Ketones in resin composites

Effect of ketone content and monomer composition on selected mechanical properties

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To optimize the improvements by diketones of the mechanical properties of resin composites, diacetyl was added to two different monomer mixtures in different quantities. There was a positive correlation between content of diacetyl and tensile strength, flexural strength, and modulus of elasticity, respectively, of both the BISGMA/TEGDMA- and the UEDMA/HEMA-based materials. Addition of diacetyl did not influence the modulus of resilience significantly. Addition of diacetyl resulted in increases in mechanical properties which were of the same relative size for BISGMA/TEGDMA-based materials as for UEDMA/HEMA-based materials. However, because of higher control values, except for modulus of elasticity, the properties of UEDMA/HEMA-based composites were superior to those of the BIGSMA/TEGDMA-based materials. A content of approximately 24 mole% diacetyl seemed to have optimum effect on mechanical properties, giving a mean increase of 25% in tensile strength, flexural strength, and modulus of elasticity. □ *Dental materials; diketones; mechanical properties; resin composites*

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In an attempt to improve the mechanical properties and wear resistance of dental resin composites, a previous study suggested the use of bifunctional ketones as cross-linking reagents to increase the degree of cross-linking (1). One cross-linking mechanism proposed was that of a diketone reacting with two remaining double bonds (Fig. 1). However, most monomers possess pendant or backbone functional groups in addition to the methacrylate double bonds. Cross-linking reagents may therefore also be used to link a functional group from one polymer chain with a functional group from a second chain. Figs. 2 and 3 show two hypothetical cross-linking reactions involving functional groups present in common dental monomers. In Fig. 2 a diketone is thought to effect a link between two amide groups present in a urethane dimethacrylate (UEDMA). The reaction propounded is based on a conjectural extension of the reaction of an aldehyde with an amide as described by March (2). Monomers such as bisphenol-A-glycidyl dimethacrylate (BISGMA) and 2-hydroxyethyl methacrylate (HEMA) contain hydroxyl groups. Through formation of two hemiketals (2), reaction with a diketone may perhaps result in the cross-linking of two polymer chains, as shown in Fig. 3.

In the study by Peutzfeldt & Asmussen (1), four bifunctional ketones were tested, and three were found to improve significantly at least one of four mechanical properties of the experimental resin composites. By a further increase in the content of the most promising ketone (diacetyl) in resin composites based on UEDMA and HEMA, the four mechanical properties measured increased between 11% and 50%.

It was the purpose of the present study to optimize the effect of diketones on mechanical properties in two different monomer mixtures.

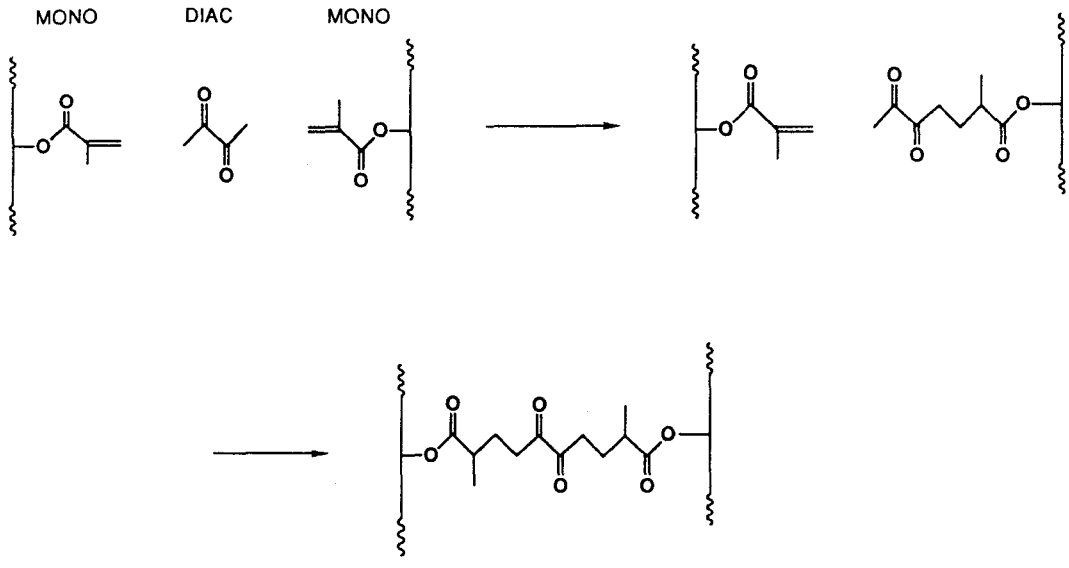


Fig. 1. Diacetyl (DIAC) reacts with two methacrylate groups. The two monomer chains are cross-linked by ester formation. MONO = monomer.

Materials and methods

The experimental resin composites were prepared from the compounds listed in Table 1, and their compositions (in mole%) are given in Table 2. To make the materials light-curing, 0.2% w/w of camphorquinone (CQ) and 0.2% w/w of *N,N*-cyanoethyl-methyl-aniline (CEMA) were dissolved in each of the monomer mixtures. After possible addition of diketone, the resins were loaded with silanized glass filler to a content of 78% w/w.

The resin composites were tested with regard to 1) diametral tensile strength (T), 2) flexural strength (S), 3) modulus of elasticity (E), and 4) modulus of resilience (R). Unpolymerized material was applied in the respective molds, covered on both sides with a clear matrix strip, and irradiated with a Visilux 2 unit (3M Company, St. Paul, Minn., USA) for 40 sec on each side. The specimens were then placed in water at 37 °C for 1 week before testing.

Diametral tensile strength

The unpolymerized material was applied in a cylindrical brass mold (height = 3.0 mm, diameter = 6.0 mm). The specimens were light-cured and stored as described. After water storage, the specimens were ground on wet silicon carbide (grit no. 1000). The length (l) and diameter (d) of the specimens were recorded, and the specimens fractured in diametral position by means of a Universal Testing Machine (Instron Ltd, High Wycombe, England) operating at a crosshead speed of 10 mm/min. The diametral tensile strength T was calculated as $T = 2F/(\pi \cdot d \cdot l)$, where F is the force at fracture.

Flexural strength

The unpolymerized material was applied in a rectangular brass mold (length = 10 mm, height = 2.0 mm, and width = 2.0 mm). The specimens were polymerized, stored, and ground on all four sides. The height (a) and the width (b) of the specimens were measured, and the specimens subjected to three-point loading at a crosshead speed of 1 mm/min with 6 mm (c) between the supports. The flexural strength S was computed as $S = (3 \cdot c \cdot F)/(2 \cdot b \cdot a^2)$, where F is the force at fracture.

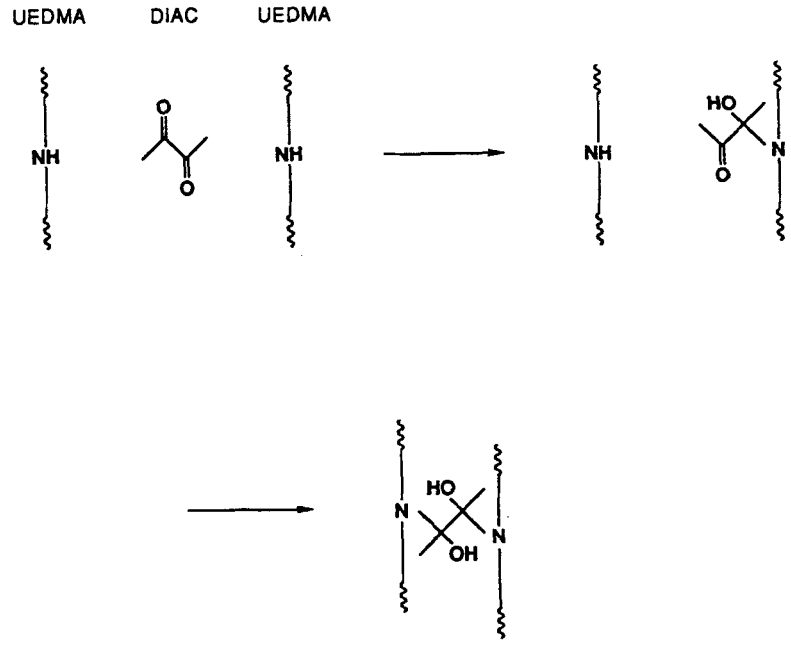


Fig. 2. Diacetyl (DIAC) reacts with the amide groups of two urethane dimethacrylate (UEDMA) chains. The two monomer chains are cróss-linked by amino-alcohol formation.

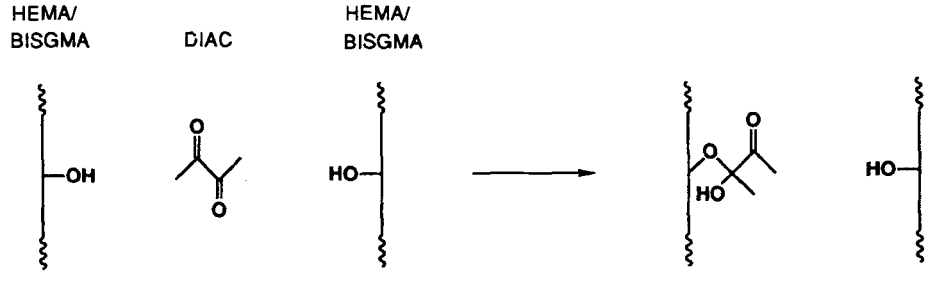


Fig. 3. Diacetyl (DIAC) reacts with two hydroxyl groups, pendant in 2-hydroxyethyl methacrylate (HEMA) and/or bisphenol-A-glycidyl dimethacrylate (BISGMA). The two monomer chains are cross-linked by formation of two hemiketals.

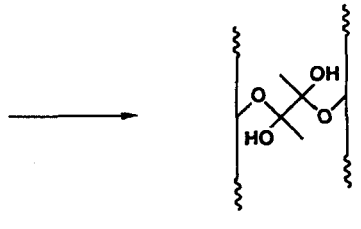
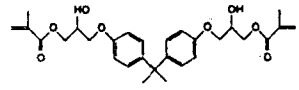
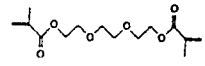
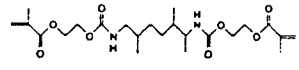
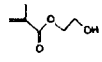


Table 1. Materials used for preparation of resin composites

Compound	Initials	Structure	Supplier
Bisphenol-A-glycidyl dimethacrylate	BISGMA		Röhm GmbH Chem. Fabrik, Darmstadt, Germany
Triethyleneglycol dimethacrylate	TEGDMA		Aldrich-Chemie, Steinheim, Germany
Urethane dimethacrylate*	UEDMA		Ivoclar AG, Schaan, Liechtenstein
2-Hydroxyethyl methacrylate	HEMA		Merck-Schuchardt, Munich, Germany
Camphorquinone	CQ		EGA-Chemie, Albuch, Germany
N,N-cyanoethyl-methylaniline	CEMA		Ivoclar AG
Diacetyl	DIAC		Merck-Schuchardt
Silanized filler	GM 31685		Schott-Schleiffer AG, Feldbach, Switzerland

* Ruyter (8).

Modulus of elasticity

The flexural strength specimens were also used for determination of the elastic moduli. With use of a chart paper speed of 500 mm/min when measuring flexural strength, the relationship between applied force and movement of the crosshead was found to be approximately linear. By hand, straight lines were fitted to the curves on the chart paper, and the slopes of these lines calculated. However, for determination of the relationship between force and deflection of the specimens, the deformation taking place within the measuring cell must be accounted for. Therefore, calibration curves were produced by use of rods of electrolytically pure copper, having a modulus of elasticity of 129.8 GPa (3), as described in detail by Asmussen & Peutzfeldt (4). Modulus of elasticity E was calculated as $E = (\alpha \cdot c^3)/(4 \cdot b \cdot a^3)$, in which α is the slope of the straight line relationship between force and deflection of the specimen, c is the distance between the two supports (6 mm), and a and b are as defined above.

Modulus of resilience

For each specimen the modulus of resilience was calculated as $R = S^2/2E$.

The measurement of T and S were done on eight specimens of each resin composite. The statistical treatment of the results involved one-way analyses of variance (5), Newman-Keuls' multiple range tests (6), and regression analyses (5) with $P = 0.05$ as the level of significance.

Results

The mean values of T, S, E, and R are presented in Table 2. The standard deviations of the four properties were pooled to give $s_T = 2.3$ MPa, $s_S = 10.9$ MPa, $s_E = 0.78$ GPa, and $s_R = 0.21$ MJ/m^3.

K1–K6 measured the effect of diacetyl on BISGMA/triethyleneglycol dimethacrylate (TEGDMA)-based resin composites. The six mean values of T, S, and E varied with statistical significance, which the mean values of R did not. From the results of the

Table 2. Composites K1–K12: composition and mean values of diametral tensile strength (T), flexural strength (S), modulus of elasticity (E), and modulus of resilience (R). Values with same lettering within each group of comparison (K1–K6 and K7–K12) were not significantly different

	Composition (mole%)					Results			
Code	BISGMA	TEGDMA	HEMA	UEDMA	DIAC	T (MPa)	S (MPa)	E (GPa)	R (MJ/m^3)
K1	25	75				52^a	126^a	7.0^a	1.2^a
K2	23	69			8	56^b	142^b	9.2^b	1.1^a
K3	21	63			16	56^b	149^b	9.6^b	1.1^a
K4	19	57			24	*58^b	*153^b	*10.3^b	1.1^a
K5	17	51			32	57^b	155^b	9.9^b	1.2^a
K6	15	45			40	57^b	153^b	10.0^b	1.2^a
K7			25	75		57^a	175^a	6.9^a	2.3^a
K8			23	69	8	64^b	183^{ab}	8.0^b	2.1^a
K9			21	63	16	65^{bc}	186^{ab}	8.9^c	2.1^a
K10			19	57	24	*68^c	192^b	9.5^c	2.0^a
K11			17	51	32	66^{bc}	*193^b	*9.5^c	2.0^a
K12			15	45	40	67^{bc}	187^{ab}	8.7^{bc}	2.0^a

* The composition with optimal effect of diacetyl.

additional statistical analyses shown in Table 2, it can be seen that K1 had lower T, S, and E than the other five composites.

The second group of comparison (K7–K12) investigated the effect of diacetyl on UEDMA/HEMA-based resin composites. Except for R, the six mean values of each mechanical property varied with statistical significance. Further, K7 had lower T than the other five materials, and K8 had lower T than K10. S was lower for K7 than for K10 and K11. As to E, K7 gave a lower value than all the other composites, while K8 gave a lower value than K9–K11.

For both monomer mixtures, linear regression analyses showed positive correlations of statistical significance between content of diacetyl and T, S, and E, respectively.

Discussion

With the exception of modulus of elasticity, the control values of the mechanical properties were higher for the resin composites based on UEDMA/HEMA than for the BISGMA/TEGDMA-based materials. T, S, and R of the composites based on UEDMA/HEMA were also all superior to those of the corresponding BISGMA/TEGDMA-based resin composites.

Despite the statistically significant linear correlations found between the content of diacetyl and T, S, and E, respectively, the beneficial influence of diacetyl seemed to lessen at high diacetyl contents. Presumably, the addition of diacetyl to resin composites could have two opposing effects on the mechanical properties dependent on the content. At lower contents a positive cross-linking effect would dominate, whereas at higher contents a negative plastifying effect would prevail. In an attempt to estimate at what content the negative effect manifested itself, regression analyses were carried out, starting with all six resin composites of each series and then eliminating one composite at a time, beginning with the resin of the highest diacetyl content. Table 2 shows which of the regression analyses gave the highest coefficients of correlation—that is, at what content the cross-linking effect was optimal.

With regard to the BISGMA/TEGDMA-based resin composites, a content of 24 mole% DIAC had optimum effect on T and S and also on E. With regard to UEDMA/HEMA-based materials, a con-

tent of 24 mole% DIAC was most favourable with regard to T, whereas 32 mole% DIAC had optimum effect on S and E. Considering all three properties, the ideal content supposedly lies between 24 and 32 mole%. In all series, the softening effect of DIAC seemed to have taken over in composites containing 40 mole% DIAC.

The possible reaction mechanisms outlined in the introduction normally require a base (Figs. 1–3) or an acid (Figs. 2 and 3) as catalyst to take place with appreciable rate. The investigated monomers are not basic or acidic, but the photoreductant CEMA is a base. Although not a strong base, it might act as a catalyst in the reactions in Figs. 1–3. It may be argued that these reactions should also take place in the uncured resin composite, leading to an increase in viscosity of the paste. This was not observed. However, it may be speculated that the catalytic effect of the CEMA is more pronounced in an aqueous environment. Therefore, the catalytic effect does not occur in the non-aqueous monomer systems but may be present in a resin composite imbued with water.

The fact that addition of diacetyl did increase three of four mechanical properties would seem to indicate a cross-linking ability of diketones. The improvements were found both in BISGMA/TEGDMA- and in UEDMA/HEMA-based resin composites. Thus, the present results did not allow the exclusion of any of the proposed cross-linking reactions. To decide whether the enhancements in mechanical properties reflected an increased conversion of double bonds (Fig. 1), a cross-linking of functional groups (Figs. 2 and 3), or even other reactions, analyses of the cross-linking mechanisms are required.

An investigation conducted by the present authors confirmed the potential of monofunctional aldehydes to improve the mechanical properties of dental resin composites (7). The improvements found after addition of propanal were generally of the same magnitude as the increases measured in the present study. Yet, for BISGMA/TEGDMA-based resin composites, addition of propanal resulted in slightly higher maximum values of flexural strength and modulus of resilience but at the same time in lower elastic moduli.

In conclusion, the results of the present study corroborated the potential of diketones to serve as cross-linking agents. Expressed in percentages, the effects of adding diacetyl on BISGMA/TEDGMA-based resin composites were approximately of the same size as the effects on UEDMA/HEMA-based composites. A content of diacetyl of about 24 mole% had optimum cross-linking effect, giving a mean increase of 25% in tensile strength, flexural strength, and modulus of elasticity.

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