

Mechanical Properties of Nanostructured Materials Determined Through Molecular Modeling Techniques

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The potential for gains in material properties over conventional materials has motivated an effort to develop novel nanostructured materials for aerospace applications. These novel materials typically consist of a polymer matrix reinforced with particles on the nanometer length scale. In this study, molecular modeling is used to construct fully atomistic models of a carbon nanotube embedded in an epoxy polymer matrix. Functionalization of the nanotube which consists of the introduction of direct chemical bonding between the polymer matrix and the nanotube, hence providing a load transfer mechanism, is systematically varied. The relative effectiveness of functionalization in a nanostructured material may depend on a variety of factors related to the details of the chemical bonding and the polymer structure at the nanotube-polymer interface. The objective of this modeling is to determine what influence the details of functionalization of the carbon nanotube with the polymer matrix has on the resulting mechanical properties. By considering a range of degree of functionalization, the structure-property relationships of these materials is examined and mechanical properties of these models are calculated using standard techniques.

I. Introduction

COMBINING nano-scale additives in polymer materials is an active area of research with the goal of greatly improving a range of physical and mechanical material properties. In particular, the use of carbon nanotubes added to various polymers to form nanocomposites has been actively pursued as a means to enhance mechanical-structural properties. Due to the great range of size scales of these nanostructured materials, experimental characterization of these materials is challenging and often limited by both time and length scale resolution. This challenge has led to the use of computational approaches to aid in understanding the key structure-property relationships relevant in these systems. One of the promising computational approaches is molecular modeling that has been applied at the atomistic scale to study the mechanical properties of polymers. This atomistic approach has been used within a context of a multi-scale modeling approach to examine structure-property relationships across a range of length scales.¹

The objective of this paper is to apply the techniques of molecular modeling to study structure-property relationships for nanostructured materials. In particular, static mechanical properties of single wall carbon nanotubes embedded in an epoxy matrix are studied. The degree of chemical functionalization of the carbon nanotube to the epoxy matrix is addressed within the computer simulation by systematically varying the number of diamine molecules which are covalently bonded to the carbon nanotube. The resultant changes in elastic mechanical properties as a function of grafting density are studied parametrically.

II. Materials

Epoxies are highly crosslinked polymeric materials formed from the reaction of two types of molecules: a molecule containing several epoxide functional groups and a molecule which serves as a crosslinker. In this paper, we consider a crosslinker with two amine functional groups (diamines) reacting with a molecule containing epoxide

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functional groups to form a crosslinked matrix. Fig. 1a shows the chemical reaction of a crosslinking molecule containing an amine group reacting with a molecule containing an epoxide functional group. Fig. 1b illustrates the product of the reaction from Fig. 1a reacting with a 2nd epoxide group. These reactions lead to the formation of highly crosslinked macromolecular structures.

The reactant molecules used in this simulation are as follows. The reaction mixture consists of epoxide group containing molecules, and crosslinking diamine molecules. The molecule which contains the reactive epoxide functional groups, the diglycidyl ether of bisphenol A (DGEBA), is shown in Fig. 2a. The crosslinker, diethyltoluene diamine (DETDA) consists of a mixture of two isomers: 3,5-diethyltoluene-2,4-diamine, and 3,5-diethyltoluene-2,6-diamine, shown in Figs. 2b and 2c respectively. A mixture of DGEBA and DETDA will react according to Figs. 1 to produce the cured epoxy network.

The carbon nanotube material is single wall with a chirality of (10, 10). The nanotube has an approximate radius of 6.74 Å and is considered continuous (no end caps) and straight. The nanotube combined with the epoxy forms a nanocomposite. Four nanocomposite models with distinct grafting densities were investigated in this study. The nanocomposite is assumed to demonstrate transverse isotropy.

III. Method

In order to achieve improvement of material properties in nanocomposite systems, load transfer between matrix and nanoparticle must be achieved. Chemical functionalization has been applied in order to achieve this goal. Recently, much experimental work has focused on the functionalization of carbon nanotubes by covalent bonding of various organic functional groups to the carbon nanotube. Single wall carbon nanotubes have been functionalized with amine groups.² Subsequently, nanocomposites were synthesized using these functionalized nanotubes in an epoxy matrix.³ Fig. 3 shows several diamine molecules covalently bonded to a carbon nanotube.

In this paper, computer simulations will be performed involving a carbon nanotube functionalized by the covalent attachment of DETDA molecules and placed in an epoxy matrix. The nanotube bound DETDA molecule is attached to the carbon nanotube through one of its two amine groups. The 2nd amine group (not attached to the carbon nanotube) is able to participate in the epoxy curing reaction as shown in Figs. 1. The degree of functionalization is varied by the number of additional DETDA molecules covalently bonded to the carbon nanotube.

The application of molecular modeling techniques to crosslinked polymer systems has been fairly limited. This is largely due to the complications involved in constructing a complex atomistic network structure representative of the crosslinked material. A recent methodology was developed to construct crosslinked molecular models of polymers.⁴ This methodology is used to generate the epoxy systems studied herein. The procedure consists of running molecular dynamics (MD) simulations of the reactant molecules, and then applying a chemical reaction to “cure” the system. Although a fairly crude technique, it does make it possible to build a representative atomistic crosslinked structure.

The modeling procedure begins by establishing the force field to be used. For its general applicability and basic form, the AMBER force field is selected.⁵ This force field can be easily used with both the Tinker⁶ and LAMMPS⁷ molecular modeling software codes, both of which are available on a no-cost basis. The LAMMPS code (Large-scale Atomic/Molecular Massively Parallel Simulator) is used for most of the MD and energy minimization simulations herein because it can be used on parallel processing machines which allows for more rapid computation times. Likewise, the Tinker software has many useful features for data analysis.

In order to simulate bulk samples of condensed matter, it is convenient to use periodic boundary conditions (PBCs).⁸ The periodic boundaries can be described with a set of vectors, \mathbf{a}_x , \mathbf{a}_y , and \mathbf{a}_z , along with an origin, $\mathbf{0}$, for this set of vectors. These vectors describe a volume in which the atoms are contained. Each atom is described by two sets of coordinates: 1) the parent chain, which ignores the PBCs and 2) the coordinates mapped into the PBC volume space. Fig. 4 shows a single DGEBA molecule subject to PBCs. The parent chain is shown in the upper right hand corner. The vectors, \mathbf{a}_x , \mathbf{a}_y , and \mathbf{a}_z , describe the PBC space (with \mathbf{a}_y pointing into the plane of the figure). When subject to the PBCs, the coordinates of the atoms lie within the volume outlined by these vectors as seen at the bottom of Fig. 4.

Simulating a single wall carbon nanotube at the atomistic level requires special considerations. Since the axial length of the nanotube is much larger than can be simulated atomistically, the nanotube must be modeled as an infinitely long tube, with the axial dimension of the tube continuing through opposing faces of the PBC volume.

This particular use of PBCs requires careful analysis. It is important not to neglect the fact that PBCs are an artificial construct, and more routinely applied to molecules much smaller than the size of the PBC volume.

The mixture of reactant molecules is prepared at low density. This reaction mixture consists of a stoichiometric ratio of DEGBA and DETDA molecules along with a carbon nanotube. The carbon nanotube is functionalized with a number of covalently bonded DETDA molecules. The grafting density of these bonded DETDA molecules ranges from 0.0 to 0.012 \AA^{-2} . The following MD and energy minimization techniques are applied using the LAMMPS software package.⁷

The initial structure is subject to an energy minimization limited to 500 steps and a convergence criteria of $0.1 \text{ kcal mol}^{-1} \text{ \AA}^{-1}$. This is followed by a constant volume (NVT) MD simulation of 10 ps in which the temperature is elevated from 300 K to 1000 K, which precedes a NVT MD simulation of 100 ps. These serve to effectively mix the reactant molecules at low density preventing any influence due to the initial placement of the reactant molecules. This simulation of the low density mixture is followed by a series of constant pressure (NPT) MD simulations. This is done in order to establish the reactant mixture at the proper density. The low density mixture is subject to an energy minimization limited to 1000 steps and a convergence criteria of $0.1 \text{ kcal mol}^{-1} \text{ \AA}^{-1}$. This is followed by a four step series of compressions: 1) A 10 ps NPT MD simulation increasing the pressure in a linear fashion from 1 to 100 atm at a temperature of 300 K. 2) A 100 ps NPT MD simulation at 100 atm and 300 K. 3) A 10 ps NPT MD simulation at 300 K in which the pressure is linearly reduced to 1 atm. 4) A 100 ps NPT MD simulation at 300 K and 1 atm of pressure which serves to produce the equilibrated final density of the reactant mixture. Finally the structure is subjected to a relatively rigorous energy minimization limited to 1000 steps and a convergence criteria of $0.01 \text{ kcal mol}^{-1} \text{ \AA}^{-1}$.

The equilibrated minimized mixture of reactants is subject to a curing methodology to produce the cured epoxy simulation. This consists of “reacting” the epoxide and amine functional groups which are part of the molecules contained in the reactant mixture. The free amine group of any of the DETDA molecules covalently bonded to the carbon nanotube is also reacted as part of this mixture. This curing methodology proceeds as follows: The positions of all reactant groups are calculated within the minimum image convention⁸ for MD simulation in periodic boundary conditions. The bond formed from curing is between the nitrogen atom on the amine group and the end carbon in the epoxide group. The distance between all pairs of these two atom types is calculated. As indicated in Fig. 1, an amine functional group ($-\text{NH}_2$) can react with two epoxide ($\text{CH}_2\text{OCH}-$) functional groups. Therefore the two epoxide functional groups with the shortest distance to each amine functional group are tabulated. If two differing amines have the same epoxide group tabulated, the one with the longer distance is eliminated from the list. If these distances are below a specified cutoff distance, r_{react} , then a chemical bond between the amine nitrogen and the epoxide end carbon is created. In addition, the chemical bond between the hydrogen and the nitrogen on the amine is eliminated and a bond between this hydrogen and the epoxide oxygen is created. The bond between the epoxide oxygen and the epoxide end carbon is also eliminated. The cutoff distance, r_{react} , of 8 \AA is used for all the curing “reactions”.

The cured epoxy network structure is subject to an energy minimization limited to 100 steps and a convergence criteria of $0.1 \text{ kcal mol}^{-1} \text{ \AA}^{-1}$. This is followed by a 100 ps NPT MD simulation at 1 atm of pressure and 300 K and a final energy minimization limited to a convergence criteria of $0.01 \text{ kcal mol}^{-1} \text{ \AA}^{-1}$. The final equilibrated model is shown in Fig. 5 with the PBC coordinates indicating the bulk nature of the epoxy matrix surrounding the carbon nanotube which extends through the z coordinate of the PBC volume.

IV. Results and Discussion

The following systems were simulated: four nanocomposite models with grafting densities 0.0, 0.004, 0.008, and 0.012 \AA^{-2} . The grafting density is calculated from the number of DETDA molecules covalently bonded to the carbon nanotube divided by the surface area of the nanotube. The surface area is calculated using a radius of 6.74 \AA for the (10,10) carbon nanotube simulate here.

The equilibrated structures obtained from the method described in Section II were simulated using the LAMMPS⁷ software which only allows rectilinear PBCs. These equilibrated structures were converted to the Tinker format for calculation of mechanical properties since it will be necessary to deform the PBCs away from their rectilinear coordinates in order to evaluate the mechanical properties in shear.

Mechanical properties are calculated by the method of Theodorou and Suter.⁹ The equilibrated atomistic models are deformed by six shear and six tension deformations corresponding to positive and negative values of ε for each of the three shear and three tension deformations. A value of $\varepsilon = \pm 0.0005$ is used for all deformations. Examples of these deformations of the periodic boundary conditions are described as follows: A shear deformation perpendicular to z along x is performed by moving the origin of the periodic boundary condition vectors, $\mathbf{0}$ and changing the

orientation of the PBC continuation vectors, \mathbf{a}_x , \mathbf{a}_y , and \mathbf{a}_z as given by Eqs. (1), where the subscript ‘0’ indicates the equilibrated undeformed reference state.

$$\mathbf{0} = \mathbf{0}_0 - (1/2)\varepsilon\mathbf{a}_{x0} \quad (1)$$

$$\mathbf{0} = \mathbf{0}_0 - (1/2)\varepsilon\mathbf{a}_{x0}$$

$$\mathbf{a}_x = \mathbf{a}_{x0}$$

$$\mathbf{a}_y = \mathbf{a}_{y0}$$

$$\mathbf{a}_z = \mathbf{a}_{z0} + \varepsilon\mathbf{a}_{x0}$$

A deformation for the uniaxial tension along x is performed by moving the origin and PBC continuation vectors as follows:

$$\mathbf{0} = \mathbf{0}_0 - (1/2)\varepsilon\mathbf{a}_{x0} \quad (2)$$

$$\mathbf{a}_x = (1 + \varepsilon)\mathbf{a}_{x0}$$

$$\mathbf{a}_y = \mathbf{a}_{y0}$$

$$\mathbf{a}_z = \mathbf{a}_{z0}$$

It should be noted that the positions of the parent chain atoms are not altered with respect to each other during this deformation step. However, the deformation does affect the mapping of the coordinates into the PBC volume. This deformation is minimal, preserving bond lengths and angles of the parent chains molecules. Only the coordinates of the atoms mapped into the PBC volume are affected. After the deformation is applied, an energy minimization is performed in Tinker, limited to a convergence criteria of $0.01 \text{ kcal mol}^{-1} \text{ \AA}^{-1}$. From this energy minimized conformation, the stress tensor is evaluated. The positive and negative deformations are compared with the undeformed reference structure for a given shear or tension deformation. The first derivative of the stress tensor is obtained through a finite difference formula, from which the 6x6 stiffness matrix of elastic constants, \mathbf{C} , is calculated.⁹ Taking the inverse of this matrix yields the compliance matrix. The compliance matrix for a transverse isotropic system is shown in Eq. (3). This expression relates the elements of the compliance matrix, \mathbf{S} , to the following variables: the Young’s modulus and Poisson ratio in the x-y symmetry plane, E_p and ν_p , the Young’s modulus and Poisson ratio in the z direction E_z and ν_{pz} , and the shear modulus in the z-direction G_{zp} .

$$\begin{bmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ \varepsilon_{yz} \\ \varepsilon_{zx} \\ \varepsilon_{xy} \end{bmatrix} = \begin{bmatrix} \frac{1}{E_p} & -\frac{\nu_p}{E_p} & -\frac{\nu_{zp}}{E_p} & 0 & 0 & 0 \\ -\frac{\nu_p}{E_p} & \frac{1}{E_p} & -\frac{\nu_{zp}}{E_p} & 0 & 0 & 0 \\ -\frac{\nu_{pz}}{E_p} & -\frac{\nu_{pz}}{E_p} & \frac{1}{E_z} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2G_{zp}} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{2G_{zp}} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1+\nu_p}{E_p} \end{bmatrix} \begin{bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{zx} \\ \sigma_{xy} \end{bmatrix} \quad (3)$$

The relative change in elastic constants due to grafting density or degree of functionalization was investigated. Fig. 6 shows the shear modulus in the z-direction, G_{zp} , as a function of grafting density of the additional diamine molecules to the nanotube. This value appears to rise sharply with the lowest non-zero grafting density (0.004 \AA^{-2}) and then decrease with increasing grafting density. One explanation for this is that the reactant mixture reaches a saturation of amine groups near the surface at high densities. Due to volume constraints, the epoxide group containing molecules (DGEBA) are excluded from the interfacial area in the region near the nanotube. Therefore, a grafting density that is too high might actually limit the effective load transfer of the matrix to the nanotube.

The Young's modulus in the x-y plane, E_p , is plotted as a function of grafting density in Fig. 7. This value appears to increase linearly with grafting density up to 0.008 \AA^{-2} and then decrease. A comparison of Figs. 6 and 7 indicates that the optimal grafting density for the enhancement of this particular mechanical property might lie at a different value than for the shear modulus in the z direction, G_{zp} .

The Young's modulus in the z direction, E_z , is plotted as a function of the grafting density in Fig. 8. The stiffness in the z direction is primarily due to the contribution of the axial stiffness of the carbon nanotube in this direction. The relatively slight decrease in this value can be attributed to the weakening of the planar aromatic carbon nanotube structure due to the functionalization.

Poisson ratio in the z direction, ν_{pz} , is plotted as function of the grafting density in Fig. 9. The results here are similar to those presented in Fig. 7, where the maximum enhancement is found at a grafting density of 0.008 \AA^{-2} . In a similar manner, Fig. 10 shows the Poisson ratio in the x-y direction, ν_p . The results here are similar to those seen in Fig. 8, with a successive though relatively small decline in this property with increasing grafting density.

V. Concluding Remarks

Elastic mechanical properties of single wall carbon nanotubes functionalized to an epoxy matrix were calculated using molecular modeling techniques. The degree of functionalization was varied by systematically changing the grafting density. It is important to note that the grafting densities used in this study are relatively high for an epoxy/nanotube nanocomposite.

To consider the accuracy of a simulation of this type, the issue of statistical sampling must be addressed. Beyond the samples considered in this study, there are numerous other configurations that can be formed from the arrangement of the reactant molecules prior to curing. In order to completely explore the statistical mechanics of this material system a statistically representative sample should be analyzed. For this study, a relatively small system size was chosen since the correlation length of the small molecules was not expected to be great. In order to produce more statistical samples, it is only necessary to repeat the low density mixing procedure, obtaining an independent configuration prior to the compression and "curing" methodology steps outlined in Section III.

The primary conclusion from this study is that for the nanocomposite systems analyzed, an optimal grafting density may exist for the enhancement of mechanical properties by the mechanism of load transfer through chemical

functionalization. Furthermore, the results indicate that each property may require differing degrees of functionalization for maximum enhancement of their respective mechanical properties (*i.e.* shear modulus in the z-direction, G_{zp} , versus Young's modulus in the x-y plane, E_p .) Some mechanical properties, such as the Young's modulus along the nanotube (the z direction, E_z) are only degraded through chemical functionalization.

References

¹Odegard, G.M., Gates, T.S., Nicholson, L.M. and Wise, K.E., "Equivalent-Continuum Modeling of Nano-Structured Materials," *Composites Science and Technology*, Vol. 62, 2002, pp. 1869-1880.

²Stevens, J.L., Huang, A.Y., Peng, H., Chiang, I.W., Khabashesku, V.N., Margrave, J.L., "Sidewall Amino-Functionalization of Single-Walled Carbon Nanotubes Through Fluorination and Subsequent Reactions with Terminal Diamines," *Nanoletters*, Vol. 3, No. 3, 2003, pp. 331-336.

³Zhu, J., Kim, J., Peng, H., Margrave, J.L., Khabashesku, V.N., Barrera, E.V., "Improving the Dispersion and Integration of Single-Walled Carbon Nanotubes in Epoxy Composites Through Functionalization," *Nanoletters*, Vol. 3, No. 8, 2003, pp. 1107-1113.

⁴Yarovsky, I., Evans, E., "Computer Simulation of Structure and Properties of Crosslinked Polymers: Application to Epoxy Resins," *Polymer*, Vol. 43, 2003, pp. 963-969.

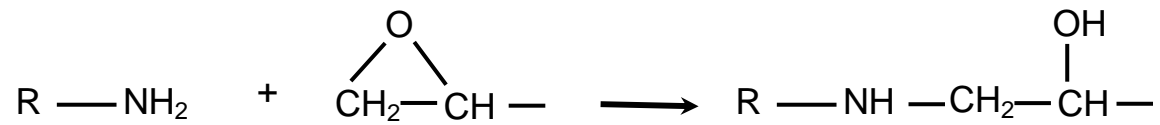
⁵Cornell, W.D., Cieplak, P., Bayly, C.I., Gould, I.R., Merz, K.M., Ferguson, D.M., Spellmeyer, D.C., Fox, T., Caldwell, J.W., Kollman, P.A., "A Second Generation Force Field for the Simulation of Proteins, Nucleic Acids, and Organic Molecules," *J. Am. Chem. Soc.*, Vol. 117, 1995, pp. 5179-5197.

⁶TINKER - Software Tools for Molecular Design, Ver. 4.2, Washington University School of Medicine, St. Louis, MO, 2004.

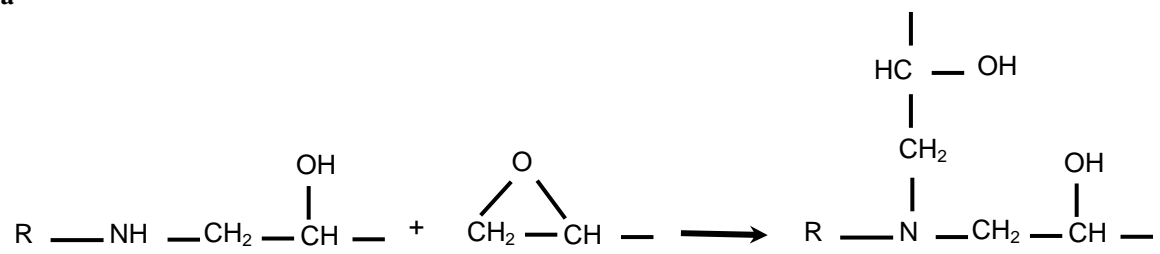
⁷Plimpton, S.J. "Fast Parallel Algorithms for Short-Range Molecular Dynamics," *J. Comp. Phys.*, Vol. 117, 1995, pp. 1-19., <http://www.cs.sandia.gov/~sjplimp/lammps.html>

⁸Allen, M.P., Tildesley, D.J., *Computer Simulation of Liquids*, Oxford University Press, New York, 1987, Chap. 1.

⁹Theodorou, D.N., Suter, U.W., "Atomistic Modeling of Mechanical Properties of Polymeric Glasses," *Macromolecules*, 1986, Vol. 19, pp. 139-154.



a



b

Fig. 1. The chemical reaction of an epoxide with an amine.

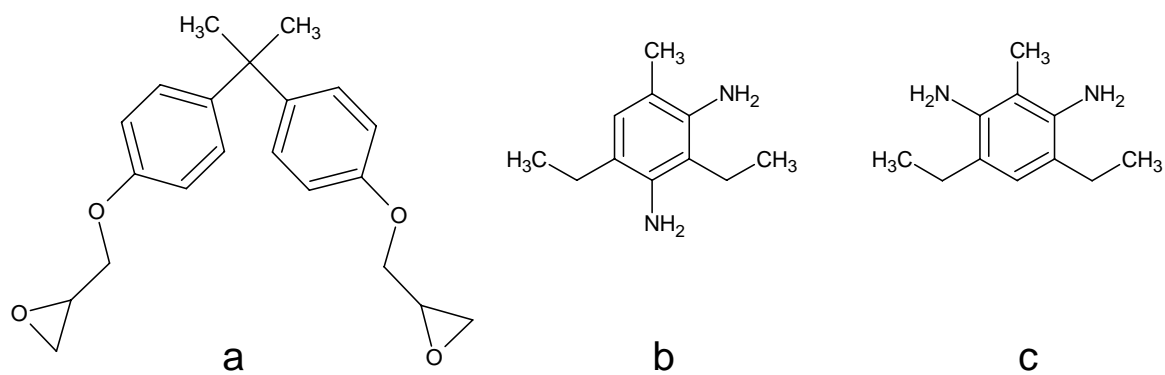


Fig. 2. a) Diglycidyl ether of bisphenol A (DGEBA). b) 3,5-Diethyltoluene-2,4-diamine. c) 3,5-Diethyltoluene-2,6-diamine.

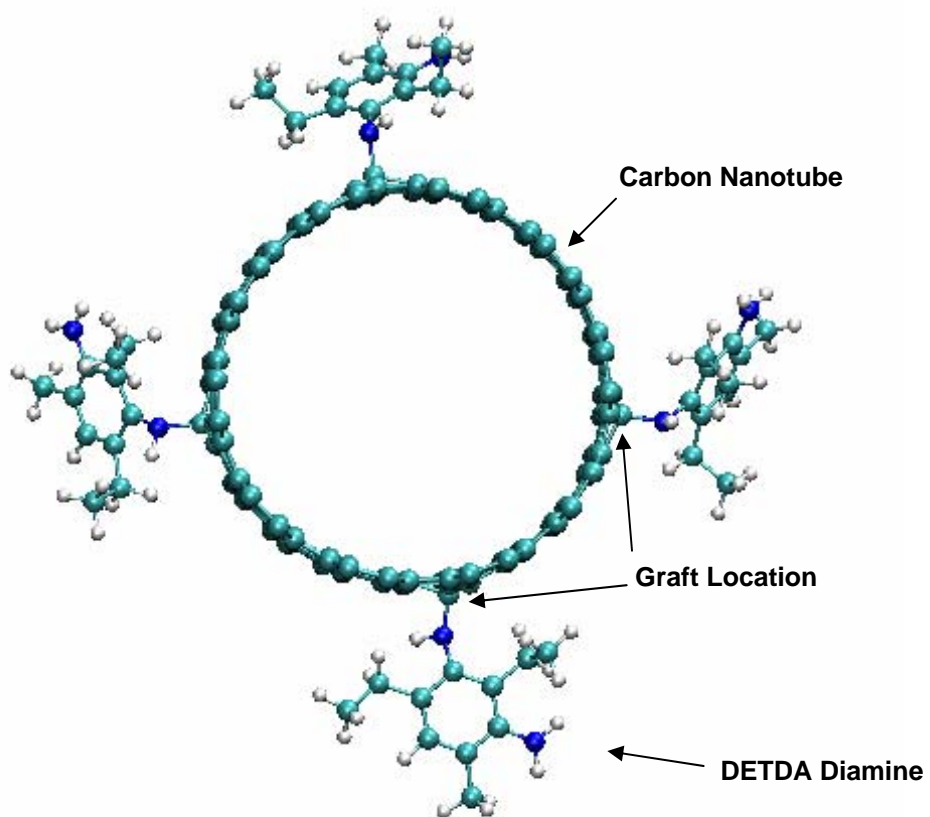


Fig. 3. DETDA diamine molecules covalently bonded to carbon nanotube.

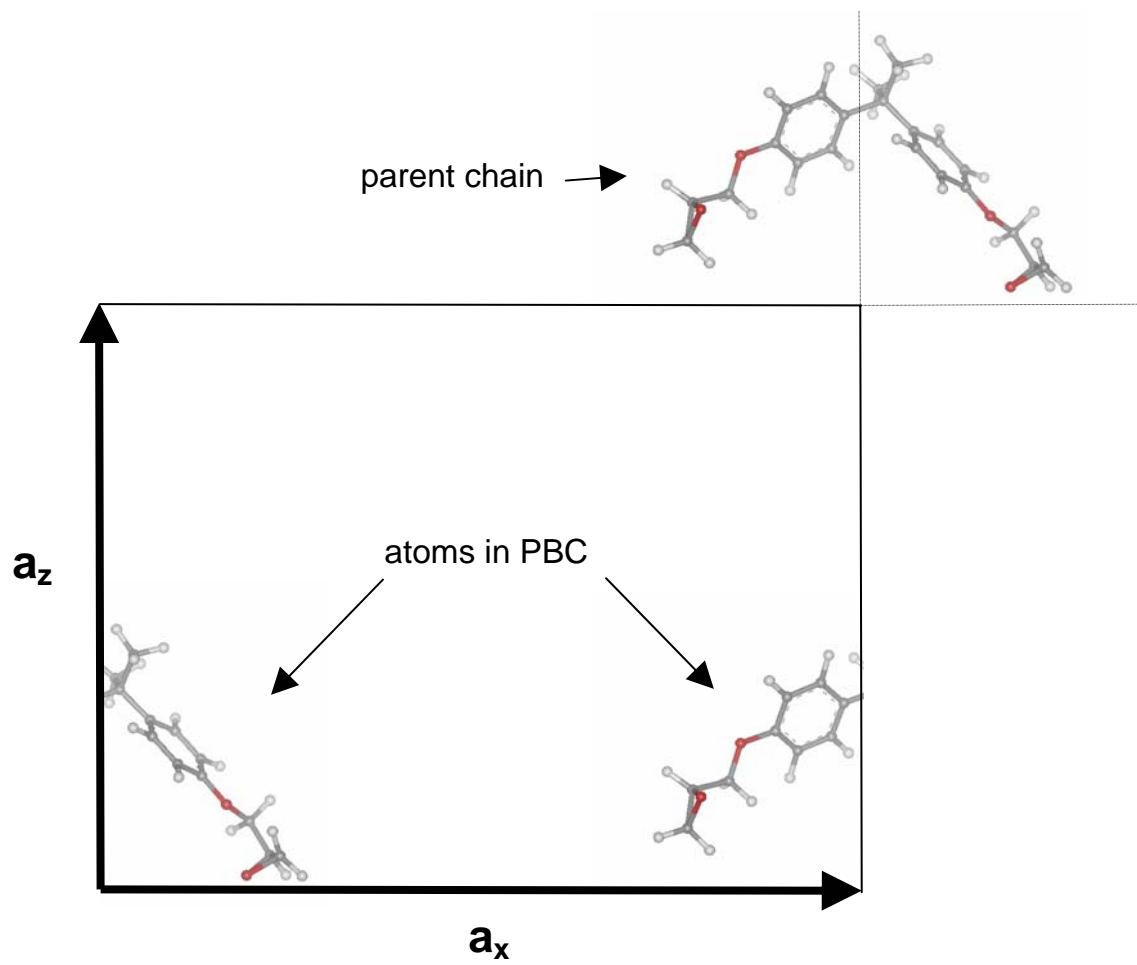


Fig. 4. The parent chain of a DGEBA molecule, mapped inside the PBC coordinate system

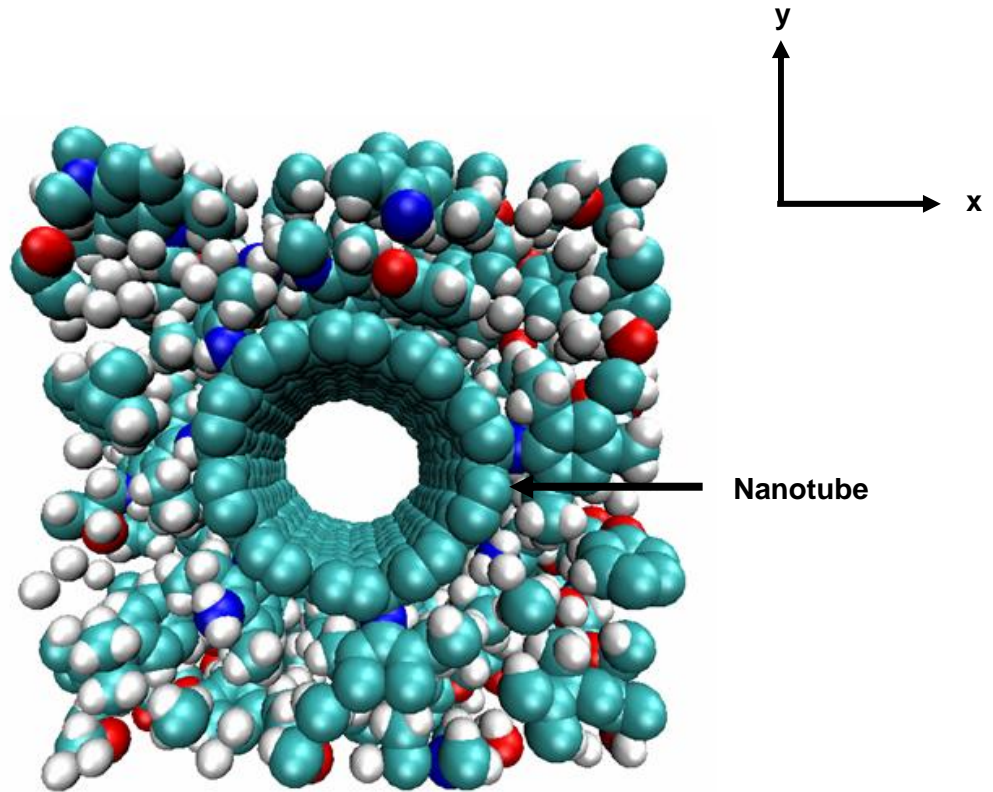


Fig. 5. The atomistic model of the carbon nanotube embedded in the epoxy matrix. The nanotube is oriented along the z axis.

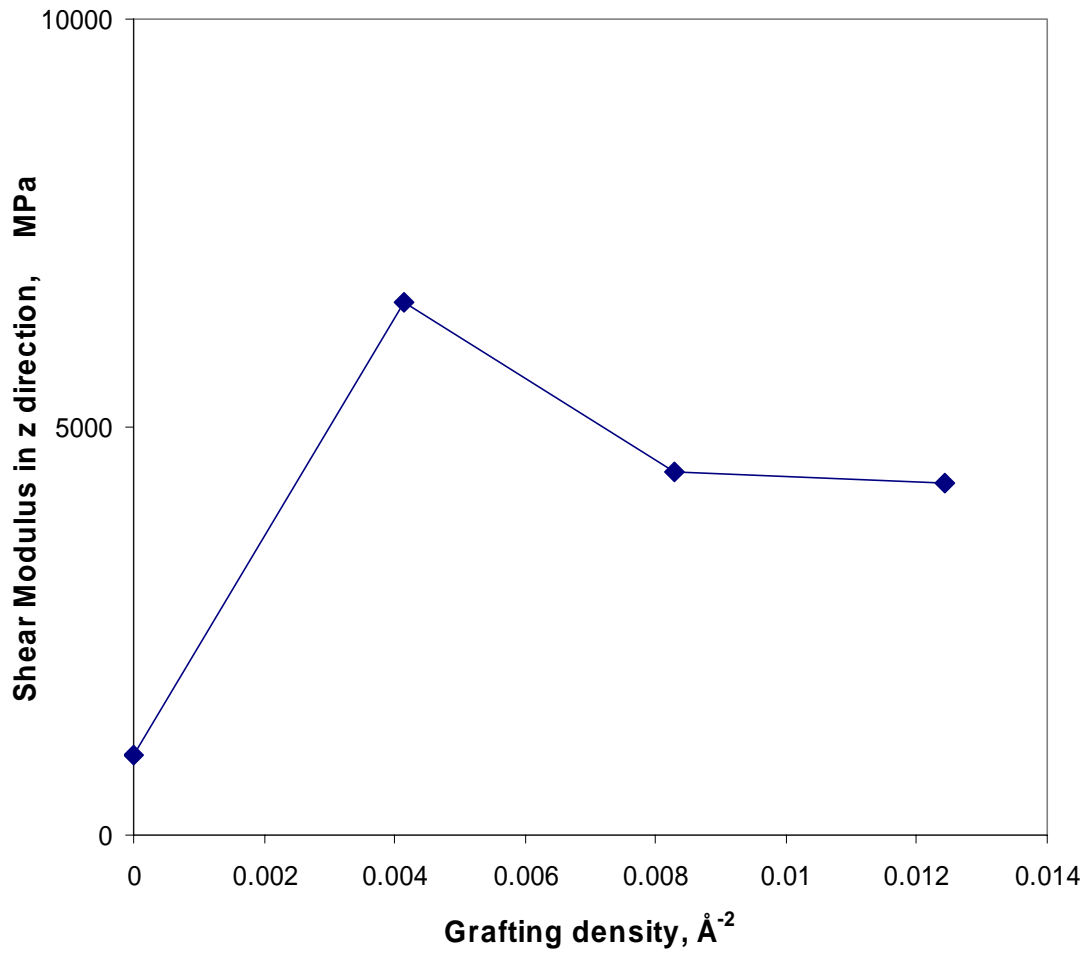


Fig. 6. The shear modulus in the z-direction, G_{zp} , as a function of grafting density of the additional diamine molecules to the nanotube.

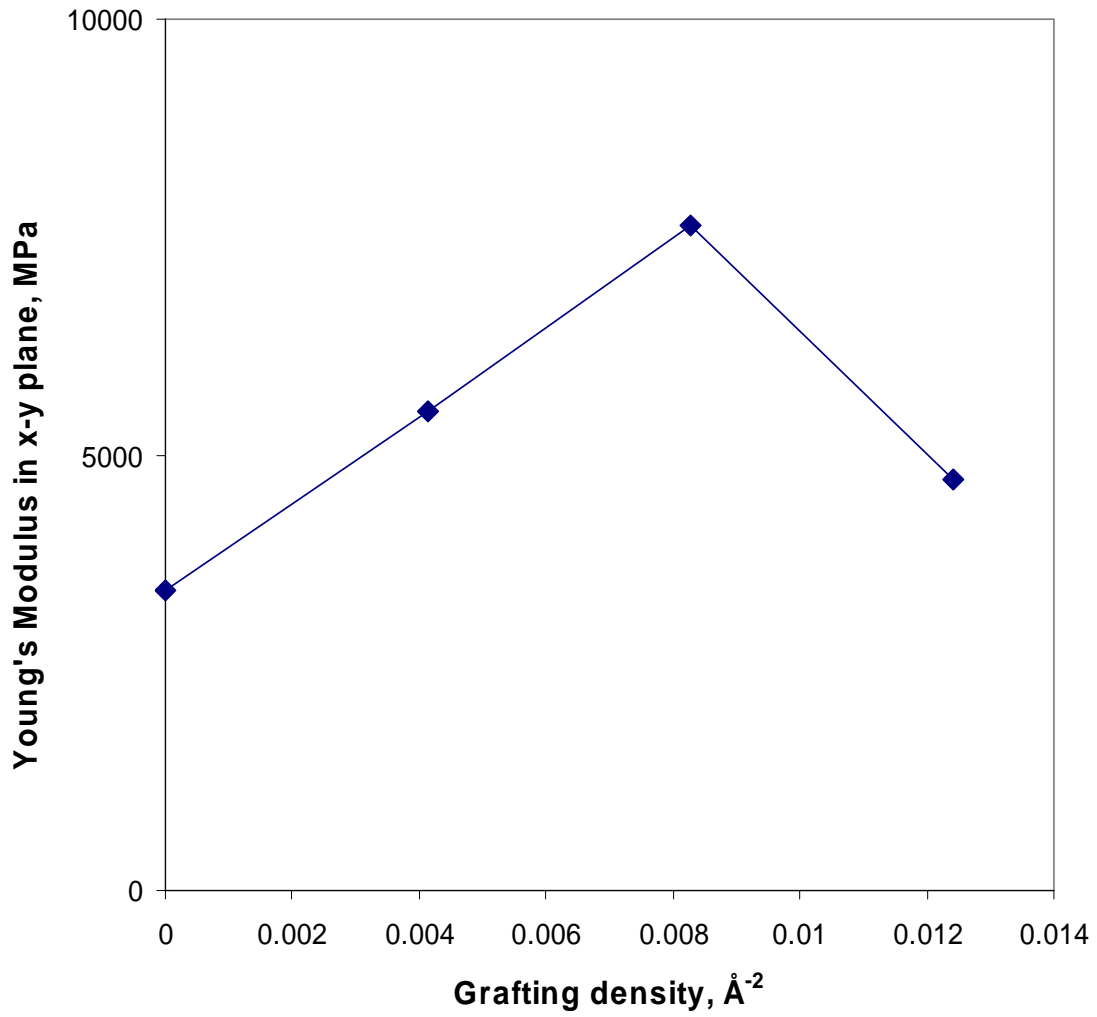


Fig. 7. The Young's modulus in the x-y plane, E_p , as a function of grafting density of the additional diamine molecules to the nanotube.

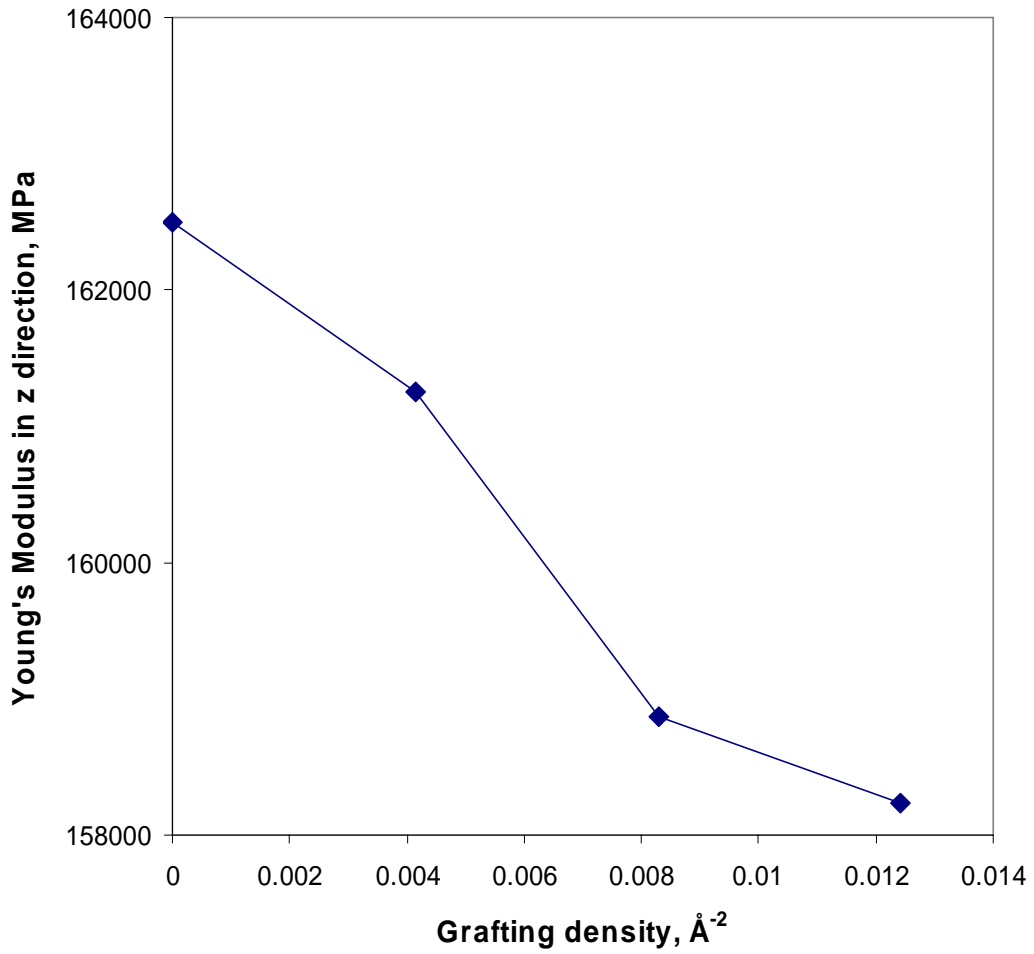


Fig. 8. The Young's modulus in the z direction, E_z , as a function of grafting density of the additional diamine molecules to the nanotube.

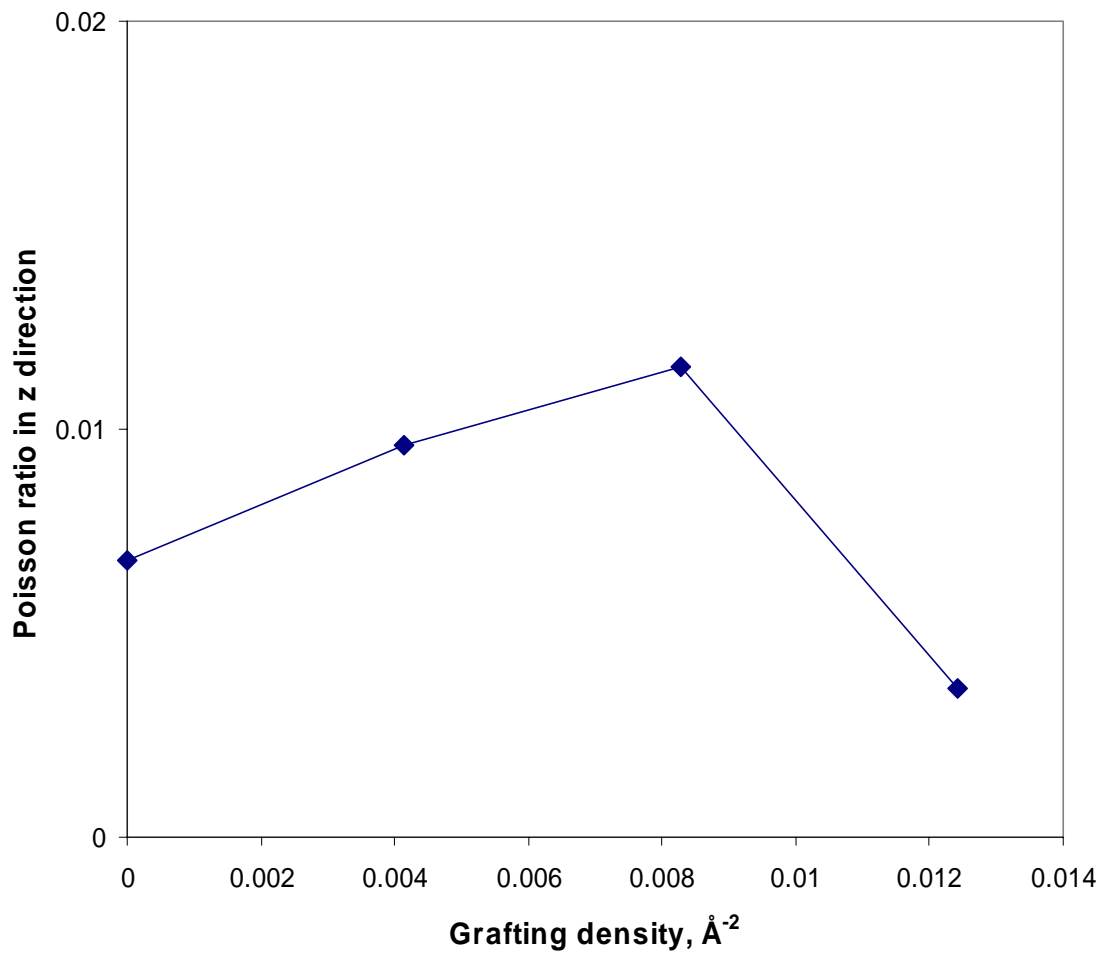


Fig. 9. The Poisson ratio in the z direction, ν_{pz} , as a function of grafting density of the additional diamine molecules to the nanotube.

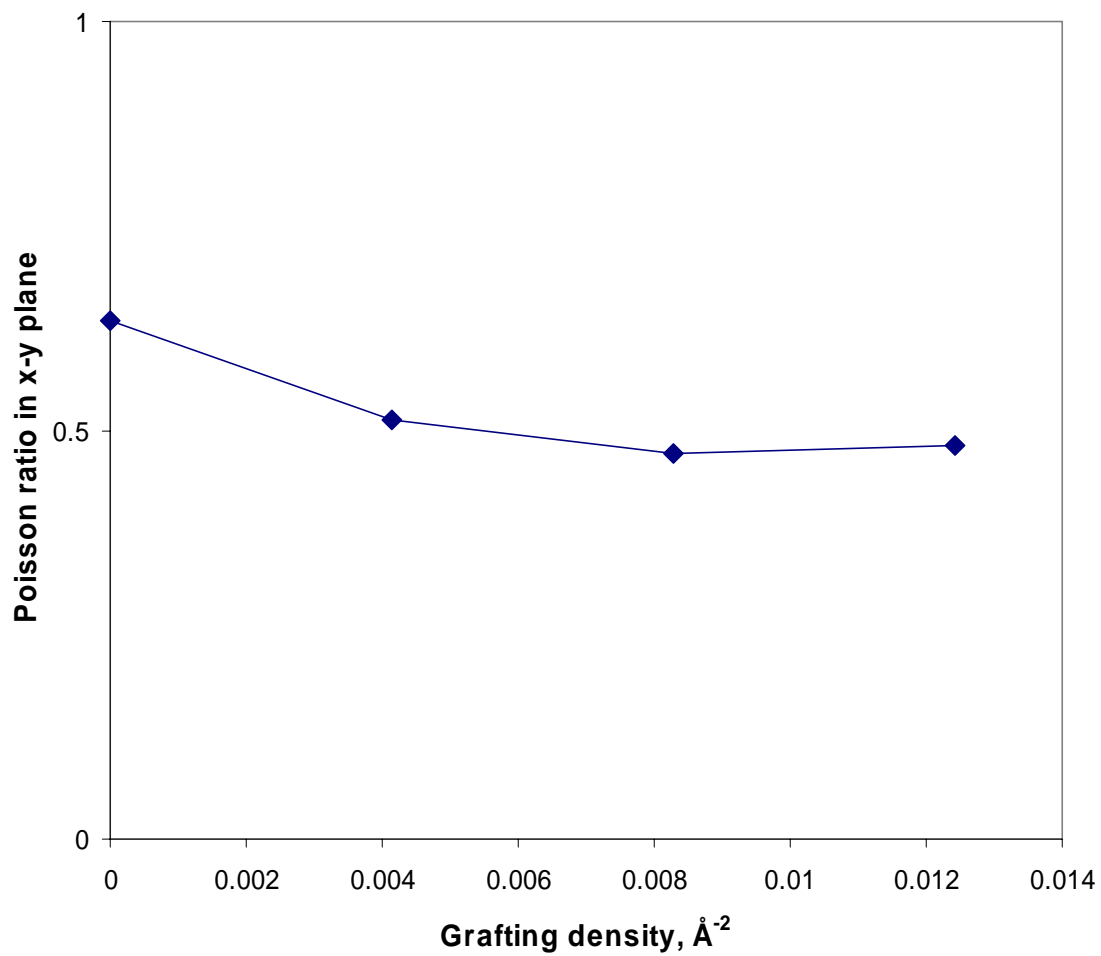


Fig. 10. The Poisson ratio in the x-y plane, ν_z , as a function of grafting density of the additional diamine molecules to the nanotube.