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An application of monomer coating for glass-cloth-reinforced acrylic resin

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This work was designed to study the application of monomer-coated glass cloths to denture base heat-curing acrylic resin, and the improvement of the bending properties and impact energy in the reinforced resins was attempted by including glass cloth with a twill weave treated by multifunctional monomers. The results, that true adhesion between fibre and resin matrix occurs, support the increases in mechanical properties when treated with the heat-cured monomer. A remarkable increase in impact energy rather than maximum strength as a bending strength was achieved in the reinforced specimen including the twill-woven glass cloth treated due to the multifunctional monomers, and the energy value in the multi-functional-treated specimen was almost twice that in the plain acrylic resin.

1. Introduction

Dentures in the dental field are frequently fractured owing to the weak fracture resistance when acrylic base resin is applied to them without a reinforcing material, because acrylic resin has a relatively poor resistance to impact, bending and fatigue [1–7]. Therefore, the following were attempted: (1) a mesh of gold wire or a stainless steel bar was applied within the acrylic resin [1]; (2) a stronger material than acrylic resin was developed, which was called a "high-impact" acrylic [2, 3, 5]; and (3) composite materials which included fibres with very high modulus (carbon, aramid and polyethylene fibres) within a resin matrix [4–8] were used. The two samples of these fibres used most were carbon fibres and organic aramid fibre, and it is thought that the fibres have the effect of resisting the applied load [5–8].

Recently the application of glass fibres and cloths to dental acrylic resin has been attempted, and the results indicate that an increase in bending strength and impact energy greater than those of acrylic resin are achieved, as reported in [9–11]. Their fibres were mainly coated by a silane coupling treatment. This reinforcement due to fibres presented some problems concerning the adhesivity of the interface between fibre and resin matrix [11]. The present study was to investigate the effect of some resin monomers for the treatment of glass cloths on the bending properties and impact energy in reinforced polymethylmethacrylate which included treated-glass cloths. We also clarified the factors which affect their properties in the reinforced resin materials.

2. Materials and methods

A commercial denture acrylic resin was selected as a control specimen (Cont, heat-curing resin; Natural resin, Nissin Co., Osaka, Japan). The resin was reinforced with seven types of glass cloths which showed the effective effect on the bending properties as reported in [11] (glass cloths: Nittobo Co., Tokyo, Japan). The specimen denoted as W1 included glass cloth WLB with a twill weave, but the other specimens (W2 to W7) included glass cloths having a plain weave [11]. The cloths with two kinds of weaves, however, had a chemical composition of non-alkali CaO–Al_2O_3–SiO_2 system with $< 8\%$ as an alkali. All glass cloths were coated by a silane coupling treatment which has often been done for filler in the composite resin [9, 12, 13]. The specimens were divided into two groups. One group was immersed in a heat-curing resin monomer for 12 h at room temperature, and the other group, which was not treated, was used for a comparison of the adhesivity at the interface between the fibre and the resin matrix. The monomer treatment was then done in the packing (Fujimaru Pakman, Fujimaru Co., Tokyo, Japan). The volume ratio (V^*/V) in the specimen was different for different glass cloths: W1, 110.0×10^{-3}; W2, 56.0×10^{-3}; W3, 30.0×10^{-3}; W4, 14.0×10^{-3}; W5, 5.0×10^{-3}; W6, 4.0×10^{-3} and W7, 3.0×10^{-3}. Each glass cloth was set in a heat-curing acrylic base resin such as Natural resin. In the case of reinforced material with the maximum strength as a bending strength, the multi-functional monomers were used as a coating agent instead of the heat-curing resin monomer. They were tried with the combination of Bis-GMA, (2,2-bis[4-(3-methacryloxy-2-hydroxy propoxy)phenyl]propane TEGDMA (triethylene glycol dimethacrylate) and TMPT (trimethylol propane trimethacrylate) as the monomers investigated when coated to the glass cloth

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TABLE I Bending properties of reinforced specimens W1, W2, W3, W4, W5, W6 and W7 containing seven types of glass cloths

Code	Glass cloth	Maximum strength ($kg\,cm^{-2}$)	Proportional limit ($kg\,cm^{-2}$)	Bending elasticity ($kg\,mm^{-2}$)
W1	WLB	1320.6 ± 143.4	866.0 ± 116.6	342.7 ± 17.9
W2	WEB	917.5 ± 21.0	731.6 ± 10.2	328.2 ± 11.6
W3	WLC	1075.2 ± 21.1	707.8 ± 30.0	304.9 ± 4.4
W4	WEA	1063.0 ± 29.6	786.2 ± 17.6	286.1 ± 9.9
W5	WLA	1065.6 ± 55.4	738.1 ± 25.6	296.5 ± 16.3
W6	WKB	1002.8 ± 62.9	652.0 ± 39.6	286.7 ± 9.4
W7	WF	1068.0 ± 24.0	728.0 ± 5.7	304.7 ± 9.0

identified as WLB according to our study on the base, and diluent monomers of Bis-GMA-based resins in [14]. The liquid/powder (L/P) ratio ranged from 1.0 to 4.0, and the immersion of glass cloth into the monomers was done within a shielded pack, which was used for the packing of meat, similarly to the treatment due to heat-curing monomer. The specimen was made using one piece of glass cloth (9.5 mm × 55 mm) by setting glass cloth along the longitudinal direction within its centre. Ten grams powder polymer and 4 ml resin monomer were then mixed at heat-curing. The methods for the preparation of bending and Charpy impact tests were similar to those reported in [9–11].

The fractured surfaces after the bending test were examined by scanning electron microscopy (Hitachi H-430, Tokyo, Japan), and two planes were cut perpendicular to the direction of the interface between the fibre and the resin matrix, as reported in [11]. That is, the adhesivity at the interface in both planes of near the fracture surface (3 mm from the fracture surface) and near the edge of the specimen (10 mm from the edge) were evaluated: + is used to denote no porosity or void found, − to denote a separated interface at both planes and ± that a separated interface was found at either side of both planes.

3. Results

In the bending test of the reinforced materials (W1 to W7) the load increased with increasing deformation and then reached a maximum. The bending strength was defined as the maximum strength at a maximum loading, and the proportional limit as the strength to which a proportional increase continues (Table I). The value of the bending elasticity was calculated according to the conventional method [15, 16]. The bending properties in the reinforced materials including monomer-treated glass cloths are shown in Fig. 1. Their values are given for the ratio (V^*/V) of volume of glass cloth (V^*) to a volume of bending specimen (V), as shown in Fig. 2 (proportional limit), Fig. 3 (maximum strength) and Fig. 4 (bending elasticity). Each full curve was expressed by each second-order equation, using the average values for the data. In Figs 5 and 6 the observations near the fracture surface are shown for typical samples of reinforced specimens W7 and W1, respectively. The treatment due to heat-curing resin monomer improved the interface between glass cloth and resin matrix, as indicated in Table II. As a typical sample the W7 specimen including untreated glass cloth was improved by the monomer treatment. As an additional study, the multifunctional monomers for the coating of glass, cloth WLB was used (Tables III and IV). In the heat-cured monomer the average values ranged approximately from 1120 to 1180 $kg\,cm^{-2}$ (maximum strength), and from 30 × 10^{-2} to 40 × 10^{-2} kg m (impact energy), showing that the effect of the L/P ratio on the values was not significant. On the contrary, the results indicate that

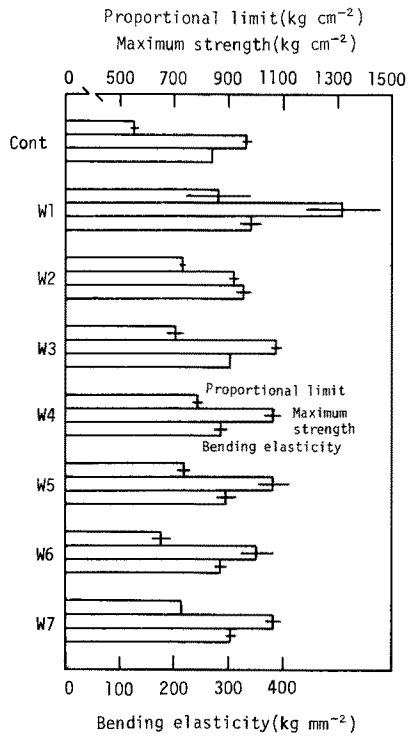

Figure 1 Bending properties (proportional limit, maximum strength and bending elasticity) in heat-curing plain acrylic resin (Cont) and glass-cloth-reinforced materials (For key, see Table I.)

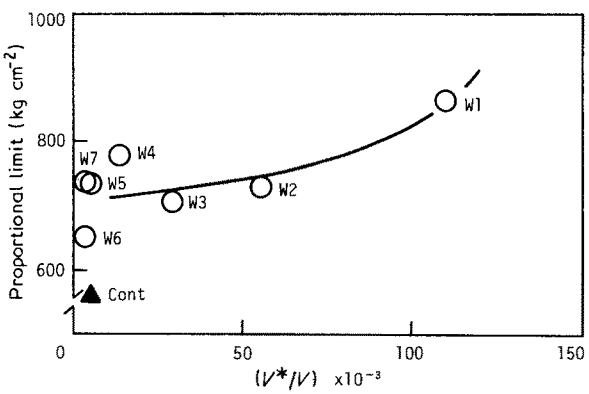

Figure 2 Change of proportional limit with volume ratio (V^*/V) in the reinforced resins tested. (The full curve was given by a second-order equation.)

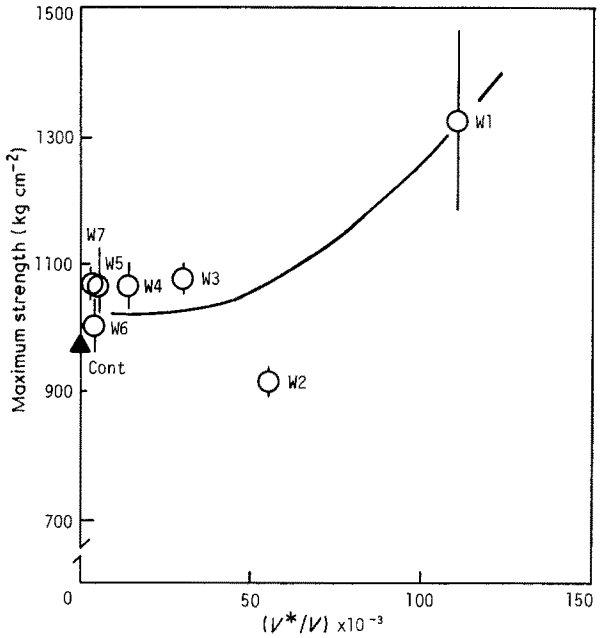

Figure 3 Maximum strength change due to the V^*/V volume ratios in the reinforced specimens.

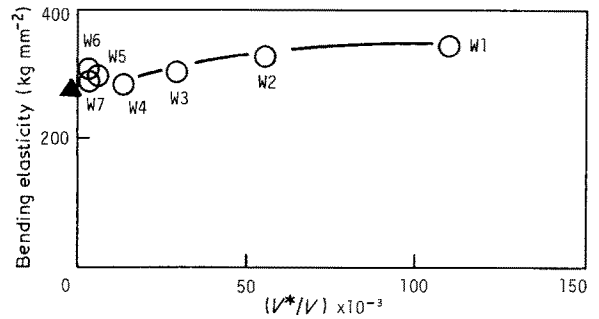

Figure 4 Bending elasticity at different V^*/V volume ratios in the reinforced specimens.

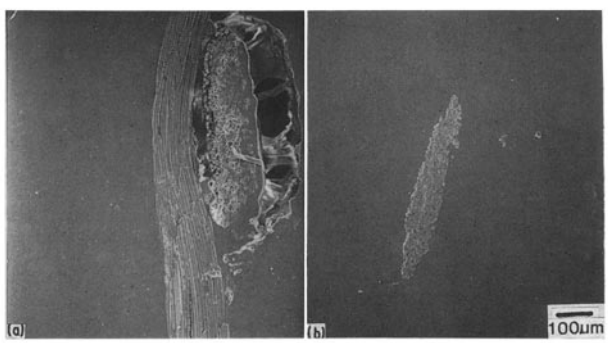

Figure 5 Observation near the fracture surface in (a) untreated and (b) treated W7 specimens.

the impact energy in multifunctional monomer (BR2 to BR5)-treated-glass-cloth-reinforced resin increases more than that in the reinforced material coated by the heat-curing monomer denoted as BR1 in Table IV, and also confirm that the fibres in glass cloth treated with the monomers tends to fit to the resin base.

4. Discussion

The treatment of glass fibres due to resin monomer demonstrates a reproducible improvement in bending

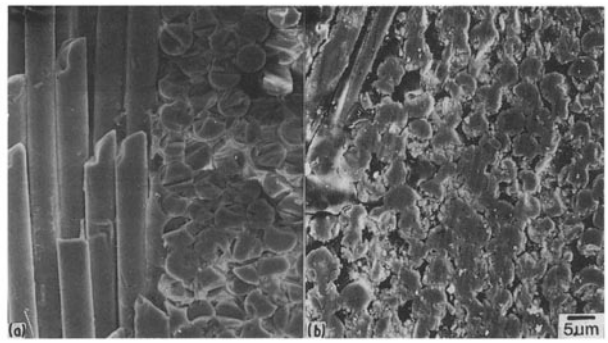

Figure 6 Observation near the fracture surface in (a) untreated and (b) treated W1 specimens.

TABLE II Adhesivity in reinforced materials including untreated or treated cloths with heat-curing monomer, evaluated by +, ± and − on the basis of scanning electron microscopy (for key, see text)

Code	Adhesivity	
	Untreated	Treated
W1	+	+
W2	+	+
W3	−	±
W4	+	+
W5	+	+
W6	+	+
W7	±	+

TABLE III Values of maximum strength and impact energy in W1 specimens which were treated with heat-cured monomer at various L/P ratios

L/P ratio at treatment	Maximum strength (kg cm^{-2})	Impact energy (kg m)
1.0	1180.8 ± 1.2	39.0×10^{-2}
1.3	1092.0 ± 24.0	33.0×10^{-2}
2.0	1165.8 ± 19.8	42.0×10^{-2}
4.0	1122.0 ± 78.0	36.0×10^{-2}

TABLE IV Impact energy in W1 specimens at five different treatments with heat-cured and multifunctional monomers

Treatment	Impact energy (kg m)
BR1	27.0×10^{-2}
BR2	33.0×10^{-2}
BR3	30.0×10^{-2}
BR4	36.0×10^{-2}
BR5	39.0×10^{-2}

BR1, heat-cured monomer; BR2, BPO (0.1 wt %) for the Bis-GMA (50 wt %) · TEGDMA (50 wt %); BR3, heat-curing monomer (50) · TEGDMA (50); BR4, Bis-GMA (50) · TMPT (50); BR5, Bis-GMA (50) · TEGDMA (50).

strength of each reinforced material including one piece of glass cloth (Figs 1 to 4). The Cont plain specimen had average values which were 968.3 kg cm^{-2} (maximum strength as a bending strength) and 21.0×10^{-2} kg m (impact energy), as reported in [9, 11]. It is suggested that the specimen W1 including twill-woven glass cloths provides a beneficial effect on the bending strength and impact

energy in the fibre-reinforced specimen. The results thus support the application multifunctional monomer to glass cloth in specimen W1 (Tables III and IV). From the results in Figs 5 and 6 and Table II, the glass fibres are wetted by the monomer during the preparation of the specimen, indicating that good adhesivity occurs at the interface between the glass fibres and the resin matrix. The largest one in volume fraction of the glass cloths tested produced an increase in bending properties compared with those of a Cont specimen or the other specimens.

In using carbon fibre in acrylic denture resin, the fibre was laid down parallel to the surface of the denture base [17]. The arrangement gave the optimized reinforcement of acrylic resin. The same arrangement in the present study on the glass cloth was used, setting the glass cloth at its centre parallel to the specimen surface. Technical difficulties of ensuring that the glass cloth was aligned were seldom found, because it became practical to make it and its cloth had a constant dimension. It is deduced that a technical error in curing the specimen would not occur. Therefore, the following points were obtained for the reinforcement of the acrylic resin: (1) the alignment of the glass cloth was longitudinally parallel to the surface of the denture base at the centre of the specimen, (2) the specimen W1 including WLB as a glass cloth coated by heat-curing monomer had the largest values of bending properties and (3) by means of the use of multifunctional monomers the impact energy became higher than those in the reinforced materials including glass cloth coated with heat-curing monomer. The value in multifunctional monomer-treated-fibre materials was 1.1 to 1.5 times that of heat-curing monomer-treated material, and the former showed a value almost twice that of a Cont plain specimen. It is presumed that the glass cloth makes widespread application to denture base acrylic resin more acceptable. In the clinical situation the use would prove to be an advantage because of the easy packing procedure, but it is important to check whether the glass cloth exists within the denture base. The inorganic reinforcing material of glass cloth WLB with a twill weave was thus beneficial to the denture base, but the heat-curing resin as an acrylic base resin had the disadvantage of the resin itself that the curing occurs by means of heat [18]. The thermal expansion effect due to the raising of the temperature during heat curing might not appear when the monomer was used to coat the glass fibres, because the interface between the fibre and the resin was without void or porosity (Table II). A simpler method of curing the base resin would be necessary to apply it to dentures in the dental field. Base resins with visible-light curing and microwave curing systems could be useful [19–21]. Therefore, a further study is needed to investigate the effects of the kinds of reinforcing materials as reinforcement and base resins as matrix on the strength of denture base resin.

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