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Research Article

Application of Simulation Molecular and Artificial Neuronal Networks in the Analysis of Adsorption of PMMA in Polyurethane/Graphene Nanocomposites

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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 remarkable properties of graphene provide essentially infinite possibilities for various applications. One such area is the biomedical applications (e.g., drug and gene delivery, nanomedicine, bioimaging and potential cancer therapies) of graphene–based polymer nano composites. The graphene, polyurethane (PU), polymethylmethacrylate (PMMA) and adsorption process of PMMA in graphene/PU nanocomposite respectively have been studied using PM3 method to determine theoretical calculations like Gibbs free energy, log P, FTIR (Fourier Transform Infrared) and molecular electrostatic potential (MESP). ΔG were spontaneous for different materials. FTIR spectroscopy reveals information about the molecular interactions of chemical components and is useful for characterization of composite. Nucleophilic and electrophilic regions were calculated using the MESP. The bonds lengths were determined with ANNs (artificial neuronal networks) for appreciate the adsorption of PMMA beside the structure of nano composite.

Keywords: MESP; Graphene; PU; PMMA; Log P; ANNs

Introduction

Biomedicine has made great progress over the past half century, of which the development and application of medical devices accounts for an important role to improve health and life quality of patients. These devices are known to be artificial cardiac pacemakers, implantable kidney dialysis machine, and joint replacements for fingers, knees, hips, and shoulders. Polymeric materials are widely employed into these medical devices to help these devices to be able to survive in the human micro environment, such as in blood and living tissues. As part of a medical device in the human body, these polymeric materials are required to be able to resist the degradation and biological rejection from the body of patients. It has been found that many polymers can be used to fabricate biomedical devices [1]. Polymer nano composites based on a range of nano fillers such as expanded graphite (EG), carbon nano tube (CNT), carbon nano fiber (CNF) have been reported [2–4].

In recent years, computational analyses are also being employed for initial optimization of design of implants before the prototypes are built and expensive experimental evaluations are conducted [5]. Molecular modeling is an aspect of computational chemistry and a particular molecular system can be modeled with the hope that it could be synthesized in the laboratory, especially for species that are too difficult, dangerous, impossible or too expensive to carry out experimentally. Molecular modeling is a quite accurate method in accounting for properties like geometric and electronic structures, frequencies, chemical shifts, bond length and angles [6].

Semi-empirical quantum chemistry attempts to address two limitations, namely slow speed and low accuracy, of the Hartree–Fock calculation by omitting or parameterizing certain integrals based on experimental data, such as ionization energies of atoms, or dipole moments of molecules. As a result, semi-empirical methods are very fast, applicable to large molecules, and may give accurate results when applied to molecules that are similar to the molecules used for parameterization. On the downside, accuracy of semi-empirical methods is erratic on many systems [7–8]. The PM3 semi-empirical model is based on grouping the electronic energies as well as that of the core-core repulsion, i.e. the molecules studied by grouping together the valence electrons on the other hand to the core [9]. Was developed with the aim to obtain a faster way the various atomic parameters through a process of parameterization of AM1 [10] model atoms C, H, O, N, F, Cl, Br. I, respectively [11].

In the past decade, artificial neural networks (ANNs) have received

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a great deal of attention among scientists and engineers and they are being touted as one of the greatest computational tools ever developed. Much of this excitement is due to the ability of neural networks to emulate the brain's ability to learn by example. Specifically, ANNs are known to be a powerful tool to simulate various non-linear systems and have been applied to numerous problems of considerable complexity in many fields, including engineering, psychology, medicinal chemistry, diagnostics, and pharmaceutical research [12]. The application of ANNs in the field of pharmaceutical development and optimization of the dosage forms has become a topic of discussion in the pharmaceutical literature [13].

The potential applications of ANNs methodology in the pharmaceutical sciences are broad as ANNs capabilities can be summarized by modeling, pattern recognition and prediction. Thus, applications of ANNs include drug modeling, dosage design, protein structure and function prediction, pharmacokinetics and pharmaco-dynamics modeling, as well as, interpretation of analytical data, and *in vitro/in vivo* correlations [12].

In this project the study of absorption process of PMMA was realized using PM3-semiempirical method for determine ΔG, structural parameters, FTIR and MESP of PU, Graphene, and absorption process of PMMA in PU/Graphene composite and through data of bond lengths, bond angles and energies, the calculus were compared with ANNs for verified the absorption process in the composite.

Materials and Methods

Geometry Optimization

In this study the PM3 semi-empirical method was used for find the potential energy minimum corresponding to the lower–energy structure. Iteration number and convergence level lead optimal structure. The optimizing process of structures used in this work was started using the PM3 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.

FTIR

The infrared spectrum is commonly obtained by passing infrared electromagnetic radiation through a sample that possesses a permanent or induced dipole moment and determining what fraction of the incident radiation is absorbed at a particular energy [14].

Electrostatic Potential

After obtaining a Gibbs free energy or optimization geometry using the PM3 method, we can plot two–dimensional contour diagrams of the electrostatic potential surrounding a molecule, the total electronic density, the spin density, one or more molecular orbital's, and the electron densities of individual orbital. Hyperchem software displays the electrostatic potential as a contour plot [15].

Artificial Neuronal Networks (ANNs)

One of the more important ANNs is the Self-Organization Map (SOM) proposed by Kohonen [16]. In this network there is an input layer and the Kohonen layer, which is usually, designed as two-dimensional arrangement of neurons that maps n-dimensional input to two-dimensional. It is basically a competitive network with the characteristic of self-organization providing a topology-preserving mapping from the input space to the clusters [16-17]. Mathematically networks and SOM require input vectors $x_j = (x_1, x_2, x_3, \ldots, x_{jp})$, training weights $w_l = (w_{l1}, w_{l2}, \ldots, w_{lp})$, where l indicates the number of nodes, w_{lj} denote the weights assigned to entry x_j of node l and p is number input variables.

One way to establish the structure of the SOM type neural network, which indicates that the basic structure of the network must be input layer, hidden layer and output layer, the number of neurons in each layer is determined by the information processing capacity and robustness to want to project the problem, the problem presented in this work a static neural network is established with a number finite neurons, 20 neurons in each of the layers of the neural network. The distance between each of the nodes is made using the equation of Euclidean distance between the input nodes and the projection (bond lengths). The neural network must be trained, to establish minimum and maximum parameters of the projection of the bond lengths, usually workouts rate applied backward propagation (BP), for study case, a training method type is batch learning.

The use of batch mode training provides an accurate gradient vector, thus ensuring convergence to a local minimum, this basically does not happen with sequential training as BP because it becomes a search in the space of weights estimation stochastically and however the stochastic nature prevents convergence of the algorithm [18].

Results

QSAR Properties

The set of thermodynamic data obtained is listed in table 1. The negative value in Gibbs free energy associated with a chemical reaction is a useful indicator of whether the reaction will proceed spontaneously. The value clearly shows that the interaction between the carbonyl and methyl groups, this indicate a spontaneous reaction of adsorption process of PMMA, as expressed by the negative Gibbs free energy.

Table 1: QSAR properties for composite.

Properties	NMC/PMMA
ΔG (Kcal/mol)	–256531
Log P	3.36

Determination of a partition coefficient (log P) is an important step in evaluating the affinity of a polymer film for one substance over another [19]. The positive value of log P (see table 1) indicates a hydrophobic effect is the observed tendency of non-polar substances to aggregate in aqueous solution and exclude water molecules [20]. Some argue that the hydrophobic interaction is mostly an entropic effect originating from the disruption of highly dynamic hydrogen bonds between molecules of liquid water by the non-polar solute [21].

FTIR

The FTIR values of NMC and the adsorption process of PMMA in NCM (see table 2) indicate the details of functional groups present in the material. A sharp intense peak at 1730 cm^{-1} appeared due to the presence of ester carbonyl group stretching vibration. The broad peak is ranging from 1150–1065 and 778cm^{-1}can be explained owing to the C–C, CH and C–O (ester bond) stretching vibration [22]. A sharp intense peaks appeared at 2036 and 1895 cm^{-1} due to the presence of ester carbonyl group stretching vibration (C=O stretching), N=C=O and C=C, respectively, in addition, suggesting the existence of carboxyl group [23-25]. The broad peak ranging from 1260–1000 cm^{-1} can be explained owing by the C–O (ester bond) stretching vibration. The broad peak ranging from 4537–4208 cm^{-1} is attributed to the presence of stretching vibration of O–CH_3 stretching vibrations [23-24]. The peaks between 1571 and 1528 cm^{-1} are attributed to the C=C stretching of PU.

Table 2: FTIR results of adsorption process of PMMA in nanocomposite.

Assignment	NMC (cm^{-1})	NMC/PMMA (cm^{-1})
CH stretching vibration	4781–4522	4913, 3786–3705
CH stretching	4384	4537–4208
NH stretching	3696–3715	3705
CH_2 stretching	3520–3350, 3218	3471
C–C	3074, 2918, 2686	3127, 2803, 2455
C=C and C=O	2966–2800,2650–2381,1752–1688, 1592–1536, 772, 728	2293–2036, 1895, 1777–1730, 1571–1528
C–O, C–C, C–N	1190–1097	1364, 1150–1065, 778
C–H	1260–1000, 841	1049

Electrostatic Potential

Figure 1 shows the MESP of adsorption process of PMMA in nanocomposite, where is appreciated that the electrostatic potential is from 1.093 at 0.067 indicated that the nucleophilic and electrophilic regions mainly involved the C=O and C–O bonds respectively. The adsorption of PMMA by the nano composite mainly involved the formation of hydrogen bonds between PU, graphene and PMMA, respectively. The scale value indicates asymmetric distribution between positive charges of 1.093 eV while the negative is 0.067 eV. This behavior arises because the electronic distribution of a core is not symmetrical in a given time.

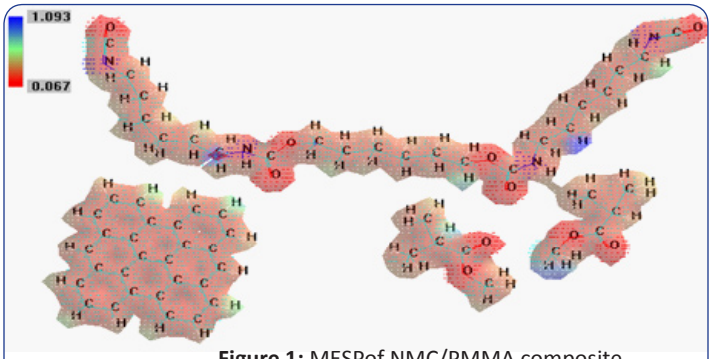

Figure 1: MESPof NMC/PMMA composite.

Artificial Neural Networks

ANNs can be applied in the recognition of images, but not only are limited in that application; these also can be applied in the estimate or projection in the molecular simulation. The application of ANNs in molecular simulation is given by estimating possible formation of molecules this is achieved by applying the neural network SOM (Self -Organizing Map), which made possible a projection of the molecule on a space in two dimensions (2-D). The projection of the molecule may be performed by data bond lengths, bond angles and energies, to the projection of this work PU molecules and graphene is performed from these two supports absorption study is performed one carbonate ion and a molecule of PMMA. The application of ANNs to obtaining of molecules provides projections of results of bond lengths, in figure 2 the bond length between the polyurethane and graphene sample, the bond length between atoms of graphene is small in comparison with the bond length between graphene and PU, demonstrating that graphene is packaged PU among atoms.

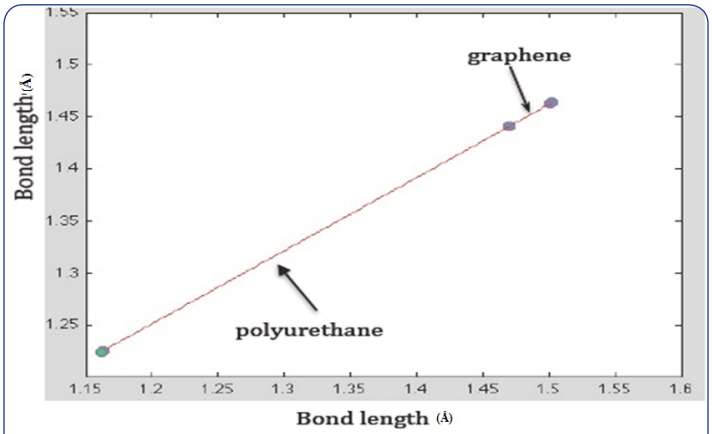

Figure 2: Simulation Bond lengths of NMC.

Similarly simulation graphene molecules and polyurethane is made, but a molecule is added PMMA, similarly as with the carbonate. PMMA have interaction between the PU and PMMA can be appreciated in figure 3. Table 3 shows the results about bond

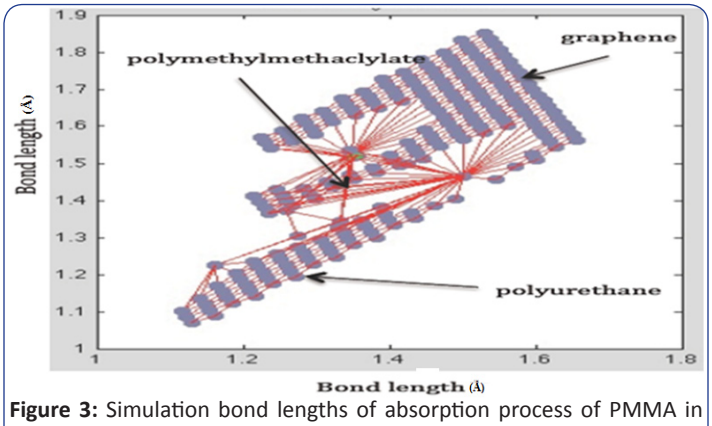

Figure 3: Simulation bond lengths of absorption process of PMMA in NMC composite.

length determinate with ANNs of bond length, where the bond length is related to bond order: when more electrons participate in bond formation the bond is shorter.

So, the structures are no planar due to the deformations of the graphene´s rings depend on the characteristics of the bonds NH, C=O, and PMMA mainly.

Conclusions

PM3 method determined that: Gibbs free energy indicated that absorption of PMMA is spontaneous; also through the electrostatic potential found reaction mechanism mainly CH groups of graphene and NH groups of PU indicating the regions for electrophilics bonds (red color) and FTIR results showed the cross linking of

Table 3: Structural parameters of adsorption PMMA in graphene/PU composite using ANNs.

Bond	ANNs (Å)	Bond	ANNs (Å)	Bond	ANNs (Å)	Bond	ANNs (Å)
PU		**Graphene**		**Graphene**		**PMMA**	
O9=C8	1.157	C1-C2	1.4932	C28-C29	1.4951	**1st mol**	
C8=N1	1.2193	C2-C3	1.4543	C29-C30	1.5338	C1=C2	1.3094
N1-C2	1.4581	C3-C4	1.4546	C30-C16	1.4933	C2-C3	1.4993
C2-C3	1.6203	C4-C5	1.4546	C25-C24	1.4551	C2-C9	1.4562
C3-C4	1.5394	C5-C6	1.4929	C24-C23	1.4518	C9=O10	1.1925
C4-C5	1.6067	C6-C1	1.5338	C23-C22	1.4571	C9-O11	1.3140
C5-C6	1.6201	C4-C7	1.4568	C22-C13	1.4577	O11-C12	1.3551
C6-C7	1.6228	C7-10	1.4568	C22-C21	1.4557		
C7-N10	1.5247	C2-C27	1.4933	C21-C20	1.4557	**2nd mole**	
N10-C11	1.4288	C27-C26	1.5337	C20-C19	1.4578	C2=C4	1.3098
C11=O13	1.2276	C26-C25	1.4947	C20-C32	1.4571	C4-C5	1.4790
C11-O12	1.3713	C25-C12	1.4538	C32-C31	1.4517	C4-C9	1.4350
O12-C15	1.4051	C12-C3	1.4539	C31-C28	1.4551	C9=O10	1.1950
C15-C16	1.6301	C12-C13	1.4566	C24-C40	1.4943	C9-O11	1.3217
C16-C17	1.6083	C13-C11	1.4560	C40-C39	1.5346	O11-C12	1.3571
C17-C18	1.5384	C11-C7	1.4565	C39-C38	1.5345		
C18-C19	1.6044	C11-C19	1.4560	C38-C37	1.4921	**3rd mole**	
C19-C20	1.6077	C19-C18	1.4566	C37-C23	1.4526	C1=C4	1.3191
C20-O21	1.4043	C18-C17	1.4540	C37-C36	1.4923	C4-C5	1.4821
O21-C22	1.3658	C18-C28	1.4539	C36-C35	1.4923	C4-C9	1.4554
C22=O25	1.2272	C10-C9	1.4546	C35-C21	1.4554	C9=O10	1.1956
C22-N23	1.4071	C9-C8	1.4921	C35-C34	1.4924	C9-O11	1.3347
N23-C26	1.4506	C8-C5	1.4921	C34-C33	1.4924	O11-C12	1.3691
C26-C27	1.6533	C10-C17	1.4545	C33-C32	1.4526		
C27-C28	1.8220	C17-C16	1.4543	C33-C43	1.4922		
C28-C29	1.6525	C16-C15	1.4932	C43-C42	1.5349		
C29-C30	1.5408	C15-C14	1.5338	C42-C41	1.5349		
C30-C31	1.6206	C14-C9	1.4929	C41-C31	1.4945		
C31-N32	1.4582						
N32=C33	1.2194						
C33=O34	1.1571						

PU/graphene for absorption of PMMA. Finally, the use of neural networks for the simulation of molecules, is a viable alternative, mainly because the networks may make projections and estimates of bond lengths as was done in this study, it is observed that the lengths obtained using neural networks are very similar to those obtained by a commercial simulator, also neural networks can be applied for obtaining new molecules and its absorption between them, as demonstrated in this work shows that the networks make predictions absorption of different molecules on the basis set.

References

1. Wang H, Rempel GL (2013) Preparation of core-shell Nanostructured PMMA-PS for prosthesis and implant material applications. Adv. Biomed. Eng. Res (ABER) 1: 62-68.
2. Das TK, Prusty S (2013) Graphene-Based Polymer Composites and Their Applications. Polym.-Plast. Technol. Eng 52(4): 319–331.
3. Aguilar Z (2012) Nanomaterials for medical applications.(1stedn), Elsevier Ed, USA.
4. Haghi AK, Zachariah AK, Kalariakkal NK (2013) Nanomaterials: Synthesis, characterization, and applications. (1stedn), CRC Press Taylor Ed, Canada.
5. Chandran KB (2010) Role of computational simulations in heart valve dynamics and design of valvular prostheses. Cardiovasc. Eng. Technol 1(1): 18-38.
6. Adejoro IA, Oyeneyin OE, Adeboye OO, Obaleye JA (2012) PM3 Semi empirical quantum mechanical calculations on a novel Dichlorobis (N-{4-[(2-pyrimidinyl-kN-amino)sulfonyl}acetamide] copper(II),containing a metabolite N-acetylsulfadiazine. J. Comput. Method. Mol. Des 2(4): 142-148.
7. Ramachandran KI, Deepa G, Namboori K (2008) Computational chemistry and molecular modelling: Principles and applications., Springer-Verlag Berlin Heidelberg Ed, Germany.
8. Dewar MJS, Zoebisch EG, Healy EF, Stewart JJP (1985) Development and use of quantum molecular models. J. Am. Chem. Soc 107(13): 3902-3909.
9. Angulo Cornejo JR, Tovar CF (2014) Utilización de la química computacional: método semiempírico PM3, para elucidar la estructura del complejo bis (1,5- difenil-1,2, 4-triazol-3-tionato) plomo (II) (Pb(DTT)). Rev. Soc. Quím. Perú 80(2): 136-143.
10. Jurema MW, Shields GC (1993) Ability of the PM3 Quantum-Mechanical method to model intermolecular hydrogen bonding between neutral molecules. J. Computat. Chem 14(1): 89-104.
11. Tubert Brohman I, Werneck Guimaraes CR, Jorgensen WL (2005) Extension of the PDDG/PM3 Semiempirical molecular orbital method to sulfur, silicon, and phosphorus. J. Chem. Theory Computat 1(5): 817-823.
12. Sutariya V, Groshev A, Sadana P, Bhatia D, Pathak Y (2013) Artificial neural network in drug delivery and pharmaceutical research. The Open Bioinformatic J 7: 49-62.
13. Ghaffari A, Abdollahi H, Khoshayand MR, Bozchalooi IS, Dadgar A, et al. (2006) Performance comparison of neural network training algorithms in modeling of bimodal drug delivery. Int. J. Pharm 327(1-2): 126–138.
14. Kumirska J, Czerwicka M, Kaczyn´ski Z, Bychowska A, Brzozowski K, et al. (2010) Application of spectroscopic methods for structural analysis of chitin and chitosan, Mar. Drug 8(5): 1567–1636.
15. Rangel Vázquez NA, Rodríguez-Felix F (2014) Computational chemistry applied in the analyses of Chitosan/Polyvinylpyrrolidone/Mimosa tenuiflore. (1stedn), Science Publishing Group Ed, Hong Kong.
16. Kohonen T (1989) Self-Organization and associative memory. (3rded), Springer-Verlag Ed, USA.
17. Gallant SI (1993) Neural network learning and expert systems. MIT Press Ed, England.
18. Kohonen T (1995) Self-Organizing maps.(3rded), Springer-Verlag Ed.Germany.
19. Plett KL (2008) Development and characterization of polysiloxane polymer films for use in optical sensor technology. Ph. D Thesis, Canada.
20. Chandler D (2005) Interfaces and the driving force of hydrophobic assembly. Nature 437: 640-647.
21. Silverstein TP (1998) The real reason why oil and water don't mix. J. Chem. Educ 75(1): 116-118.
22. Balamurugan A, Kannan S, Selvaraj V, Rajeswari S (2004) Development and spectral characterization of Poly(methyl Methacrylate). Trends Biomater. Artif. Organs 18(1): 41-45.
23. Singho ND, CheLah NA, Johan MR, Ahmad R (2012) FTIR studies on silver-poly(methylmethacrylate) nanocomposites via in-situ polymerization technique.Int. J. Electrochem. Sci 7: 5596–5603.
24. Tomar AK, Mahendiaa S, Kumar S (2011) Structural characterization of PMMA blended with chemically synthesized PAni. Adv. Appl. Sci. Res 2(3): 327-333.
25. Ren ZY, Wu HP, Ma JM, Dezhu M (2004) FTIR studies on the model polyurethane hard segments based on a new waterborne chain extender dimethylolbutanoic acid (DMBA). Chinese J. Polym. Sci 22(3): 225-230.