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A Study of Probe Characteristics on the Diffusion Process in Materials Containing Acryloxy and Acrylate Units

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Summary: We study the diffusion of an atomic probe in materials used in restorative dentistry. We rely on computer simulation and on a version of transition state theory to access the diffusion regimes of interest. We find that the calculated logD values are in good agreement with reported results in other glassy polymeric materials. We report the effect of atomic mass and probe radius on the diffusion process.

Keywords: molecular dynamics; molecular modeling; Monte Carlo simulation; noncrystalline polymers; structure-property relations

Introduction

We study the diffusion of an atomic probe in systems consisting of 2,2-bis[4-(2-methacryloxypropoxy)phenylene]propane (Bis-GMA), ethoxylated bisphenol-A dimethacrylate (EBPADM) and a mixture of Bis-GMA and triethylene glycol dimethacrylate (TEGDMA) (70%/30%) (See Figure 1). Bis-GMA is one of the most commonly used polymeric dental restorative materials. It is part of several polymeric composite resins currently used for tooth restoration. A major drawback of the polymeric composite resins is their overall lack of durability. The typical lifespan for posterior composite resins varies between 3 and 10 years; it is typically less than 5 years for large fillings.[1] This lack of durability is attributed to internally induced stresses in the material. Interaction with food, differences in thermal expansion and volume shrinkage during polymerization contribute to those stresses.

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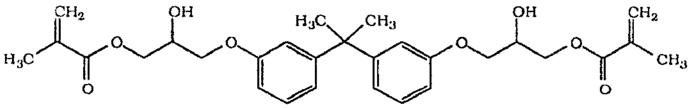
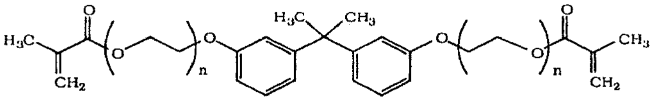
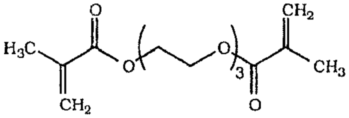


2,2-Bis[4-(2-methacryloxypropoxy)phenylene]propane



Ethoxylated bisphenol A dimethacrylate



Triethylene Glycol dimethacrylate

Figure 1. Chemical structure from top to bottom of Bis-GMA, EBPADM and TEGDMA.

We aim to understand the free volume and diffusion characteristics of some of the components of dental restoratives. Molecular dynamics may be used for evaluating diffusion coefficients D by monitoring the mean-squared displacement $\langle r^2 \rangle$ of the diffusing species as a function of time. The Einstein relation $D = \lim_{t \to \infty} \left\langle (r_t - r_0)^2 \right\rangle / 6t$, is known to hold in the diffusive regime. Here r_t denotes the position of the diffusing particle at time t and the angle brackets denote an average over an ensemble of systems. If the slope of a plot of $\langle r^2 \rangle = \langle (r_t - r_0)^2 \rangle$ with time is constant, the Einstein formula gives the diffusion coefficient of interest. The process of diffusion in rubbery and glassy polymers may be studied by using transition state theory, as originally formulated by Suter and co-workers.[2-5]

Methodology

Bis-GMA, EBPADM and TEGDMA, were built and minimized using MSI/Accelrys Insight version 2.3.7, Discover version 2.9.5 and Amorphous Cell version 7.0. All simulations were performed at 308 K. In addition to the molecules of interest, the density of the system, as well as the number of atoms to be used in a cell were used as input. Relying on the experimental density of the materials and choosing a number of atoms that insures no interchain interaction, around 2400 atoms (30 to 37 molecules), the average amorphous cell size is approximately 28-29 Å per side. Three to five different configurations of each cell were created to ensure reproducibility.

The refinement was performed on the built amorphous cell. An initial minimization of 200 steps was used to eliminate any unrealistic bond lengths or angles. A molecular dynamics run of 60,000 steps, 60 ps, was then performed. Densities for the systems were 1.133 g/cm^3 for the Bis-GMA system and 1.100 g/cm^3 for both the EBPADM and the Bis-GMA/TEGDMA mixed systems. The duration of this dynamics run affords standard deviations of the total energy of the system between 2 and 5% for each of the configurations. A final, 1500 step, minimization is then performed on the system, again to ensure all bond lengths and angles are correct. To validate the system, a cohesive energy density calculation was performed on the cells. The average of the cohesive energy density over the given number of configurations is studied. The system was considered valid if the cohesive energy densities from the two methods agreed within 10%.

After the cell was constructed, refined, and validated another molecular dynamics run was performed. This time a constant pressure dynamics run was performed with the value used for the pressure taken from the constant volume dynamics run, careful to confirm that the density of the system does not change after the constant pressure run has completed. With the constant pressure run complete, the free volume was studied by application of transition state theory.

For all results reported here a cell grid step of 0.5 Å is used. This grid step size was chosen based on computational considerations. Temperature was the temperature of the typical experimental setup and the cutoff distance was 8.0 Å, a reasonable number with respect to the 0.5 Å grid step size. The final input parameter was that of the smearing factor, a value between 0 and 1.

Results and Discussion

We adressed the question of how large a probe can be used and still have realistic computer simulation run times (less than the time incurred by performing the same experiment in the laboratory). To address this issue, the next largest probe, neon, with a radius of 2.78 Å and a mass of 20.183 amu was used. A trial run using neon as the probe in a Bis-GMA/TEGDMA mixture showed that the diffusion run for one configuration alone would have taken over three weeks to obtain diffusion coefficients in the true diffusion regime. Subsequently, a probe with 20% less mass and the same radius as neon was studied in the same resin system. Unfortunately, this probe also required simulation times much longer than a time that could be considered realistic. It was apparent from these simulations that, even with probes as small as neon, realistic simulation times could not be achieved. The focus of the probe size effect on diffusion turned then to using smaller probes that afford reduced simulation times.

The initial probe size used for the diffusion simulation was a He-like probe with a radius of 3.100 Å and a mass of 4 amu. The next probe to be studied was a He-like probe but with the smaller radius. It was decided to create larger probes moving up gradually in radius and mass. The mass was increased moderately due to its apparently large effect in simulation time as seen in the attempts to simulate neon diffusion. The choices for the probe sizes are listed in Table 1.

Table 1. Mass and corresponding radius of the four different sizes of probes used in this study.

Probe description	**Radius (Å)**	**Mass (amu)**
Probe (3100_4)	3.100	4.0
Probe (2556_4)	2.556	4.0
Probe (2828_6)	2.828	6.0
Probe (3100_8)	3.100	8.0

The results in Table 2 below are the values found by simulations for the different size probes in each of the different resin systems.

Table 2. LogD values (units of cm^2/s) for the four different probe sizes.

	3100_8	**2828_6**	**2556_4**	**3100_4**
Bis-GMA	-6.85	-6.71	-6.30	-6.70
Ethoxylated Bisphenol A Dimethacrylate	-5.85	-5.68	-5.36	-5.70
Bis-GMA/TEGDMA System	-6.09	-5.92	-5.58	-5.90

We see that for the same resin system logD decreases with increasing probe radius as expected. Values of logD also decrease with increasing probe mass, a reasonable outcome. We notice that the logD values for Bis-GMA are an order of magnitude smaller than those of the other two systems.

Conclusions

We have shown that logD values of an atomic probe in the true diffusion regime, for two of the systems studied here, are in the order of 10^{-6} cm^2/s. This is in satisfactory agreement with other glassy systems. LogD values for Bis-GMA are in the order of 10^{-7} cm^2/s. This is an order of magnitude smaller than expected. Future work will concentrate on identifying the reasons behind the difference in logD between Bis-GMA and the other two systems.[6] Additional effort will be directed in studying larger, and perhaps more representative, systems of Bis-GMA/TEGDMA.

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