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## Simulation of dental resin monomer mixtures

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**Abstract.** In this work, molecular dynamics simulations of Bis-GMA/TEGDMA resin systems were carried out to investigate the rheological and dynamic properties of dental materials. The effect of the resin diluent monomer TEGDMA content  $r_d$  on the viscosity and diffusion behaviors of the resin monomer mixtures was studied as well. The viscosity of the resin monomer mixture was calculated using the Green-Kubo method. It was shown that the mixture viscosity decreases apparently with  $r_d$ , showing good agreements with experiments. Moreover, the diffusion coefficient of the Bis-GMA/TEGDMA monomer mixtures was evaluated, and it rises from  $0.273 \times 10^{-11}$  m/s to  $9.710 \times 10^{-11}$  m/s as  $r_d$  increases from 0 to 100 wt%. In particular, as  $r_d$  is < 50 wt%, the diffusion dynamics of the resin monomer system was significantly suppressed due to the rigid benzene rings and hydroxyl groups in Bis-GMA. On the other hand, the diffusion coefficient of the materials increases rapidly with  $r_d$  at  $r_d > 50$  wt%. The findings in this work are believed to improve the atomic/molecular scale understanding of the rheological and dynamic performances of Bis-GMA/TEGDMA dental materials.

### 1. Introduction

In the state-of-the-art restorative dentistry, resin composites are becoming increasingly important and prevalent as compared to silver amalgams ascribing to their superior mechanical properties, excellent esthetics, and good biocompatibility [1-2]. Dental resin composites usually consist of a continuous polymeric matrix, a photoinitiator system, and nano/micron dispersed inorganic fillers. The widely used matrix contains the bisphenol- $\alpha$ -glycidyl methacrylate (Bis-GMA) and triethylene glycol dimethacrylate (TEGDMA) monomers. In the resin matrix, Bis-GMA monomer reduces the volume shrinkage, while TEGDMA monomer has considerable mobility and improves degree of conversion [3-4].

Dental resin composites are usually incorporated with inorganic fillers by varying filler compositions, content and size. The fillers could improve mechanical strength, and weaken water sorption and thermal expansion. However, the filler loading is limited by the dental rheological properties [5]. For example, the resin matrix viscosity, as a measure of the resistance opposed by the material itself to an imposed flow motion, influences the maximum filler content. It is reported that a lower viscosity matrix can



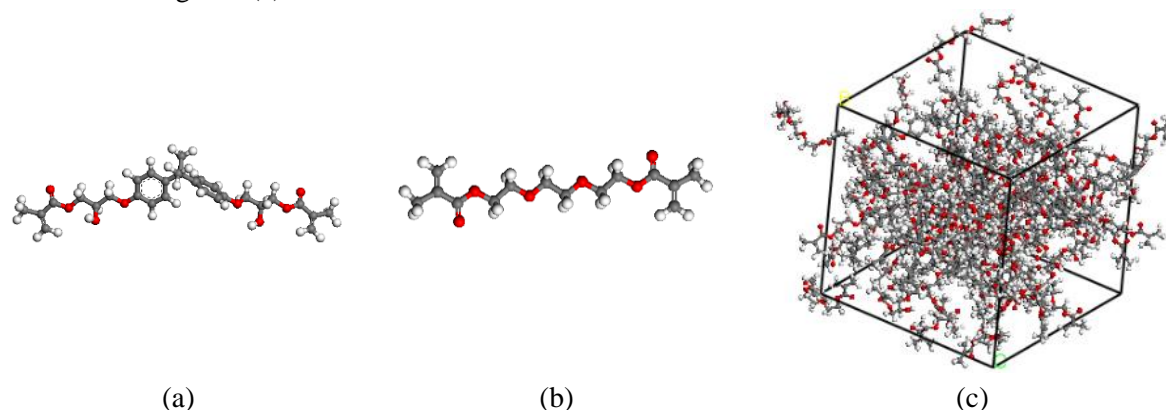
accept more fillers at constant plasticity [5]. Moreover, the matrix viscosity also affects the handling characteristics of the dental resin composite, i.e., its flowability, ease of placement and shaping on the restored site, and adherence to the tooth tissues [6]. Besides, it is well established that the dental resin matrix could absorb liquids from saliva and food, and this in return affects clinical performance [7]. Therefore, it is crucial to explore dynamic features and rheological performance of the resin models to produce restorative materials with better handling and clinical behaviors.

Meanwhile, computational simulations are widely adopted in examining features and behaviors in physics, chemistry, material, and biological science. Among them, molecular dynamics (MD) method characterizes organic-inorganic hybrid materials from an atomic/molecular perspective quite well [8]. As such, we employ an MD simulation method to study the dynamic and rheological features of Bis-GMA/TEGDMA resin models. It is expected to increase our fundamental understanding of the structure and performance of dental materials.

## 2. Methods

### 2.1. Molecular Model

In the MD simulations, we created Bis-GMA monomer and TEGDMA monomer via Materials Studio, as shown in Figures 1(a) and (b). The Bis-GMA monomer has a symmetrical structure with two rigid benzene rings and two methacrylate moieties, giving rise to high viscosity and the hydrophilic nature of the resin composites. The diluent TEGDMA is incorporated into different proportions of Bis-GMA to tune the viscosity of the resulting resin monomer blends. Six different mixtures of Bis-GMA and TEGDMA with varying TEGDMA mass ratios  $r_m$ , that is, 0, 30, 50, 60, 80 and 100 wt%, were modeled. According to the content of the diluent agent, the systems were designated as S0, S30, S50, S60, S80, and S100, respectively. The typical equilibrated atomic structure of the mixture (i.e.,  $r_m = 30$  wt%) is also shown in figure 1(c).



**Figure 1.** (a) Bis-GMA monomer model, (b) TEGDMA monomer model, and (c) the final snapshot of the Bis-GMA/TEGDMA monomer mixtures with  $r_m = 30\%$ .

### 2.2. MD Simulation Details

We chose COMPASS II force field [9] to describe the interactions between atoms and molecules. The Bis-GMA monomer and TEGDMA monomer were at first optimized using the steepest descent method during energy minimization. Then, Bis-GMA and/or TEGDMA molecules were randomly placed in a cubic domain to represent the monomer mixture with a given  $r_m$ . For each mixture, the number of atoms was around 2500 ~ 4000 to improve computational efficiency. The systems were relaxed at 296 K and 1 bar for a period of 1 ns to obtain reasonable densities as compared with experiments, as illustrated in table 1.

Then, the resin blend systems were further equilibrated at 296 K for 10 ns. The system temperature was retained constant using the Nosé-Hoover-Langevin thermostat [10], and the pressure was coupled

to the Berendsen barostat [11]. The long-range electrostatic interactions were computed with the Ewald summation method [12].

**Table 1.** Comparison of density (g/cm<sup>3</sup>) of the Bis-GMA/TEGDMA mixtures using MD simulations and experiments.

Bis-GMA/TEGDMA monomer mixture	Density	
	Simulation	Experiment [13-14]
S0	1.147	1.151
S30	1.133	1.142
S50	1.117	1.121
S60	1.100	1.113
S80	1.082	1.096
S100	1.072	1.072

### 3. Results and Discussions

#### 3.1. Viscosity

The shear viscosity of the Bis-GMA/TEGDMA mixtures was evaluated according to the Green-Kubo (GK) expression as [15]

$$\eta = \frac{V}{3K_B T} \int_0^\infty \langle \sum P_{xy}(t) P_{xy}(0) \rangle dt \quad (1)$$

where  $\eta$  is the shear viscosity,  $V$  is the cell volume,  $T$  is the ambient temperature,  $K_B$  is the Boltzmann constant, and  $P_{xy}$  represents the  $xy$  component of the stress, respectively.

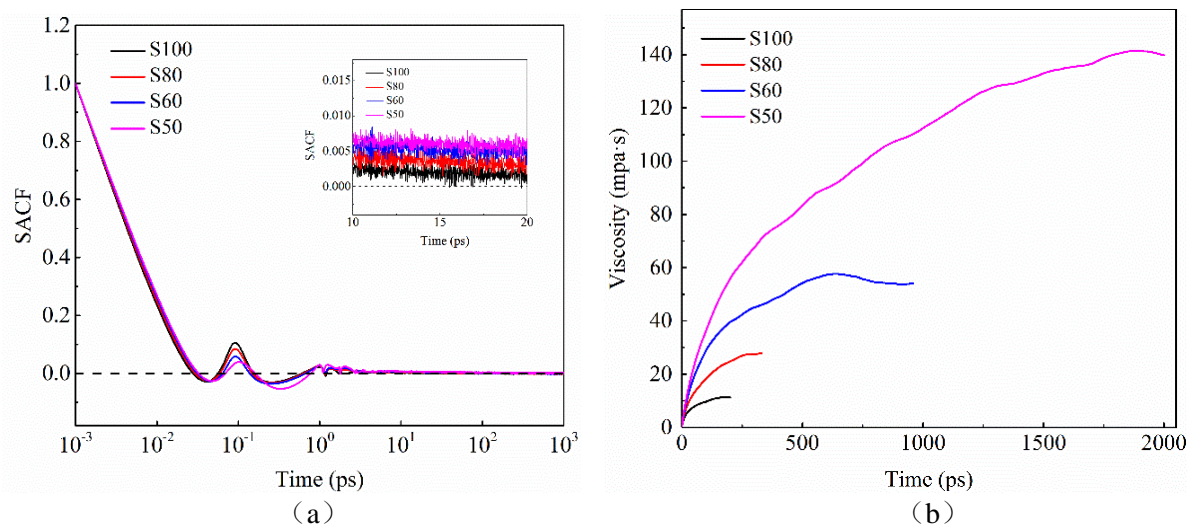
It is known that the angle brackets in equation (1) indicates an ensemble average. In the GK computation, it requires deliberate selection of some quantities including the MD simulation time,  $t_D$ , the time length over which the stress autocorrelation function (SACF) is calculated,  $t_w$ , and the time interval between time windows,  $t_s$ . Generally,  $t_D$  is in order of a few nanoseconds and  $t_s$  is some femtoseconds for systems with particles ranging from 258 to 25,800 [16]. The time window  $t_w$  should be large sufficiently to observe the SACF decay, and it may range from a few to hundreds of picoseconds. However, these relatively small values of  $t_w$  were chosen mostly when the shear viscosities of the systems of interest are only about a few mPa·s. If target systems with ultrahigh viscosities like Bis-GMA/TEGDMA mixtures are modeled, a much larger  $t_w$  is required to obtain the computation accuracy of Equation (1). In this regard, we calculated the shear viscosity of the mixtures using a rather large  $t_w$  ( $t_w = 1$  ns) and the results are shown in figure 2.

Figure 2(a) shows the normalized SACF as a function of  $t_w$  at various TEGDMA mass ratios  $r_m$ . For all the systems, the SACF fluctuates and decays quickly towards zero. More importantly, the SACF curves approach to zero after 10 ps, indicating that the selection of  $t_w$  ( $t_w \geq 10$  ps) might be appropriate in cutting off the contribution of SACF at longer integration time in equation (1). However, if we examine the integrals of the shear viscosities with  $t_w$  in the insets of figure 2(a), the viscosities continue to increase with  $t_w$ , and no acceptable plateau was observed. This implies that the contribution of SACF after 10 ps should not be neglected and a more massive effective  $t_w$  is required. In this work, we took 0.20, 0.33, 0.96, and 2 ns as the effective  $t_w$  where the plateau of the shear viscosity curves begin for the mixtures with various TEGDMA mass ratios  $r_m$  respectively, as seen in figure 2(b). The calculated shear viscosities and the experimental values are also listed in table 2. As expected, the shear viscosity decreases with  $r_m$  from both the simulations and experiments. For S80 and S100 samples, the simulated viscosities agree well with the experimental observations. While for S50 and S60, the discrepancy between them increases significantly. This is probably due to two reasons. Firstly, the simulation time  $t_D$  is not sufficiently long at high values of  $t_w$  (i.e., around 1 ~ 2 ns) to provide enough sampling when calculating SACF. Secondly, the SACF contribution beyond  $t_w$  is still non-negligible, and it should be

taken into consideration. While in the case of low  $r_m$  ( $\leq 50$  wt%), the lack of computational power and longer simulation time make it difficult to verify the detailed viscosity convergence to a reasonable accuracy. However, the results indeed demonstrated the precise quantification of viscosity increment as  $r_m$  decreases.

**Table 2.** Comparison of shear viscosity (mPa·s) of the Bis-GMA/TEGDMA mixtures using the MD simulations and experiments.

Bis-GMA/TEGDMA monomer mixture	Viscosity	
	Simulation	Experiment [6]
S50	139.81	144
S60	54.21	66
S80	27.87	22
S100	11.27	7.7



**Figure 2.** (a) The normalized SACF as a function of  $t_w$  at various TEGDMA mass ratios  $r_m$  and (b) the effective  $t_w$  where the plateau of the shear viscosity curves begin for the mixtures with various TEGDMA mass ratios  $r_m$ .

### 3.2. Diffusion Coefficient

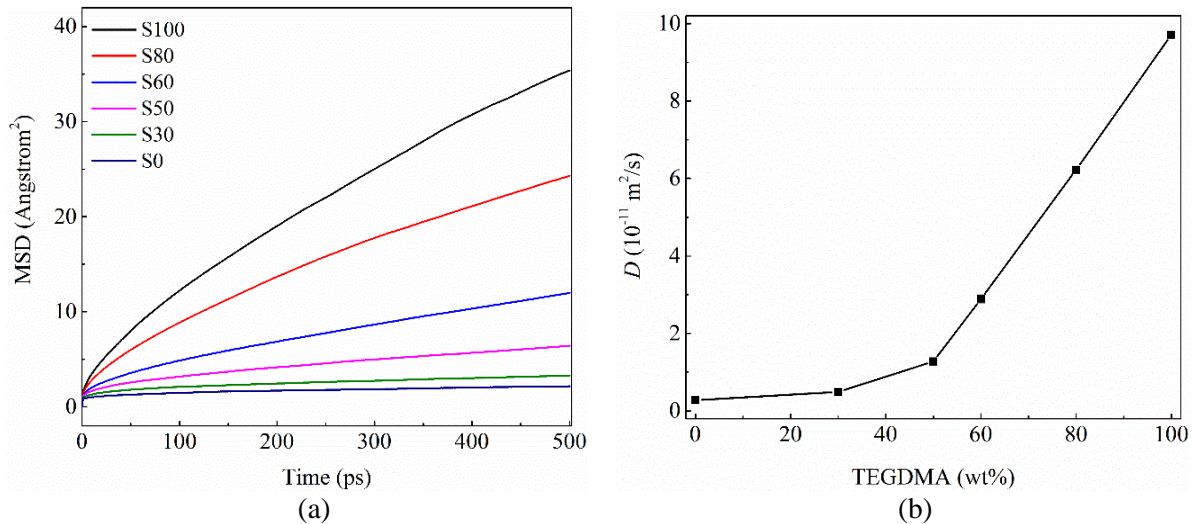
In addition to shear viscosity, the mixture dynamics was investigated by calculating diffusion coefficient  $D$  of the monomers, and it was computed using the Einstein relationship, as in [17]:

$$\langle \Delta r(t)^2 \rangle = \frac{1}{N} \sum_{i=1}^N [r_i(t) - r_i(0)]^2 \quad (2)$$

$$D = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle \Delta r(t)^2 \rangle \quad (3)$$

where  $\langle \Delta r(t)^2 \rangle$  is the mean square displacement (MSD) of  $N$  molecules. The diffusion coefficients of the monomer mixtures were calculated by directly fitting a straight line in the MSD plots from 150 to 400 ps in Figure 3(a). The diffusion coefficients rise from  $0.273 \times 10^{-11}$  m/s of S0 (pure Bis-GMA monomers) to  $9.710 \times 10^{-11}$  m/s of S100 (pure TEGDMA monomers), and more results were shown in Figure 3(b), where the curve might be divided into two straight lines intersected at 50 wt%. When  $r_m$  is  $< 50$  wt%, the diffusion coefficients of the mixtures are mainly dominated by the rigid Bis-GMA monomer, and the increment is quite small, due to the two stiff benzene rings and hydroxyl groups in

Bis-GMA. In contrast, the vise versa was an observer at  $r_m > 50$  wt% and the mixtures exhibit much higher mobility as the diluent agent content increases.



**Figure 3.** (a) The MSD of the Bis-GMA/TEGDMA mixtures and (b) the diffusion coefficient  $D$  at various  $r_m$ .

#### 4. Conclusions

In the present work, we carried out MD simulations to study the viscosity and diffusion coefficient of Bis-GMA/TEGDMA monomer mixtures. The viscosity of the mixtures was fundamentally calculated by the GK method. It was shown that the time window  $t_w$  plays an essential role in determining the computation accuracy of the viscosities and a large  $t_w$  should be adopted for systems of interest with high target viscosities. By choosing appropriate  $t_w$ , the simulated viscosities agree well with experimental observations. Moreover, the dynamic property of the monomer mixtures was quantified by calculating the monomer diffusion coefficients. It was found that the two rigid benzene rings and hydroxyl groups in Bis-GMA result in suppressed diffusion dynamics of the mixtures when the TEGDMA mass ratio  $r_m$  is  $< 50$  wt%. When  $r_m$  is  $> 50$  wt%, the diffusion coefficient of the materials increases rapidly as the diluent agent content increases. The findings in this work could enhance our fundamental understanding of the dynamics and rheological features of resin materials.

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