

Synthesis and Characterization of BTDA-Based Dimethacrylate Dental Adhesive Monomer and Its Interaction with Ca^{2+} Ions

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ABSTRACT: A BTDA-based dimethacrylate monomer was synthesized via reaction of 3, 3', 4, 4'-Benzophenone tetracarboxylic dianhydride (BTDA) and 2-Hydroxyethyl methacrylate (HEMA). The reactions were followed using FTIR spectroscopy and the product was characterized and confirmed using FTIR, $^1\text{H-NMR}$, and Elemental Analysis. The effects of temperature and pyridine as catalyst were investigated. The water contact angle on the surface of cured

BTDMA and Bis-GMA-based resins were also measured and compared. FTIR studies showed an interaction between carboxylic acid groups of BTDMA and Ca^{2+} ions of CaO. The interaction of the resin with hydroxyapatite and tooth ash was also investigated. The interaction was also studied using thermogravimetric analysis (TGA). © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3246–3249, 2002

INTRODUCTION

Bis-GMA monomer has widely been used in the composition of dental composites since the 1960s when Bowen introduced it.^{1–5} Although the monomer has given good physical and mechanical properties to dental composites, lack of good adhesion between tooth structure and restoration has led to improve dental bonding systems and methods for enhancing the adhesion.^{6–8} The problem is more evident in adhesion to dentin because it is a wet and dynamic substrate.⁸ Bonding systems containing hydrophilic monomers such as Hydroxyethyl methacrylate (HEMA) and monomers having carboxylic acid groups have been introduced and used to improve the adhesion of the composites and tooth structure.^{8–11} The adduct of HEMA and BTDA (3,3', 4,4'-Benzophenone tetracarboxylic acid dianhydride) has been used, in some cases, in the composition of dental bonding systems, and it has been claimed that carboxylic acid groups of the monomer can interact with the Ca^{2+} ions of tooth minerals,¹² but there are no details on the characterization of product and its interaction with Ca^{2+} ions. Many studies have been done on the interaction of carboxylic acid groups of poly(acrylic acid) with metal ions^{13–16} and hydroxyapatite,^{17,18} but we have not found many studies on the interaction of adhesive monomers containing carboxylic acid groups with such minerals.

In this work BTDA-dimethacrylate (BTDMA), which has carboxylic acid groups in its structure, was synthesized via reaction of BTDA and HEMA. The product was then purified and characterized. The interaction of BTDMA, which contains carboxylic acid groups, with minerals of tooth structure was studied. To see the hydrophilicity of samples the water contact angles on the surface of cured BTDMA- and Bis-GMA-based resins were also measured and compared.

EXPERIMENTAL

Materials

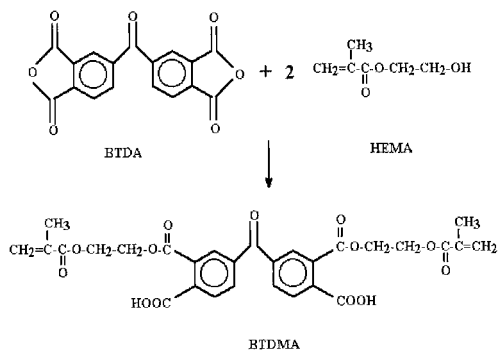
3,3', 4,4'-Benzophenone tetracarboxylic dianhydride (BTDA, 96%) was obtained from Aldrich. 2-Hydroxyethyl methacrylate (HEMA, 95%) was purchased from Fluka, Hydroquinone (HQ, >99%) and pyridine were obtained from Merck. *N,N*-Dimethylformamide (DMF, >99%) was obtained from Merck and was dried by distillation under reduced pressure and stored over 4 Å molecular sieves.

METHODS

Synthesis and characterization of BTDMA

BTDMA was synthesized by the reaction of BTDA and HEMA. The reactions were done in a three-necked flask equipped with a magnetic stirrer, reflux condenser, and nitrogen inlet tube; 0.01 mol of BTDA, 0.025 mol of HEMA, and 0.008 g of HQ were added to 30 mL of DMF in the reaction flask, respectively. The reactants were warmed up to the reaction temperature under an N_2 blanket. The nitrogen gas was dried

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Scheme 1 Synthesis of BTDMA.

before entering the flask by passing over silica gel desiccant.

The reactions were done at 60 and 80°C to investigate the effect of temperature. To study the effect of catalyst, the reaction temperature was held at 60°C, and pyridine was added to the reaction mixture in the weight percents of 0.1, 0.5, and 2. The completion of the reaction was demonstrated by the disappearance of C=O stretching of the anhydride group at 1860 and 1790 cm^{-1} from FTIR spectra.

After completion of the reaction, the product was washed with distilled water and separated by a centrifuge. The purification was repeated several times and the product then dried under reduced pressure at 50°C overnight. The FTIR and $^1\text{H-NMR}$ of the product (BTDMA) were then obtained.

FTIR spectra of the product and reaction mixtures were obtained using a Bruker Model IFS 48 spectrophotometer and $^1\text{H-NMR}$ spectrum of the product was recorded on a Bruker Advance 500 MHz FT-NMR using CDCl_3 as the solvent and TMS as the reference. The elemental analyses were done on an Elementar-Analysensysteme GmbH.

Preparation of the samples for contact angle measurements

To measure the contact angle of cured BTDMA and compare it with that of Bis-GMA, mixtures of the two

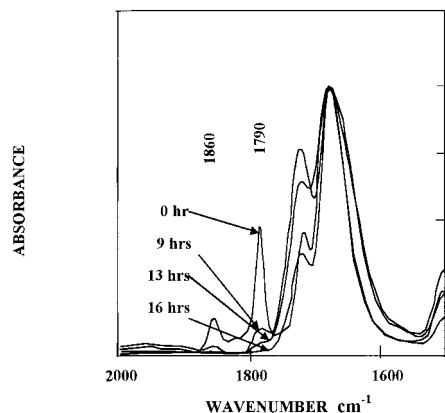


Figure 1 Disappearance of anhydride characteristic peaks of 60°C.

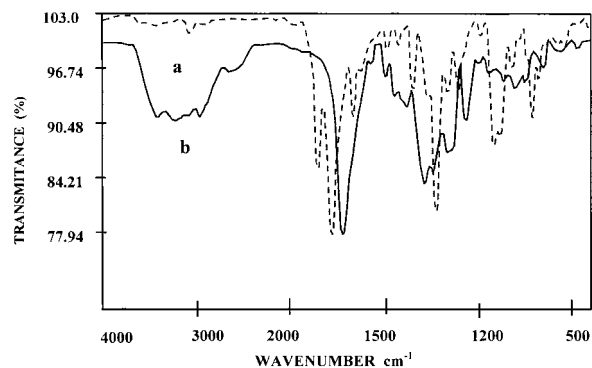


Figure 2 500 MHz $^1\text{H-NMR}$ spectrum of BTDMA.

resins with 30% (wt %) of ethylene glycol dimethacrylate (EGDMA) and 1% (wt %) of benzoyl peroxide (BP) were prepared and cured in a mold between two glass slides for 2 h at 80° and 2 h at 110°C. The contact angle of water droplets on the surface of the samples were then measured on the surface of samples using a KRÜS G40 contact angle measuring system. The values reported for contact angles are the average of five measurements.

Interaction of BTDMA with Ca^{2+}

The interaction of carboxylic acid groups of BTDMA with Ca^{2+} ions was investigated using FTIR spectroscopy. The stretching band of the carbonyl group, which appears at about 1720 cm^{-1} in a carboxylic acid group, will shift to lower wave numbers after the interaction with ions such as Ca^{2+} .^{13,14,16,19} A solution of BTDMA and ethanol (50/50 wt %) was prepared and mixed with CaO, synthetic hydroxyapatite, and the ash of natural tooth. The mixtures were stored at 37°C for 1 day, dried under reduced pressure at 60°C for 10 h, and then their FTIR spectra and TGA thermograms were obtained. To ensure that there were enough Ca^{2+} ions to interact with BTDMA, excess amount of the minerals were mixed with the solution.

RESULTS AND DISCUSSION

Synthesis and characterization of BTDMA

Scheme 1 summarizes the reaction of BTDA and HEMA. The reactions were followed by FTIR spectroscopy every hour. As shown in Figure 1, the absorption characteristic peaks of anhydride (BTDA) at 1860 and 1790 cm^{-1} disappeared gradually with increasing the time of the reaction. The disappearance of the peaks was checked every hour, and the reactions were judged to be completed when the peaks completely disappeared.

Figures 2 and 3 show the FTIR and $^1\text{H-NMR}$ spectra of purified BTDMA, respectively. As can be seen in the FTIR spectrum of BTDMA, the characteristic peaks of

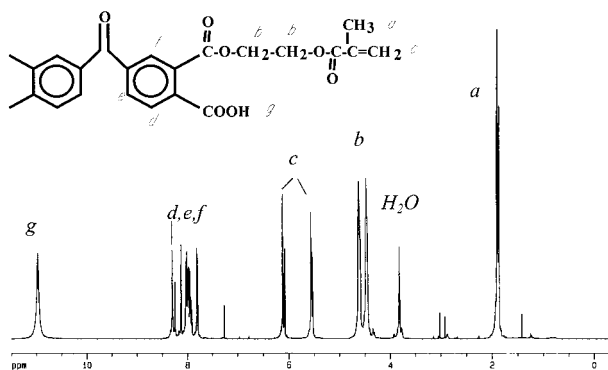


Figure 3 Infrared spectra of BTDA (a) and BTMDA (b).

anhydride disappeared. The peaks at 1720 cm^{-1} , and in the range of 2700 to 3500 cm^{-1} , indicate formation of carboxylic acid groups. The peak at the chemical shift of 11 ppm, in the $^1\text{H-NMR}$ spectrum of the monomer that is related to the acidic proton, also confirms it.

Results obtained from elemental analysis for the product and the calculated values based on the molecular structure are compared in Table I. The results confirm the formation of BTMDA and its purification.

Effect of temperature on reaction

As shown in Figure 1, the reaction was completed in 16 h. The time of completion of the reaction was decreased from 16 to 8 h by increasing the temperature from 60 to 80°C . Although the reaction time was decreased at 80°C , the color of product was darker, and it was observed that the viscosity of the reaction solution increased probably due to some side reactions.

Effect of catalyst on reaction

Pyridine has been used as a suitable catalyst for alcoholysis of anhydrides.²⁰ In the presence of pyridine, the completion time for reaction of BTDA and HEMA was decreased. Table II shows the effect of catalyst percentage on the time of the reaction. Increasing percentage of catalyst decreased the reaction time from 16 to 6 h. Reduction of the reaction time was not significant when the catalyst percentage increased from 0.5 to 2%.

TABLE I
Elemental Analysis Results for BTMDA

	% N	% C	% H
Experimental	0.00	59.02	4.63
Calculated	0	59.79	4.47

TABLE II
Effect of Catalyst Percentage on the Reaction Time at 60°C

Pyridine Concentration (wt %)	Reaction Time (h)
0	16
0.1	14
0.5	7
2	6

Interaction of BTMDA with Ca^{2+} ions

Although the interaction of carboxylic acid groups with hydroxyapatite is complex and several factors may affect it,^{17,18} formation of ionic interactions and/or chelate between carboxyl and calcium or phosphate groups of hydroxyapatite can be one of the possible mechanisms, as such interactions have been observed between carboxylic acid groups of polyacrylic acid and Ca^{2+} and some other metal ions.^{13,14} To investigate the interaction, CaO was used as a material containing Ca^{2+} ions, and synthetic hydroxyapatite and natural tooth ash were used to simulate more realistic conditions. The FTIR spectra were obtained from mixtures of the minerals and BTMDA. As shown in Figure 4, peaks appeared between 1550 and 1650 cm^{-1} , indicating some interaction between BTMDA and CaO. Because of the existence of carbonyl groups in ester form in the structure of BTMDA, the peak at 1720 cm^{-1} did not disappear completely. Appearance and enhancement of COO^- stretching bands of carboxylates observed in the regions 1500 to 1650 cm^{-1} for asymmetric stretch [$\nu_a(\text{COO}^-)$] and 1390 to 1420 cm^{-1} for symmetric stretch [$\nu_s(\text{COO}^-)$] are indicative of an acid-base interaction.^{13-15,21,22} So the peak at 1570 cm^{-1} in Figure 4 can be assigned to $\nu_a(\text{COO}^-)$, corresponding to carboxylate complexes of carboxylic acid groups of BTMDA and ions of the minerals. The peak at 1404 cm^{-1} is attributed to ν_s

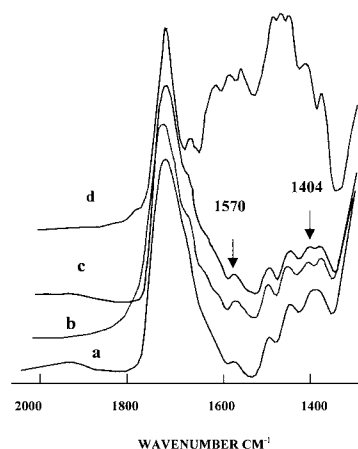


Figure 4 Infrared spectra of BTMDA (a), the mixture of BTMDA with: hydroxyapatite (b), toothash (c), and CaO (d).

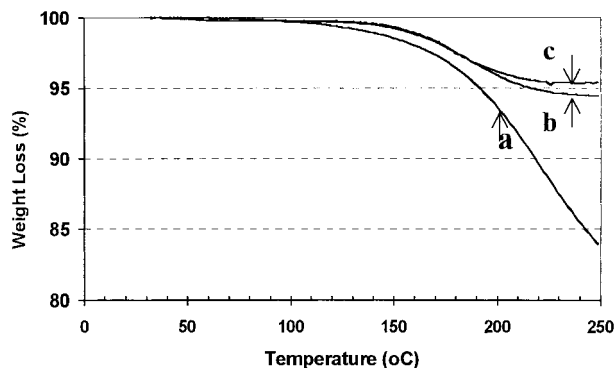


Figure 5 TGA thermograms of BTDMA (a), its mixture with hydroxyapatite (b), and tooth ash (c).

(COO⁻) of the carboxylate, and confirms the interaction of BTDMA with the minerals.

Figure 5 shows the thermogram of BTDMA containing hydroxyapatite tooth ash and the pure one. It can be seen that the onset of the weight loss at about 12°C has transferred to about 150°C for the samples containing the minerals. The weight loss is due to the starting of the reformation of anhydride. The interaction between carboxylic acid groups of BTDMA and ions of the minerals shifts the onset to higher temperatures because of some ionic and/or physical crosslinking. TGA results confirm the FTIR results and the interaction.

Contact angle measurements

The contact angles of water on the surface of cured BTDMA/EGDMA and Bis-GMA/EGDMA samples are 50 and 60°, respectively. The contact angle, in the case of BTDMA, is about 10° smaller than the Bis-GMA one. It indicates that the hydrophilicity of BTDMA is more than that of Bis-GMA. The higher hydrophilicity of BTDMA causes more wetting of the tooth surface, more penetration of resin into the dentin tubules, and more micromechanical retention.

CONCLUSION

The BTDA-based dimethacrylate monomer (BTDMA) was synthesized and characterized using FTIR, ¹H-NMR, and elemental analyses. The effects of temperature and catalyst were investigated. The water contact angle on the surface of cured resins was also measured. The following results were obtained:

1. Increasing the reaction temperature from 60 to 80°C decreased the time of completion of reaction dramatically, but the viscosity of the reaction

mixture was higher and the color of product was darker.

2. Pyridine as a catalyst decreased the time of reaction from 16 to 6 h. The time of reaction decreases rapidly to 7 h for 0.5% of pyridine but, by increasing the percentage of pyridine further to 2%, it decreased only 1 more hour.
3. The dimethacrylate monomer, which contains carboxylic acid groups, interacts with Ca²⁺ ions of CaO and the ions of hydroxyapatite and tooth ash.
4. The contact angle of water on the surface of cured BTDMA was smaller than that of Bis-GMA, which is an indication of more hydrophilicity of BTDMA in comparison with Bis-GMA.

The authors believe that the adhesion-promoting effect of these kinds of dental adhesive monomers is a combination of ionic interactions and their wetting efficiency.

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