Effect ofCamphorquinone with 2, 2-Bis-[4-(2-hydroxy-3-methacryloxyprop-1-oxy) phenyl]propane in dental coating

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Abstract: Several formulations were prepared with the prepolymer, 2, 2-bis-[4-(2-hydroxy-3-methacryloxy prop-1-oxy) phenyl] propane in combination with the diluent, tri (ethylene glycol) dimethacrylate, the photoinitiator, camphoroquinone and the coinitiator, 2-(diethylamino) ethyl methacrylate. Thin polymer films were obtained by coating the formulated solutions on the thin glass plates and then cured under visible light radiation. The degree of conversion and rate of polymerization of the irradiated photopolymer samples were determined by Fourier Transform Infrared Spectra. The aim of the work is to determine the parameters such as the rate of polymerization, activation energy, enthalpy of activation, the entropy of activation, and Gibbs free energy of activation by using various concentrations of the photoinitiating system, camphoroquinone/2-(diethylamino) ethyl methacrylate and tri (ethyleneglycol) dimethacrylate at the various temperature of 30, 40, 50, 60 and 70°C respectively. The results have shown that degree of conversion increases with increase in camphoroquinone concentration in all temperatures.

Keywords: Visible light radiation, polymer films, Fourier Transform Infrared spectra, degree of conversion, rate of polymerization, effect of temperature.

1. Introduction

A numerous visible light curable polymeric composites are now routinely used as filling materials for dental restorations[1-2]. These materials are based on difunctional methacrylate monomers and prepolymers along with silane-coated inorganic fillers. The major feature of the composites are the use of visible blue light (420-500 nm) for activating photopolymerization in a tooth cavity. The polymeric dental composite generally consists of a multifunctional methacrylate prepolymer, a dimethacrylate diluent, a photoinitiating system and a large quantity of inorganic fillers[3-6]. The polymeric composite is then photopolymerized intra-orally by visible light to form network structures with adequate shaping[7]. The polymeric dental restorative composites require such important properties and aesthetics close matching with those of tooth structure along with acceptable bio-compatibility[8].

The prepolymer, 2,2-bis-[4-(2-hydroxy-3-methacryloxyprop-1-oxy)phenyl]propane(BISGMA), a multifunctional methacrylate was used as a major component in dental composite material. The rigid aromatic backbone structure of BISGMA based on bisphenol A (BPA) provides a superior toughness and desirable properties for final applications[1, 9]. The high molecular weight prepolymer, BISGMA is extremely viscous at room temperature. The diluents were used to attain high filler levels and to produce a paste of clinically usable consistencies. TEGDMA is used as diluent on to reduce the viscosity of BISGMA significantly[10]. The effect of dilution, temperature and structural modification of prepolymer on the kinetics of thermal polymerization of dental composite-matrix resins were studied by several authors[11-17].

In the present work is to find out the thermodynamic parameters, enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$) and Gibbs free energy of activation ($\Delta G^{\#}$). In this article, the prepolymer,BISGMA is mixed with the diluent, TEGDMA at various temperatures to determine the various thermodynamic parameters, $\Delta H^{\#}$, $\Delta S^{\#}$, and $\Delta G^{\#}$, which helps to know the kinetics and mechanism of reaction[18-21].

2. Experimental

2.1 Materials

The diluent, tri(ethylene glycol)dimethacrylate (TEGDMA), prepolymer, 2,2-bis-[4-(2-hydroxy-3-methacryloxyprpoxy)phenyl]propane (BISGMA), photoinitiator, camphoroquinone (CQ) and coinitiator, 2-(dimethylamino)ethylmethacrylate (DMAEMA) were purchased from Aldrich (USA) and used without further purification.

2.2. Photocrosslinking

The photocurable formulation containing camphorquinone(2.5%) and dimethylaminoethyl methacrylate (2.5%) as a photoinitiating system were dissolved in a mixture of BISGMA (70%) and TEGDMA (30%) andwere coated on glass plate. The coated samples were irradiatedusing the visible light with an intensity of 120W/cm^2 at various temperature in the temperature range from 30 to 70°C. Simultaneously infrared spectra ofrecorded. Absorbance of the methacrylate C=C at 1638 cm^{-1} was measured before and after exposure. The absorption band of aromatic rings at 1609 cm^{-1} was used as an internal standard. The ratio of absorbanceintensities of two bands before and after photopolymerization was compared to determine the degree ofconversion of the methacrylate C=C bonds. The effect of temperature, photoinitiator concentration and degreeof conversion of the methacrylate were investigated.

3. Results and Discussion

3.1 Photocuring by visible light

Photocurable formulations comprising a prepolymer with a mixture of CQ and DMAEMA as photoinitiating system were irradiated using visible light (420-500 nm) and their photoactivities were investigated by FTIR spectra analysis. The absorption band at 1638 Cm^{-1} representing the methacrylate C=C stretching vibration of the multimethcaylates gradually decreases with increasing irradiation time. The absorption band at 1609 Cm^{-1} originating from the aromatic ring was used as an internal standard for calculating the photopolymerization.The ratio of the calculated areas of the two absorption bands before and after exposure were compared to determine the degree of conversion of the methacrylate C=C bonds. The photopolymerization were carried out at different time intervals. The spectra were taken simultaneously after curing.

3.2 Degrees of conversion

The degree of conversion, DC (%) was calculated from the following Equation[20, 22].

$$DC(\%) = \left\{ 1 - \frac{\left(\dfrac{A_{methacrylate\ C=C}}{} A_{aromatic} \right) \text{crosslinked polymer}}{\left(\dfrac{A_{methacrylate\ C=C}}{A_{aromatic}} \right) \text{prepolymer}} \right\} \times 100$$

The decrease in the intensity of methacrylate C=C absorbance ($A_{metacrylate}$) at 1635-1640 Cm^{-1} was monitored. The phenyl absorbance ($A_{aromatic}$) at 1605-1610 Cm^{-1} used as the internal standard. Figures 1 and 2 shows the influence photoinitiator system and temperature in DC (%) respectively. The result shows that the DC (%) increases with increase in photoinitiator system concentration and temperature is due to increase in formation and reactivity of free radicals with methacrylate prepolymer[20].
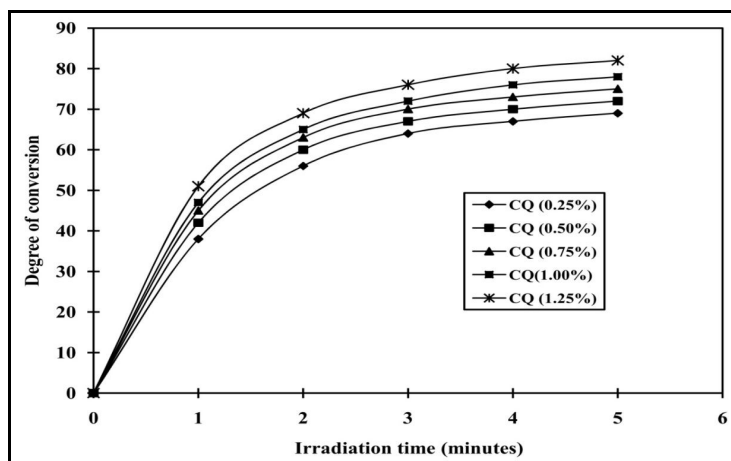
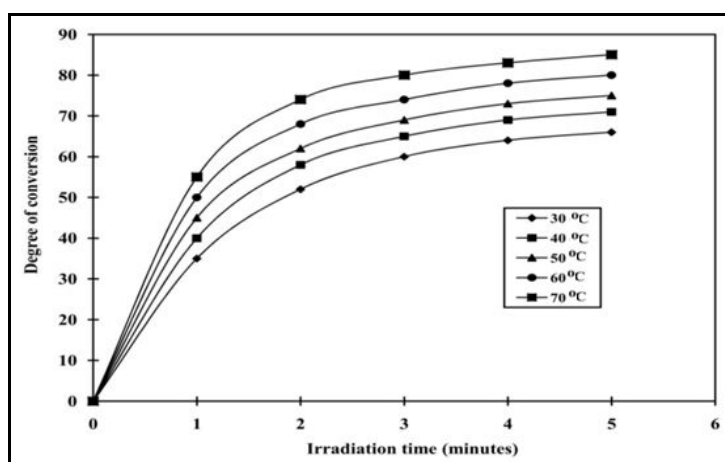**Figure 1. Influence of photoinitiator system concentration on DC (%)**

Figure 2. Influence of temperature on DC (%)
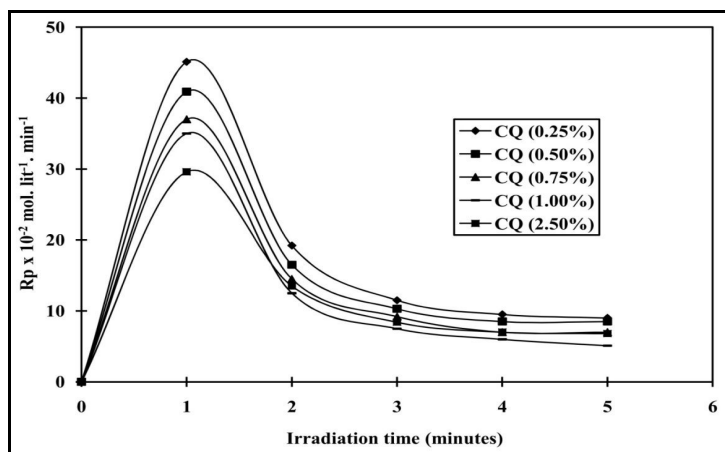
3.2   Rate of polymerization

Figure 3. Influence of photoinitiator system concentration on Rp

The rate of polymerization (Rp) was calculated using by the following Equation[20, 23].

$$R_p = [M_0] \times \left[\frac{(A_{810})t_1 - (A_{810})t_2}{(A_{810})t_0 \,(t_2 - t_1)} \right]$$

Where, $[M_0]$ is the diluent concentration before irradiation, $(A_{810})t_0$, $(A_{810})t_1$ and $(A_{810})t_2$ represent the

absorption due to >C=C< double bond before and exposure during t_1 and t_2 time, respectively. The influence photoinitiator system and temperature on Rp are shown in Figure 3 and 4 respectively. The rate of polymerization depends on the bond conversion. An increasing photoinitiator concentration and temperature Rp value increases due to increase in degree of conversion[16].
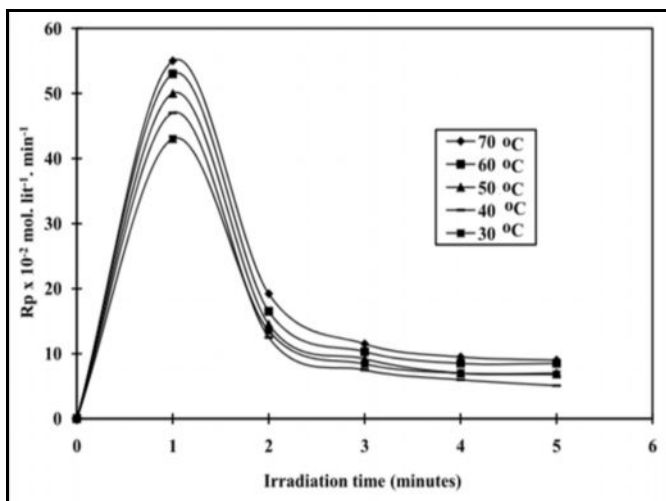

Figure 4. Influence of temperature on Rp

3.4   Rate Constant

The absorbance is related to the concentration by the following Equation (2). Assuming it is a second order reaction, we can use the nth order reaction kinetics (Equation), when the stoichiometric ratio is used[24].

$$\frac{A_0}{A_t} = \frac{C_0}{C_t} = \frac{1}{1-p} = k.t + b \qquad (2)$$

Where, A_0, A_t, C_o and C_t are initial absorbance, absorbance at 't' time, initial concentration and concentration at 't' time respectively. Figure 5 shows the relationship between 1/ (1-p) and t. The rate constant (k) is calculated from the slope of the plot of ln 1/(1-p) vs t^{24}. The rate constant value at various temperatures are given in Table 1.
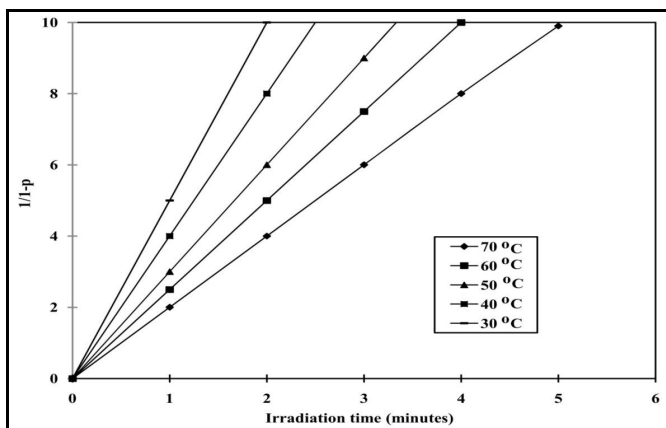

Figure 5. The relationship between 1/(1-p) and t

Table 1.Rate constant for the photopolymerization of BISGMA with TEGDMA

S. No	Temperature (^{o}C)	k (x 10^2 lit. mol^{-1}. min^{-1})
1	30	0.52
2	40	0.61
3	50	0.68
4	60	0.82
5	70	1.13

3.3   Thermodynamic parameters

Thermodynamic parameter, activation energy (Ea), enthalpy of activation (**Δ** H), and entropy of activation (**Δs**) can be calculated with the Arrhenius law (Equation 3) and the Eyring law (Equation 4)[24]:

$$k = \left(\frac{-Ea}{2.303\,RT}\right) + A \tag{3}$$
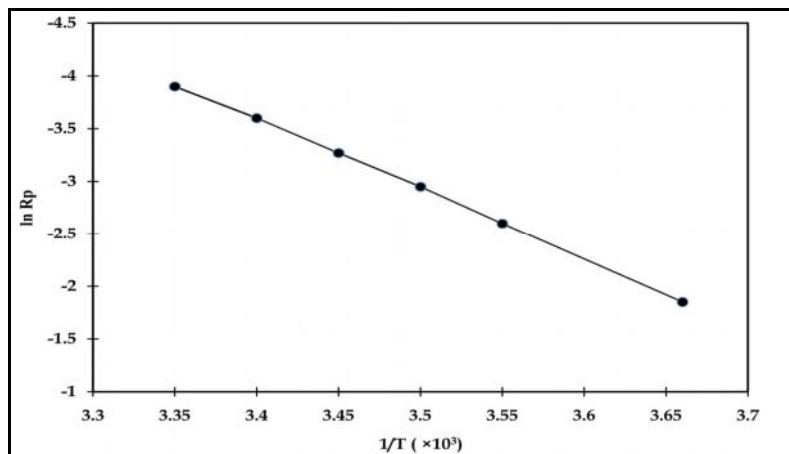
$$lnk = \left(\frac{-Ea}{RT}\right) + ln\,A \tag{4}$$

Figure 5. Arrhenius plot of lnk vs 1/T (x 10³)

$$\Delta H = Ea - RT \tag{5}$$

$$ln\,k/T = -\ [\Delta H]^{\dagger}\#/(RT) + [\Delta S]^{\dagger}\#/R + ln\,R/Nh \tag{6}$$

Where R is the gas constant (R = 8.314 J.mol⁻¹.K⁻¹), N is Avogadro's constant (N = 6.02 x 10²³), and h is planck's constant (h = 6.62 x 10⁻³⁴ J.s). The values of Ea,,,are given in Table 2. The negative value of the entropy of activation suggested that the transition state formed was considered as rigid and complex resulting in a reduction in the degrees of freedom of the molecule,

Table. 2. Apparent activation energy (Ea) and thermodynamic parameters of the prepolymer, TEGDMA and the diluent, TEFDMA in the presence of the photoinitiating system, CQ and DMAMA.

S. No	Ea $J.mol^{-1}$	$J.mol^{-1}$	$J.K^{-1}.mol^{-1}$	$J^{-1}.K^{-1}.mol^{-1}$
1	8. 2065	- 2560.608	-261. 9602	76.3663

4. Conclusion

The influence of temperature of the photopolymerization of BISGMA and TEGDMA was studied by FTIR spectroscopy. The result shows that the Rpincreases with increasing temperature is due to the drop in viscosity of the system. The degree of conversion increases with increases in camphoroquinone concentration. The thermodynamic parameters were calculated from the plot of log Rpvs 1/T. The activation energy Ea, enthalpy of activation,, entropyof activation,, were found to be 8.2065 J..mol⁻¹,-2560.608 J. mol⁻¹ --261. 9602 J. K⁻¹mol⁻¹, respectively. Further investigation in this study will be carried out in order to predict the mechanism of the reaction.

5. Acknowledgement

6. References

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