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Properties of Experimental Resins Based on Synthesized Propoxylated bis-GMA with Different Propionaldehyde Ratios

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The effect of different propionaldehyde ratios on the properties of bis-GMA-based comonomers and copolymers diluted with propoxylated bis-GMA (CH₃bis-GMA) was evaluated. Five experimental comonomers were prepared combining bis-GMA with CH₃bis-GMA and propionaldehyde at 0, 2, 8, 16, 24 mol%. Light polymerization was effected with the use of 0.2 wt. (%) each of camphorquinone and *N,N*-dimethyl-*p*-toluidine. Resin degrees of conversion (%DC) were evaluated by FT-IR spectrophotometry and T_g by Differential Scanning Calorimeter. Complex viscosity (η^*), the effect of temperature on η^* , and Microhardness (*H*) for dry and wet samples were also determined. Data were analyzed by Student's t-test, one-way ANOVA and Tukey-Kramer test ($\alpha = 0.05$). The group with 24 mol% additive had a significant increase in %DC and *H*, and the lowest comonomer T_g and η^* . No remarkable variation was noted in copolymers T_gs. All resins presented Newtonian behavior of viscosity, which linearly decreased with increased temperature. The η^* decreased sigmoidally as the additive ratio increased.

Keywords: aldehyde, bis-GMA analog, microhardness, rheology

1. Introduction

It has been reported that the incorporation of propionaldehyde as an additive to bis-GMA/TEGDMA (bisphenol glycidyl dimethacrylate/triethyleneglycol dimethacrylate) and UDMA/HEMA (urethane dimethacrylate/hydroxyethyl methacrylate) resins significantly improved their degree of conversion^{1,2}, mechanical properties³ and in vitro wear resistance⁴. The extent of conversion continuously increased as the propanal content increased from 0 to 40 mol%¹. Properties such as flexural strength, diametral tensile strength, modulus of elasticity, and wear resistance improved up to an additive content of 24 to 32 mol%, above which the properties did not present significant changes^{3,4}. The possibility should, however, be considered that in excess this rather volatile and relatively toxic component may leach and evaporate from the resin affecting its biocompatibility.

In Dentistry, dilution of bis-GMA with the more hydrophilic TEGDMA is known to cause clinical adverse effects, mainly because of the increase in water sorption and polymerization shrinkage^{5,6}. To overcome these unwanted effects studies have been directed toward developing low viscosity, hydroxyl free, more hydrophobic bis-GMA analogs such as the propoxylated bis-GMA (2,2-bis(4-(2-methacryloxyprop-1-oxy)phenyl)propane), as a replacement for TEGDMA in bis-GMA mixtures^{7,8}. The properties of

bis-GMA copolymers and composites containing CH₃bis-GMA (Figure 1) have been evaluated. Due to TEGDMA being a more flexible monomer, with a higher degree of conversion, the Young's modulus and flexural strength values of bis-GMA/TEGDMA systems were higher⁹.

To improve its mechanical properties, propionaldehyde has been incorporated into the bis-GMA/CH₃bis-GMA system. The ratios of 24 mol and 32 mol% were used because they were shown to promote the highest increases in the properties of methacrylates^{3,4}. In this latter system, a significant increase was also noted in the degree of conversion¹⁰ and properties such as wear, strength, modulus of elasticity and hardness^{11,12}. Considering the lack of studies with regard to incorporation of lower ratios of aldehyde into the mentioned developmental resin, the objective of this study was to evaluate the physical, rheological, and mechanical properties of bis-GMA diluted with CH₃bis-GMA containing 0, 2, 8, 16 and 24 mol% propionaldehyde.

2. Materials and Methods

2.1. Materials

Bis-GMA, the photosensitizer camphorquinone (CQ, Kerr Corp., CA 92867-5422, USA), reducing agent *N,N*-dimethyl-*p*-toluidine (DMPT, Alfa Aesar, NH 03087-

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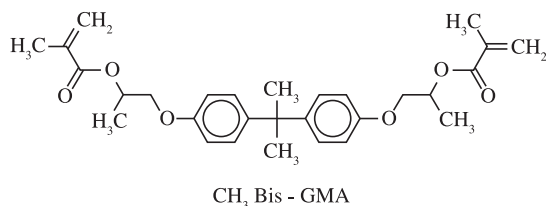


Figure 1. Molecular Structure of CH_3 bis-GMA.

9977, USA), and propionaldehyde (Acros Organics, NJ 07410, USA) were all used as received. The bis-GMA analog, CH_3 bis-GMA was synthesized, purified and stored according to reported methods⁷. Synthesized monomer was characterized by ^1H NMR and ^{13}C NMR, providing spectra that were consistent with the expected product (Figures 2a and b).

2.2. Formulation of comonomers

Five experimental resin formulations were prepared comprising 5 groups. For the control group bis-GMA/ CH_3 bis-GMA (without additive – G0) the comonomer ratio (mol%) was 75/25. For the other groups (G2, G8, G16 and G24) containing bis-GMA/ CH_3 bis-GMA/aldehyde the comonomer ratios (mol%) were G2: 72/26/2; G8: 69/23/8; G16: 63/21/16, and G24: 57/19/24. Resins were activated for visible light polymerization (LED Ultrablue IS, DMC Ltda, São Carlos, SP, Brazil; 350 $\text{mW}\cdot\text{cm}^{-2}$ and 470 ± 10 nm) by the addition of CQ and DMPT (0.2 wt. (%) each).

2.3. Degree of conversion (%DC)

The %DC test was performed ($n = 3$) by means of a FT-IR spectrophotometer (FTS 700-ATR, Varian Inc., Palo Alto, CA, USA) in transmission mode. Spectra were obtained in the region from 2000 to 1200 cm^{-1} and were acquired at a 4 cm^{-1} resolution and a total of 30 scans per spectrum. For comonomers, absorbance peaks were recorded by inserting the material into a Teflon disk-shaped mold (1 mm height \times 5 mm diameter) adapted to a NaCl plate. A Mylar strip was used to press the unpolymerized material inside the mold in order to produce a very thin layer. The samples were then light polymerized for 40 seconds and the absorbance peaks of the copolymers were recorded. The percentage of monomer conversion was determined from the ratio of absorbance intensities of aliphatic $\text{C} = \text{C}$ (peak at 1637 cm^{-1}) against the internal reference aromatic $\text{C} = \text{C}$ (peak at 1607 cm^{-1}) peaks before and after the samples were polymerized. The %DC was calculated as¹³:

$$\%DC = \left[1 - \left(\frac{(\text{abs } \text{C} = \text{C}_{1637\text{cm}^{-1}} / \text{abs } \text{C} = \text{C}_{1607\text{cm}^{-1}})_{\text{polymerized}}}{(\text{abs } \text{C} = \text{C}_{1637\text{cm}^{-1}} / \text{abs } \text{C} = \text{C}_{1607\text{cm}^{-1}})_{\text{unpolymerized}}} \right) \right] \times 100 \quad (1)$$

2.4. Glass transition temperature (T_g)

Comonomers and corresponding copolymers T_g were obtained using a differential scanning calorimeter (DSC 2010, TA Instruments, New Castle, DE, USA) each in duplicate, at heating rates of 20 $^{\circ}\text{C}/\text{min}$ (1st run) and 10 $^{\circ}\text{C}/\text{min}$ (2nd run). For each experiment (comonomers

or copolymers), about 15 mg of resin per sample were proportioned, mixed, and in the case of copolymers, light activated (40 s irradiation; LED Ultrablue IS) prior to testing. In both tests, samples were scanned from -60 to 200 $^{\circ}\text{C}$ under a nitrogen atmosphere. The T_g was determined from the mid-point in the curve, as measured from the extensions of the pre- and post- transition baselines^{10,14}.

2.5. Rheological measurements

Viscosity (η) of the resins as a function of shear rate and the effect of temperature on complex viscosity (η^*) were performed by a dynamic oscillatory rheometer (AR1000-N rheometer, TA Instruments, New Castle, DE, USA) equipped with a stainless steel cone/plate geometry (2 $^{\circ}$ cone angle/20 mm diameter; gap 0.69 μm) and strain amplitude set at 1% (25 $^{\circ}\text{C}$). Each comonomer was proportioned and mixed prior to testing. The frequency sweep test was completed over a range of 0.1-100 rad/s. To evaluate the effect of temperature on η^* , measurements were taken as the temperature was increased from 25 to 40 $^{\circ}\text{C}$ at intervals of 1 $^{\circ}\text{C}$ at a frequency of 1.0 Hz. Viscosity was measured at the shear rate of 5×10^{-4} to 10 s^{-1} (shear stress of 0.05 to 500 Pa) at 25 $^{\circ}\text{C}$.

2.6. Microhardness measurements (H)

An H tester (VMHT MOT, Leica Microsystems Wetzlar GmbH, Germany) with Knoop diamond indenter was used under a 5 gf load for 15 seconds. The test was performed for dry and wet disk-shaped (1 mm thick \times 5 mm in diameter) specimens ($n = 5$). Wet specimens were tested after 7 days storage in deionized water (37 $^{\circ}\text{C}$). The Knoop hardness number was determined by the arithmetic mean of five indentations randomly performed for each specimen and group. H changes were obtained for each group by the percentage difference between baseline (dry) and final (wet) means¹¹.

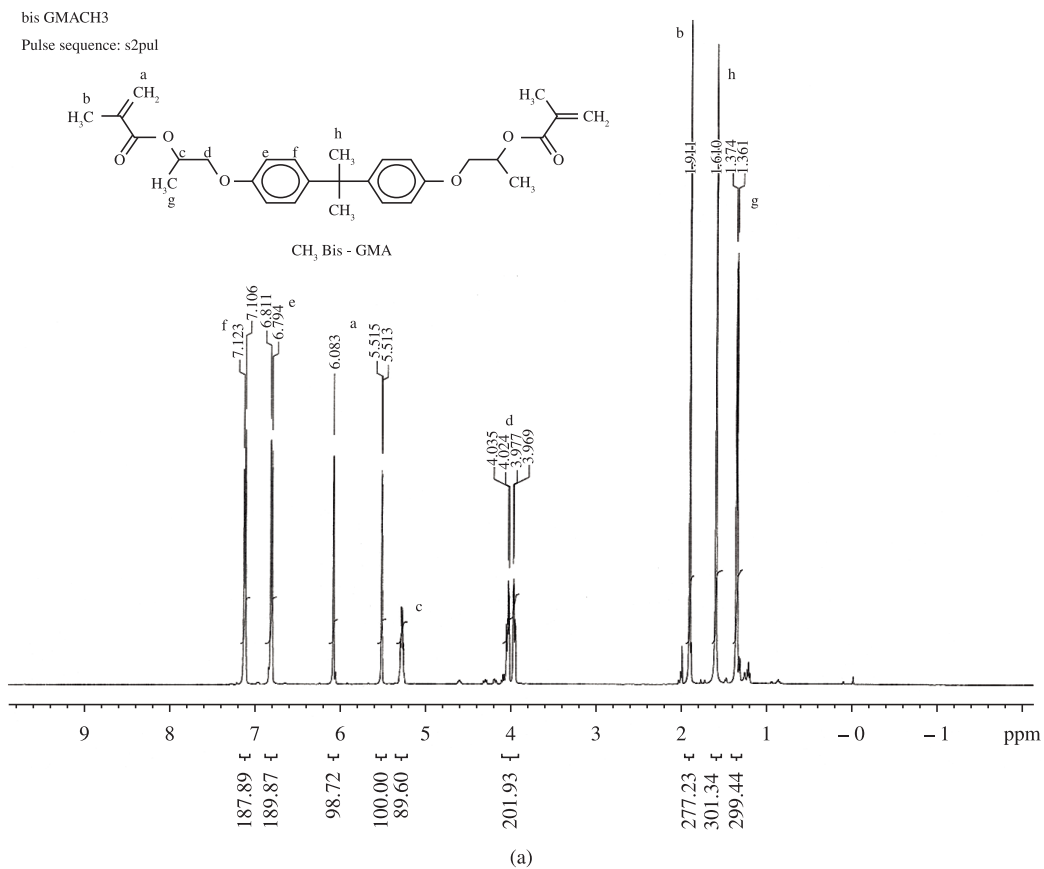
2.7. Statistical analysis

The %DC and H (dry, wet and %change) data were analyzed by one-way ANOVA followed by Tukey-Kramer post hoc test. Differences between H in dry and wet condition were analyzed by Student's t-test. Significance level was set at 0.05.

3. Results

Mean %DC values, T_g of comonomers and copolymers are given in Table 1. A gradual increase in %DC from G0 to G24 was noted. G24 had a significantly higher degree of conversion than all other evaluated groups ($p < 0.001$). The %DC of G16 also differed statistically from G0 and G2. Inclusion of propionaldehyde in comonomers resulted in a reduction of T_g values as the mol% additive increased. Conversely, no remarkable variation was seen in the copolymer T_g s.

Figures 3a-c show representative rheological curves of the evaluated comonomers. All resins presented Newtonian behavior of viscosity (Figure 3a), which decreased linearly with increased temperature (Figure 3b). The η^* decreased sigmoidally as the additive ratio increased (Figure 3c). G24



bis GMACH3
in COCl₃ 25C
13C 1d
nt = 160
Pulse sequence: s2pul

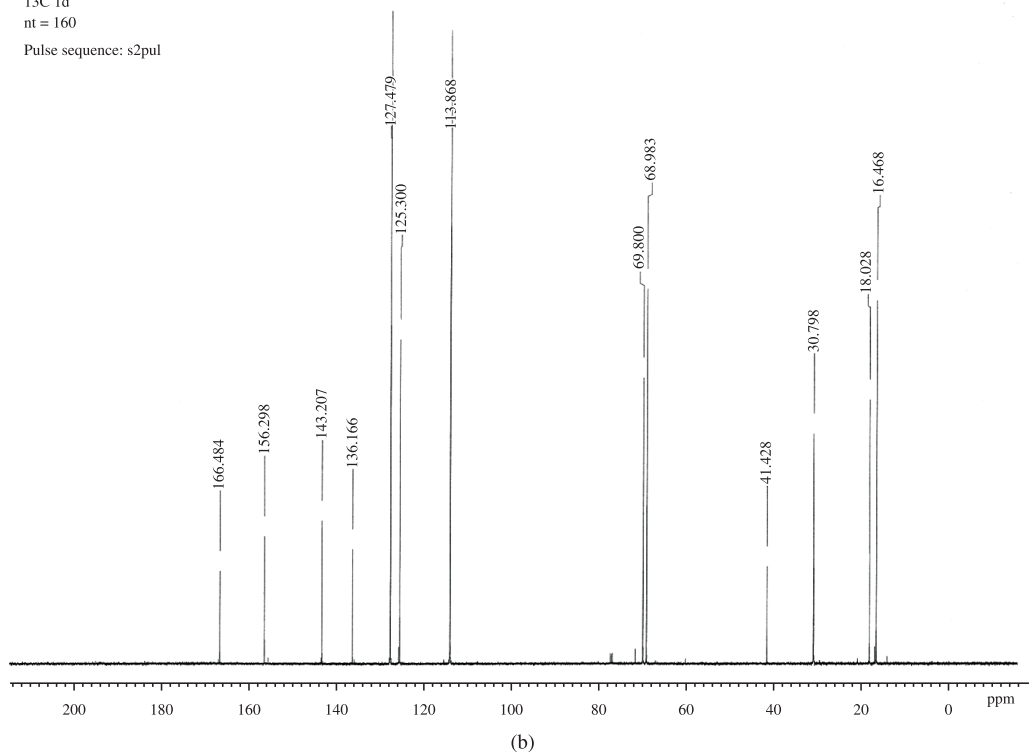


Figure 2. a) ¹H NMR spectrum of CH₃bis-GMA: the lower case letters correspond to the structures shown in the molecular structure; and b) ¹³C NMR spectrum for CH₃bis-GMA.

Table 1. Mean degree of conversion (%DC), comonomer and copolymer T_g values.

Groups	%DC (s.d.)	T_g (°C)	
		Comonomers	Copolymers
G0	38.0 (2.6) ^a	-0.4	48
G2	38.6 (3.0) ^a	-5.4	48
G8	40.0 (1.7) ^{a,b}	-5.4	49
G16	44.3 (1.5) ^b	-6.5	49
G24	53.3 (1.5) ^c	-7.0	50

ANOVA and Tukey-Kramer, $\alpha = 0.05$; s.d.: standard deviation; same letters indicate no statistical difference within same column.

had the lowest η^* (Table 2). Mean H values are shown in Table 2. A gradual increase in H values from G0 to G24 was also noted. G24 showed a significant difference ($p < 0.0001$) when compared with the other groups for either dry or wet conditions. None of the groups had significant changes in H from the dry to wet condition ($p > 0.05$). G0 had the highest H change percentage ($p < 0.05$), whereas G2 to G24 did not differ statistically from each other.

4. Discussion

The present findings revealed that the incorporation of propionaldehyde into the experimental resins gradually increased %DC as the mol% of the additive increased (Table 1). These results are in agreement with a previous study that reported increase in the conversion of comonomers based on bis-GMA/TEGDMA containing additive², which was significant at higher ratios (24 to 32 mol%). With regard to the bis-GMA/ $\text{CH}_3\text{bis-GMA}$ system, G16 differed significantly from G0 and G2, and G24 differed from all groups. According to Peutzfeldt (1997)¹⁵, propanal acts on resin conversion mainly by the chain transfer mechanism. The reaction would turn the transfer agents into free radicals. Due to their small size, they are able to react with double bonds in a growing polymer by hydrogen abstraction, which otherwise would not have reacted¹².

Assessment of comonomer T_g s (Table 1) was considered important as it has been shown that aromatic methacrylates with low T_g and viscosity values exhibit higher degrees of conversion¹⁶. With the addition of propanal, the bis-GMA/ $\text{CH}_3\text{bis-GMA}$ system presented a decrease in comonomer T_g s as the ratio of additive increased. Resins with lower T_g s also tend to reach vitrification at a higher extent of conversion¹⁰. For instance, among the evaluated groups, G24 exhibited the largest slot in T_g values between comonomer and copolymer (-7 to 50 °C) and the highest %DC (53.3), followed by G16 (-6.5 to 49 °C/%DC = 44.3). On the other hand, copolymer T_g s were very similar, indicating that at ambient temperature, vitrification during polymerization of the samples tended to limit complete conversion¹⁴. It is also worth mentioning that since the reaction involved in this process is a free radical reaction, even at low conversion rates (i.e., group G0) the polymer attained a sufficiently high molecular mass in which the T_g value remained stable and independent of the %DC.

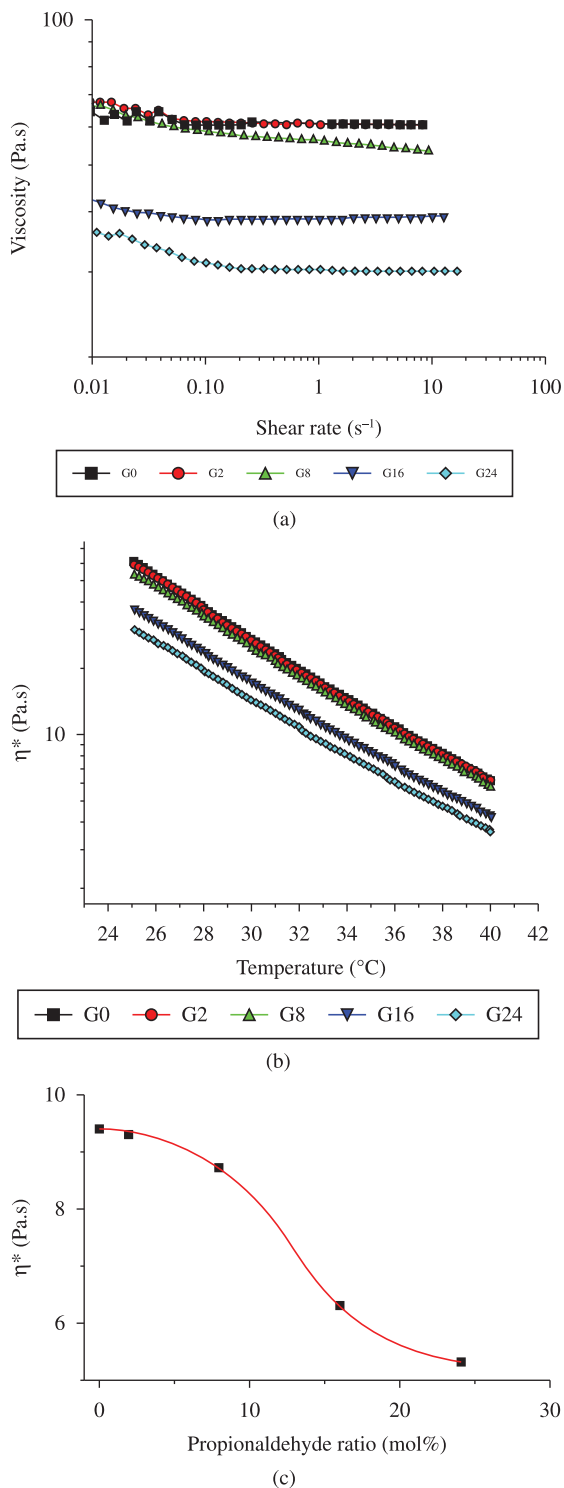


Figure 3. a) Viscosity as a function of shear rate; b) Complex viscosity as a function of temperature; and c) Complex viscosity as a function of mol% propanal.

It has been reported that the viscosity of propionaldehyde is 3×10^{-5} Pa.s and its incorporation into comonomers significantly lowers the viscosity of $\text{CH}_3\text{bis-GMA}$ -based resins¹⁰. Thus, alternatively to the chain transfer reactions,

Table 2. Complex viscosity (η^*), Knoop Hardness Number (KHN), and hardness change in experimental resins.

Groups	η^* (Pa.s) 37 °C	KNH (s.d.) Dry	KNH (s.d.) Wet	KNH (s.d.) Change (%)
G0	9.41	13.3 (1.2) ^{Ad}	12.6 (0.8) ^{Af}	9.18 (3.4) ⁱ
G2	9.28	14.0 (0.7) ^{Bd}	13.3 (0.6) ^{Bfg}	4.80 (2.6) ^{ji}
G8	8.72	14.2 (1.0) ^{Cd}	14.0 (0.7) ^{Cg}	2.21 (1.6) ^j
G16	6.31	14.6 (0.6) ^{Dd}	14.1 (0.3) ^{Dg}	3.86 (2.7) ^j
G24	5.33	17.2 (0.9) ^{Ee}	16.5 (0.8) ^{EH}	4.26 (1.7) ^j

ANOVA and Tukey-Kramer, $\alpha = 0.05$; s.d.: standard deviation; same lower case letters indicate no statistical difference within same column. Student's t-test, $\alpha = 0.05$: same upper case letters indicate no statistical difference within same line.

the sigmoidal decrease observed in comonomer viscosities (Table 2, Figure 3c) due to the presence of additive is likely to be the main contributory factor to their increased conversions. The sigmoidal curve describes phenomena in which very little change is apparent as a variable response (0 and 2 mol% propanal), until a threshold that marks the onset of dramatic change is reached (from approximately 8 to 16 mol% propanal) until a new stable state is reached. This reduced viscosity would delay the formation of cross-linked networks, thus increasing the collision and diffusion of newly formed free radicals. This enhanced mobility of reactive species also delays the auto-acceleration effect usually seen in bulk polymerization, facilitating more reaction between free radicals and double bonds, leading to increased conversion.

Moreover, all evaluated comonomers presented Newtonian behavior (Figure 3a) of η , i.e., relationship between the shear stress and strain rate was linear therefore the constant of proportionality = coefficient of viscosity. Differently from resin composites, which usually present pseudoplastic properties, the comonomer matrix usually displays Newtonian behavior in which their η is independent of the shear rate¹⁷. With regard to composites, as the shear rate increases the comonomer molecules and inorganic particles undergo a change in the direction of alignment resulting in reduced interlocking between filler particles, and between filler particles and organic matrix, decreasing η ¹⁸. Figure 3b shows that η^* linearly decreased with the increase in temperature. This is expected to occur as the temperature rise provides the systems with higher activation energy, therefore increasing the agitation and motion of chain segments, and lowering the comonomer η ¹⁹.

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An ongoing increase in H values for dry and wet samples from G0 to G24, and a concomitant decrease in H percentage change were observed (Table 2). There were no significant differences in H values between dry and wet samples. In the wet condition, G24, G16 and G8 differed statistically from G0. In the dry condition, G24 differed significantly from baseline following the same trend as for %DC in which G24 also presented the highest value and significance. Increased %DC is known to improve resin mechanical properties such as surface hardness²⁰. In the present study, group G24 indeed exhibited the significantly highest changes in the evaluated properties. However, G8 and specially G16 also exhibited differences for some properties (%DC, H wet, H change) when compared with G0, falling within the range of the viscosity change curve. Therefore, future studies should assess the mechanical properties of G8 (8 mol% propanal) and G16 (16 mol% propanal) as well as the biocompatibility of these experimental resins.

5. Conclusion

Based on the foregoing experiments on the influence of different propanal ratios on bis-GMA/CH₃bis-GMA experimental resins, the following conclusions were drawn:

- Incorporation of either 16 or 24 mol% of propionaldehyde significantly increased comonomer degree of conversion;
- The group with 24 mol% additive had the lowest comonomer T_g , whereas no remarkable variation was noted in copolymer T_g s;
- Increased propionaldehyde ratio led to lower comonomer viscosity values. All resins presented Newtonian behavior of viscosity, which linearly decreased with increased temperature;
- In the dry condition, the group with 24 mol% additive had the highest microhardness value. In the wet condition, the groups with 8, 16, and 24 mol% propionaldehyde had significantly increased microhardness values.

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