UNIVERSITÉ PARIS-EST

MSME Laboratoire Modélisation et Simulation Multi Echelle

Modélisation et Simulation Multi Echelle **MSME UMR 8208**

équipe Biomécanique Salah NAILI, Professor

Créteil, July 19, 2017

Object: **Revised version, manuscript COMMAT-D-17-00680**

Dear Professor Jeffrey Hoyt,

Thank you for the opportunity you gave us to revise our Manuscript COMMAT-D-17-00680 entitled "From morphology to thermodynamics and mechanical properties of epoxy/clay nanocomposite: investigation by molecular dynamics simulations" by Van Son Vo, Vu-Hieu Nguyen, Samia Mahouche-Chergui, Benjamin Carbonnier, Devis Di Tommaso and Salah Naili.

As suggested by the referee 3, the title of the revised manuscript is henceforth "From atomistic structure to thermodynamics and mechanical properties of epoxy/clay nanocomposites: investigation by molecular dynamics simulations".

You will find with this letter for your convenience a point-by-point answer to the points made by the referees. All of the changes are explained in detail. We deal with the points sequentially, with their comments indented in a small font size and our response in a normal font size.

Given the overall positive recommendations of the referees, we trust that the manuscript is now acceptable for publication in Computational Materials Science.

Correspondence should be addressed to Professor S. Naili.

With all best wishes,

Salah NAILI,
on behalf of the authors.

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équipe Biomécanique Salah NAILI, Professor

Créteil, July 18, 2017

Response to the referee on the Manuscript COMMAT-D-17-00680 presented by Van Son Vo *et al.*
via
Professor Jeffrey Hoyt (Editor)
Computational Materials Science

Dear referee,

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We thank the referee for his helpful and comments regarding our work and we are pleased that his opinion is "It establishes a clear computational methodology to simulate the properties of PCNs. So, I will recommend this draft to publish on the journal of Computational Materials Science.".

As suggested by one of the referees, the title of the revised manuscript is henceforth "From atomistic structure to thermodynamics and mechanical properties of epoxy/clay nanocomposites : investigation by molecular dynamics simulations".

Please see our detailed responses below. As a result of the comments, we have modified the paper and we hope that the referee will be satisfied with the revised version.

Referee comment :

> "This work presents a novel method to study the structural and mechanical properties of complicated polymer/clay nanocomposites, combining several different levels of computational approaches and analyses. This draft provides atomic insights to study PCNs and is able to compute the related thermodynamic and elastic properties of the

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multi-functional materials. It establishes a clear computational methodology to simulate the properties of PCNs. So, I will recommend this draft to publish on the journal of Computational Materials Science."

Author response :

We thank the referee for his positive evaluation of our manuscript and for his support for the publication of our manuscript in Computational Materials Science.

Referee comment :

"In general, the figures are nice. However, if fussily, nearly all the fonts of the labels of x- and y-axis as well as the legends are smaller than their captions and text. It would be great if those labels can be enlarged. Particularly Figure 3, the atoms are too small to be clearly viewed. I will suggest the authors enlarging the four snaps of Figure 3, also the atomic labels."

Author response :

The font size of the labels and of the legends has been increased to improve the readability the Figure's text.

Salah NAILI,
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We thank the referee for his helpful and comments regarding our work and we are pleased that his opinion is "The calculations have been carried out with care and are reproducible. The results on mechanical properties are interesting, and the reported elastic constants and radial distribution functions contribute to better understanding of composite properties."

As suggested by one of the referees, the title of the revised manuscript is henceforth "From atomistic structure to thermodynamics and mechanical properties of epoxy/clay nanocomposites : investigation by molecular dynamics simulations".

Please see our detailed responses below. As a result of the comments, we have modified the paper and we hope that the referee will be satisfied with the revised version.

Referee comment :

> "The authors report a study of mechanical properties of a model clay/epoxy polymer composite. I am somewhat confused about the model choices. The clay parameters in CLAYFF are not suited to study interfacial adsorption and binding mechanisms - they are good for high temperature glasses only. Some sources have shown that

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cleavage and organic binding energies are 100% off compared to experiment whereas interface FF gives ¡ 10% deviation. See, for example, Chem. Mater. 2005, 17, 5658, and a review in Clay Miner. 2012, 47, 205. The reason for this are poor choices of atomic charges in CLAYFF that do not reproduce dipole moments and interfacial interactions. I think the authors should discuss these issues and references in the paper as the assumptions affect the reported results. It is known that CLAYFF can calculate better mechanical properties than Interface FF as many bonding terms therein plus the nonbond terms overestimate the in-plane stiffness (J. Phys. Chem. C 2010, 114, 1763). These differences, however, have little impact at low filler fraction."

Author response :

We agree with referee that InterfaceFF would give more accurate cleavage energies and binding energies for the PCNs system. However, these quantities have not been computed in the present work because its main goal was to evaluate the thermodynamic and mechanical properties of PCNs at different temperatures temperature (300 K to 600 K). Moreover, InterfaceFF contains several intramolecular terms that can overestimate the in-plane stiffness of the PCNs system [1] and increase the computation time of the molecular dynamics simulations. Given that the CLAYFF force field has been previously adopted to calculate the structural and mechanical properties of clays and other PCNs systems [1, 2, 3, 4], given that CLAYFF has a rather simple functional form, which makes this force field computationally fast and robust for the simulation of multicomponent systems, CLAYFF is a suitable potential model to accurately simulate the structural and thermodynamic properties of epoxy/clay nanocomposite.

The following paragraph and references given below have been added to the revised manuscript at the end of Section 2.3 "Force field description".

Given that the CLAYFF forcefield has been previously adopted to calculate the structural and mechanical properties of clays and other PCNs systems [2, 3, 4, 5, 6], given that CLAYFF has a rather simple functional form, which makes this forcefield computationally fast and robust for the simulation of multicomponent complex systems, CLAYFF is a suitable potential model to accurately simulate the structural and thermodynamic properties of epoxy/clay nanocomposite. It was previously pointed out that this forcefield is not appropriate to compute cleavage and binding energies [1, 7, 8], but the evaluation of these properties is not the focus of the present study.

[1] Heinz, H. (2012). Clay minerals for nanocomposites and biotechnology : surface modification, dynamics and responses to stimuli. Clay Minerals, 47(2), 205-230.

[2] Mazo, M.A., Manevitch, L.I., Gusarova, E.B., Shamaev, M.Y., Berlin, A.A., Balabaev, N.K., Rutledge, G.C. (2008). Molecular dynamics simulation of thermomechanical properties of montmorillonite crystal. 1. Isolated clay nanoplate. The Journal of Physical Chemistry B, 112(10), 2964-2969.

[3] Liu, X., Lu, X., Wang, R., Zhou, H., Xu, S. (2007). Interlayer structure and dynamics of alkylammonium-intercalated smectites with and without water : A molecular dynamics study. Clays and Clay Minerals, 55(6), 554-564.

[4] Anoukou, K., Zaoui A., Zaïri F., Nait-Abdelaziz, M., Gloaguen, J.-M. (2013). Molecular dynamics study of the polymer clay nanocomposites (PCNs) : Elastic constants and basal spacing predictions, Computational Materials Science, 77, 417-423.

[5] Suter, J.L., Coveney, P.V. (2009). Computer simulation study of the materials properties of intercalated and exfoliated poly (ethylene) glycol clay nanocomposites. Soft Matter, 5(11), 2239-2251.

[6] Carrier, B., Vandamme, M., Pellenq, R.J.M., Van Damme, H. (2014). Elastic properties of swelling clay particles at finite temperature upon hydration. The Journal of Physical Chemistry C, 118(17), 8933-8943.

[7] Heinz, H., Koerner, H., Anderson, K.L., Vaia, R.A., Farmer, B.L. (2005). Force field for mica-type silicates and dynamics of octadecylammonium chains grafted to montmorillonite. Chemistry of materials, 17(23), 5658-5669.

[8] Zartman, G.D., Liu, H., Akdim, B., Pachter, R., Heinz, H. (2010). Nanoscale tensile, shear, and failure properties of layered silicates as a function of cation density and stress. The Journal of Physical Chemistry C, 114(4), 1763-1772.

The following criteria have been used to verify the accuracy of the molecular model and simulations :

- The structural parameters obtained from the density profile of the epoxy matrix as well as the polymer confined between the clay layers agree with experimental characterisation of PCNs reported in the literature [9, 10, 11].
- The presence of the interphase revealed in our study was inferred by Chen et al. [12].
- The elastic tensors obtained from our simulations for the PCNs system are agree with the orthorhombic symmetry [13].
- The CLAYFF forcefield has been widely previously adopted to calculate the structural and mechanical properties of clays.

The following paragraph has been added to the revised manuscript in section 2.1.

It is also important to point out that the molecular models used in this manuscript are "clay clusters" and not true PCNs. Real PCNs should be the mixture of clay clusters with polymer matrix, and they have a very complex structure [12, 13]. Therefore, a comparison with the real PCNs in the experimental part will be not appropriate. Moreover, it should be noted that, in the experimental part, it is impossible to make the nanocomposites with a specific control interlayer distance. Thus, the molecular dynamics simulation has been used to investigate the properties of the nanocomposites.

[9] Tack, J L., Ford, D.M. (2008). Thermodynamic and mechanical properties of epoxy resin DGEBF crosslinked with DETDA by molecular dynamics. Journal of Molecular Graphics and Modelling, 26(8), 1269-1275.

[10] Fan, H.B., Yuen, M.M. (2007). Material properties of the cross-linked epoxy resin compound predicted by molecular dynamics simulation. Polymer, 48(7), 2174-2178.

[11] Chen, Y., Chia, J.Y.H., Su, Z.C., Tay, T.E., Tan, V.B.C. (2013). Mechanical characterization of interfaces in epoxy-clay nanocomposites by molecular simulations. Polymer, 54(2), 766-773.

[12] Suter, J.L., Coveney, P.V. (2009). Computer simulation study of the materials properties of intercalated and exfoliated poly (ethylene) glycol clay nanocomposites. Soft Matter,

5(11), 2239-2251.

[13] Anoukou, K., Zaoui A., Zaïri F., Nait-Abdelaziz, M., Gloaguen, J.-M. (2013). Molecular dynamics study of the polymer clay nanocomposites (PCNs) : Elastic constants and basal spacing predictions," Computational Materials Science, 77, 417-423.

Referee comment :

> "Can the authors confirm the (supposedly) correct in-plane modulus of neat montmorillonite of 160 GPa (+/-10 GPa) in their calculations ?"

Author response :

In the literature, the values of the in-plane *moduli* E_{xx} and E_{yy} of neat montmorillonite layer are in the range of $160 - 400$ GPa (see Tab. 1).

Authors	h (nm)	E_{xx} (GPa)	E_{yy} (GPa)
Manevitch *et al.* [15]	1-0.6	250-420	250-420
Mazo *et al.* [16]	0.6-0.65	442	399
Suter *et al.* [17]	6.69-9.37	210-331	245-356
Carrier *et al.* [18]	0.656	292.3	274.2
Xu *et al.* [19]	0.615	277	277.8
Zartman *et al.* [20]	0.955	160	160

TABLE 1 – Values of the in-plane *moduli* E_{xx} and E_{yy} of neat montmorillonite layer issues of the literature.

It should be noted that the thickness of clay layer is small (around to 0.65 nm), this is why the molecular model with only clay layer can not be computed because the limit of R_{cut}. Basically, in order to overcome this problem, the calculation was performed with the interlayer distance in the literature. The reported value in Tab. 1 was determined in function of the thickness of the clay layer. Moreover, the method using stress-strain behavior seems to be more suitable to determine the mechanical properties of clay layer. In this study, we used the strain fluctuations method for determining the mechanical properties of the PCNs system. Due to the issues mentionned above, we are not able to confirm the value of the in-plane *modulus* of neat montmorillonite of 160 GPa ($\pm$ 10 GPa). However, the value of $160 - 230$ GPa used for the in-plane *modulus* of neat montmorillonite layer in the calculation with the finite element method give results suitable.

[15] Manevitch, O.L., Rutledge, G.C. (2004). Elastic properties of a single lamella of montmorillonite by molecular dynamics simulation. The Journal of Physical Chemistry B, 108(4), 1428-1435.

[16] Mazo, M.A., Manevitch, L.I., Gusarova, E.B., Shamaev, M.Y., Berlin, A.A., Balabaev, N.K., Rutledge, G.C. (2008). Molecular dynamics simulation of thermomechanical

properties of montmorillonite crystal. 1. Isolated clay nanoplate. The Journal of Physical Chemistry B, 112(10), 2964-2969.

[17] Suter, J.L., Coveney, P.V., Greenwell, H.C., Thyveetil, M.A. (2007). Large-scale molecular dynamics study of montmorillonite clay : emergence of undulatory fluctuations and determination of material properties. The Journal of Physical Chemistry C, 111(23), 8248-8259.

[18] Carrier, B., Vandamme, M., Pellenq, R.J.M., Van Damme, H. (2014). Elastic properties of swelling clay particles at finite temperature upon hydration. The Journal of Physical Chemistry C, 118(17), 8933-8943.

[19] Xu, W., Zeng, Q., Yu, A. (2012). Young's modulus of effective clay clusters in polymer nanocomposites. Polymer, 53(17), 3735-3740.

[20] Zartman, G.D., Liu, H., Akdim, B., Pachter, R., Heinz, H. (2010). Nanoscale tensile, shear, and failure properties of layered silicates as a function of cation density and stress. The Journal of Physical Chemistry C, 114(4), 1763-1772.

Referee comment :

> "The calculations have been carried out with care and are reproducible. The results on mechanical properties are interesting, and the reported elastic constants and radial distribution functions contribute to better understanding of composite properties."

Author response :

We thank referee for the overall positive assessment and we anticipate that the new version of the manuscript is now acceptable for publication in Computational Materials Science.

Salah NAILI,
on behalf of the authors.

*Response to Reviewers

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We thank the referee for his helpful and comments regarding our work and we are pleased that his opinion is "This subject may be attractive.".

Please see our detailed responses below. As a result of the comments, we have modified the paper and we hope that the referee will be satisfied with the revised version.

Referee comment :

> "0. Authors claimed that they have proposed a novel molecular approach to study the morphology and thermomechanical properties of epoxy/clay nanocomposites. They utilized molecular dynamic simulations to determine structural arrangement of the constitutive components PCNs, the molecular interactions and the influence of silicate layer on the thermodynamic and elastic properties of these materials. Also, they investigated the thermodynamic properties of the confined polymer in each structure to characterize the role of silicate layer on the properties of nanocomposites. This subject may be attractive. However, the biggest challenge is its novelty, because the similar

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works may be found in the literature. Therefore, I think that the authors should explain clearly the originality and novelty of their work as well as revise the manuscript substantially for consideration again."

Author response :

Polymer/clay nanocomposites (PCNs) materials have been previously studied by means of computational methods but only few studies have considered the structure and thermodynamic properties of thermosetting polymers/clay nanocomposites (see reference 16 in the manuscript). To the best of our knowledge, this work reports the first computational model and molecular dynamics simulations of PCNs composed of silanilized-clay and thermosetting epoxy resin. Three nanocomposite structures consisting of different representative cross-linked epoxy molecules were considered to represent intercalated or exfoliated structures.

To put this work in the context of previously published theoretical studies of PCN materials and to highlight our novel contribution to this field, the following text has been added in the section 1 "Introduction".

The molecular structures of intercalated and exfoliated poly ϵ-caprolactone (PCL) nanocomposites have been previously studied by means of the molecular dynamics (MD) technique [7, 8]. Gardebien et al. [7] investigated the effect of the number and length of polymer chains on the structure of intercalated nanocomposites. By examining the interlayer density profiles, the authors found that the interlayer phase organizes into four layers while the charged heads of the surfactants remained at the surface. On the other hand, for the exfoliated nanocomposites it was found a layered structure with high density of organic phase near the clay surface. The different arrangement of poly (ethylene oxide) (PEO) in the intercalated and exfoliated nanocomposites was considered by Suter and Coveney [9] using large-scale MD simulations, where non-modified montmorillonite (MMT-Na) was used to model the inorganic phase. It was found that the PEO chains organize in layers parallel to the clay surface, and because of the sodium ions and the charges within the clay surface the conformation of the polymer in the exfoliated structure was significantly different from the intercalated system.

Elastic coefficients of PCNs are important properties that can be used as parameters in continuum mechanical models to estimate other macroscopic properties of PCNs [10,11]. However, only Xu et al. has used computational methods to predict the longitudinal and lateral Young's *moduli* of the exfoliated and partially intercalated/exfoliated clay clusters.

So far, computational models of PCNs were restricted to the cases of clay with pristine surface or chemically modified through cationic exchange with surfactant molecules.

In the works cited above, the pristine clay of organically modified clays with cationic surfactants were modelled. Modification of the clay surface by the covalent grafting was, for the first time, modelled using in the work of Piscitelli et al. [13]. Their MD simulations

revealed that an increase of aminosilanes concentration and the use of shorted aminosilane chains contribute to the extent of the *d*-spacing in the clay.

To the best of our knowledge, there is no computational study where these silanized clays served as fillers in polymer matrix, despite these techniques are extensively used in the synthesis of epoxy/clay nanocomposites [14, 15, 16, 17, 18]. Moreover, there is only a single computational study on the structural and thermosetting properties of polymer/clay nanocomposites [14], where Chen and co-workers considered intercalated and exfoliated clay-nanocomposites based on epoxy matrix cross-linked from Diglycidyl ether of bisphenol-A and Diethylmethylbenzenediamine (DGEBA and DETDA). In this study, a series of surfactants with a single ammonium group and one alkyl chain of various length were used and the failure behaviour of the interphase in terms of quantifiable parameters such as peak strength, fracture energy and final separation distance were determined. However, details of the molecular structures and overall thermomechanical properties of these nanocomposites were not investigated.

In the present work, we propose a molecular model based on the epoxy-based nanocomposite and silanized-clay models of Piscitelli et al. [13] to investigate the structural, thermodynamic and mechanical properties of thermosetting clay nanocomposites. The arrangements of the constitutive components of PCNs, and the effect of silicate layer on the thermodynamic and elastic properties of these multifunctional materials are quantified by means of molecular dynamics simulations of three nanocomposite structures consisting of different representative cross-linked epoxy molecules to represent intercalated or exfoliated structures.

Referee comment :

> "1. Title does not represent the main work of the research ? Please, revise it. "

Author response :

In our manuscript, we introduced an atomistic model to study the structural, thermodynamic and mechanical properties of epoxy/clay nanocomposite using molecular dynamics simulations. It is the reason for which we slightly change the title to "From atomistic structure to thermodynamics and mechanical properties of epoxy/clay nanocomposites : investigation by molecular dynamics simulations".

Referee comment :

> "2. Literature reviews are not complete. Many researches have been conducted on the issues raised in the manuscript. I recommend to add the manuscript the suitable references ; such as, (Molecular dynamics study of epoxy/clay nanocomposites : rheology and molecular confinement, Journal of Polymer Research 19 (6), 9897 , 2012), etc."

Author response :

Previously published computational studies of PCNs are now referenced in the section 1 "Introduction".

Referee comment :

"3. Please, the necessity of performing this work should be clarified ?"

Author response :

This point has been addressed in the response of the item 0.

Referee comment :

"4. What are the criteria for evaluating the accuracy of the obtained results ? Also, is there any experimental data to check and compare the results ?"

Author response :

The following criteria have been used to verify the accuracy of the molecular model and simulations :

- The structural parameters obtained from the density profile of the epoxy matrix as well as the polymer confined between the clay layers agree with experimental characterisation of PCNs reported in the literature [1, 2, 3].
- The presence of the interphase revealed in our study was inferred by Chen et al. [4].
- The elastic tensors obtained from our simulations for the PCNs system are agree with the orthorhombic symmetry [5].
- The CLAYFF force field has been widely previously adopted to calculate the structural and mechanical properties of clays.

The following paragraph has been added to the revised manuscript in section 2.1.

It is also important to point out that the molecular models used in this manuscript are "clay clusters" and not true PCNs. Real PCNs should be the mixture of clay clusters with polymer matrix, and they have a very complex structure [4, 5]. Therefore, a comparison with the real PCNs in the experimental part will be not appropriate. Moreover, it should be noted that, in the experimental part, it is impossible to make the nanocomposites with a specific controlled interlayer distance. Thus, the molecular dynamics simulation has been used to investigate the properties of the nanocomposites.

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Referee comment :

"5. What are the statistical measures for analyzing the final results ?"

Author response :

It is not clear to us what referee means by this question. Molecular dynamics is a statistical mechanics technique and for the systems considered in the present study (the molecular systems 100E, N − 20E, N − 60E and N − 100E simulated at temperature conditions in the range of 300 − 600 K) all computed properties have been averaged over the configurations generated during the production phase of the simulations.

Referee comment :

"6. Page 6, line 106, does the 200 ps is sufficient ? The energy graph should be presented. Furthermore, why was this step carried out at 600 K ?"

Author response :

During the preparation and equilibration stages of the computational protocol, MD simulations have been conducted in the NVT (600 K) ensemble for 200 ps to provide sufficient kinetic energy to the system and obtain a homogeneous polymer network near the clay surface and an equilibrated state. This procedure has been adopted in previous MD studies of similar systems [1, 2, 3, 4, 5]. The plot of total energy *versus* time for the N − 100E system is reported in Fig. 1. The total energy converges quickly indicating that the system is at equilibrium within the first 100 ps.

[1] J. Suter and P. Coveney, Computer simulation study of the materials properties of intercalated and exfoliated poly (ethylene) glycol clay nanocomposites," Soft Matter, vol. 5, no. 11, pp. 2239-2251, 2009.

[2] S.-C. Shiu and J.-L. Tsai, Characterizing thermal and mechanical properties of graphene/epoxy nanocomposites," Composites Part B : Engineering, vol. 56, pp. 691-697, 2014.

[3] K. Anoukou, A. Zaoui, F. Zaïri, M. Nait-Abdelaziz, and J.-M. Gloaguen, Molecular dynamics study of the polymer clay nanocomposites (PCNS) : Elastic constants and basal spacing predictions," Computational Materials Science, vol. 77, pp. 417-423, 2013.

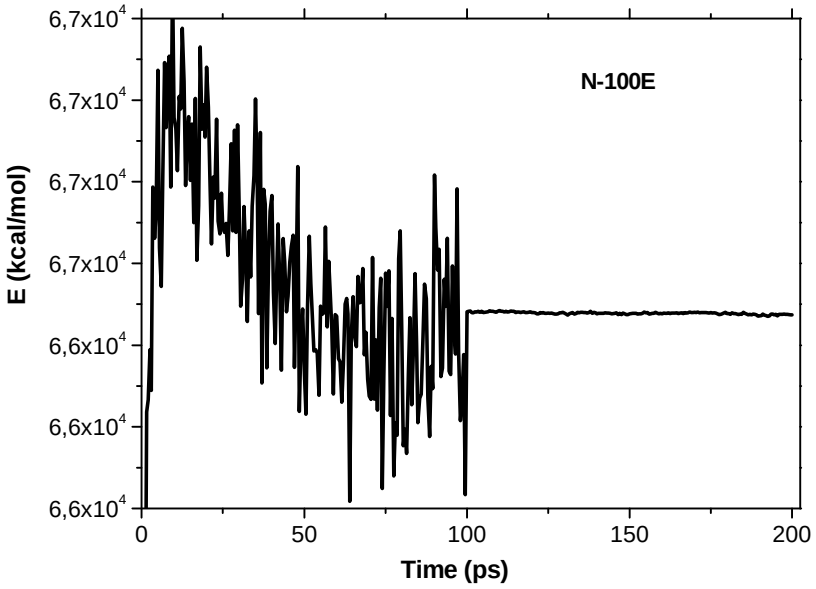

FIGURE 1 – Total energy *versus* time in NVT ensemble at 300 K for the case N − 100E. The first 100 ps correspond to the equilibration time.

[4] C. Li, A. Browning, S. Christensen, A. Strachan, Atomistic simulations on multilayer graphene reinforced epoxy composites," Composites Part A : Applied Science and Manufacturing, vol. 43, no. 8, pp. 1293-1300, 2012.

[5] W. Xu, Q. Zeng, A. Yu, Young's modulus of effective clay clusters in polymer nanocomposites, Polymer, vol. 53, no. 17, pp. 3735-3740, 2012.

The following paragraph has been added to the revised manuscript in section 2.3.

This procedure has been adopted in previous MD studies of similar systems [1, 2, 3, 4, 5].

Referee comment :

"7. Please, in Figure 8(b), explain the range of time that the graph has been obtained ?"

Author response :

We thank the referee for his remark and we apologize for this lack of information.

We have now added the following sentence in the revised version of manuscript to clarify this point.

To clarify this behavior, the temperature dependence of the MSD of the carbon species of pure epoxy matrix and its nanocomposites at 100 ps is reported.

We have also added the paragraph below in order to justify the typical behavior of the considered systems.

It should be emphasized that the chosen time (100 ps) for the comparison purpose may have a certain influence on the obtained results. In order to ensure the reliability of the result, other choices have also been tested (50, 150 and 200 ps) in the current work and the similar results have been observed. Thus, the reported results are the typical ones for the considered systems.

Salah NAILI,
on behalf of the authors.

From atomistic structure to thermodynamics and mechanical properties of epoxy/clay nanocomposites: investigation by molecular dynamics simulations

Van Son Vo[a,b], Vu-Hieu Nguyen[a], Samia Mahouche-Chergui[b], Benjamin Carbonnier[b], Devis Di Tommaso[c], Salah Naili[a]

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[b] *Université Paris-Est, Institut de chimie et des matériaux Paris-Est, ICMPE UMR 7182 CNRS, UPEC, 94320 Thiais, France*
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Abstract

Polymer/clay nanocomposites (PCNs) are multi-functional materials that have superior mechanical and thermal properties than polymer-based materials while maintaining their characteristic properties of lightweight and optical clarity. These materials are obtained by adding small amounts of clay nanofillers to a polymer matrix. In this work, we proposed a molecular model to investigate the morphology and thermomechanical properties of thermoseting clay nanocomposites. The epoxy matrix was composed of several representative cross-linked epoxy units, and different structures of PCNs, which correspond to intercalated or exfoliated status, were considered by varying the amount of polymer phase in the interlayer space. Molecular dynamics simulations of different nanocomposite structures were used to provide atomistic insights into the arrangement of the constitutive components of PCNs, the molecular interactions occurring in the interphase zone, and the influence of silicate layer on the thermodynamic and elastic properties of these multi-functional materials.

Keywords: clay, epoxy resin, exfoliated, intercalated, interphase, molecular dynamics simulations

1. Introduction

Polymer/clay nanocomposites (PCNs) materials are obtained by adding small amounts of clay nanofillers that have an extremely high aspect-ratio (up to 0.5 µm in length and width, but only 1 nm in thickness) and great mechanical properties (strength and flexibility) to a polymer matrix. PCNs exhibit significant enhancements in mechanical and thermal properties while maintaining

the characteristic of lightweight and optical clarity of polymer-based materials [1, 2, 3, 4]. To date, the physical behavior of PCNs is not yet well understood and to the best of our knowledge, few studies have considered the molecular structures and overall thermomechanical properties of polymers/clay nanocomposites. So, the physical behavior of this kind of nanomaterial is not yet well understood and still stimulate numerous research activities [5, 6].

The molecular structures of intercalated and exfoliated poly ϵ-caprolactone (PCL) nanocomposites have been previously studied by means of the molecular dynamics (MD) technique [7, 8]. Gardebien *et al.* [7] investigated the effect of the number and length of polymer chains on the structure of intercalated nanocomposites. By examining the interlayer density profiles, the authors found that the interlayer phase organizes into four layers while the charged heads of the surfactants remained at the surface. On the other hand, for the exfoliated nanocomposites it was found a layered structure with high density of organic phase near the clay surface. The different arrangement of poly (ethylene oxide) (PEO) in the intercalated and exfoliated nanocomposites was considered by Suter and Coveney [9] using large-scale MD simulations, where non-modified montmorillonite (MMT-Na) was used to model the inorganic phase. It was found that the PEO chains organize in layers parallel to the clay surface, and because of the sodium ions and the charges within the clay surface the conformation of the polymer in the exfoliated structure was significantly different from the intercalated system.

Elastic coefficients of PCNs are important properties that can be used as parameters in continuum mechanical models to estimate other macroscopic properties of PCNs [10, 11]. However, only Xu *et al.* [12] has used computational methods to predict the longitudinal and lateral Young's *moduli* of the exfoliated and partially intercalated/exfoliated clay clusters.

So far, computational models of PCNs were restricted to the cases of clay with pristine surface or chemically modified through cationic exchange with surfactant molecules.

In the works cited above, the pristine clay of organically modified clays with cationic surfactants were modelled. Modification of the clay surface by the covalent grafting was, for the first time, modelled using in the work of Piscitelli et al. [13]. Their MD simulations revealed that an increase of aminosilanes concentration and the use of shorted aminosilane chains contribute to the extent of the d-spacing in the clay.

To the best of our knowledge, there is no computational study where these silanized clays served as fillers in polymer matrix, despite these techniques are extensively used in the synthesis of epoxy/clay nanocomposites [14, 15, 16, 17, 18]. Moreover, there is only a single computational study on the structural and thermosetting properties of polymer/clay nanocomposites [14], where Chen and co-workers [14] considered intercalated and exfoliated clay-nanocomposites based on epoxy matrix cross-linked from Diglycidyl ether of bisphenol-A and Diethylmethylbenzenediamine (DGEBA and DETDA). In this study, a series of surfactants with a single ammonium group and one alkyl chain of various length were used and the failure behaviour of the interphase in terms of quantifiable parameters such as peak strength, fracture energy and final separation distance were determined. However, details of the molecular structures and overall thermomechanical properties of these nanocomposites were not investigated.

In the present work, we propose a molecular model based on the epoxy-based nanocomposite and silanized-clay models of Piscitelli *et al.* [13] to investigate the structural, thermodynamic and mechanical properties of thermosetting clay nanocomposites. The arrangements of the constitutive components of PCNs, and the effect of silicate layer on the thermodynamic and elastic properties of these multifunctional materials are quantified by means of molecular dynamics simulations of three nanocomposite structures consisting of different representative cross-linked epoxy molecules to represent intercalated or exfoliated structures.

The influence of the silanized clay on the morphology and density of polymers and the molecular interactions occurring at the issue of the resulting interphase region was analysed. In addition, the effect of the end functional groups of the grafted aminosilane molecules, on their interactions with the host epoxy polymer was also discussed by examining the local structure of nanocomposites. The thermodynamics and physical properties, including the glass transition temperature, the time-dependent mean squared displacement (MSD), the elasticity coefficients, and the isothermal bulk *modulus* of the epoxy matrix and PCNs were also computed.

After this introduction on the rationale for studying the polymer/clay nanocomposites materials, the paper is organized as follows. In section 2, the methodology adopted to construct the molecular models of sodium montmorillonite and polymer clay nanocomposites, and the force fields used to conduct the molecular dynamics simulations are discussed in detail. The methods adopted to determine the glass transition temperature and the mechanical properties of the PCN models

are also discussed in this section. The results of our simulations are presented in section 3, where the effect of different cross-linked epoxy-units are discussed by comparing radial distribution function, glass transition temperatures, translational dynamics of the polymer and elastic properties. Finally, in section 4, we draw the conclusion of this work.

2. Computational Methods

It is also important to point out that the molecular models used in this manuscript are "clay clusters" and not true PCNs. Real PCNs should be the mixture of clay clusters with polymer matrix, and they have a very complex structure [9, 19]. Therefore, a comparison with the real PCNs in the experimental part will be not appropriate. Moreover, it should be noted that, in the experimental part, it is impossible to make the nanocomposites with a specific controlled interlayer distance. Thus, the molecular dynamics simulation has been used to investigate the properties of the nanocomposites.

2.1. Molecular model of polymer/clay nanocomposites

2.1.1. Pristine and silanized clay

Let us consider a sodium montmorillonite ($MMT - Na^+$) which has the chemical structure $Na_x(Si_8)(Al_{4-x}Mg_x)O_{20}(OH)_4$ where x = 0.67 presents a cation exchange capacity of 91 meq/100g. This structure corresponds to the sodium montmorillonite provided by Souther Clay Products. Starting from the crystallographic unit cell [20], an orthogonal basis was defined with the Z-axis being perpendicular to the clay surface of the cell. Next, the unit cell was replicated 4 times according to the X-axis and 3 times according to the Y-axis. Then, 8 atoms of Al^{3+} were randomly chosen and replaced by Mg^{2+} in the octahedral layer, which resulted in a charge deficiency of -8 for the clay layer. Finally, 8 sodium ions Na^+ were added in the interlayer space to obtain the complete $MMT - Na^+$ cell. The size of the $MMT - Na^+$ cell were $21.12 \times 27.42 \times 6.56$ $Å^3$.

For the silanized clay, the size along the Z-axis of the $MMT - Na^+$ cell was fixed at 18 Å, which corresponds to the bilayer organization of aminosilanes within the clay interlayer space [21, 16, 17, 13, 22]. Grafting of aminosilanes onto the clay surface was carried out following the procedure proposed by Piscitelli *et al.* [13]. Herein, it is assumed that the silane molecules can be grafted covalently with the oxygen atoms on the surface of clay [13]. We only considered the case where the 3-aminopropyltrimethoxysilane molecules were linked with clay surface through three

covalent bonds [13]. The molecular structure of this aminosilane molecule is shown in Fig. 1(a). In this model, 8 aminosilanes were grafted on each clay surface. This corresponds to the number of monocationic surfactant needed to obtain a fully treated clay surface based on its cation-exchange capacity.

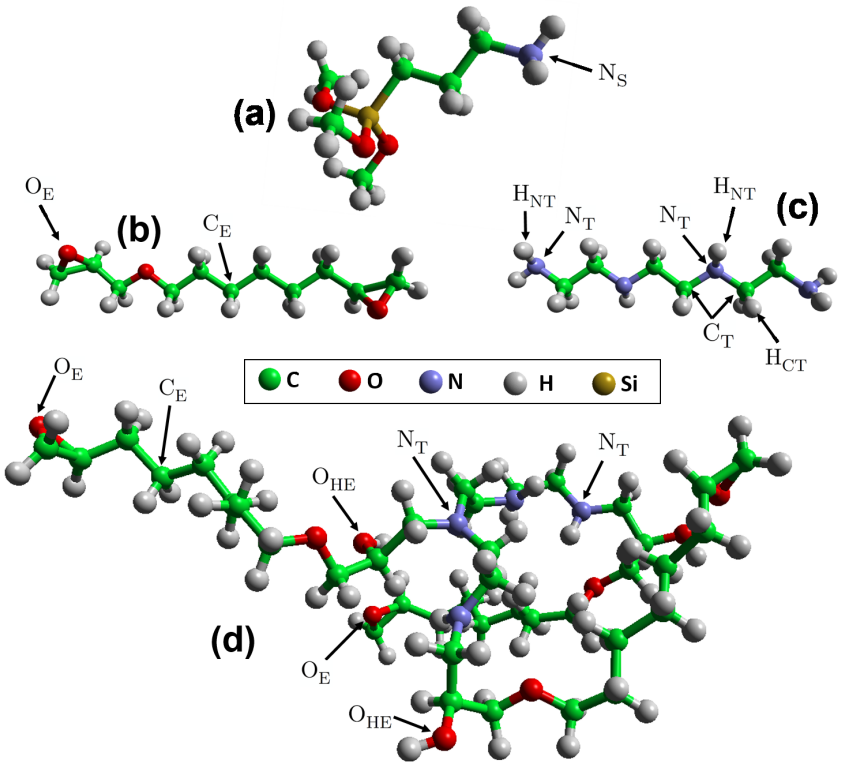


Figure 1: The molecular structure of (a) aminosilane molecule, (b) epoxy monomer molecule, (c) amine-based hardener molecule and (d) the representative cross-linked molecule. The cross-linked molecule (d) is obtained from the cross-linking reaction between three epoxy monomers (b) and one hardener (c).

2.1.2. Polymer clay nanocomposites

In our PCN model, the polymer matrix consists of representative cross-linked molecules as shown in Fig. 1(d). This type of cross-linked molecules has been previously used for simulating thermoset polymers [23, 24, 25, 26]. The use of these representative cross-linked molecules was also shown to be suitable for estimating thermodynamic and mechanical properties of thermoset polymer [27]. Figure 2 reports the curing reaction mechanism between the epoxy group and the

primary amine group. The carbon-oxygen bond in the epoxy monomers is broken through opening of the epoxy ring. The oxygen-end of the opened epoxy ring takes over the hydrogen atom from a nearby amine group in the hardener molecule and leaves a dangling nitrogen in the hardener molecule, which forms a covalent bond with the carbon-end of the opened epoxy ring. This process allows the epoxy monomer to link to an amine based hardener.

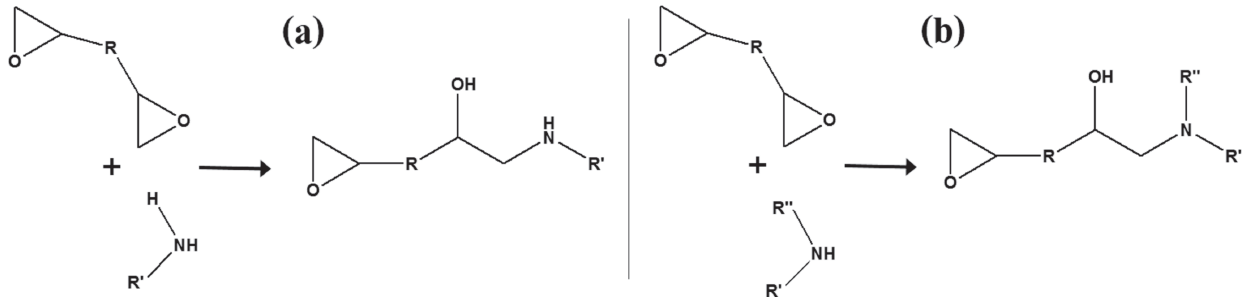


Figure 2: Curing reaction between the epoxy resin and (a) primary amine or (b) secondary amine of hardener.

The structures of the epoxy monomer and of the hardener used in this work are reported in Fig. 1(b) and (c), respectively. Each epoxy monomer has two reactive epoxy groups and the hardener has six reactive amine groups. The representative cross-linked molecule was build from the cross-link process between three linear epoxy monomers and one chain of curing agent. Therefore, as suggested in the work of Yu *et al.* [27], a cross-linking ratio of 50 % is used for this representative molecule based on the consummation of the reactive functions on both epoxy monomer and hardener molecules. Figure 1(d) shows the configuration of the representative cross-linked molecule.

The procedure used to build the nanocomposite structures from the organically modified clay followed the work of Anoukou *et al.* [19]. Firstly, the silanized system was relaxed in NVE (constant Number, Volume and Energy) ensemble for 200 ps. Then, the simulation cell was replicated 2 times in both X- and Y-axes in order to have enough surface before adding the representative cross-linked molecules. As a consequence, its surface dimensions became 42.24×54.84 Å^2 in the XY-plane geometry. The size of the c-cell (Z-direction) of the simulation box was shifted to insert the cross-linked molecules in the interlayer space. Three PCNs containing 20, 60 and 100 cross-linked molecules (denoted by $(N-20E)$, $(N-60E)$ and $(N-100E)$) which correspond to three interlayer distances. For the purpose of comparison, a model that contains only cross-linked molecules (100

molecules), designated as pure epoxy, was also built. Note that the orthorhombic symmetry was assumed for all molecular systems in this study. The orthorhombic symmetry corresponds to $\alpha = \beta = \gamma = 90°$, where the three angles α, β and γ are the angles between the Y- and Z-axes, between the X- and Z-axes, and between the X- and Y-axes, respectively. The initial structures of the aminosilane and cross-linked molecules were generated by using the Aten package [28].

2.2. Force fields description

Electrostatic charges and interatomic potential parameters for all atoms in the montmorillonite layer $MMT - Na^+$ were taken from CLAYFF [29]. For the organic phase, the molecular structures and Mulliken charges of organosilane and cross-linked molecules were optimized at the $B3LYP/6-311^{++}G^*$ level using the Gaussian 09 program [30]. For the organic phase, the geometries of both organosilane and cross-linked molecules were optimized by using the DFT method at $B3LYP/6-311^{++}G^*$ level implemented in Gaussian 09 program [30]. The electrostatic charges of these optimized molecules were calculated at $B3LYP/6-311^{++}G^{**}$ level by using the mulliken population analysis. The potential parameters for the organic phase were taken from the INTERFACE-FF force field [31]. In particular, we used the 12-6 van der Waals (vdW) form instead of 9-6 vdW in the INTERFACE-FF for polymer and aminosilan molecules as described in the conversion method presented by Heinz *et al.* [31]. The FIELD file for the DL_POLY molecular dynamics code was generated using the DL_FIELD program [32].

Given that the CLAYFF force field has been previously adopted to calculate the structural and mechanical properties of clays and other PCNs systems [33, 34, 19, 9, 35], given that CLAYFF has a rather simple functional form, which makes this force field computationally fast and robust for the simulation of multicomponent complex systems, CLAYFF is a suitable potential model to accurately simulate the structural and thermodynamic properties of epoxy/clay nanocomposite. It was previously pointed out that this force field is not appropriate to compute cleavage and binding energies [36, 37, 38], but the evaluation of these properties is not the focus of the present study.

2.3. Molecular dynamics simulation procedure

The molecular dynamics (MD) simulations were performed using DL_POLY 4.5 [39]. The integration algorithms were based on a Verlet leap-frog scheme. Periodic boundary conditions were applied to three directions of the simulation box. The Nosé-Hoover algorithm was used to control

the temperature and pressure of molecular systems. The long-range electrostatic interactions between the charges of all species were computed using the Smoothed Particle Mesh Ewald (SPME) method with the relative error of 10^{-6} [40]. The time step of 0.5 fs was chosen for all MD simulations to maintain the system stability. The system properties were recorded every 5 fs, whereas the mean square displacements of atoms were recorded every 2 ps.

The molecular system were sequentially simulated in two types of thermodynamic ensembles, NVT (constant Number, Volume and Temperature) and NPT (constant Number, Pressure and Temperature). At first, simulations in the NVT ensemble at 600 K and 200 ps were carried out. The objective of this step is to provide a sufficient kinetic energy to the cross-linked epoxy molecules, so that the homogeneous polymer layers can be achieved near the clay surface. Then, the MD simulations in NVT ensemble were conducted at 300 K for another 200 ps. After this step, the size according to Z-axis of the simulation box was adjusted by removing the empty space between the clay layers in order to approach the equilibrium configuration of the molecular systems. This procedure has been adopted in previous MD studies of similar systems [9, 25, 19, 24, 12].

Simulations in the NPT ensemble with $P = 0$ atm and $T = 300$ K were then conducted for 500 ps in order to equilibrate the volume of the unit cell and ring the system in a stress-free state [25]. The production stage of the simulations was carried out in NPT ensemble at room temperature (300 K) and atmospheric pressure (1 atm) for 2000 ps. During the simulation process, the positions of the atoms in two silicate layers were kept fixed whereas the atoms in all organic components were free to move. The stabilization of the total energy, pressure and temperature of the molecular system was monitored to ensure that the system was at equilibrium during the production phase of the MD simulations. The configurations at equilibrium state of the pure epoxy matrix (N − 20E) and of the nanocomposites ((N − 20E), (N − 60E) and (N − 100E)) are shown in Fig. 3. The interlayer distance d-spacing is $3.01, 5.57$ and 7.77 nm respectively (see Tab. 1). The density of all molecular systems at the equilibrium state is also reported in Tab. 1.

2.4. Determination of glass transition temperature

At the glass transition temperature T_g, the polymer changes from a 'glassy' state (an amorphous solid trapped in a non-equilibrium state) to a rubber (for cross-linked systems over the gel point) or liquid (when chains are not covalently bonded to each other as in the thermoplastics) state [41]. For a molecular system, the value of T_g is defined by the temperature at which the density-

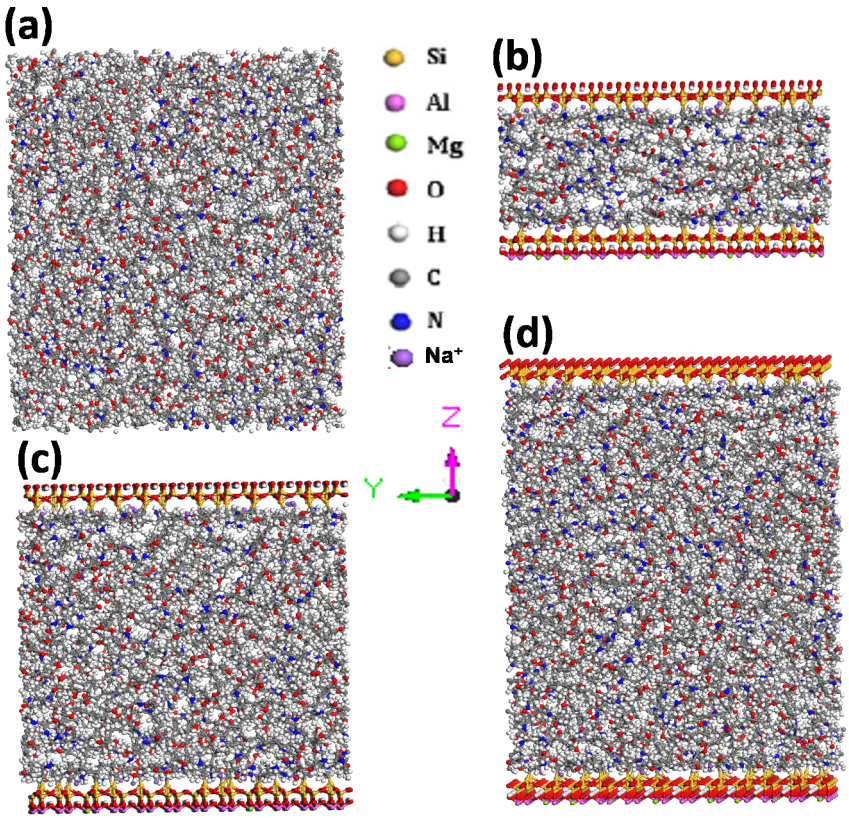


Figure 3: The configuration at equilibrated state of (a) pure epoxy matrix 100E, (b) nanocomposite containing 20 representative molecules (N − 20E), (c) nanocomposite containing containing 60 representative molecules (N − 60E) and (d) nanocomposite containing 100 representative molecules (N − 100E).

temperature relation becomes discontinued. At the transition temperature, the motion of polymer chain segments increases significantly and the mechanical properties of polymers become very different from those below the value of T_g. The value of the transition temperature T_g is governed by local chain dynamics and represents an intrinsic signature of the molecular structure [41].

The determination of T_g was performed by varying the system temperature from 300 K to 500 K at a constant heating rate of 20 K/500 ps and at the pressure $P = 1$ atm. At each temperature, the density was only averaged over the last 200 ps.

Besides of using the density-temperature relationship, the quantity T_g can also be obtained from the mean squared displacement-temperature relationship of some typical atom types where the mean squared displacement (MSD) stands the time-dependent.

2.5. Determination of mechanical properties

In this work, the elastic properties of the PCNs considered were quantified using the strain fluctuations method proposed by Parrinello and Rahman [42], which was then further developed in the work of Ray [15], and Van Workum and de Pablo [43]. This approach allows to determine the elasticity properties of a molecular system from using a single MD simulation. Particularly, the elasticity properties of the system can be determined at a specific temperature [35]. This is particularly important for the polymeric materials because their mechanical behaviours strongly depend on the temperature.

In order to perform the MD calculation with strain fluctuations method, the equilibrated systems obtained in NPT ensemble were used as describe in the section 2.3. It is worth noting that at this step, all atoms were free to move. During the simulation, the system was subjected to a three-dimensional stress field in the NσT ensemble (constant Number, Stress and Temperature). The obtained strain field was determined in each case of temperatures. The components of the 4-th order effective compliance tensor s_{ijkl} of the considered molecular system are given by:

$$s_{ijkl} = \frac{\langle V \rangle}{K_b T}(\langle \epsilon_{ij}\epsilon_{kl}\rangle - \langle \epsilon_{ij}\rangle\langle \epsilon_{kl}\rangle), \tag{1}$$

where K_b, ϵ_{ij}, T and V are the Boltzmann constant, the components of strain tensor, the imposed temperature and the volume of the molecular system, respectively. The angular brackets $\langle\star\rangle$ designates the ensemble average of the cell volume. Each index varies from 1 to 3, where each value of these indexes 1, 2 and 3 is associated with the X-axis, Y-axis and Z-axis, respectively. The stiffness tensor $\mathbb{c}$ can be then computed according to the relation $\mathbb{s}^{-1} = \mathbb{c}$ whose the components are given by s_{ijkl}.

To determine the isothermal bulk *modulus* κ_T, the temperature was set at the temperature $T = 300$ K and MD simulations were conducted in NPT ensemble with different values of the pressure in range 0.1 MPa (*i.e.* $P = 1$ atm) to 2.5 GPa (*i.e.* $P = 25$ katm) [19]. Each simulation was carried out for 500 ps and the average volume was taken for the last 200 ps.

The bulk *modulus* κ_T is related with the compressibility of the substance. It is defined as the ratio of the infinitesimal pressure increase to the resulting relative decrease of the volume. As a consequence, the bulk *modulus* κ_T at temperature T is determined by using a relationship between

P and V as follows [19]:

$$\kappa_T = -V \left(\frac{\partial P}{\partial V} \right)_T , \tag{2}$$

where P is pressure, V is volume, and $(\partial P/\partial V)_T$ denotes the partial derivative of pressure with respect to volume at constant temperature T.

3. Results and discussion

3.1. Structural characterization of PCNs

3.1.1. Density distribution profiles

Figure 4 compares the density profiles of pure epoxy matrix and different nanocomposite systems at room temperature (*i.e.* $T = 300$ K). The position $z = 0$ along the Z-axis corresponds to the median plane of the simulation box, whereas the two dash lines present the positions of clay surfaces. The positions of clay surfaces were determined from the density profile of surface oxygen atoms of silicate layer.

In the pure epoxy matrix system (see Fig. 4(a)) the density profile of polymer is almost constant along the Z-axis with a mean value $d_m = 1.038\,\mathrm{g \cdot cm^{-3}}$, which is similar to the values derived from the diglycidyl ether of bisphenol F (DGEBF) cross-linked with curing agent diethyltoluenediamine (DETDA) ($d_m = 1.07 - 1.075\,\mathrm{g \cdot cm^{-3}}$ given by Tack and Ford [44]) and from the epoxy network composed of EPON 862 epoxy resin and triethylenetetramine (TETA) curing agent ($d_m = 1.08\,\mathrm{g \cdot cm^{-3}}$, given by Fan and Yuen [45]). These values are slightly smaller than the ones obtained by experimental measurements of epoxy networks ($d_m = 1.13\,\mathrm{g \cdot cm^{-3}}$ in [46], or $d_m = 1.16\,\mathrm{g \cdot cm^{-3}}$ in [47]). The experimental density of epoxy cross-linked matrix was determined using fully cross-linked epoxy resin whereas in this study, to reduce the computational cost, a low cross-link density has been adopted. The difference between the result obtained herein and the ones presented in the other works may be associated to the small cross-link density, the type of epoxy and hardener, or the force field adopted in this study [44, 23, 48, 49].

Significant variations of the density profiles are observed in Figs. 4(b), (c) and (d) indicating the influence of silicate layers on the molecular configuration of the epoxy matrix. In all three nanocomposite structures, the confined polymer region near the clay surface becomes similar to a layered structure with the density much higher than the density of the bulk polymer.

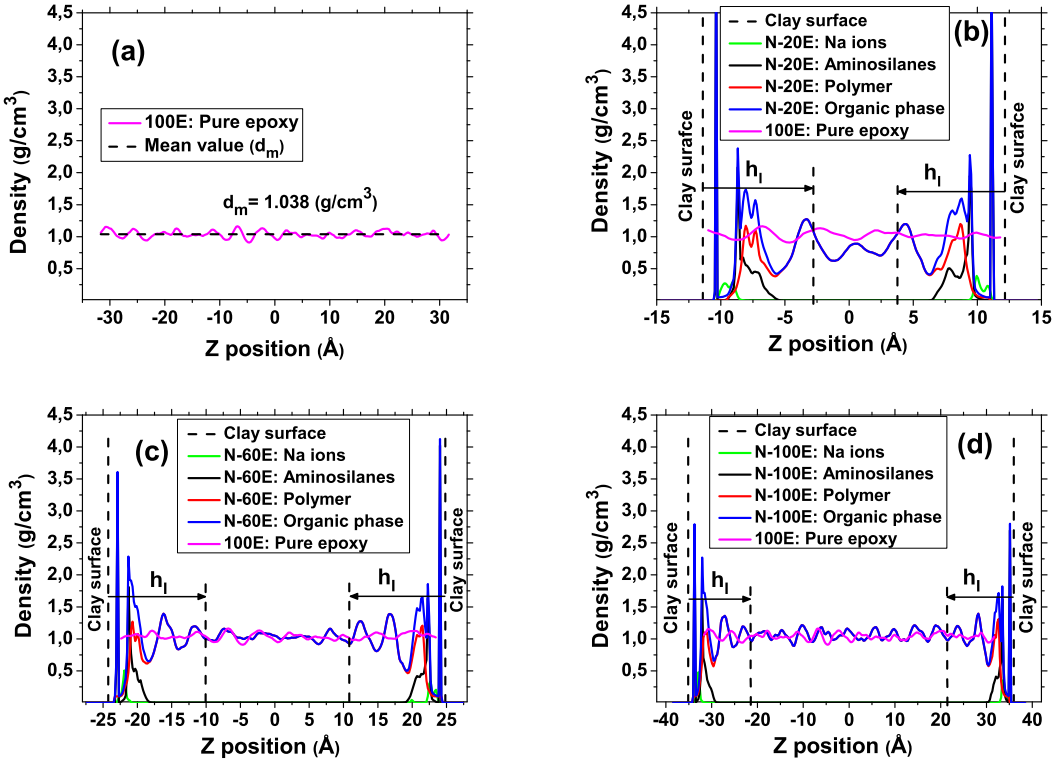


Figure 4: Density profiles of the different simulated systems: (a) Pure epoxy matrix containing 100 representative molecules, (b) Nanocomposite containing 20 representative molecules (N − 20E), (c) Nanocomposite containing 60 representative molecules (N − 60E), (d) Nanocomposite containing 100 representative molecules (N − 100E). For the purpose of comparison, the density profile of the pure epoxy matrix is put together with that one of nanocomposite.

Our results are similar to other MD simulations of poly ϵ-caprolactone/clay nanocomposites [9] and the graphene/epoxy nanocomposites [25, 24, 50]. In particular, Suter and Coveney [9] suggested that the high density of organic phase in the region close to the clay surface shows a strong affinity between the polymer matrix and the clay platelets.

On contrary, by studying epoxy/clay nanocomposite models using MD simulations, Chen *et al.* [14] have shown that the density of epoxy resin near clay surface is slightly lower than that of bulk matrix. Moreover, no layering configuration has clearly been observed. This may be explained in terms of different models used for the surfactants. In fact, in our model, the grafted aminosilanes have reactive amino functions NH_2 to epoxy matrix, whereas in [14], different organic molecules composed of a single ammonium head group NH_3^+ and one alkyl chain of various lengths C_n have

been used.

Therefore, one may suggest that the presence of the reactive functions NH_2 on the grafted aminosilanes is the main cause of the high density of organic phase near the clay surface. As a consequence, this interphase may enhance the mechanical properties as well as the adhesion between the clay layer and polymer matrix, in agreement with what suggested in previous works [21, 17].

Besides, the results show that aminosilane molecules are always found in the range $[0, 7]$ Å from the clay surface thanks to its covalent bonds with clay surface. Moreover, all sodium ions are close to clay surface due to its strong electrostatic interactions with the negatively charged silicate layer. From the density profile of nanocomposite structures, we can also estimate the thickness of interphase region [12, 51]. In Fig. 4, it can be observed that the thickness of the interphase of the exfoliated (N − 100E) or nearly exfoliated structures (N − 60E) is approximately 15 Å. For the intercalated structure (N − 20E), only a 10 Å thickness interphase layer was found.

The density profiles in three nanocomposite structures are presented in Figs. 4(b), (c) and (d). For the intercalated structure (N − 20E), the density of interlayer epoxy resin ($0.77\ \mathrm{g \cdot cm^{-3}}$) is smaller than the bulk epoxy matrix ($1.038\ \mathrm{g \cdot cm^{-3}}$). This result is similar to the one given by Chen *et al.* [14] who found an average density of $0.76\ \mathrm{g \cdot cm^{-3}}$ for organic phase in case of intercalated nanocomposite, and may be explained by strong confined effects in the narrow space between silicate layers, particularly for non-flexible polymers as epoxy resins [14].

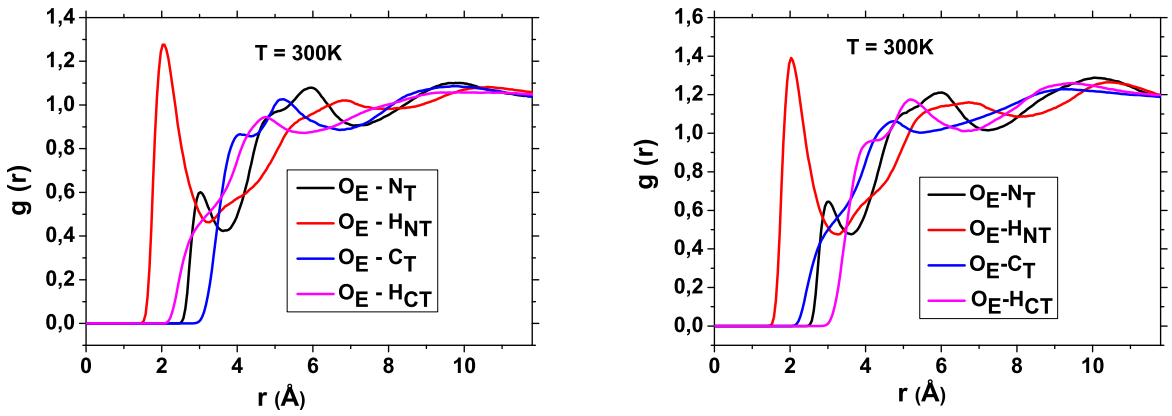
When the number of representative molecules increases, the configuration of nanocomposite structures changes from intercalated to the exfoliated one. In Figs. 4(c) and (d), one may observe that the density of polymer matrix in the region far away from the clay surface tends to that of the bulk polymer matrix. Compared to the intercalated structure, in the exfoliated systems (N − 60E and N − 100E), individual silicate layers with reactive surface may locally reinforce the interphase while maintaining the behavior of bulk polymer matrix for the confined polymer.

3.2. Radial distribution function

The radial distribution function (RDF), denoted by $g(r)$, is defined as the probability of finding a given particle at a distance r from a reference particle. In this work, the radial distribution functions were studied in order to better understand the short- and medium-range structure in PCNs.

For the pure epoxy matrix, which is composed of numerous cross-linked representative molecules, Fig. 5(a) compares the RDF of the reactive oxygen atoms in epoxy functions with other atom types in the hardener backbone, such as the reactive nitrogen N_T, the hydrogen linked to nitrogen H_{NT}, the carbon C_T and the hydrogen linked to carbon H_{CT} (see Fig. 1).

There are two peaks at approximately 2 Å and 3 Å that correspond to the short-range interaction between $O_E - N_T$ and $O_E - H_{NT}$ atoms, respectively. The RDFs between the oxygen atoms in epoxy with the carbon (C_T) and hydrogen (H_{CT}) atoms do not display peaks at distance lower than 3.5 Å. The peaks smaller than 3.5 Å in the RDF curves are mainly due to hydrogen and chemical bonds between atoms, whilst those beyond 3.5 Å correspond to van der Waals and electrostatic interactions. Thus, small distances between these reactive atoms show their tendency to cross-link together. In fact, by checking the close contact between these pairs of reactive atoms, several authors suggested the formation of the cross-linking between the epoxy resin and the hardener [52, 48, 53, 54]. Besides, some small peaks within the range $[4, 7]$ Å could contribute to the inter- or intra-molecular RDF of the cross-linked representative molecules. The case with the nearly exfoliated structure ($N - 60E$) is reported in Fig. 5(b) showing the analogous RDF profiles at the ones found for epoxy matrices in PCN structures.



(a) (b)

Figure 5: RDF's of reactive oxygen atoms in epoxy functions (O_E) to other atoms in hardener backbone such as reactive nitrogen N_T, hydrogen linked to nitrogen H_{NT}, carbon C_T and hydrogen linked to carbon H_{CT} of two cases (a) pure epoxy matrix and (b) a nanocomposite that contains 60 epoxy representative molecules.

The local interactions between the confined polymer matrix and the grafted aminosilanes were

also quantified in terms of the RDF profiles. The RDFs of reactive nitrogen atoms of grafted aminosilanes N_S to some typical atoms in cross-linked representative molecules such as O_E, C_E, C_T and N_T are reported in Fig. 6, where an intense peak at 3 Å can be seen in the N_S-O_E RDF indicating a string interaction between the nitrogen atoms of primary amine functions N_S on the grafted aminosilanes and the oxygen atoms in epoxy groups O_E. The profile of this peak is similar to the one of $O_E - N_T$ in pure epoxy matrix presented in Fig. 5(a). A peak located at 3 Å between the N_S atoms of the grafted aminosilanes and the N_T atoms of the cross-linked molecule is associated to the hydrogen bonding between two amine groups. In summary, these RDF's profiles show a strong affinity between the grafted aminosilanes and the cross-linked polymer matrix.

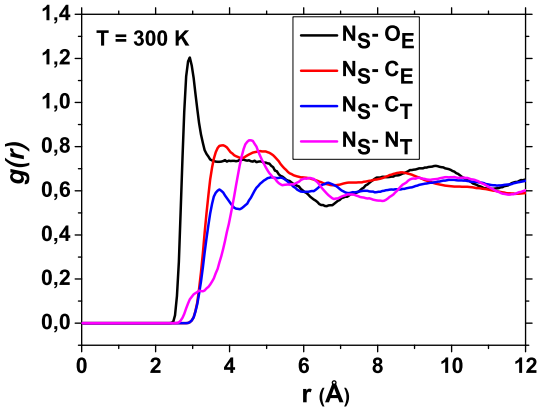


Figure 6: RDF's of reactive nitrogen atoms in surfactant (N_S) to other atoms in the cross-linked representative molecule such as reactive oxygen O_E, carbon in epoxy backbone C_E, carbon in hardener backbone C_T, reactive nitrogen in hardener backbone N_T,

3.3. Glass transition temperature

Figure 7(a) shows the variation of the density of pure epoxy matrix and its nanocomposites as a function of temperature. For all systems, the density decreases with increasing temperature and there are two linear regions, which correspond to the glass and rubber states of the polymeric material, respectively. The abscissa of the intersection of two linear curves, which are obtained by taking a linear fitting of the data, corresponds to T_g. As the value of T_g is somewhat dependent on the method and number of data used for the linear regression fitting, here we report the temperature range where there is a slope change. Therefore, it is more suitable to take into account a range of

temperature in which there is a slope's change. For the pure epoxy matrix, T_g was found in the range $[380, 385]$ K, which is in line with the results reported in several other MD works of epoxy matrix [45, 55, 56, 25, 57].

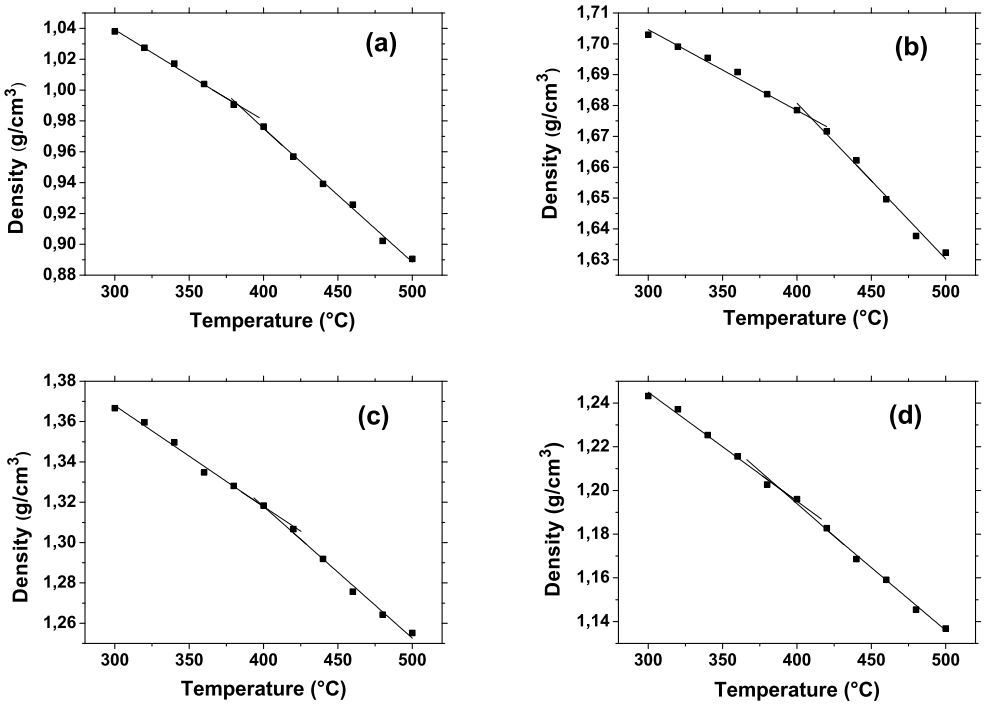


Figure 7: Plots of unit cell density of MD simulation versus temperature used to estimate the glass transition temperature T_g for epoxy and epoxy/clay nanocomposites: (a) pure epoxy matrix, (b) nanocomposite containing 20 representative molecules (N20 − E), (c) nanocomposite containing 60 representative molecules (N60 − E), (d) nanocomposite containing 100 representative molecules (N100 − E).

The results shown in Fig. 7(b), (c) and (d) highlight the effect of clay layers on the glass transition temperature T_g of the epoxy matrix. The intercalated structure (N − 20E) has the largest glass transition temperature T_g, which is in the range $[415, 425]$ K. The glass transition temperature decreases when the number of cross-linked epoxy molecules increases, with values in the range $[395, 415]$ K for (N − 60E) and in the range $[385, 395]$ K for (N − 100E) systems, respectively. The exfoliated structure (N − 100E) and pure epoxy matrix have very similar T_g values.

This result can be explained in terms of the few polymer molecules inserted into the interlayer space in the (N20 − E) system, where all polymer molecules are located close to the clay surfaces

and the grafted aminosilanes. These polymer molecules strongly interact with the reactive grafted aminosilanes as well as the clay surfaces as shown by the RDF profiles in Figs 5 and 6 and consequently the mobility of the polymer is reduced. As the number of cross-linked molecules in the three PCNs increases on going from (N − 20E) to (N − 100E) then the proportion of polymer molecules that do not interact with the surface decreases, and the thermodynamic behaviour tends to that of the bulk polymer matrix.

3.4. Translational dynamics of polymer

The translational dynamics of polymer in pure epoxy matrix and its nanocomposites have been quantified in terms of the mean square displacement of the carbon atoms in the epoxy backbone. Figure 8(a) reports the MSD of the C species along the MD trajectories in the temperature range $[300, 480]$ K for the nanocomposite containing 100 cross-linked molecules (N − 100E). As expected, diffusional behaviour consistently increases with temperature. Moreover, the mobility of the carbon atoms in epoxy backbone, and consequently the polymer, shows transitional behaviour as a function of temperature.

To clarify this behavior, the temperature dependence of the MSD of the carbon species of pure epoxy matrix and its nanocomposites at 100 ps is reported. As can be seen from the Fig. 8(b), a gradual change in the MSD value of the pure epoxy matrix is found at around 380 K, whereas it becomes bigger for all nanocomposite structures. The intercalated structure (N − 20E), which shows the highest T_g due to the stronger interaction with the clay surface, is characterized by the slowest increase of MSD with the temperature. Particularly, it is observed that the MSD value of the pure epoxy quickly increases once the glass transition temperature has been reached. From these observed behaviour on the glass transition temperature, it is possible to conclude that the addition of reactive clay significantly enhances the thermal stability of epoxy-based materials. It should be emphasized that the chosen time (100 ps) for the comparison purpose may have a certain influence on the obtained results. In order to ensure the reliability of the result, other choices have also been tested (50, 150 and 200 ps) in the current work and the similar results have been observed. Thus, the reported results are the typical ones for the considered systems.

3.5. Bulk modulus

The isothermal bulk *modulus* of pure epoxy system and nanocomposites determined using Eq. (2) are reported in Tab. 1. The isothermal bulk *modulus* of the pure epoxy matrix is larger

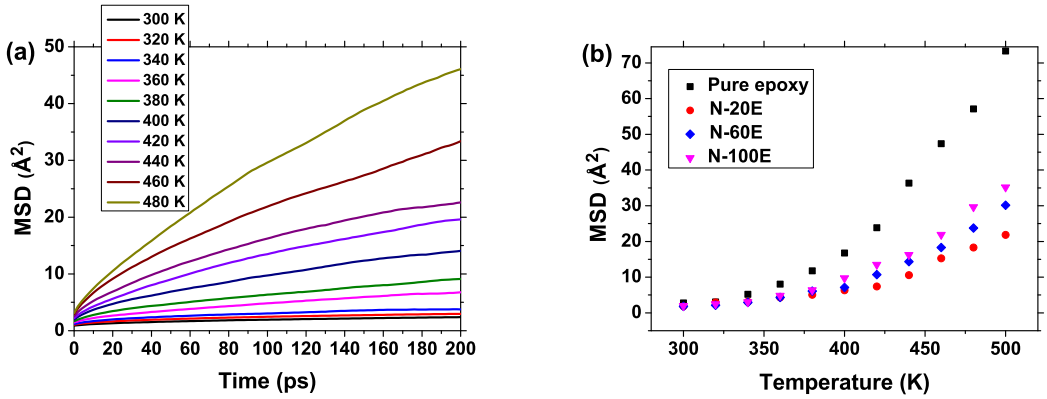


Figure 8: Mean square displacement of carbon atoms in the backbone of cross-linked molecules: (a) case of a nanocomposite containing 100 representative molecules (N − 100E) at different temperatures; (b) pure epoxy and its nanocomposites at $t = 100$ ps.

than the bulk *moduli* computed for the nanocomposite structures. There is a slight difference between κ_T for (N − 60E) and (N − 100E). The bulk *modulus* of (N − 20E) structure is significantly smaller than the ones obtained for (N − 60E) and (N − 100E) as well as the pure epoxy. Note that the isothermal bulk *modulus* represents the volume variation of the molecular system with respect to the pressure. This volume variation mainly depends on changes of the organic phase volume and density. A small volume of organic phase in the intercalated structure is likely to be the reason for the observed results.

Table 1: Physical and structural properties of several molecular systems at 300 K determined by using MD simulations. κ_T is the isothermal bulk *modulus*.

Molecular systems	κ_T (GPa)	Density (g/cm^3)	d_{001} (nm)
Pure epoxy 100E	15.65	1.038	–
(N − 100E)	15.28	1.24	7.77
(N − 60E)	15.05	1.37	5.57
(N − 20E)	12.20	1.70	3.01

3.6. Elasticity coefficients

The elasticity properties of the pure epoxy matrix and its nanocomposites at various temperatures were computed using the strain fluctuations method (see Eq. (1)). The 4-th order tensors in three dimensions can be represented in a Euclidian six-dimensional space as (6×6) matrices. To this end, the representation adopted in this work is called the *Voigt*'s representation in which the new indexes I and J vary in the set $\{1, ..., 6\}$ such as $I = (i, j)$ and $J = (k, l)$, where the indices i, j, k and l vary in the set $\{1, ..., 3\}$. The relation between these indices is the following $1 = (1, 1), 2 = (2, 2), 3 = (3, 3), 4 = (2, 3), 5 = (1, 3)$ and $6 = (1, 2)$. So, the the relation between symmetric matrix $\mathbf{C}$ with the 4-th order tensor $\mathbf{c}$, whose the components are c_{ijkl} is given by these components:

$$C_{IJ} = c_{ijkl}. \tag{3}$$

Table 2: The elastic constants (in GPa) at various temperature conditions

Molecular systems	Temperature	C_{11}	C_{22}	C_{33}	C_{12}	C_{13}	C_{23}	C_{44}	C_{55}	C_{66}
Pure epoxy	(300 K)	3.38	3.46	3.28	2.52	2.18	1.93	1.69	2.28	1.84
Pure epoxy	(350 K)	1.97	1.83	1.87	1.56	1.51	1.43	0.98	0.685	0.818
Pure epoxy	(400 K)	0.84	0.75	0.70	0.66	0.54	0.52	0.20	0.25	0.49
(N – 100E)	(300 K)	39.5	38.2	4.37	17.3	3.2	2.82	2.77	2.33	32.3
(N – 100E)	(350 K)	37.06	32.96	3.39	15.82	2.85	3.65	1.40	1.32	26.46
(N – 100E)	(400 K)	24.1	25.47	1.49	11.11	1.02	0.77	0.26	0.49	19.66
(N – 60E)	(300 K)	59.8	60.2	5.26	24.3	1.9	2.2	1.93	3.85	49.2
(N – 60E)	(350 K)	46.1	56.2	3.13	27.0	1.23	0.93	1.03	1.46	49.1
(N – 60E)	(400 K)	31.2	39.8	1.87	15.9	1.1	1.31	0.534	0.586	33.6
(N – 20E)	(300 K)	127	122	3.77	48.5	2.39	2.68	5.63	2.44	117
(N – 20E)	(350 K)	106	113	3.70	47.90	1.50	1.15	3.21	2.78	92.10
(N – 20E)	(400 K)	96.2	98.7	3.99	47.8	1.29	1.06	1.67	1.83	69.8

Because of the orthorhombic crystal systems, the components of the elasticity tensor of the pure polymer matrix rest always nearly the one of a isotropic tensor whose the components obey to the following conditions:

$$C_{11} = C_{22} = C_{33}, \quad C_{12} = C_{13} = C_{23}, \quad C_{44} = C_{55} = C_{66} = \frac{1}{2}(C_{11} - C_{12}). \tag{4}$$

In contrast, all nanocomposite structures exhibit highly anisotropic behaviors. Indeed, the elastic constants in XY-plane (C_{11} and C_{22}), which have similar values, are larger than the one along the Z-axis (C_{33}). The nanocomposites' stiffness in XY-plane strongly depend on the in-plane stiffness of clay platelets whereas its stiffness along the Z-axis strongly depends on the soft polymeric phase. This result agrees well with previous numerical simulations of the mechanical properties of clay cluster based on micromechanics methods, and the results obtained from these atomistic MD simulations suggest that the anisotropic properties of PCN clusters should be taken into account in continuum mechanics approaches to estimate the effective mechanical properties of PCNs.

As can be seen from the Tab. 2, the elastic constants along the XY-plane decreases with increasing number of cross-linked polymers in nanocomposite structures. This can be explained by the fact that the elasticity *moduli* in the lateral directions are strongly affected by the stiffness of clay layer due to the small volume of the organic phase in the intercalated structure. In this case, the high values (around 125 GPa) have been derived. When the number of polymer increases, the properties of the nanocomposites in lateral directions become more pronounced by the elastic properties of polymer components, which show an approximative value of 60 GPa and 39 GPa for the (N − 60E) and (N − 100E) systems, respectively. Interestingly, it is found that the the elastic constant in the vertical direction of intercalated clay cluster (N − 20E) is smaller than that for nearly exfoliated (N − 60E) or exfoliated structures (N − 100E). The small density of polymer phase in the intercalated structure (N − 20E) discusses in the previous section, could contribute to a bigger strain in the Z-axis, resulting to a smaller stiffness in comparison with two others systems (N − 60E) and (N − 100E).

Moreover, one can observe that the elasticity constants of pure epoxy matrix and its nanocomposites decrease with increasing temperature. This statement reflects the typical behaviour of thermoset polymer-based materials [55]. The stiffness of the pure epoxy matrix drastically decreases between 350 K and 400 K. However, much smaller change has been observed for the nanocomposite cases.

The elastic properties of intercalated structure are less affected by the temperature than two other nanocomposite structures, a result that is consistent with the behaviour of the glass transition temperature previously discussed.

4. Conclusion

This work presents a novel molecular model approach to investigate the morphology and thermomechanical properties of epoxy/clay nanocomposites. The reactivity of the clay layer has been taken into account using the reactive organomodifiant as aminosilanes, which are covalently grafted to clay surface. The cross-linked epoxy molecules have been used as the polymer matrix. Different molecular structures of PCNs, from intercalated to exfoliated one, have been generated based on the amount of the polymer phase between the interlayer space. Molecular dynamics simulations were conducted in order to determine structural arrangement of the constitutive components of PCNs, the molecular interactions occurring in the interphase zone, and the influence of silicate layer on the thermodynamic and elastic properties of these multi-functional materials. The interphase thickness near the clay surface was identified as varying with the density of the organic phase. The exfoliated structure showed a thicker interphase. The reactivity of the clay surface was quantified in terms of RDFs between the reactive atoms, which are in the polymer phase and silane layer grafted on the clay surface. The thermodynamic properties of the confined polymer in each structure were also investigated in detail to identify the role of silicate layer on the properties of nanocomposites. It has been showed that the polymer located close to clay surface strongly interacts with clay surface and surfactant, hence enhancing its thermal stability. In addition, these molecular models allowed us to estimate the effective elastic properties of the PCN models at different temperatures. A high anisotropic behaviour of the PCNs at the nanoscale has been observed.

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