seem to behave similarly. The most likely explanation for this enhanced wear rate is that it is associated with more rapid chipping of the particles and matrix at the interfaces. This effect can be seen in the silicon carbide-abraded samples (Fig. 2), where the particle is below the level of the matrix. The holes seen in the surface profile would then represent this undercutting at particle-matrix boundaries. These holes are generally too shallow to be due to pull-outs of particles and pull-outs are not

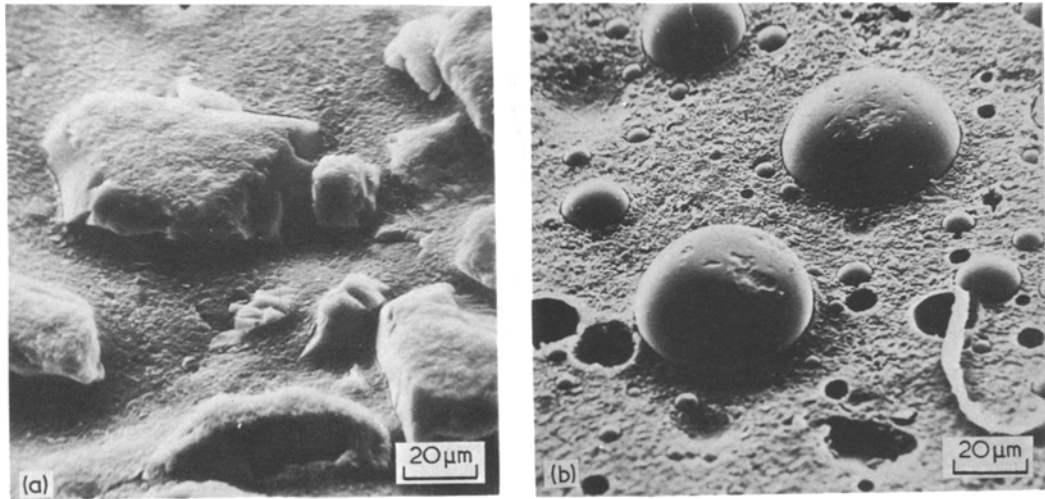


Figure 10 Surface of calcite abraded composites. (a) untreated quartz filler. (b) glass-bead filler.

seen frequently enough in the micrographs to explain the surface profiles. With silicon carbide abrasive the excess interfacial wear is within the particle. With the much larger quartz abrasive there is some evidence in the micrographs for excess matrix wear at the interface but the rounded shapes of the particles clearly show that they are wearing in from the boundaries. With glass beads the wear seems to take the form of the particles fracturing completely and pulling out. The role of the silane in reducing composite wear is clearly to improve the particle-to-matrix bond so that the matrix supports the particle at the

boundary and reduces the tendency of these regions to chip off when loaded.

Crimes [11] and Lawn and Wilshaw [13] have studied abrasive wear of brittle solids such as silica and glass and find that wear occurs primarily through a chipping mechanism. Wear material is removed as a result of cracks radiating from the original indentation intersecting the surface. PMMA, however, is a much tougher material and it is not clear whether removal is mainly by chipping or by some sort of ploughing mechanism. Crimes has shown that chips form on glass as the result of only a single indentation whilst in metals material

TABLE II Matrix, filler and composite wear rates

Abrasive system	Particle size (μm)	Composite system	Wear rates (m^2TN^{-1})			
			Composite*	Matrix	Filler [†]	Filler in bulk
3-body, SiC	4.5	Untreated quartz/PMMA	23	16	130	5-9
3-body, SiC	4.5	Treated quartz/PMMA	19	16	35	5-9
3-body, quartz	10	Untreated quartz/PMMA	18	20	16	1.6
3-body, quartz	10	Treated quartz/PMMA	11	20	6	1.6
3-body, calcite	3	Untreated quartz/PMMA	0.4	5	0.1	
3-body, calcite	3	Treated quartz/PMMA	0.1	5	0.03	
3-body, quartz	10	Untreated glass beads/PMMA	24	20	80	25
3-body, calcite	3	Untreated glass beads/PMMA	2	5	0.8	
2-body, SiC	10	Sevitron, PMMA		259		
2-body, SiC	10	Smile, glass/bis GMA	150	331	97	
2-body, SiC	10	Untreated glass/bis GMA	268	331	226	
2-body, SiC	10	Adaptic, quartz/bis GMA	75	366	42	
2-body, SiC	10	Untreated quartz/bis GMA	110	366	64	
SiC abrader	100	Adaptic, quartz/bis GMA	86	61	80	

*Results from this work, composite 30 vol% filler.

† Results calculated from [12, 13], composite 50 vol% filler.

‡ Calculated using Equation 7.

removal seems to occur only after the surface layer has been work-hardened by several indentation events. Similarly, observations of wear of dental materials by a slider suggest that subsequent passes are more effective than the first in removing material. Even in brittle materials cracks remaining after the first indentations will enhance subsequent loss of material. Crimes [11] also showed that in this type of three-body abrasion the depth of the abrasive bed was generally equal to the particle diameter, i.e. the bed consisted of a single layer of particles.

Wear by particle pull-out clearly dominates the abrasive wear by calcite. The relative apparent wear rates of silanated and unsilanated quartz and of glass beads is the same as in quartz abrasion indicating that these differences mainly reflect interfacial bonding and that this is much poorer with the glass beads than with unsilanated quartz. In principle, it should be possible to develop a model to calculate wear rates with pull-outs but a simple, parallel, model just allows the matrix to wear at its normal rate until the particles are undermined and fall out; in this case, the wear rate of the composite is the same as the pure matrix. That this is not so demonstrates that the matrix wears more slowly when it is recessed between the filler particles.

Powers *et al.* [14] measured abrasive wear of composite materials against silicon carbide paper. From Table II it can be seen that their composite wear rates, converted into our units, are higher than those we observe. This is usually the case between two-body and three-body abrasion. However, using Equation 7, the apparent filler wear rates are similar to ours whilst the matrix wear rates are greatly increased. Thus it appears that the polymer wear rate is much more dependent on the abrasion test than is the filler. Lugassy and Greener [15] measured wear using an abrasive wheel and found polymer wear rates similar to ours.

A major motivation for wear testing of dental composites is to find a test that will emulate *in vivo* wear and so provide a convenient screening test. It is generally agreed that such a test should place classes of filling materials in the same order as is observed *in vivo*, that is unfilled resin > composite > amalgam, and that the various composites should be ordered correctly. Lee *et al.* [16] found that an impact abrasion test and compressive strength gave approximately the right order, whilst a tooth brushing test was unsatisfactory. Craig and

Powers [5] find that their two-body abrasion test is reliable only within the composites but slider tests seem more generally applicable. From our work it seems that the range of fracture processes involved in wear is such that more needs to be known about the actual wear process *in vivo* from careful surface examination before a trustworthy wear model could be devised. Compressive strength measurements seem to be the most convenient guide to behaviour, although attention should probably be paid to fatigue and to long-term effects of water.

Our measurements do show that a soft abrasive such as in toothpaste will tend to cause little wear but will give rise to a rough surface with the particles standing out. Thus Chandler *et al.* [17] have prepared much smoother composite surfaces with diamond abrasives than with a soft, cuttlefish disc. However, with two-body abrasion, at least, abrasive particle size is also important in that coarse tungsten carbide burrs used in dentistry give rise to rough, ploughed, surfaces [18].

7. Conclusions

The abrasive wear of particle-reinforced polymer composites can be described by a simple additive equation based on a series model. The apparent filler wear rate in the composite is higher than that measured for the same material in sheet form and this increase is very dependent on the type of particle surface treatment. Surface profile measurements and electron microscopy suggest that the enhanced wear rate is due to enhanced chipping of the filler at the interface.

With soft abrasives, filler removal is mainly by particle pull-out which is again very dependent on the interfacial strength.

Acknowledgements

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References

1. S. SAHU and L. J. BROUTMAN, *Polymer Eng. Sci.* **12** (1972) 91.
2. J. LEIDNER and R. T. WOODHAMS, *J. Appl. Polymer Sci.* **18** (1974) 1639.
3. K. L. TRACHTER and A. T. DIBENEDETTO, *Int. J. Polymer. Mater.* **1** (1971) 75.
4. R. L. BOWEN, *J. Amer. Dent. Assoc.* **66** (1963) 57.
5. R. G. CRAIG and J. M. POWERS, *Int. Dent. J.* **26** (1976) 121.

6. E. RABINOWICZ, "Friction and Wear of Materials" (Wiley, New York, 1965).
7. B. LAWN and R. WILSHAW, *J. Mater. Sci.* **10** (1975) 1049.
8. B. R. LAWN, *Wear* **33** (1975) 369.
9. K. PHILLIPS, G. M. CRIMES and T. R. WILSHAW, *ibid.* **41** (1977) 327.
10. S. V. PRASAD, D.Phil. Thesis, University of Sussex (1977).
11. M. G. CRIMES, D.Phil. Thesis, University of Sussex (1973).
12. N. G. HARTLEY, D.Phil. Thesis, University of Sussex (1971).
13. B. R. LAWN and T. R. WILSHAW, "Fracture of Brittle Solids" (Cambridge, 1975).
14. J. M. POWERS, L. J. ALLEN and R. G. CRAIG, *J. Amer. Dent. Assoc.* **89** (1974) 1118.
15. A. A. LUGASSY and E. H. GREENER, *J. Dent. Res.* **51** (1972) 967.
16. H. -L. LEE, J. A. ORLOWSKI, P. D. KIDD, R. W. GLACE and E. ENABE, in "Advances in Polymer Friction and Wear", edited by H. -L. Lee, Polymer Science and Technology, Vol. 5B (Plenum Press, New York, 1974).
17. H. H. CHANDLER, R. L. BOWEN and G. C. PAFFENBARGER, *J. Amer. Dent. Assoc.* **83** (1971) 344.
18. W. CAMPBELL-KEYS and R. J. VERRALL, *Dental Update* (1978) 105.

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