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Increased strength of polyethylene glycol dimethacrylate doped with polymethyl methacrylate

M. ATSUTA*, D. T. TURNER†
Dental Research Center, University of North Carolina, Chapel Hill, NC 27514, USA

Polymethyl methacrylate (PMMA) powder was stirred into ethylene glycol dimethacrylate (EGDM) to give an apparently homogeneous solution. The EGDM was then polymerized to give a range of composite materials with from 0.5 to 50 wt % PMMA. Phase separation was observed in specimens with 2 and 5% PMMA. Flexural strength was increased by about 40% by as little as 1% PMMA. In order to account for the increase in strength of a predominantly brittle material, it was suggested that the presence of PMMA served to increase localized plastic deformation. Supporting evidence was obtained from studies of fracture surfaces by scanning electron microscopy.

1. Introduction

Glassy polymethacrylates are used in many applications in dentistry and in orthopaedics which call for a rigid load-bearing polymer. Crosslinked polymethacrylates are used in cases where resistance to crazing is important. For convenience of processing, and especially for use *in vivo*, a plastic dough is made by mixing methacrylate monomers with polymethyl methacrylate (PMMA) powder. After placement and shaping, rigidity is attained by free radical polymerization of the monomer. The present work was undertaken in order to study the mechanical strength of networks formed from mixtures of PMMA powder and ethylene glycol dimethacrylate (EGDM) over the widest practicable range of compositions [1]. The unexpected discovery was made that doping with as little as 1% PMMA significantly increased flexural strength without causing turbidity. Thus the method allows preparation of highly crosslinked glassy networks which are transparent and fairly strong. Previously the preparation of such networks was rather impractical because of fragmentation during polymerization, caused by shrinkage and by embrittlement. The purpose of the present paper is to describe the preparation of these new doped networks and to suggest an explanation for their increased strength.

2. Experimental

Spherical particles of PMMA (viscosity-average molar mass, $M_v = 3.2 \times 10^5$) were used having an average diameter of about 30 μm and a maximum value of about 100 μm (Ivoclar-Williams-Justi, Lichtenstein). Azobisisobutyronitrile (0.2 mol%) was dissolved in EGDM (Polysciences Inc., Warrington, Pa). Slurries of powder and liquid were heated at 60° C with stirring until the solution became viscous and no particles remained visible; this took from 5 to 60 min. The solutions were syringed into a vertical mould made from two glass plates separated by a gasket of polytetrafluoroethylene; the plates were held together with spring clips. The solutions were heated under nitrogen (4 atm) in consecutive stages: 5 h at 70° C; 1 h at 85° C; 1 h at 100° C; and 2 h at 125° C (the glass transition temperatures of PMMA and polyethylene glycol dimethacrylate (PEGDM) are about 100 and 120° C, respectively). The resulting fully polymerized sheet (75 mm × 50 mm × 1 mm) was slowly cooled to room temperature. Because of its brittleness and also

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*Presently Professor of Prosthodontics, Nagasaki University, Japan.
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because of the large contraction during polymerization, PEGDM always cracked into a number of fragments. In contrast, and suggestively, sheets made with $\geqslant 1$ wt % PMMA were either uncracked or else obtained in just a few fragments. On account of the brittlness of PEGDM it appeared to be impracticable to prepare the large specimens needed for sophisticated analyses of strength in terms of inherent flaw size and fracture surface energy. On the contrary, it was only practicable to make specimens suitable for three-point bending tests. These specimens were made from fragments of sheet by scratching followed by bending; the fracture surfaces were finely polished with emery papers. Specimens (1 mm, (depth, d) x 5 mm (breadth, b) x 15 mm) were broken on an Instron machine running at 2 mm min^{-1}. Values of Young's modulus (E) and flexural strength (S) were calculated from Equations 1 and 2 where P is the load, δ is the deformation and l (= 10 mm) is the span length.

$$E = \frac{Pl^3}{4\delta bd^3} \tag{1}$$

$$S = \frac{3Pl}{2db^2} \tag{2}$$

Such values are approximations, particularly on account of the low span length, but serve for purposes of comparison [2].

Load–deflection curves obtained in Instron tests were approximately linear up to fracture. Therefore, a strain at fracture was calculated as S/E, for the surface under tension.

More limited experiments were made using two other powders (Aldrich, Milwaukee, Wis.): PMMA ($M_v = 12\,000$) and polystyrene (number average molar mass, $M_n = 84\,000$; $M_w/M_n = 3.8$).

3. Results

Values of flexural strength are plotted against wt % PMMA in Fig. 1, where an interval scale is used in order to include all the results and yet to emphasize those with up to 5% PMMA. The first point which should be made in connection with these results concerns the appearance of the specimens. With exceptions at two loadings of PMMA, specimens were transparent and appeared to be homogeneous. In contrast, specimens with 5% PMMA were completely white and opaque. With 2% PMMA, specimens were transparent in some parts and opaque in others. With 1% PMMA, specimens were usually transparent but occasionally a small amount of opacity was seen in the form of whitish cloudy streaks. Presumably the whiteness is due to phase separation and therefore the low values of flexural strength obtained with 2 and 5% PMMA are disregarded, in the first analysis, as being due to an obvious complicating factor. The interpretation of the results, then, is that as little as 1% PMMA considerably increases flexural strength and thereafter, in the absence of complications caused by phase separation, produces relatively small changes for higher concentrations up to 50%. In any event, the important finding is that 1% PMMA causes a marked increase in strength. The reality of this effect was decided on the grounds that an increase was reproduced in experiments on a fairly large number of separately prepared sheets. A more objective statement can be made

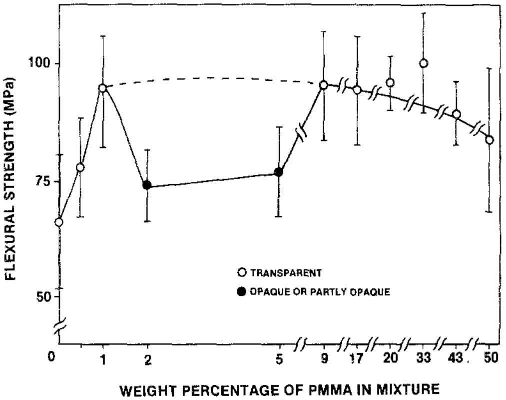

Figure 1 Interval dependence of flexural strength on the amount of PMMA in the network.

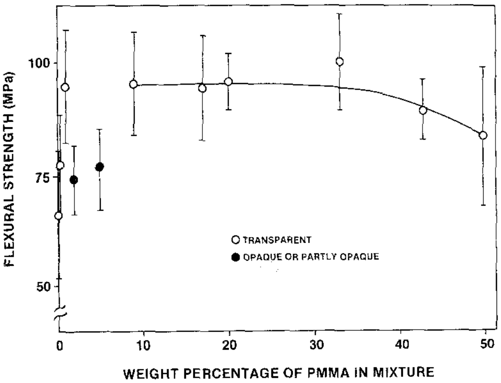

Figure 2 Dependence of flexural strength on the feed of PMMA.

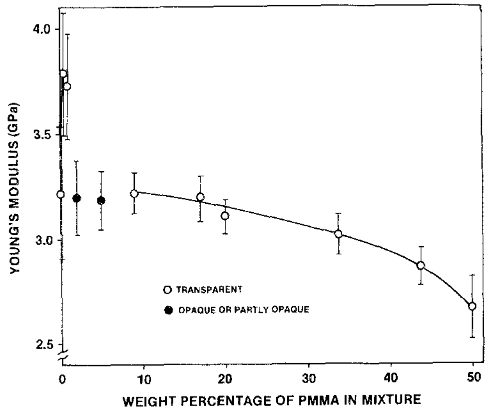

Figure 3 Dependence of Young's modulus on the feed of PMMA.

by comparing values obtained for 100 specimens (from 12 sheets) at 0% PMMA with 84 specimens (from 10 sheets) at 1% PMMA. By reference to Student's t-test, the probability that these two sets of values come from the same population is less than 1 in 1000. Therefore, it is concluded that a significant increase in flexural strength results from addition of 1% PMMA to EGDM.

For convenience of comparison with other results, values of flexural strength are shown replotted against percentage PMMA on a linear scale in Fig. 2. Young's modulus shows a pronounced peak effect with as little as 0.5% PMMA (Fig. 3). In this case the occurrence of phase separation seems to have little influence on values of E for amounts of PMMA $\geqslant 2\%$. Rather, except for the striking peaking phenomena, they seem to fit in a gradual decline in values up to the maxima studied of 50% PMMA. The strain at fracture gradually increases with increasing amounts of PMMA. However, opaque samples appear to be more brittle, in that results obtained with 2 and 5% PMMA fall below the curve for transparent samples (Fig. 4).

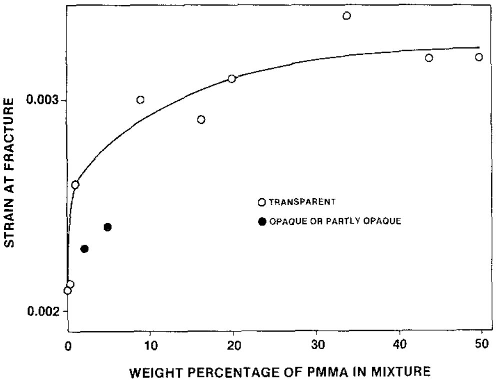

Figure 4 Dependence of strain at fracture on the feed of PMMA.

Addition of PMMA of low molecular weight was studied up to a maximum feed of 5%. The specimens were all transparent and there was no increase either in flexural strength or in Young's modulus. In the same feed range, addition of polystyrene gave white opaque specimens. Values of both flexural strength and Young's modulus were decreased, relative to PEGDM alone (results not shown).

In order to obtain information about the mode of fracture, surfaces were examined by scanning electron microscopy (SEM). In opaque specimens distinctive microstructures were observed. Addition of polystyrene resulted in discrete particles which have poor cohesion which adversely affected both strength and Young's modulus (Fig. 5a). Indications of a particulate microstructure were also found in specimens with 5% PMMA but in this case there was much more extensive coalescence of the particles (Fig. 5b). The boundaries between particles sometimes include dark features which might be voids although it is impossible to be certain about this point, in view of the roughness of fracture surfaces. In an attempt to get further information, specimens were given a fine polish and examined under an optical microscope. No evidence of the presence of voids was obtained using the maximum readily available magnification of x 1260.

In the SEM work, because of the remarkable effects on mechanical properties, most attention was given to the characterization of transparent specimens with 1% PMMA. This matter is sufficiently complex and important to be the subject of a separate report [3]. However, the main point coming from this work is that fractographic evidence shows that 1% PMMA serves to increase localized plastic deformation. An important source of evidence is that high magnification of mist regions reveals linear features with a morphology which could not arise by fracture of an ideally brittle material or, as a practical reference material, by fracture of a silicate glass. Instead it has been reasoned that the observed morphology provides evidence of fracture which, though predominantly brittle, is, nevertheless, greatly modified by localized plastic deformation. An example of the appearance of such linear features is given in Fig. 5d. In contrast, in brittle fracture the cross-section of such linear features would

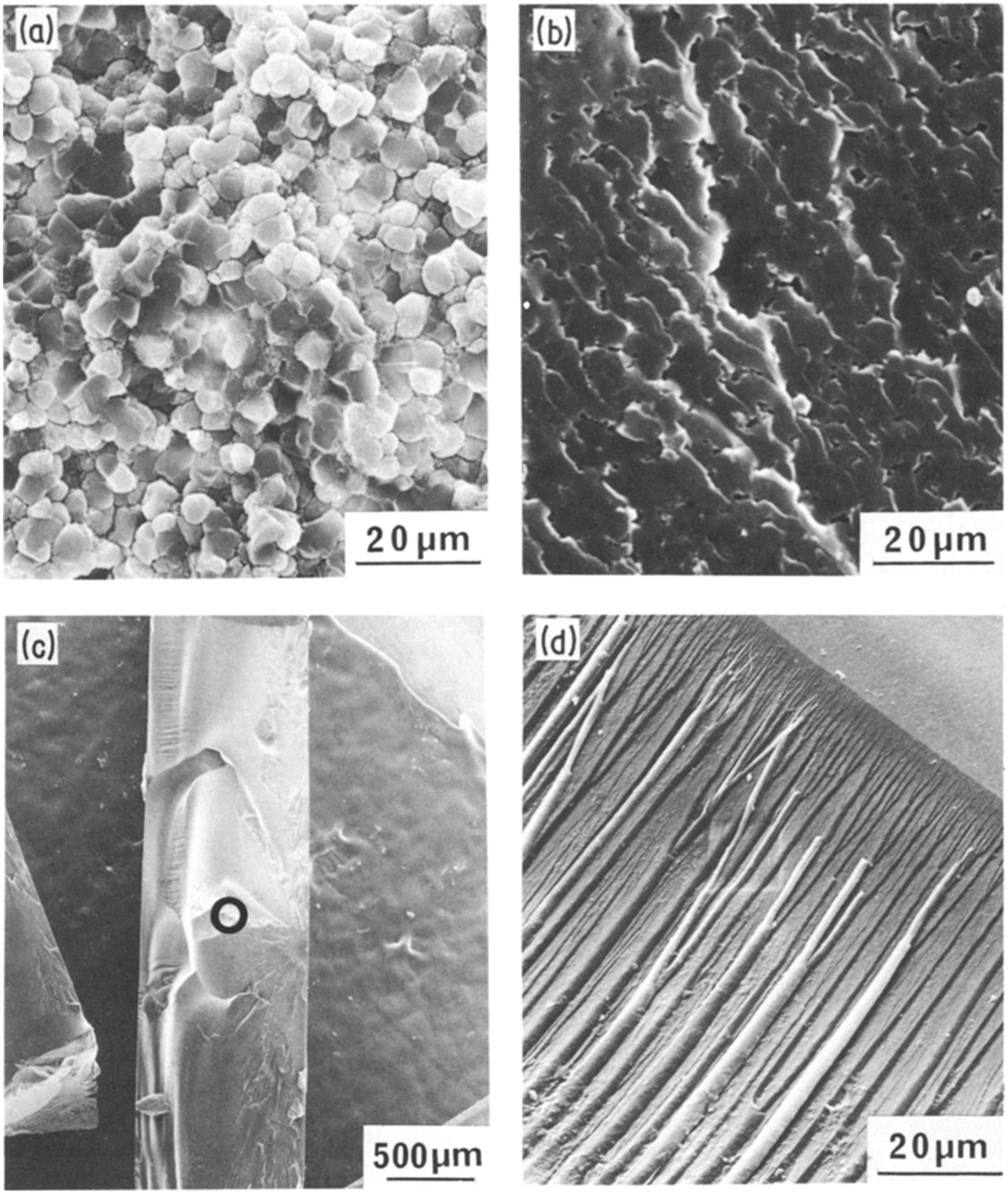

Figure 5 Morphology of fracture surfaces by scanning electron microscopy. Key: (a) 5% polystyrene; (b) 5% PMMA; (c) 1% PMMA; (d) a detail from (c).

not be circular but of a cross-section characteristic of extremely brittle materials such as silicate glass [4].

4. Discussion

Little is known about factors which govern the strength of highly crosslinked organic glassy networks [5]. In fact little progress has been made in this subject since the early studies of phenol–formaldehyde polymers [6]. Most pertinently, Houwink [7] and de Boer [8] were especially concerned about the large discrepancy between theoretically calculated and experimental values of tensile strength. Houwink attributed the much lower experimental values to flaws in the chemical regularity of the crosslinking and suggested how such "lockerstellen" might be formed. "Lockerstellen" may be regarded as intrinsic flaws, as distinct from extrinsic flaws which are introduced either adventitiously or deliberately by controlled crack initiation. In either case the weakness may be rationalized, in a first approach [9], by invoking Griffith's concepts about the role of flaws as stress concentrators in an ideal brittle material [10]. However, organic polymeric materials depart from ideal brittle behaviour because of their greater susceptibility to localized plastic deformation. In the case of linear polymers, such as PMMA and polystyrene, it is known that this can result in an increase in strength because of stress relaxation near the crack tip, through crazing [11]. Crazing does not occur in highly crosslinked networks but nevertheless modes of localized plastic deformation have been detected by fractographic studies of materials made by polymerization of EGDM. It has been argued that it is the occurrence of such localized plastic deformation that accounts for the formation of moderately strong materials [12, 13]. Now this argument will be extended in an attempt to explain the role of PMMA in increasing the strength of PEGDM networks.

The general explanation offered for the role of PMMA is that, somehow, it serves to limit crack initiation by increasing localized plastic deformation in regions of high stress concentration. Any further detailed explanation should take account of the following observations. First, that as little as 1% PMMA increases strength. Second, that 1% PMMA also increases Young's modulus. Third, that PMMA of low molecular weight is ineffective. Fourth, that the efficacy with 1% PMMA can be obtained without sufficient phase separation to cause turbidity. Nevertheless, segregation might play a role as has been envisaged previously for other possibly related systems. For example, de Gennes wrote "Segregation effects in mixtures of two polymers are sometimes welcome, e.g. for the preparation of *composite materials* with special resistance of fracture ––– but they are often unwelcome because resulting structures scatter light and result in a loss of transparency [14]."

In addition to taking account of the above observations, any explanation should also be consistent with the little that is known about the structure of highly crosslinked networks. In this respect, it is known that the preparation of such materials is usually accompanied by the formation of a particulate microstructure [15, 16]. This was first recognized in the case of phenol–formaldehyde polymers which were said to have a "porridge" structure [15]. From a consideration of the chemical mechanism of polymerization it is believed that such particles are highly crosslinked (microgels), which is in contrast to the much lower levels of crosslinking between particles. Actually, particles have not been detected in PEGDM by SEM [12]. However, transient particles have been detected in the course of polymerization by spectroturbidimetric analysis [17]. Colloidal particles are formed at the beginning of the polymerization reaction but eventually disappear, presumably because of coalescence. When polymerization is carried out with PMMA dissolved in EGDM, it is possible that the linear polymer is rejected to the surface of colloidal particles of microgel. As a consequence, the PMMA is segregated into just those loci, between particles, which are the main sites of potential flaws. Presumably this potential would be diminished by the presence of long linear macromolecules which could bridge flaws via entangled regions. In order to account for the observed increase in Young's modulus (Fig. 3), it is supposed that small amounts of PMMA are able to bear a part of an imposed stress, in addition to that borne by the crosslinked network.

The above suggestions are made partly by analogy with the relationship between structure and strength for bulk PMMA. Only above a critical molecular weight ($M_n = 10\,000$ to $20\,000$) does the strength increase markedly due to formation of an entangled network [18–20]. This sort of sensitivity to molecular weight is consistent with the inefficiency, in crosslinked PEGD, of a PMMA additive of low molecular weight, i.e. $M_n \sim 7000$. A more detailed study of molecular weight dependence would indicate the extent to which this analogy is valid.

Segregation of PMMA around particles of microgel is also consistent with the observation that evidence of plastic deformation is often accompanied by the appearance of a particulate microstructure. In Fig. 5d the presence of linear features provides evidence of localized plastic deformation, for reasons already mentioned. Towards the bottom left hand corner of the picture, rather gross (about 1 μm) particles can just be discerned. The correlation between these two types of morphological features has been documented more fully elsewhere [3].

4. Conclusions

1. Inclusion of 1 wt% PMMA in networks made by polymerization of ethylene glycol dimethacrylate raised flexural strength by 40% (to 95 MPa) and Young's modulus by 20%.

2. One factor contributing to the increase in strength was an increase in localized plastic deformation during fracture. The latter effect was deduced from fractography.

3. Phase separation was observed for PMMA inclusions of 2 and 5%. Both lower and higher inclusions gave transparent specimens.

Acknowledgements

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