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Photopolymerization of Dimethacrylamide with (Meth)acrylates

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***Abstract*—**A photopolymerizable dimethacrylamide was synthesized and copolymerized with the selected (meth)acrylates. The polymerization rate, degree of conversion, gel time, and compressive strength of the formed neat resins were investigated. The results show that in situ photo-polymerization of the synthesized dimethacrylamide with comonomers having an electron-withdrawing and/or acrylate group dramatically increased the polymerization rate, degree of conversion, and compressive strength. On the other hand, an electron-donating group on either carbon-carbon double bond or the ester linkage slowed down the polymerization. In contrast, the triethylene glycol dimethacrylate-based system did not show a clear pattern. Both strong hydrogen-bonding between (meth)acrylamide and organic acid groups may be responsible for higher compressive strengths. Within the limitation of this study, the photo-polymerization of dimethacrylamide can be greatly accelerated by copolymerization with monomers having electron-withdrawing and/or acrylate groups. The monomers with methacrylate group can significantly reduce the polymerization rate and degree of conversion.

***Keywords*—**Photopolymerization, dimethacrylamide, degree of conversion, compressive strength.

I. Introduction

PHOTO- or redox-initiated (meth)acrylate-based polymerizations are very popular and useful in biomedical research [1], [2]. Due to the fast in situ polymerization rate and user friendly nature [3], methacrylates or acrylates have been used for a long time [4]. However, recent studies found that methacrylates and dimethacrylates are vulnerable to oral esterase [5], [6] and/or highly acidic environment [7] due to instability of ester bonds [5]-[7]. It was found that acrylamide and methacrylamide-based oligomers have showed a hydrolytical stability in acidic environment and in the presence of esterase [8]. Nevertheless, these alternative oligomers are still not popular as methacrylates due to their slow polymerization kinetics [9]. It was reported that photo-polymerization of diacrylamide, N,N'-diethyl-1,3-bis(acrylamido)propane (DEBAAP) alone showed lower polymerization rate as well as lower degree of conversation under visible light illumination as compared to methacrylate- or acrylate-based systems [9], [10]. Interestingly acrylamide containing a phosphoric acid was reported to increase the polymerization rate and degree of conversion of DEBAAP when they were copolymerized each other [10]. It was also found that the polymerization rate and degree of conversion were increased with DEBAAP in the presence of non-polymerizable organic phosphoric acid [11]. Then, it was concluded that the photo-polymerization of acrylamide oligomer such as DEBAAP could be enhanced by the increase of medium polarity brought by the presence of phosphoric acid groups [11]. Our preliminary study on dimethacrylamide also indicated that the monomer itself was harder to be homo-polymerized under blue light or even visible light in the presence of camphorquinone and N,N'-dimethylaminoethyl methacrylate photo-initiation system [12]. However, it was found that the polymerization was much faster if we incorporated acrylic acid into the system. To extend the preliminary study, we proposed to investigate the effect of the selected (meth)acrylate monomers which are often used in biomedical/dental applications on photo-polymerization of dimethacrylamide and tried to find some correlation between dimethacrylamide and the selected (meth)acrylate monomers.

The objective of this study was to investigate the photopolymerization rate, degree of conversion, and compressive strength of the newly synthesized dimethacrylamide copolymerization with the selected (meth)acrylates.

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II. Experimental

A. Materials

Acrylic acid (AA), methacrylic acid (MAA), ethylene glycol methacrylate phosphate (EGMAP), hydroxyethyl acrylate (HEA), hydroxyethyl methacrylate (HEMA), methyl acrylate (MA), methyl methacrylate (MMA), triethylene glycol dimethacrylate (TEGDMA), 1,8-diamino-3,6-dioxaoctane (DADO), methacrylic anhydride (MAAn), triethylamine (TEA), camphorquinone, N,N-dimethylaminoethyl methacrylate, acetone and diethyl ether were used as received from Sigma-Aldrich Chemical Co (Milwaukee, WI, USA) without further purification.

B. Synthesis and Characterization

Synthesis of dioxaoctane dimethacrylamide (DDM) is described below. Briefly, to a flask containing DADO (0.05 mol) and acetone in an ice-bath, MAAn (0.11 mol) was added dropwise with stirring. After addition was completed, the reaction was run at room temperature overnight. The solution was concentrated with a rotary evaporator, followed by dissolving in ether, washing with sodium bicarbonate solution and barine, drying with anhydrous $MgSO_4$ and then concentrating in vacuo to obtain the purified product DDM (yield > 85%). The synthesis scheme is shown in Fig. 1.

The synthesized oligomer was characterized by Fourier transform-infrared (FT-IR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. The proton NMR (^{1}HNMR)

spectra were obtained on a 500-MHz Bruker NMR spectrometer (Bruker Avance II, Bruker BioSpin Corporation, Billerica, MA) using deuterated dimethyl sulfoxide as solvents and FT-IR spectra were obtained on a FT-IR spectrometer (Mattson Research Series FT/IR 1000, Madison, WI).

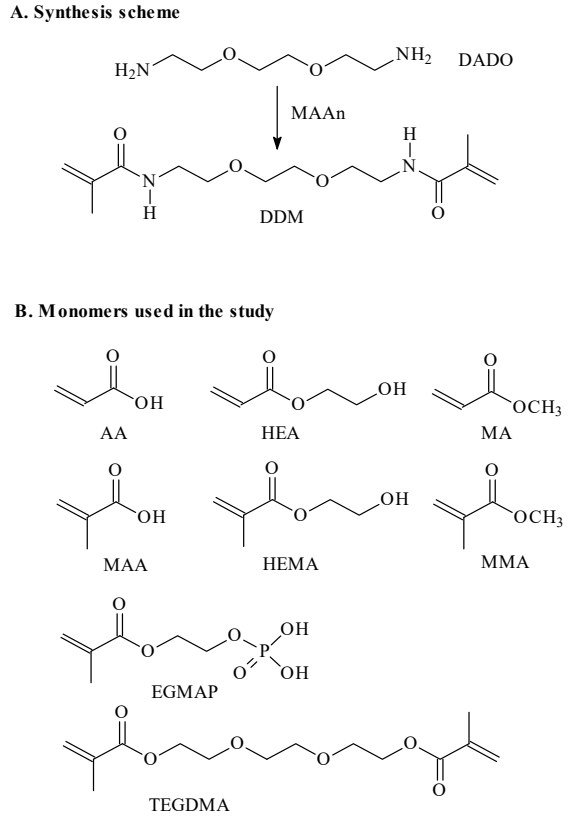


Fig. 1 Schematic diagrams for synthesis of DDM and structures of the monomers used in the study: A. DDM synthesis; B. Structures of AA, HEA, MA, MAA, HEMA, MMA, EGMAP, and TEGDMA

C. Evaluation

The resin liquid was formulated with DDM or TEGDMA, commercial monomers, 1.5% camphorquinone (photo-initiator, wt./wt.) and 3.0% N,N-dimethylaminoethyl methacrylate (activator), where DDM or TEGDMA was either formulated alone or mixed with a comonomer in a ratio of 50:50 (wt./wt.) [12].

Polymerization conversion was evaluated by measuring degree of monomer conversion via a FT-IR spectrometer, following the published protocol [13]. Briefly, liquid resin sample was cast within two KBr crystals, followed by illuminating with a visible light device (Tungsten halogen light source, 250 W, Tricure 2000, Dentsply, York, PA). Immediately after illumination, the KBr crystal sandwich was mounted on the FT-IR sample holder and scanned for acquiring a FT-IR spectrum. The peak areas on the absorbance spectra of the samples were used to determine degree of conversion (DC). The areas under the peaks (cm^{-1}) at 1637 and 2957, assigned to vinyl C=C and amide H stretching for the DDM-based resin, and at 1637 and 1722, to vinyl C=C and ester for the TEGDMA-based resin, were used to calculate DC. DC was determined using the equation of $1-[(A_{C=C,\ cured}/A_{amide\ or\ ester,\ cured})/(A_{C=C,\ uncured}/A_{amide\ or\ ester\ uncured})] \times 100$, where A = measured peak area. The gel time was estimated by visual observation where the resin or composite sample starts to shrink under the light illumination.

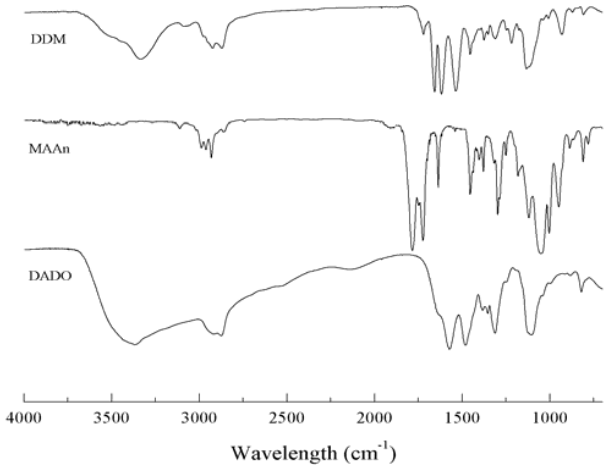
Cylindrical specimens were fabricated at room temperature according to the published protocol [12]. Briefly, the thoroughly mixed resin liquid was placed into a cylindrical glass mold with dimensions of 4 mm in diameter by 8 mm in length. Then, the specimens were exposed to visible light for 10 min to ensure a complete polymerization. The sample sizes were n = 6-8 for each formulation. The compressive strength test was performed on a screw-driven mechanical tester (QTest QT/10, MTS Systems Corporation, Eden Prairie, MN, USA) with a crosshead speed of 1 mm/min [14]. Compressive strength was calculated using an equation of $P/\pi r^2$, where P = the load at fracture and r = the radius of the cylinder. Compressive yield strength, modulus, toughness and energy to yield were obtained from the stress-strain curves of the compressive strength tests. One-way analysis of variance (ANOVA) with the post hoc Tukey-Kramer multiple range test was used to determine significant differences of the compressive strength among the materials in each formulation. A level of $\alpha = 0.05$ was used for statistical significance.

III. Results

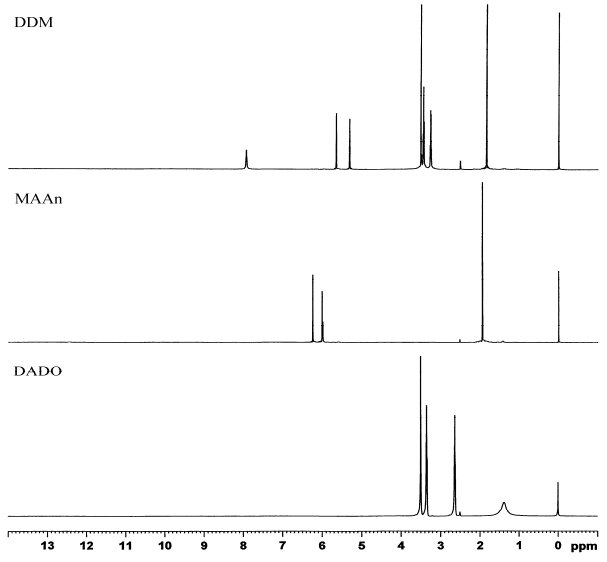
Fig. 2 shows the FT-IR and ^{1}HNMR spectra of DADO, MAAn, and DDM. Fig. 2 (a) shows the FT-IR spectra for DADO, MAAn, and DDM. The characteristic peaks are listed below: (1) DADO: 3368 and 1573 (-N-H stretching and deformation) for primary amino group; 1480, 1383, and 1105 (-C-O-C- and $-OCH_2-$ stretching and deformation) for ether group; and 2874, 1354, 819, 698, 624, and 583 (C-H stretching and deformation) for methylene and methyl groups. (2) MAAn: 1783 and 1723 (-C=O stretching) for anhydride group; 1636, 1454 and 1297 (-C=C- stretching and vibration) for methacrylate group; 1050 (-C-O-C- deformation) for anhydride group; and 2930, 1403, 1379, 1181, 1119, 1003, 948, 809, and 641 (C-H stretching and deformation) for methylene and methyl groups. (3) DDM: 3331 and 3086 (-N-H stretching) for amide group; 1719, 1657, and 1534 (-CONH- stretching and deformation) for amide group; 1617, 1454, and 1311 (-C=C- stretching and vibration) for methacrylamide group; 1454 and 1133 (-C-O-C- and $-OCH_2-$ stretching and deformation) for ether group; and 2924, 1412, 1375, 1218, 1007, 931, 808, and 650 (C-H stretching and deformation) for methylene and methyl groups. Disappearance of the broad peak at 3468 for amino group on DADO as well as the strong peaks at 1783 and 1723 for anhydride on MAAn, appearance of strong new peaks at 3331, 1657 and 1534 on DDM, and slightly downshift of the peak at 1636 to 1617 for C=C group on DDM confirmed the formation of the oligomer DDM.

Fig. 2 (b) shows the ^{1}HNMR spectra for DADO, MAAn, and DDM. The chemical shifts (ppm) were: (1) DADO, 3.5, 3.35 and 2.65 (12H on $-CH_2CH_2-$) and 1.40 (4H on $-NH_4$); (2)

MAAn, 6.25 and 6.0 (-4H on C=C), 1.95 (6H on $–CH_3$); (3) DDM, 7.95 (2H on -CONH-), 5.65 and 5.35 (4H on C=C), 3.5, 3.45 and 3.25 (12H on $-CH_2CH_2-$), and 1.85 (6H on $–CH_3$). Significant chemical shifts of C=C from 6.25 and 6.0 to 5.65 and 5.35, disappearance of the chemical shift at 1.4 ($-NH_2$), and formation of all the new chemical shifts on DDM confirmed the successful synthesis of DDM.



(a)

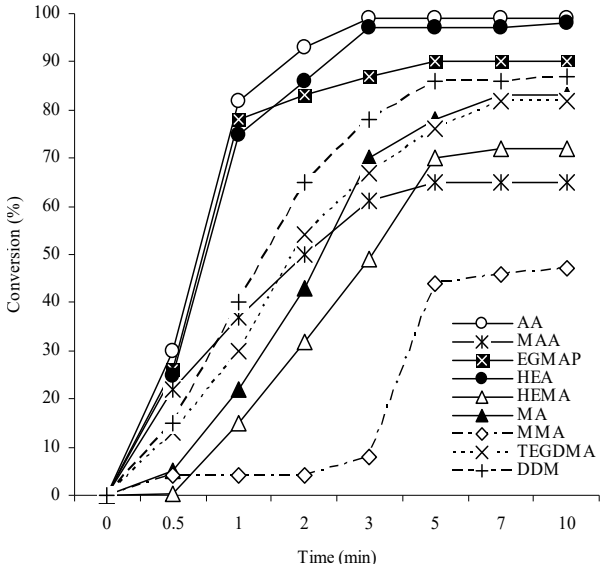


(b)

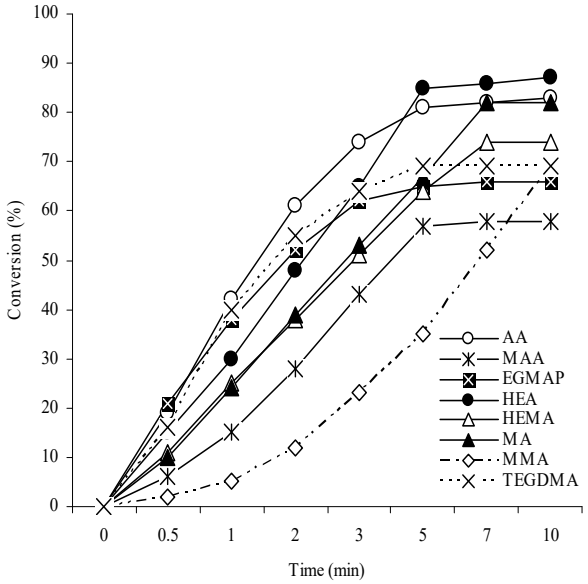
Fig. 2 FT-IR and ^{1}HNMR spectra for DODA, MAAn, and DDM: (a) FT-IR and (b) ^{1}HNMR

Fig. 3 shows the conversion curves of the DDM- and TEGDMA-based resins vs. time. In Fig. 3 (a), both polymerization rate and DC were in the decreasing order of AA > HEA > EGMAP > MAA > DDM > TEGDMA > MA > HEMA > MMA. In Fig. 3 (b), the polymerization rate was in the decreasing order of AA > TEGDMA > EGMAP > HEA > MA > HEMA > MAA > MMA. DC was in the decreasing order of HEA > AA = MA > HEMA > TEGDMA > EGMAP > MMA > MAA.

Table I shows the observed gel points of the tested formulations. The gel point in second (sec) was in the increasing order of AA > EGMAP > HEA > MAA > DDM > TEGDMA > MA > HEMA > MMA for DDM-based resins and EGMAP > TEGDMA > HEA > MA = MAA > AA > DDM > HEMA > MMA for TEGDMA-based resins.



(a)



(b)

Fig. 3 Conversion of the DDM- and TEGDMA-based resins: (a) DDM-based resins; (b) TEGDMA-based resins. The conversion values were calculated based on absorbance in FT-IR

Fig. 4 shows the compressive strength (MPa) values of the DDM-based resins and TEGDMA-based resins. For the DODAM-based resins (Fig. 4 (a)), the compressive strength

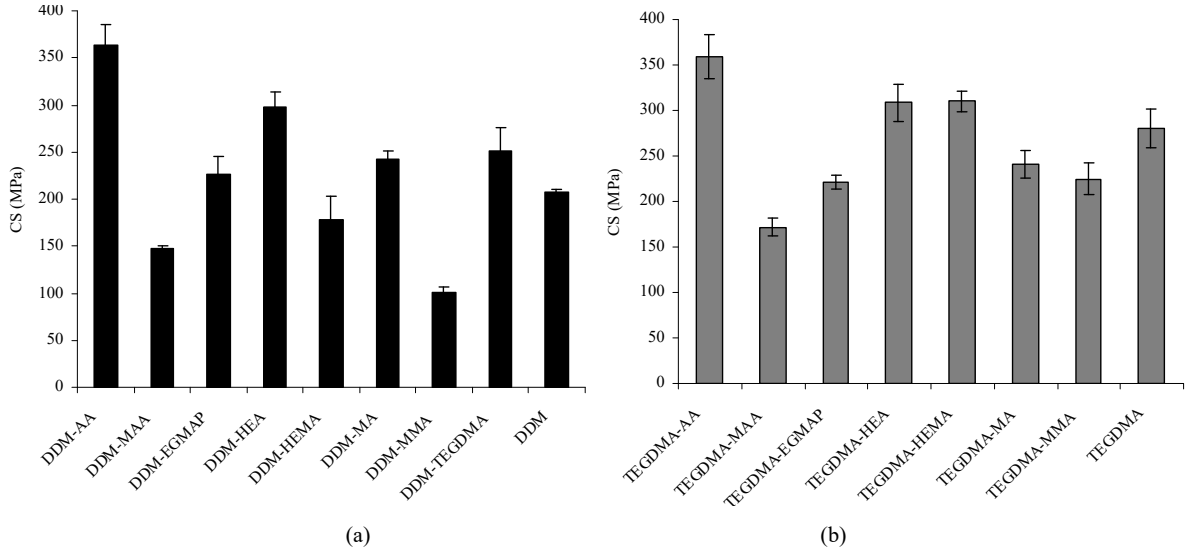
values were in the decreasing order of AA > HEA > TEGDMA > EGMAP > MA > DDM > HEMA > MAA > MMA. For the TEGDMA-based resins (Fig. 4 (b)), the compressive strength values were in the decreasing order of AA > HEMA = HEA > TEGDMA > MA > MMA > EGDMA > MAA, where there were no significant differences between HEA and HEMA and between MA and MMA ($p > 0.05$).

Fig. 5 shows the stress-strain curves of the DDM-based resins and TEGDMA-based resins. In Fig. 5 (a), (1) Yield strength (MPa): AA > EGMAP > MAA > TEGDMA > HEMA > MMA > DDM > HEA > MA; (2) Modulus (GPa): AA > MAA > EGMAP > TEGDMA > HEMA > DDM > MMA > HEA > MA; (3) Energy to yield (Nmm): AA > EGMAP > MAA > TEGDMA > MMA > HEMA > DDM > HEA > MA; (4) Toughness (KNmm): AA > EGMAP > TEGDMA > HEMA > HEA > MAA > MMA > DDM > MA. In Fig. 5 (b), (1) Yield strength: AA > MAA > HEMA > MMA > TEGDMA = EGMAP > MA > HEA; (2) Modulus: MAA > AA > HEMA > MA > MMA > EGMAP > TEGDMA > HEA; (3) Energy to yield: AA > MAA > TEGDMA = MMA > HEMA > EGMAP > MA > HEA; (4) Toughness: AA > HEMA > TEGDMA > HEA = MA > EGMAP > MMA > MAA.

TABLE I
GEL POINTS OF THE TESTED RESIN FORMULATIONS

Name	Ratio	Gel time (s) DDM	Gel time (s) TEGDMA
AA	50/50	40	138
MAA	50/50	100	115
HEA	50/50	75	86
HEMA	50/50	318	202
EGMAP	50/50	45	61
MA	50/50	230	113
MMA	50/50	420	238
TEGDMA	50/50	190	71
DDM	100	170	190

[1][I] = 3-arm BPB initiator concentration; [2]Conversion was determined from [1]HNMR spectrum at reaction time = 2 h; [3]MW was determined from [1]HNMR spectrum; [4]MW = calculated theoretical MW; [5]Temperature change was measured *in situ* during ATRP reactions.



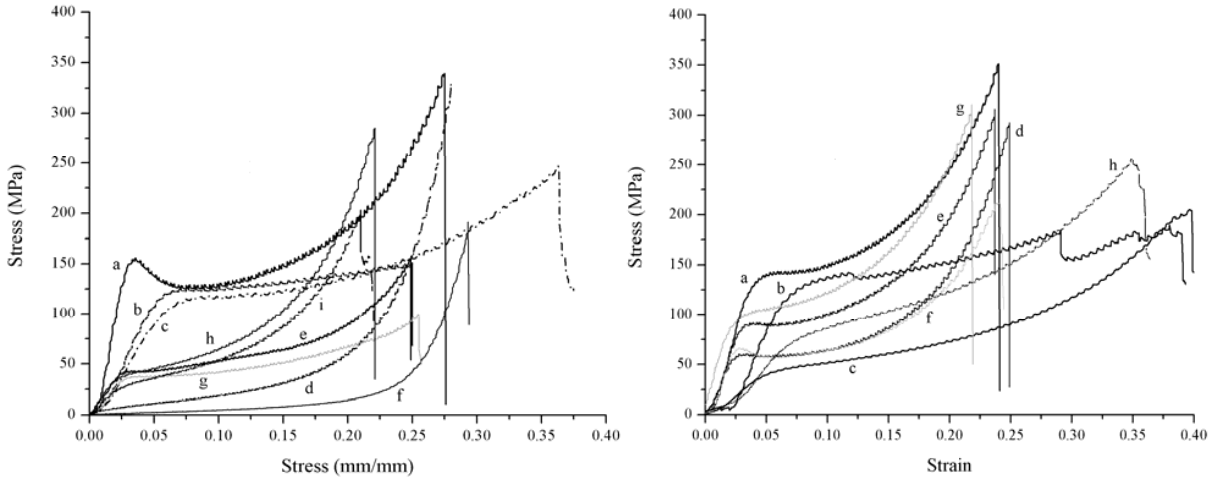
(a) (b)

Fig. 4 CS of the DDM- and TEGDMA-based resins: (a) DDM-based resins; (b) TEGDMA-based resins

IV. DISCUSSION

In current photo-cured polymer resin and composite applications, most resin and composite systems are methacrylate- or acrylate-based. Only a few research reports were focused on in situ curable methacrylamides or acrylamides, probably due to their slower in situ polymerization [9], [10]. In this study, a liquid dimethacrylamide – DDM was synthesized and used to construct a polymerizable liquid resin system with different acrylates or methacrylates, in order to study their in-situ curing rate and degree of conversion. Before the study was started, we have tried two different photo-curing sources - blue-light and visible light, to see if the system can be cured in situ. It was found that DDM was relatively hard to be polymerized in situ via a blue light source but relatively easier and faster to be cured using a visible light source although the curing was still not fast enough. Therefore, we decided to use visible light to study the proposed system. We evaluated the DC, gel time as well as compressive strength of the DDM-based resins and compared them with its methacrylate counterpart - TEGDMA-based system (TEGDMA or triethylene glycol dimethacrylate is a commonly used commercial dimethacrylate). Polymerization rate was used to measure how fast the reaction would start under visible light illumination, whereas DC was used to investigate how long it would take to complete the reaction. Gel time was used to evaluate when the photo-initiation would start while the material was in a practical form for compressive strength evaluation – cylinder. Compressive strength was used to evaluate how strong the formed resins would be after light illumination, which is another indication of degree of conversion. The details are discussed below.

Fig. 3 shows the conversion curves of the DDM- and TEGDMA-based resins vs. time. From Fig. 3 (a), when DDM was mixed with different comonomers, AA, HEA and EGMAP showed the highest polymerization rate and DC, followed by MAA, DDM, TEGDMA, MA, HEMA and MMA. AA, HEA, EGMAP and MAA all contain either carboxylic acid (-COOH), hydroxyl (-OH), or phosphoric acid (-OP(OH)$_2$) groups, which belong to an electron-withdrawing group [15]. Furthermore, both AA and HEA are acrylate without a methyl (-CH$_3$) group on carbon-carbon double bond (C=C) but EGMAP and MAA are methacrylate although both also contain -OP(OH)$_2$ and -COOH groups, respectively. Obviously, the acrylate group activates C=C, but the methyl group deactivates it. It is also evident that either methyl group on C=C or alkyl group on the ester linkage can deactivate C=C group, thus leading to slower polymerization (lower rate) and lower DC [15]. It was reported that the monomer containing phosphoric acid can increase the conversion and curing rate of the diacrylamide [10] and even the reaction rate can be enhanced in the presence of non-polymerizable organic phosphoric acid-containing reaction medium [11]. Hydrogen bonding between amides on DDM and acid groups on AA, MAA and EGMAP may be another reason to show higher polymerization rate and DC. It was reported that the polymerization rate was higher for monomers that are capable of forming hydrogen-bonding [16]-[18]. Those authors suggested that a higher dipole moment of the polymerizing medium reduced the termination rate k_t but hydrogen-bonding raised the propagation rate k_p, thus leading to an increased polymerization rate [16], [17]. In our study, AA, MAA or EGMAP and even HEA can be regarded as either reaction medium or comonomer that are capable of forming strong hydrogen-bonding with DDM and with themselves. That may be why AA showed the highest reaction rate and DC, but MMA showed the lowest one. On the other hand, the case is quite different for TEGDMA. From Fig. 3 (b), AA, when TEGDMA was mixed with the above comonomers, TEGDMA, EGMAP and HEA showed the highest polymerization rate, followed by MA, HEMA, MAA and MMA. HEA showed the highest DC, followed by AA = MA > HEMA > TEGDMA > EGMAP > MMA > MAA. There seems no clear correlation to be found from the molecular structure viewpoint. It is known that DDM is an amide, whereas TEGDMA is an ester. When DDM was mixed with any monomer in the study except for MA, MMA and TEGDMA, the two-way hydrogen-bonding would form because amides in DDM provide H-bonds. In contrast, when TEGDMA was used, only one-way hydrogen-bonding formed because TEGDMA does not have any hydrogen-bonds on it. It seems that the DDM polymerization is more vulnerable to the surrounding groups whether they are electron-withdrawing or donating, polar or non-polar.



(a) (b)

Fig. 5 Stress-strain curves of the DDM-based resins and TEGDMA-based resins: (A) DDM-based resins: a = AA, b = MAA, c = EGMAP, d = HEA, e = HEMA, f = MA, g = MMA, h = TEGDMA, i = DDM; (B) TEGDMA-based resins: a = AA, b = MAA, c = EGMAP, d = HEA, e = HEMA, f = MA, g = MMA, h = TEGDMA.S of the DDM- and TEGDMA-based resins: (a) DDM-based resins; (b) TEGDMA-based resins

The gel time can be roughly used to evaluate the starting point of curing [8], although it is not as accurate as the conversion measured by FT-IR. For the DDM-based resins, it was found that incorporation of the acid-containing and/or acrylate-containing monomer led to a shorter gel time or faster curing (see Table I). On the other hand, the comonomers composed of methacrylate and/or methyl or alkyl groups next to the ester linkage showed the opposite. The result from the gel time measurement was fairly consistent with that for the polymerization rate from the DC curves by FT-IR, indicating that gel time may be used to roughly estimate the polymerization rate of DDM with its comonomers in situ. In the case of the TEGDMA-based resins, however, the curing pattern did not follow the above discussion for the DDM-based system, although there is some similarity. It seems that the electron-withdrawing group still shows some effect on polymerization rate but the electron-donating group on C=C or the ester linkage plays little role.

Figs. 4 and 5 show the compressive strength and stress-strain curves of the DDM- and TEGDMA-based resins. The stress-strain curves can be illustrated by yield strength, modulus, energy to yield, and toughness in addition to compressive strength. Yield strength and modulus are often used to evaluate brittleness or stiffness of materials [19]. Compressive strength represents compressive break strength. Energy to yield is defined as the area under stress-strain curve before plastic deformation [19], which only covers elastic portion and is closely related to yield strength and modulus. It represents consumed energy to yield. Toughness is defined as the area under stress-strain curve before break, which covers both elastic and plastic portions [19]. It represents consumed energy before break. The data from Figs. 4 and 5 strongly support the viewpoints discussed above. In Fig. 4 (a), AA showed the highest compressive strength, followed by HEA, MA, TEGDMA, EGMAP, DDM, HEMA, MAA and MMA. All the acrylate-containing comonomers showed much higher compressive strength values than their corresponding methacrylate counterparts. The trend is similar to that for the gel time shown in Table I. The lower compressive strength values exhibited by EGMAP and MAA can be attributed to their lower DC. From Fig. 5 (a), AA, EGMAP and MAA showed the highest yield strength, modulus and energy to yield, indicating that these resins are much stiffer than the other resins, probably due to strong hydrogen-bonding between DDM and acid groups. HEA and MA were the softest resins with nearly no yield strength, very low modulus and low energy to yield. For toughness, AA was the highest, followed by EGMAP and TEGDMA, suggesting that these three resins are the toughest. The low yield strength and modulus of HEA, low compressive strength of HEMA and MAA, and relatively low yield strength and modulus of DDM and MMA made these resins to show lower toughness. The lower toughness value exhibited by MAA can also be attributed to its lower DC due to the negative effect of methyl group on C=C.

Regarding the TEGDMA-based resins (see Figs. 4 (b) and 5 (b)), although AA was still the highest in all the measured strengths, EGMAP and MAA were not ranked as high in all the strengths as those shown in the DDM-based system. MAA was ranked the 2nd in yield strength, followed by HEMA, MMA, TEGDMA, EGMAP, MA and HEA. MAA was ranked the 1st in M, followed by AA, HEMA, MA, MMA, EGMAP, TEGDMA and TEA. HEMA was ranked the 2nd in compressive strength, followed by HEA, TEGDMA, MA, MMA, EGMAP and MAA. HEMA was ranked the 2nd in toughness, followed by TEGDMA, HEA, MA, EGMAP, MMA and MAA. MAA was ranked as the 2nd in energy to yield, followed by TEGDMA, MMA, HEMA, EGMAP, MA and HEA. Except for AA and MAA, it seems that there is no negative influence from methyl group on C=C if one compares HEA with HEMA and MA with MMA, unlike in the DDM-based system. The effect of the electron-withdrawing group was not significant either if one compares AA, MAA and EGMAP with HEA, HEMA, MA and MMA. The effect of the electron-donating group was not significant at all, which can be easily observed between HEA and HEMA and between MA and MMA (no difference in compressive strength at all). Obviously, there is no clear pattern to follow for the strength ranking in the TEGDMA-based resins, suggesting that there is no special interaction between TEGDMA and acid-containing co-monomer including AA, MMA and EGMAP, unlike that in the DDM-based system.

V. Conclusions

The photopolymerization of the dimethacrylamide-based resins was studied. Generally speaking, when dimethacrylamide was copolymerized with the monomer having an electron-withdrawing group and/or an acrylate group, shorter gel time, faster polymerization rate, higher DC and higher mechanical strength were obtained and vice versa. In contrast, the TEGDMA-based system did not show a clear pattern. This may be attributed to the molecular structure difference between dimethacrylamide and dimethacrylate because the former is a hydrogen-bonding provider but the latter is not. The strong hydrogen-bonding between (meth)acrylamide and organic acid groups may be responsible for higher strengths exhibited. It is suggested that monomers containing electron-withdrawing and acrylate groups would favor in situ curing of (meth)acrylamide or di(meth)acrylamide.

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