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ORIGINAL RESEARCH ARTICLE

Molecular dynamic study of abrasive wear, viscosity and moduli of UDMA: A component of dental composite

M. Maurya[1], H. Somashekarappa[2,*], M. B. Nandaprakash[3], S. R. Kumaraswamy[4], K. Hemalatha[4], R. Somashekar[5]

[1] *Department of Public Health Dentistry JSS Dental College and Hospital, JSS Academy of Higher Education and Research, Mysuru 570015, Karnataka, India*

[2] *Department of Physics Yuvaraja's College, University of Mysore, Mysuru 570005, Karnataka, India*

[3] *Department of Studies and Research in Physics Karnataka State OpenUniversity, Mysuru 570006, Karnataka, India*

[4] *Department of Physics Maharani's Science College forWomen, Mysuru 570005, Karnataka, India*

[5] *Department of Physics and Materials Science University of Mysore, Mysuru 570006, Karnataka, India*

*** Corresponding author:** H. Somashekarappa, drhssappa@gmail.com

ABSTRACT

Among the dental composites, Urethane Dimethacrylate (UDMA) is commonly used as a component in treating oral complications. Many molecular dynamics approaches are used to understand the behaviour of the material at room temperature as well as at higher temperatures to get a better insight after comparison with experimental values at the atomic level. There are three critical physical properties associated with these components, like abrasive wear, viscosity, and moduli, which play an essential role in determining the treatment and can be computed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS), the general-purpose quantum chemistry program package (ORCA), and the General Utility Lattice Program (GULP) molecular dynamics methods. A radial distribution function plot is generated using visual molecular dynamics (VMD) for UDMA and BisGMA. A comparison of these parameters with BisGMA, another component of dental composites, along with experimental results, is carried out in the present investigation. Further, since radiation also matters for settling the materials in dental treatment, we have computed absorption spectra from 200 nm to 800 nm using LAMMPS/ORCA.

Keywords: UDMA; BisGMA; dental resin

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1. Introduction

Abrasive wear normally deals with the loss of material due to hard particles that are forced against and move along a solid surface and is measured as weight loss (in mg) per number of cycles[1,2]. This being associated with the movement of the molecules, we have also quantified viscosity and hardness, which are important in the field of dental composites and their applications. UDMA, being a component of the dental composite, is used regularly because of its flexibility and influence on physicomechanical properties[3–13]. For polymer and metallic samples, an experimental study has shown that there is a distinct correlation between abrasive wear and the cohesive energy of materials[14]. To understand the distinct features of the components UDMA and BisGMA used in dental composites, we have undertaken a molecular-dynamic study of the abrasive wear, viscosity, absorption, and moduli of both BisGMA and UDMA of dental resins. Molecular dynamics (MD) has been extensively used for the study of dental

materials by earlier investigators[15–18]. We have employed a method reported earlier for the computation of absorption spectra for polymers using LAMMPS and the ORCA procedure here for computing the same for BisGMA and UDMA molecules[19–22]. For this purpose, we have used the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)[23,24] and the General Utility Lattice Program (GULP)[25,26] to compute the cohesive energy, viscosity absorption spectra, and elastic constants of UDMA and BisGMA molecules.

2. Material and method

The UDMA's chemical name is Urethane Dimethacrylate, and the formula written in smiles as CC(CCNC(=O)OCCOC(=O)C(=C)C)CC(C)(C)CNC(=O)OCCOC(=O)C(=C)C[27] and for BisGMA as Propane-2,2-diylbis[4,1-phenyleneoxy(2-hydroxypropane-3,1-diyl)] bis(2-methylprop-2-en oate) with smiles as CC(=C)C(=O)OCC(COC1=CC=C(C=C1)C(C)(C)C2=CC=C(C=C2)OCC(COC(=O)C(=C)C)C)O)O. These smiles are essential for input to an online program to generate a set of parameter files, which includes *.pdb file for LAMMPS, ORCA, and GULP developed by Jorgensen group[28–31]. Using Visual Molecular Dynamics (VMD)[32] and *.pdb file generated, with the following command lines in extension/Tkconsole, one can create input LAMMPS data files for the molecule UDMA. The LAMMPS script for computing cohesive energy, viscosity, heat capacity, and radial distribution function with Linard-Jonnes potential is given here, along with the LAMMPS manual, which is essential in the absence of types of bonds, bond angles, and dihedral angles, and to write the output for use in the execution of the LAMMPS script.

```
topo retypebonds
topo guessangles
topo guessdihedrals
topo writelammpsdata file.data

#initialization
units        real
boundary   f f f
atom_style full
read_data
udm.data log
udm_log.dat
```

For computing the viscosity of the molecule, the following statement was included in the LAMMPS input script:

```
#viscosity calculations reset_timestep 0
variable     pxy equal pxy variable   pxz equal pxz variable   pyz equal pyz
fix SS all ave/correlate $s $p $d &
v_pxy v_pxz v_pyz type auto file S0St.dat ave running
variable     scale equal ${convert}/(${kB}*$T)*$V*$s*${dt}
variable     v11 equal trap(f_SS[3])*${scale}
variable     v22 equal trap(f_SS[4])*${scale} variable          v33 equal trap(f_SS[5])*${scale}
thermo_style custom step temp press v_pxy v_pxz v_pyz v_v11 v_v22 v_v33 run     100000
variable     v equal (v_v11+v_v22+v_v33)/3.0
variable     ndens equal count(all)/vol
print        "average viscosity: $v [Pa.s] @ $T K, ${ndens} atoms/A^3"
```

For computing the cohesive energy, we have incorporated the appropriate changes in the input script and they are:

```
#cohesive energy calculations eset_timestep 0
fix 1 all box/relax iso 0.0 vmax 0.001
thermo 10
thermo_style custom step temp pe lx ly lz press pxx pyy pzz c_eatoms min_style cg
minimize 1e-25 1e-25 5000 10000
print "Cohesive energy (eV) = ${ecoh};" print "Temperature = $T K;"
```

From the cohesive energy, we could estimate the abrasive wear rate using the linear relationship between these two parameters as reported based on experiment data[14] and its temperature variation is shown in **Figure 1** for both UDMA and BisGMA. A linear fit to the computed abrasive wear rate shows that for BisGMA, there is a slight increase with the increase in temperature, which is not so for UDMA. The computed values are in the range for some of the polymers determined experimentally[14].

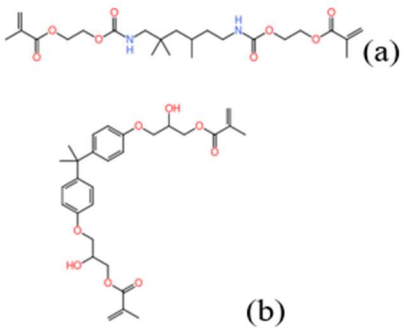


Figure 1. (a) UDMA and **(b)** BisGMA molecules used independently for computation.

For computing the absorption, we have used the software ORCA along with the LAMMPS input script file. It has two stages of computing. Firstly, we have to use udma.pdb file to create the input file udma.xyz with the following instructions:

```
! B3LYP DEF2-SVP Opt
* xyz 0 1
```

#along with fractional coordinates from udma.pdb file and then in the second stage we have to use

```
! PBE0 D3BJ RIJCOSX CPCM
%tddft nroots 50
maxdim 5 end
* xyzfile 0 1 udma/udma.xyz*
```

for creating absorption data files. Normally for molecules like UDMA and BisGMA, the computation time is around 8 to 10 hours on a dual-core desktop computer. To convert the output file into two column files x in units of nm and y in arbitrary units, we use the command (./orca_mapspc output.file ABS-w1000) which can be used to plot as shown in **Figure 2**.

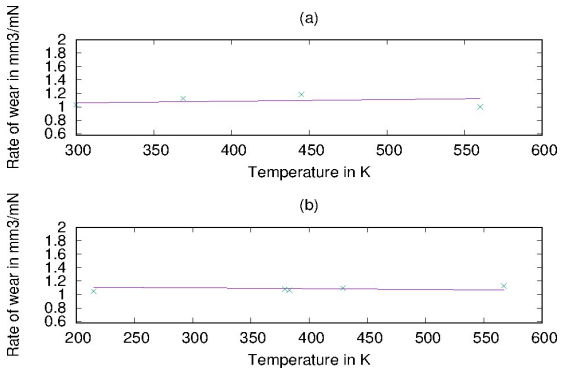


Figure 2. Temperature variation of abrasive wear rate for **(a)** BisGMA and **(b)** UDMA.

From **Figure 3,** the absorption peak was observed at 273 nm for BisGMA, which is in agreement with the experimentally reported value of 230 nm[33]. For UDMA, the absorption starts at 257 nm and is in agreement with the experimental observation of the same feature[33].

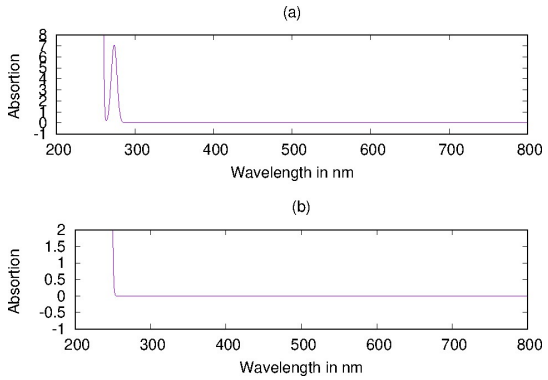


Figure 3. Absorption spectra for **(a)** BisGMA and **(b)** UDMA.

The computed viscosity for UDMA is 7.5E-7 Pa-s, and for BisGMA, it is 5.6E-7 at 300 K. The experimental value of the viscosity of UDMA is 7.054 (0.005) Pa-s[34] which is rather high. For BisGMA, the experimental value is 1200 Pa-s[35] (one poise is 0.1 Pa-s). The viscosity value in BisGMA is due to strong hydrogen bonding interactions and π-π interactions, which result in low flexibility. Computation has been carried out for 8.98E-6 atoms/*A˚3* in the case of BisGMA and 8.6E-6 atoms/*AA˚3*. As the particle's volume fraction rises, the fluid viscosity increases. Further, there is a scaling factor involved in the LAMMPS computation for viscosity[36]. The temperature variation of viscosity for UDMA and BisGMA is shown in **Figure 4**.

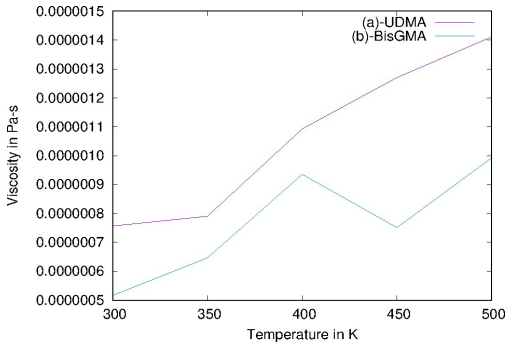


Figure 4. Temperature variation of viscosity for **(a)** UDMA and **(b)** BisGMA.

From **Figures 2** and **4**, it is evident that even though abrasive wear remains constant with temperature for both UDMA and BisGMA, viscosity indicates a broad increase, which has till now not been reported. To understand this behaviour at the atomic level, we have computed the radial distribution function for both UDMA and BisGMA and represented it in **Figure 5**.

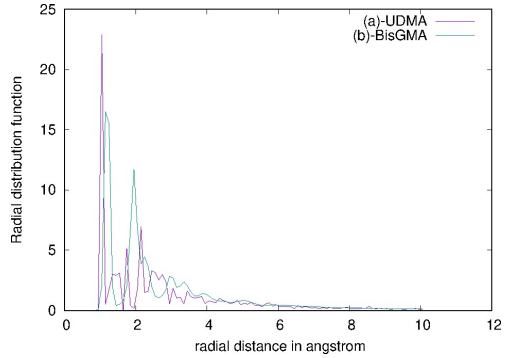


Figure 5. Radial distribution function for **(a)** UDMA and **(b)** BisGMA.

It is evident from **Figure 5** that the first peak in UDMA occurs for an *r*-value less than that for BisGMA, leading to a stronger interaction between the molecules and hence the corresponding behaviour of abrasive wear and viscosity.

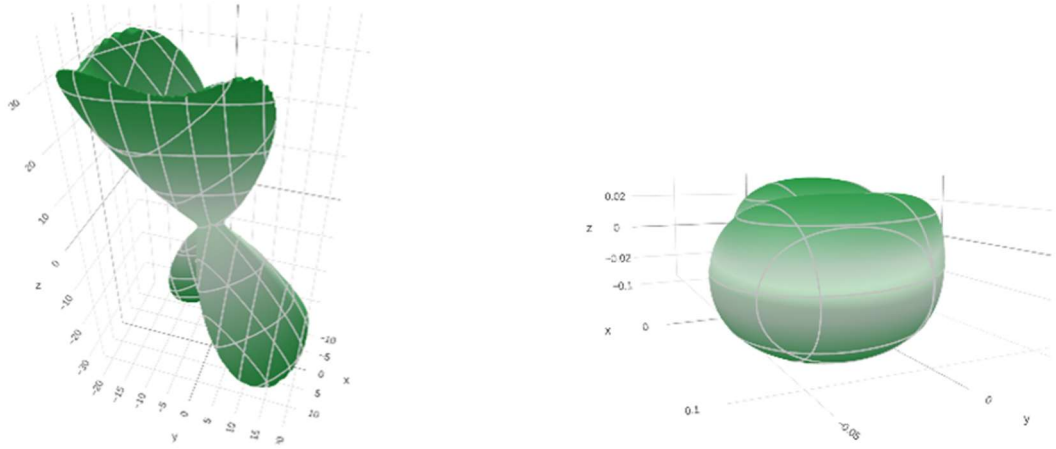
Radial distribution function (RDF) can be used to determine the state of the particles in a system. We have identified carbon-carbon atoms for the computation of RDF. **Figure 5** shows the RDF plot generated using VMD[37,38] procedure.

The GULP program, along with appropriate potential constant parameters, can obtain 21 symmetric elastic constants for UDMA, as given in **Table 1**. Details for the procedure can be obtained from our earlier paper[34].

Table 1. Computed elastic constants C_{ij} for I, j = 1 to 6.

0.1109	0.0023	0.0038	0.0377	−0.0079	0.0024
−0.0032	0.0501	−0.0047	0.0023	0.0065	−0.0166
−0.0056	−0.0047	0.0102	0.0038	0.0002	0.0061
−0.0032	0.0023	0.0038	0.0377	−0.0079	0.0024
−0.0064	0.0065	0.0002	−0.0079	0.0489	0.0051
−0.0195	−0.0166	0.0061	0.0024	0.0051	0.0562

For UDMA, Young's modulus is 0.03 GPa(experimental value being 1.8 Gpa[35] and for BisGMA, it is 0.06 GPa (experimental value being 3.55 GPa[40]). The spatial variation of these moduli is represented in **Figure 6**. Flexural modulus is Young's modulus(Y) and Bulk modulus(K) is $K = Y/3(1 - 2\mu)$ which can be calculated using the experimental value of Y and Poisson's ratio (μ) and is given in **Table 2**.



(a) (b)

Figure 6. 3-D spatial behaviour young's modulus in **(a)** BisGM and **(b)** UDMA.

Electronegativity, which defined the tendency of an atom to attract electrons towards itself, has been computed and given in **Table 2** and is of the same order for BisGMA reported earlier[40]. Self-energy, which is the potential energy generated by the electron due to its surrounding environment, is of the same order as the BisGMA value. Total lattice energy, which is the energy required to convert one mole into its constituents, is greater than what is observed for BisGMA[40]. Human sound P-wave and S-wave velocities are 6.0 km/s and 4.00 km/s, which is less than the values for UDMA material. Zero-point energy, which is the lowest energy of an electron in a system, is 3.17 eV, which is the value normally observed for polymers. The bulk modulus for UDMA agrees with the experimentally reported value.

Table 2. Computed parameters for the molecules UDMA.

Parameter	Comp	Expt UDMA
Electronegativity self energy	6.62 eV	6.00 km/s
Total lattice energy	26.74 eV	
P-wave velocity	3942.0 eV	
	48.03 km/s	
S-wave velocity	37.82 km/s	4.00 km/s
Zero point energy bulk modulus *(GPa)	3.17 eV	1.67[35]
	0.01	
Poisson's ratio *(GPa)	−0.32	-

* Reuss averaging procedure is used.

Electronegativity, which defined the tendency of an atom to attract electrons towards itself, has been computed and given in **Table 2** and is of the same order for BisGMA reported earlier[40]. Self-energy, which is the potential energy generated by the electron due to its surrounding environment, is of the same order as the BisGMA value. Total lattice energy, which is the energy required to convert one mole into its constituents, is greater than what is observed for BisGMA[40]. Human sound P-wave and S-wave velocities are 6.0 km/s and 4.00 km/s, which is less than the values for UDMA material. Zero-point energy, which is the lowest energy of an electron in a system, is 3.17 eV, which is the value normally observed for polymers. The bulk modulus for UDMA agrees with the experimentally reported value.

3. Conclusion

Abrasive wear, viscosity, optical absorption, radial distribution function, and elastic constants of UDMA have been computed using GULP, VMD, LAMMPS, and ORCA to understand their behaviour while they are used in dental treatments. Based on this, the following results emerge from our study: (i) Abrasive wear computed using cohesive energy indicates that there is a slight difference between the values for BisGMA and UDMA materials, and it is constant for a temperature range of 300 K–600 K. (ii) The value of abrasive wear is in the range of experimental values observed for polymers, which are small compared to metals. (iii) The experimental and computed absorption spectra of both BisGMA and UDMA are in total agreement, which justifies the strength of the computational physics carried out here. (iv) viscosity and its temperature variation bring out the differences in the values for BisGMA and UDMA. In both cases, it increases with temperature. (v) There is a broad agreement for the computed values of Young's and Bulk's modulus for both UDMA and BisGMA materials with the reported experimental values, and (vi) a 3-D representation of Young's modulus for UDMA and BisGMA shows the changes in the values along the different directions within the material.

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Author contributions

Conceptualization MM; validation KH; formal analysis MBN; resources, SRK; data curation, HS; writing—original draft preparation, RS; supervision, RS.

Conflicts of interest

The authors declare no conflict of interest.

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Appendix

Abrasive wear, viscosity, moduli and absorption spectra of UDMA molecule have been carried out and compared with reported experimental values.

Moduli represented in 3-d space for UDMA and BisGMA are compared.

Quantified wear and tear of these materials in dental composites will be an added advantage.