

DMD2018-6934**Molecular Analysis of Polymeric Nanocomposites on Prosthesis Design****Norma-Aurea Rangel-Vázquez**

1 Department of Chemistry, University of
Minnesota

Smith Hall, 207 Pleasant St SE, ZC. 55455
Minneapolis, Minnesota, USA

2 Department of Posgrade, Instituto Tecnológico
de Aguascalientes

Ave. Adolfo Lopez Mateos #18001 Fracc. Bona
Gens CP. 20256

Aguascalientes, Aguascalientes, México

Juan-Ramón Campos-Cruz

Department of Posgrade, Instituto Tecnológico de
Aguascalientes

Ave. Adolfo Lopez Mateos #18001 Fracc. Bona
Gens CP. 20256

Aguascalientes, Aguascalientes, México

Jonathan Kalla

Department of Chemistry, PCC

9633 Hampshire Ln, 55347

Eden Prairie, Minnesota, USA

ABSTRACT

There has been an increasing amount of interest in the design and preparation of new biomaterials that can be used in the fabrication of medical devices for artificial prostheses or implant applications. The use of molecular modeling and computational chemistry aids in the design of these materials by calculating different structural properties such as molecular energy, geometry optimization, dipole moments, FTIR, UV-vis, NMR, and others. In this study graphene, polyurethane (PU), polymethylmethacrylate (PMMA) and PU/graphene/PMMA composites have been studied using theoretical calculations. For this work, the AMBER and AM1 simulation methods were used. The results indicate the favorable formation of a cross-linked PU/Graphene composite and adsorption of PMMA.

INTRODUCTION

Biomedical implants are artificial replacements of original structural components of a biological system, such as the human body, that try to supplant the function of the original element. Depending on the use, these artificial replacements can be constructed in metallic, polymeric, ceramic materials or combinations thereof. The first requirement to implant a material in the body is its biocompatibility, equivalent to the absence of organic rejection [1].

A large variety of polymers such as Polyurethane (PU) or Polymethyl methacrylate (PMMA) can be used as biomaterials because the physical properties and chemical stability of these depend on a set of variables such as the chemical composition of the polymer and the degree of cross-linking [2]. Thus, through computational simulation, which includes areas of chemistry, biology and physics combined with computation, it allows the investigation of atoms, molecules and macromolecules through a computer system [3]. There are several simulation methods, however in this research AMBER and AM1 were used to design polymeric nanocomposites from PU, PMMA and graphene, able to replace any bony part of the human body without generating secondary reactions.

METHODS

a) Geometry optimization. The optimizing process of structures used in this work was started using the AM1 method, because it generates a lower-energy structure even when the initial structure is far away from the minimum structure. The Polak-Ribiere algorithm was used for mapping the energy barriers of the conformational transitions.

b) FTIR. The FTIR was obtained by first selecting menu Compute, vibrational, rotational option, once completed this analysis, using the option vibrational spectrum of FTIR spectrum pattern is obtained from the method of analysis.

c) Molecular electrostatic potential (MESP). After obtaining an optimization geometry or Gibbs free energy using the AM1 method, a menu plot molecular graph, the electrostatic potential property is selected and then the 3D representation mapped isosurface for both methods of analysis. Atomic charges indicate where large negative values (sites for electrophilic attack) are likely to occur. However, the largest negative value of the electrostatic potential is not necessarily adjacent to the atom with the largest negative charge.

RESULTS

PU/Graphene crosslinking.

Table 1 shows a stoichiometric relationship and the optimization geometries or corresponding Gibbs free energies obtained by means of the AM1 method, which shows that by means of a minimum ratio (1-1) a spontaneous cross-linking reaction is obtained. In addition, through the optimization geometry it was possible to determine that the cross-linking originates between the carbonyl group of PU and the C-H bond of graphene. Because the PU molecule has two carbonyl groups that need to bind in the same way to two C-H bonds of graphene to generate a stable matrix. That is why the ideal relationship is that of 2 PU molecules and 2 graphene molecules (see Figure 1) [4].

Table 1. Gibbs free energy for different PU-graphene ratios

PU/Graphene	ΔG (Kcal/mol)
1-1	- 09,839.0279
1-2	- 15,246.9720
2-2	- 19,616.7780

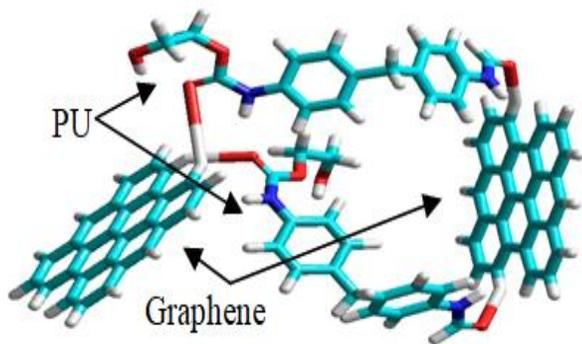


Figure 1. Optimized molecular geometry of the system 2 PU/2 Graphene, where: \circ hydrogen, \bullet carbon, \bullet oxygen and \bullet nitrogen, respectively.

Subsequently, the FTIR signals of the PU/Graphene composition where the OH bond (PU) was observed at 3805 and 3233 cm^{-1} , the CH bond of graphene was appreciated at 3756-2901 cm^{-1} , and the C=O bond of PU was obtained at 2035-1996 cm^{-1} .

The MESP of Figure 2 presents a high electronegative density, with slightly neutral zones, mainly in the carbon-hydrogen bonds of both PU and graphene. The most positive areas where the electronegative density is less are found in one of the graphene carbon atoms that are in the central zone of the molecule.

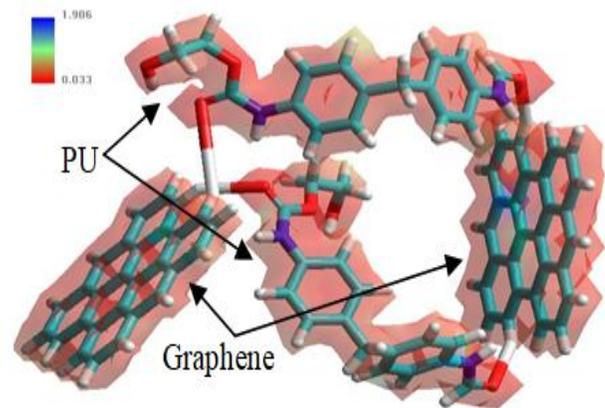


Figure 2. MESP of the PU/Graphene composite in where: \circ hydrogen, \bullet carbon, \bullet oxygen and \bullet nitrogen.

Adsorption of PMMA in PU/Graphene

For the adsorption of PMMA, the amounts of PMMA with respect to PU/Graphene (2-2) were varied, obtaining the results shown in Table 2. The optimized molecular geometry that was obtained from the PU/Graphene/PMMA ratio (2-2-2) is shown in Figure 3. It shows an attraction of the carbonyl group of PMMA towards the C-H bonds of graphene, giving rise to the spontaneous formation of a new O-H bond between graphene and PMMA through a hydrogen bond. The Log P value for the structure shown is +24.67 so there is little affinity for polar substances such as water, so it is a system with a hydrophobic tendency.

Table 2 Comparison of Gibbs free energy with different amounts of PMMA.

PU-Graphene-PMMA	ΔG (Kcal/mol)
2-2-1	+244,876.23
2-2-2	-22,876.4608
2-2-3	-24,478.7738

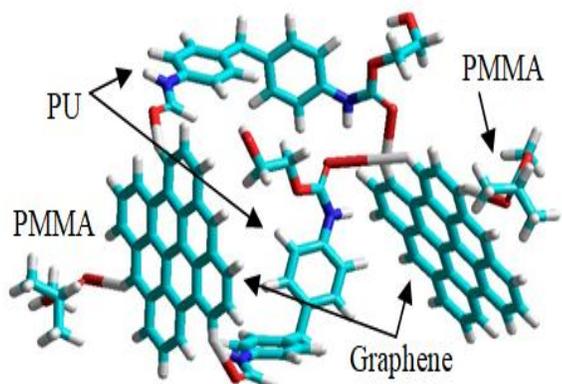


Figure 3. Molecular geometry of PU/Graphene/PMMA in where: ○ hydrogen, ● carbon, ● oxygen and ● nitrogen, respectively.

The main assignments of the vibrational analysis corresponding to the PU/Graphene/PMMA composition showed the main displacement found in the O-H bond of the PU moved from 3805 and 3233 cm^{-1} towards 3485 and 3453 cm^{-1} due to the presence of PMMA. Another bond that changes frequency in its symmetric vibration is the carbonyl group (C=O) of 2543 and 2151 cm^{-1} the vibration was appreciated at 2056 and 1908 cm^{-1} .

In addition, the C=O bonds of the PMMA and the CH bond of the graphene present a simultaneous vibration at the frequencies of 2118 and 1659 cm^{-1} , thereby checking the reaction between the PMMA and the graphene, giving rise again to another OH bond through a hydrogen bond. Figure 4 shows the MESP of the adsorption of PMMA in the PU/Graphene composite where it can be seen that the nucleophilic zones have a slightly lower density in the C-H groups of graphene. The vast majority of the molecular structure is in a red hue so it has high electron density [5-6].

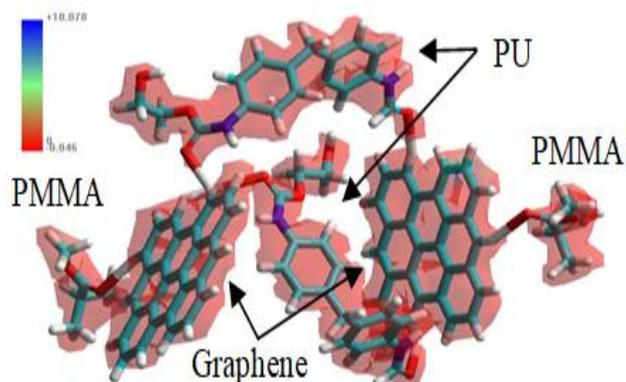


Figure 4. MESP of the PU/Graphene/PMMA composite in where: ○ hydrogen, ● carbon, ● oxygen and ● nitrogen.

INTERPRETATION

The cross-linking observed in figure 1 has a free energy of -19,628.2332 Kcal/mol, which shows that the established reaction occurs spontaneously giving rise to a stable system. The structure shown above has a Log P value of +20.99, so it is indicated that the system as well as the individual components have a low affinity to polar substances such as water, that is, it would be resistant to oxidation caused by the water present in the human body.

The adsorption of PMMA generates that the chemical structure has a high electronegative density almost completely distributed homogeneously, only has some areas that have neutral and slightly positive charges. This behavior indicates that the composite will maintain the property of graphene which is a very good electrical conductor, which is suitable for the design of prostheses.

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