Remaining methacrylate groups in composite restorative materials

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The quantity of the remaining unreacted methacrylate groups in polymerized composite materials has been determined. Six proprietary composites were investigated by infrared multiple internal reflection spectroscopy. Infrared reflectance measurements were made before polymerization and repeated after the composites were subjected to polymerization at 37 °C for 24 hours. The quantities of remaining unreacted methacrylate groups were determined and the data expressed as percentages of the total amount of methacrylate groups in the unpolymerized materials. The specimens were specially prepared to ensure that the surface properties simulated the bulk properties of the polymerized composites. The quantities of remaining methacrylate groups in the six composites determined by this surface measuring technique ranged from 25 to 48 %. The results demonstrate that commercially available composite materials exhibit different degrees of conversion 24 hours after the start of polymerization. These differences can be correlated to the different monomer compositions of the composite restorative resins.

Key-words: Dental materials; infrared reflectance; MIR-spectroscopy; polymer chemistry; structure

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Commercially available dental composite resin materials vary in composition (2). Their properties may consequently be different. A review of data available from clinical and laboratory studies of dental composite resin materials (24) indicate that these materials are susceptible to wear and loss of "anatomic form" (6, 15, 16, 23, 25, 26). They also discolor and tend to shift in time toward yellow (7, 16, 17, 25, 32).

The typical pattern of attrition of occlusal composite resin restorations in posterior teeth after two years of service, shows a uniform loss of substance giving exposed enamel walls of the original cavity preparation. It has been postulated that the susceptibility to wear and loss of "anatomic form" results from loss of surface filler particles, followed by the attrition of the exposed polymer matrix (4, 5, 20). The mechanism for the attrition of the exposed polymer matrix could be postulated to be both mechanical wear and chemical degradation.

The discoloration of composite resin restorations can also be ascribed to chemical degradation and the presence of porosities. Apart from the molecular structure of the

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monomers, it is likely that the degree of conversion after polymerization will also affect the properties of the products. It is known that residual double bonds in polymeric materials make them less resistant to degradation reactions (8).

The monomer bisphenol A diglycidyl dimethacrylate (BIS–GMA) (Fig. 1) is not quite color stable (1). It tends to turn yellow. This tendency to yellowing may remain in the polymerized material, if all of the methacrylate groups of this monomer have not been converted. Polymerized proprietary dental sealants, which are similar to the matrix of the composites, contain different quantities of remaining unreacted methacrylate groups (28).

Investigations of multifunctional methacrylate polymerizations by means of dilatometric (18, 19) calorimetric (11) or thermometric (30) techniques have been conducted for some years. Comparison of the formation of homopolymers from multifunctional methacrylates have been made (13, 22, 30).

Transmission infrared spectroscopy has been used for determination of remaining unreacted methacrylate groups (18, 28); or residual monomer in methacrylate polymers (31).

The present study was designed to analyze quantitatively the remaining unreacted methacrylate groups in polymerized commercial restorative composite resin materials.

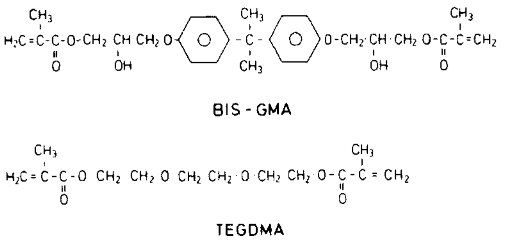

Fig. 1. Two monomers bisphenol A diglycidyl dimethacrylate (BIS-GMA) and triethyleneglycol dimethacrylate (TEGDMA), commonly used in composite resins.

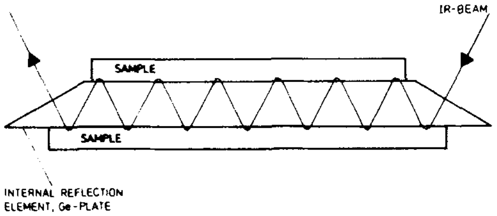

Fig. 2. Schematic representation of multiple internal reflection effect.

MATERIALS AND METHODS

The six dental composite resin materials used in this investigation are listed in Table 1. The six brands were available as two-paste systems consisting of inorganic fillers and an organic phase comprising mainly different methacrylate monomers. The chemically induced polymerization of these pastes gives a composite material with a noncrystalline organic phase.

Transmission infrared spectroscopy techniques cannot satisfactorily be adapted to composite materials, because of the inorganic fillers. The amounts of unreacted methacrylate groups can, however, be determined with another infrared spectroscopy technique, the so-called multiple internal reflection (MIR) spectroscopy (9). The principles of this technique are demonstrated in Fig. 2. The technique involves molecular absorption of infrared radiation during the process of reflections in specimen surface, and it may be used for quantitative measurements.

MIR-spectroscopy

The multiple internal reflectance technique is based on the total reflection of radiation

Table 1. *List of brands used in the investigation*

Name	Code	Batch no.	Manufacturer
Adaptic Dental Restorative®	AD	6C009	Johnson & Johnson, N.J., USA
Compact Composite Restorative®	CP	Univ.: 760217 Cat.: 760203	Svedia Dental Industri, Sweden
Concise Composite®	CC	6271S14	3M Company, Minn., USA
Epolite 100 Dental Restorative®	EP	JM 3	G-C Dental Industrial Corp., Japan
Prestige Dental Restorative®	PS	Univ.: HPR 0118 Cat.: MPR 0119	Lee Pharmaceuticals, Cal., USA
Protosit Composite®	PR	Univ.: 202–13 Cat.: 202–12	A. Kettenbach, W-Germany

at the boundary between media of different refractive indices provided the angle of incidence is larger than the critical angel (a function of refractive index). Internal reflection per se implies that all the energy is reflected. However, the beam appears to penetrate slightly beyond the reflecting surface before returning. When a material which selectively absorbs radiation is placed in contact with the reflecting surface, the beam will loose energy at the wavelengths where the material absorbs owing to an interaction with the penetrating beam. In order to obtain internal reflection spectra which are nearly identical to transmission spectra, a reflector with a relatively high refractive index should be used. A germanium crystal with the refractive index of 4,02 was employed in the present study.

Since internal reflection spectroscopy is essentially a surface measuring technique, the spectra reveal the absorption in the actual region representative of the top five microns of the specimens. For this reason special precautions were taken during preparation of specimens to ensure that the surface properties simulated the bulk properties.

Preparation of specimens

The composite components were mixed according to the manufacturers instructions in air. However, the end of mixing was performed in an argon atmosphere using a polyethylene glove bag (Model S–1, I2R, Instruments for Research and Industry, PA., USA). The composite pastes were pressed to one side of a 52 x 18 x 2 mm 30° germanium crystal (Dr. Karl Korth Monokristalle-Kristalloptik oHG, Germany) in an argon atmosphere. In order to protect and to ensure good contact between the sample and the germanium plate, the prismatic material was covered with a thin film of an argon saturated hydrocarbon oil. These precautions were taken to minimize the inhibiting effects of oxygen in air. The germanium crystal with the composite was installed in the MIR accessory of a grating infrared double beam spectrophotometer (Model 577, Perkin Elmer Corp., CT., USA). The operating conditions of the spectrophotometer were: time constant, 2 sec; scan mode, 560; slit program, 7. The sample tray of the infrared spectrophotometer was kept at 37 °C.

Rationale of test method

The main constituent in the organic phase of most composite resins is the difunctional monomer BIS–GMA. In addition one or more difunctional dimethacrylates like triethylene glycol dimethacrylate (TEGDMA) (Fig. 1) are used as liquifying monomer. Also the monofunctional monomer 2-hydroxyethyl methacrylate is found in one of the brands investigated.

The monomers used in the commercial products exhibit absorption bands in the infrared region that may be used to determine the remaining methacrylate groups, i.e. carbon-carbon double bonds in the unreacted methacrylate groups, after polymerization. The quantity of remaining methacrylate groups are determined in per cent of the methacrylate groups originally present in the unpolymerized material. The absorption band at approximately 1640 cm^{-1} is caused by C=C stretching vibrations (Fig. 3). The intensity of the C=C stretching absorption band is relatively high because the olefinic bond is in conjugation with the ester carbonyl group (18). From the spectrum in Fig. 3 it is evident that the C=C stretching absorption band can suitably be used for quantitative determination of unsaturation.

Internal reflectance spectra in the actual region were recorded for each composite component before the start of polymerization. After mixing, the composites were kept at 37 °C for 24 hours. After 24 hours infrared spectra were recorded, and the amounts of remaining unreacted methacrylate groups were determined. The C=C stretching absorption band at 1640 cm^{-1} representative for a composite material is shown in Fig. 4.

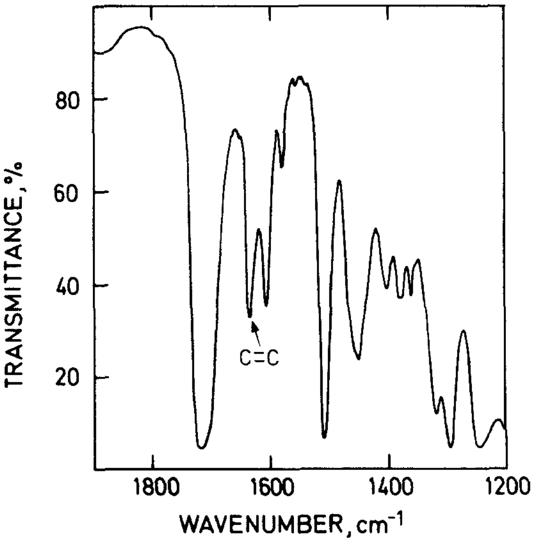

Fig. 3. Internal reflection spectrum, region 1900–1200 cm^{-1}, of Concise Composite Universal paste with C=C absorption bands at 1640 cm^{-1}.

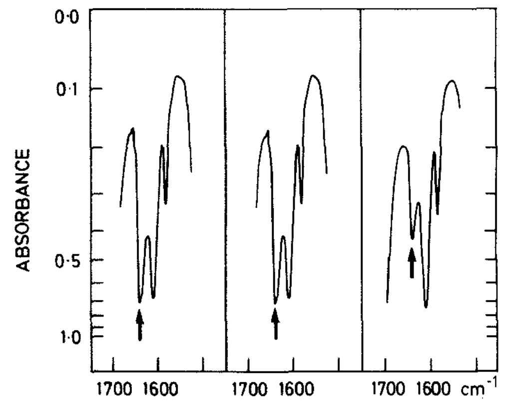

Fig. 4. Internal reflection spectrum of Concise Composite. To the left and in the center the components Universal and Catalyst respectively, prior to polymerization. To the right the mixed components 24 hours after the start of polymerization.

The baseline method for determining peak absorbance was used (10, 27, 34). Appropriate baselines were drawn, and the baseline absorbance value subtracted from the peak absorbance value as read at the wavenumber of the peak, i.e. 1640 cm^{-1}, directly from the non-linear absorbance paper (Perkin Elmer, Part No 5 1004366, Perkin Elmer Corp., CT., USA) used to record the spectra.

The quantitative measurements were made on a *relative basis* (21, 33) where the absorption band of the methacrylate C=C bond at 1640 cm^{-1} and the aromatic C...C stretching band at 1610 cm^{-1} were compared. In this way the ratios of the two bands before and after polymerization were etstablished.

The validity of the infrared spectroscopic procedure is based on the fact that there should be similar absorptivity values at 1640 cm^{-1} for all monomers included in the brands. Transmission infrared absorptivity values at 1639 cm^{-1} determined for the actual monomers in diglyme solutions are indeed of the same magnitude (28).

The absorbance measurements also have to follow Beer's law and no interfering bands should be present.

The linear relationship between absorbance and quantity of C=C bonds is verified by the calibration curves shown in Fig. 5 which are based on MIR spectra of mixtures. These mixtures were made of TEGDMA and bisphenol A in ethanol solution (a) and of TEGDMA and BIS-GMA in ethanol solution (b). An appropriate abscissa description for curve (a) is the *mole ratio* of TEGDMA to bisphenol A since there are two absorbing groups, C=C and aromatic C...C respectively per molecule. In case (b) where BIS-GMA exhibit two absorbing groups of each kind, C=C and aromatic C...C, the abscissa representation is *mole ratio + 1.*

The baseline method used for peak absorbances permits accuracies by the MIR technique of ± 3 % in concentration determinations (21). The investigated brands contain two or more monomers. Various dimethacrylate monomers exhibit different reactivities (13, 22). At a given time this may lead to different degrees of conversion for the various brands. The error in concentration of remaining methacrylate groups in the brands investigated was estimated to be ± 4 to ± 5 % absolute.

RESULTS

The quantities of remaining unreacted methacrylate groups in the six investigated brands are shown in Fig. 6. The amounts of remaining methacrylate groups constitute mean values and estimated errors of five determinations. The results demonstrate that commercially available composite restorative resin materials have different amounts of remaining unreacted methacrylate groups 24 hours after start of polymerization, i.e. they exhibit different degrees of conversion.

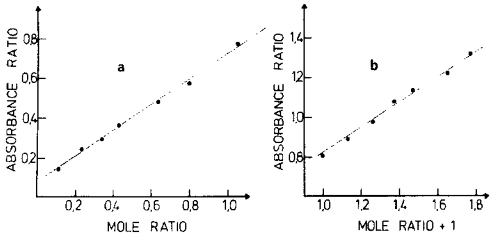

Fig. 5. MIR calibration curves. The ratio of C=C stretching band absorption at 1640 cm^{-1} and the aromatic C...C band at 1610 cm^{-1} as a function of the amounts of C=C bonds. (a) Mixtures of TEGDMA and bisphenol A. (b) Mixtures of TEGDMA and BIS-GMA.

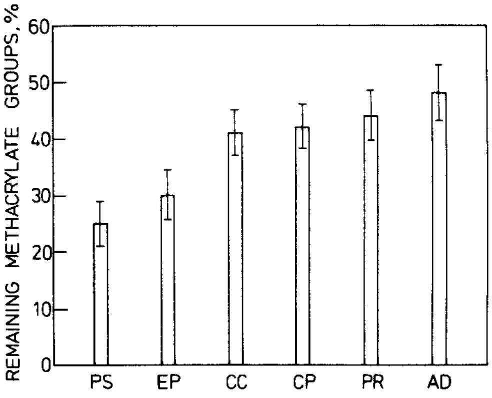

Fig. 6. Remaining unsaturated methacrylate groups in six composite restorative materials. Vertical lines on bars indicate estimated errors. Codes of products refer to those used in Table 1.

DISCUSSION

Composite resorative resin materials are based on multicomponent systems of methacrylate monomers. These monomers are usually difunctional. Monofunctional monomers are also used. The functionality is based upon the polymerization reactive methacrylate groups.

The present data indicate that the different amounts of residual methacrylate groups in the polymerized materials of the brands investigated are related to their different resin formulations, i.e. the unpolymerized pastes contain various monomers in different amounts.

Dimethacrylate monomers polymerize to highly crosslinked three-dimensional network systems. Investigations have demonstrated that even at low degrees of conversion primary polymer chains become coiled with formation of microregions (12) or microgels (11). Within these regions polymerization occurs at higher rates than in a space which is free of these regions because of a local gel effect (12). The formation of homopolymers from dimethacrylates of mono-, di-, tri-, and tetraethylene glycol shows that with increasing distance between the methacrylic groups the reactivity of the monomers increases (3, 22). By the formation of homopolymers, the highest conversions are also obtained with the dimethacrylate of the long chain flexible glycols. This may be explained by stereochemical considerations. The presence of ether bridge linkages in the dimethacrylate monomers increases the flexibility of the chains (14). With increasing distance and increasing number of ether bridge linkages between the methacrylate groups, both flexibility of the monomers and the mobility of the elements containing the unreacted methacrylate groups in the polymer matrix increase.

The materials investigated contain the aromatic monomer BIS-GMA and in addition the material Adaptic contains the aromatic monomer bisphenol A dimethacrylate (BIS-MA) (2, 29). Apart from these aromatic monomers the materials investigated contain the diluting aliphatic monomer triethylene glycol dimethacrylate. According to high performance liquid chromatography analysis (29) the material Prestige with the lowest content of residual methacrylate groups 24 hours after start of polymerization contains in addition to BIS-GMA the dimethacrylates of monoethylene glycol and of the higher ethylene glycols. The same material also contains the monofunctional monomer 2-hydroexyethyl methacrylate (HEMA) and the reaction products of 1, 2, 3, 6-tetrahydrophtalic anhydride, 2, 3-epoxypropyl methacrylate and HEMA. The reason for the low content of the remaining unreacted methacrylate groups after curing in the product Prestige is the low content of the relatively heavy and rigid monomer BIS-GMA and the high concentrations of the nonfunctional monomers and the oligoethylene glycol dimethacrylates.

The five other investigated materials contain only difunctional dimethacrylate monomers, i.e. the diluting monomer TEGDMA and the aromatic monomers BIS-GMA and BIS-MA (Adaptic). Within these groups of composite materials the degree of conversion can be correlated with the quantity of the relatively heavy and rigid aromatic monomers BIS-GMA and BIS-MA. With increasing concentration of the aromatic monomers, the quantities of remaining methacrylate groups also increase.

In composite dental materials the dimethacrylates polymerize to form an organic matrix of three-dimensional network systems (Fig. 7). The illustration represents a condition corresponding to 20–30 % pendant methacrylate groups randomly distributed in the polymeric matrix. As a result of the influence of microregions or microgels during the polymerization of dimethacrylates (12), the organic matrix in the polymerized composite materials should consist of regions, i.e. clusters, with higher crosslinking density than the regions between each cluster with higher concentration of unreacted methacrylate groups.

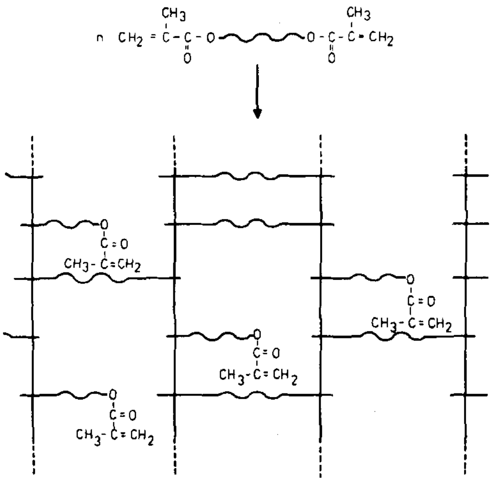

Fig. 7. Simplified and idealized structure of polymerized dimethacrylates with remaining unsaturated groups.

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