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Young's and shear moduli of ceramic particle filled polyethylene

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Tensile and shear properties were determined for hydroxyapatite reinforced polyethylene composites (HAPEX™) for medical applications. Properties of talc or alumina filled polyethylene were also obtained. Hydroxyapatite particles of different median sizes and morphologies were used to reinforce the polyethylene. Furthermore, chemical coupling of hydroxyapatite to polyethylene was investigated. The obtained results are discussed in terms of possible use as orthodontic materials. © *1998 Kluwer Academic Publishers*

1. Introduction

The hydroxyapatite reinforced polyethylene (HAPEX™) composites were originally developed as bone substitute materials [1]. However, there are other possibilities, such as dental orthodontic brackets. These are traditionally made of stainless steel, which function satisfactorily, but are unaesthetic. Ceramic brackets are also used, but are brittle, expensive, and can damage the tooth on removal. Polymers themselves have insufficient rigidity, unless reinforced with fibers.

Earlier experiments [2] with hydrostatically extruded polyethylene achieved high Young's moduli, and hence enhanced resistance to bending; unfortunately, being anisotropic, their shear moduli were similar to unoriented polyethylene, with corresponding poor resistance to torsion. In practice, orthodontic brackets encounter complex modes of deformation.

A priori, HAPEX™ composites are an attractive potential possibility, because reinforcement is isotropic, they are relatively easy to mold, and bonding to dental enamel should be improved by the presence of hydroxyapatite (HA). This contribution describes the determination of Young's and shear moduli of a range of ceramic particle reinforced polyethylene composites.

2. Materials and methods

2.1. Materials

Prior to composite processing, the as-received particulate ceramics and polyethylene were characterized by means of particle size analysis, surface area measurement (BET method) and scanning electron microscopy. The morphology of the hydroxyapatite particles is shown in Fig. 1 and their size distribution in Fig. 2. Characteristic values of the ceramics used are tabulated in Table I. All ceramic particle reinforced polyethylene composites without chemical coupling were manufactured through the established route [3], which consisted of blending, compounding, centrifugal milling and compression molding. The injection-molded plaques used calcined bone ash (CBA) as the filler [4]. Chemically coupled HAPEX™ composites were produced by either introducing a coupling agent or a grafting polymer [5]. Table II gives the polymer details. The compositions of the composites are listed in Table III. The distribution of ceramic particles in the polymer matrix was homogeneous, as was shown in a previous publication [3].

2.2. Tensile testing

Tensile specimens were made from 4 mm thick compression-molded plates according to ISO527 standard. They were subsequently heat treated at 80 °C for 24 h and tensile tested 48 h after heat treatment. The tensile tests were conducted on an Instron 6025 testing machine at a crosshead speed of 0.5 mm min^{-1}. An Instron extensometer was mounted on to the test piece for accurate measurement of strain and hence Young's modulus. At least five specimens were tested for each composition of the composites.

2.3. Shear testing

Shear specimens (2 mm × 2 mm × 25 mm) were machined from the 4 mm thick composite plates, and cooling water aimed at the specimen was circulated throughout machining. The specimens were then tested as described previously [2]. At least ten specimens were tested for each composition of the composites.

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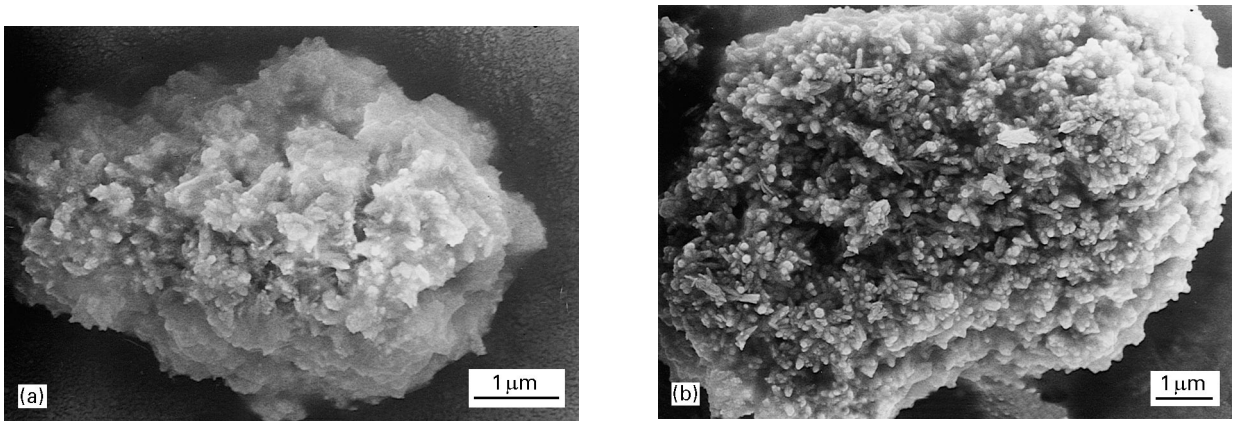

Figure 1 Morphology of particulate hydroxyapatite used to reinforce polyethylenes: (a) HA P88; (b) HA P81B.

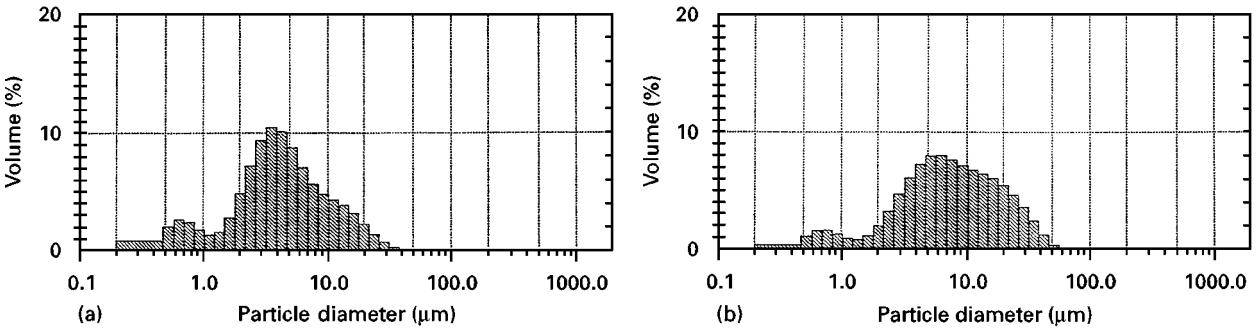

Figure 2 Size distribution of particulate hydroxyapatite used to reinforce polyethylenes: (a) HA P88; (b) HA P81B.

TABLE I Particle size and surface area of ceramic particles

Ceramic	Particle size (μm)[a]			Surface area ($m^2 g^{-1}$)
	$D_{0.5}$	$D_{0.1}$	$D_{0.9}$	
Hydroxyapatite P88	4.14	1.08	13.50	8.27
Hydroxyapatite P81B	7.32	2.07	23.97	7.61
Talc	9.78	2.43	26.01	
Alumina	1.03	0.38	11.21	
Calcined bone ash (CBA)	5.5[b]			

[a] $D_{0.5}$, median particle size; $D_{0.1}$ and $D_{0.9}$, the sizes below which 10% and 90% of the particle diameters lie, respectively.
[b] Estimated from Fig. 2 of [4].

TABLE III Composition of ceramic–polymer composites

Composite	Ceramic	Polymer	Chemical coupling
A	HA P88	HDPE	No
B	HA P81B	HDPE	No
C	HA P88	XPE	No
D	HA P81B	XPE	No
E	HA P88	HDPE	Silanation (5%)
F	HA P88	HDPE	Silanation (5%) + grafting
G	HA P88	HDPE	Silanation (2%) + grafting
H	HA P88	HDPE	Silanation (5%) + grafting
K	CBA	HDPE	No
M	Talc	HDPE	No
N	Alumina	HDPE	No

3. Results

Modulus data are summarized in Tables IV–VI. Figs 3 and 4 show typical plots of Young's and shear moduli, respectively, as a function of filler loading, and Fig. 5 plots Young's modulus, E, as a function of the corresponding shear modulus, G, value.

4. Discussion

Obviously, both moduli increase monotonically with filler loading. The maximum modulus enhancement is, at 45% loading, with Composite C, using a particular grade hydroxyapatite (HA P88) in the DePuy polyethylene. Surface treatment of either ceramic or

TABLE II Characteristics of polyethylenes

Polymer type	Polymer manufacturer	Weight average molecular mass, ($\bar{M}_w$)	Polydispersity	Designation
High density	BP chemicals	270 000	16	HDPE
Cross-linkable	DePuy	200 000	22	XPE

TABLE IV Young's and shear moduli of HAPEX™ composites

HA volume (%)	Composite A		Composite B		Composite C		Composite D	
	E (GPa)	*G* (GPa)	*E* (GPa)	*G* (GPa)	*E* (GPa)	*G* (GPa)	*E* (GPa)	*G* (GPa)
0	0.65 ± 0.02	0.281 ± 0.098	0.72 ± 0.03	0.281 ± 0.098	1.37 ± 0.07	0.302 ± 0.050	1.37 ± 0.07	0.302 ± 0.050
10	0.98 ± 0.02	0.388 ± 0.162	0.98 ± 0.07	0.266 ± 0.037	2.04 ± 0.11	0.389 ± 0.076	2.07 ± 0.03	0.494 ± 0.084
20	1.60 ± 0.02	0.479 ± 0.068	1.55 ± 0.04	0.389 ± 0.046	2.77 ± 0.14	0.516 ± 0.068	3.05 ± 0.09	0.725 ± 0.111
30	2.73 ± 0.10	0.709 ± 0.169	2.46 ± 0.21	0.617 ± 0.072	4.38 ± 0.18	0.864 ± 0.150	4.48 ± 0.17	1.085 ± 0.157
40	4.29 ± 0.17	1.180 ± 0.074	3.74 ± 0.14	1.032 ± 0.163	5.97 ± 0.25	1.179 ± 0.230	6.48 ± 0.17	1.289 ± 0.117
45	5.54 ± 0.62	1.461 ± 0.261	5.39 ± 0.81	1.237 ± 0.214	7.63 ± 0.42	1.526 ± 0.487	6.95 ± 0.40	1.635 ± 0.170

TABLE V Young's and shear moduli of chemically coupled HAPEX™ composites

HA volume (%)	Composite E		Composite F		Composite G		Composite H	
	E (GPa)	*G* (GPa)	*E* (GPa)	*G* (GPa)	*E* (GPa)	*G* (GPa)	*E* (GPa)	*G* (GPa)
20	1.54 ± 0.02	0.426 ± 0.048	1.81 ± 0.05	0.435 ± 0.071	1.74 ± 0.05	0.389 ± 0.076	1.74 ± 0.04	0.393 ± 0.058
40	3.66 ± 0.20	0.773 ± 0.104	3.87 ± 0.21	0.742 ± 0.140	2.30 ± 0.12	0.566 ± 0.085	3.11 ± 0.12	0.621 ± 0.194

TABLE VI Young's and shear moduli of other composites

Ceramic volume (%)	Composite K		Composite M		Composite N	
	E (GPa)	*G* (GPa)	*E* (GPa)	*G* (GPa)	*E* (GPa)	*G* (GPa)
0	1.3 ± 0.2		0.65 ± 0.02	0.281 ± 0.098	0.71 ± 0.04	0.281 ± 0.098
10	1.4 ± 0.2	0.128 ± 0.026	1.19 ± 0.01	0.404 ± 0.064	1.42 ± 0.07	0.303 ± 0.083
20	2.0 ± 0.1	0.427 ± 0.103	2.12 ± 0.04	0.516 ± 0.053	2.23 ± 0.10	0.471 ± 0.083
30	3.0 ± 0.2	0.644 ± 0.094	2.82 ± 0.08	0.633 ± 0.128	3.52 ± 0.11	0.743 ± 0.130
40	4.4 ± 0.7		3.97 ± 0.33	0.869 ± 0.115	5.20 ± 0.25	1.089 ± 0.204
45	5.9 ± 0.5	1.159 ± 0.305	4.56 ± 0.35	0.888 ± 0.206	7.55 ± 0.35	1.457 ± 0.245
50	7.7 ± 1.3		5.06 ± 0.22	1.250 ± 0.160		
60			5.87 ± 0.83	1.387 ± 0.183		

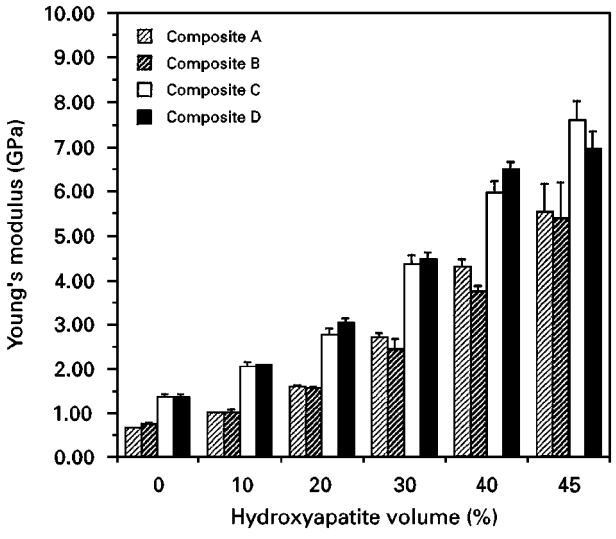

Figure 3 Variation of Young's modulus with hydroxyapatite volume for HAPEX™ composites.

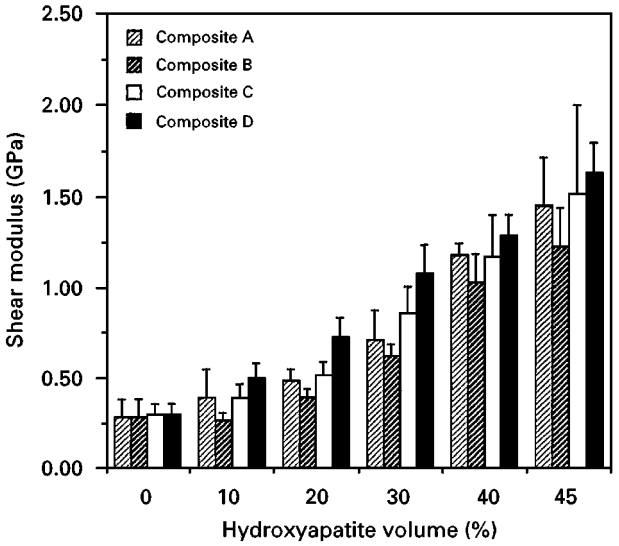

Figure 4 Variation of shear modulus with hydroxyapatite volume for HAPEX™ composites.

polymer seems to have had little effect on the modulus of the composite. The values of moduli for Composite C ($E = 7.63$ GPa, $G = 1.53$ GPa) are roughly twice those of glassy polymers, such as polymethylmethacrylate (PMMA) and polycarbonates, and similar to those of fiber-reinforced polymers. Young's modulus values are in reasonable agreement with those published previously [3]. As noted previously, the modulus enhancement is much less than that predicted by the simple "Rule of Mixtures".

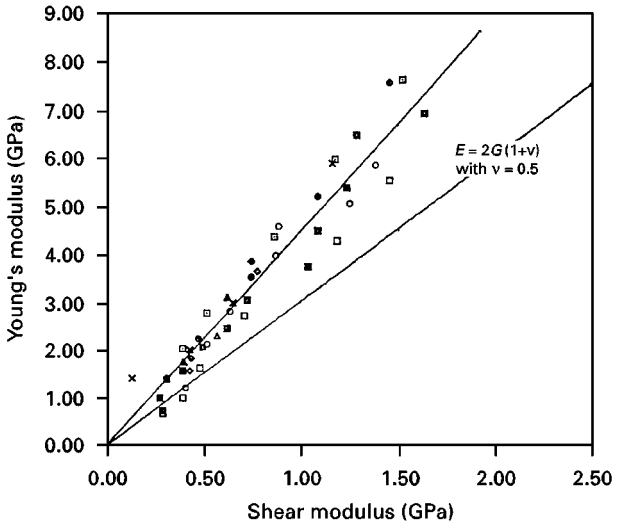

Figure 5 Relation between Young's moduli and shear moduli for ceramic–polymer composites (□) A, (■) B, (⊡) C, (■) D, (♦) E, (◆) F, (▲) G, (▲) H, (×) K, (○) M, (●) N.

While there is no clear guide as to what is exactly required, these materials obviously merit further study with respect to stress relaxation, and bonding to dental enamel. From Fig. 5, there is a general linear correlation between Young's and shear moduli; however, the ratio of E/G gives rise to a Poissons's ratio, v, of > 0.5, using the classical elasticity theory formula

$$E/2G = 1 + v \quad (1)$$

Because the torsional test used to determine shear modulus is a quasi-static method, stress relaxation may have probably given rise to lower values than would a continuous deformation method, as used to determine Young's modulus.

5. Conclusion

The enhanced Young's and shear moduli obtained with polyethylene composites, particularly with hydroxyapatite as a filler, indicate these materials to have potential as orthodontic brackets. The shear moduli values are lower than expected from predictions of classical elasticity theory, probably due to stress relaxation effects consequent to the quasi-static torsion method used.

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References

1. W. BONFIELD, J. A. BOWMAN and M. D. GRYNPAS, UK Pat. GB 2085461B (1984).
2. M. SOMERTON, M. BRADEN, I. M. WARD and D. W. WOODS, *Biomaterials* **12** (1991) 13.
3. M. WANG, D. PORTER and W. BONFIELD, *Br. Ceram. Trans.* **93** (1994) 91.
4. J. ABRAM, J. BOWMAN, J. C. BEHIRI and W. BONFIELD, *Plastics Rubber Process. Applic.* **4** (1984) 261.
5. M. WANG, S. DEB, K. E. TANNER and W. BONFIELD, in "Proceedings of the Seventh European Conference on Composite Materials". Vol. 2, edited by M. Bader *et al.* (Woodhead, Cambridge, UK, 1996), pp. 455–60.

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