Assessing hBN Nanoparticles Stability in Trimethylolpropane Triester Based Biolubricants Using Molecular Dynamic Simulation

Rizky, Ruliandini
Faculty of Engineering, Universitas Indonesia

Nasruddin
Faculty of Engineering, Universitas Indonesia

Tokumasu, Takashi
Institute of Fluid Science, Tohoku University

https://doi.org/10.5109/4055225

出版情報：Evergreen. 7 (2), pp.234-239, 2020-06. 九州大学グリーンテクノロジー研究教育センター
バージョン：

Assessing hBN Nanoparticles Stability in Trimethylolpropane Triester Based Biolubricants Using Molecular Dynamic Simulation

Rizky Ruliandini[1,2*], Nasruddin[1] and Takashi Tokumasu[3]

[1]Faculty of Engineering, Universitas Indonesia, Indonesia

[2]Faculty of Science and Technology, Universitas Ibn Khaldun, Indonesia

[3]Institute of Fluid Science, Tohoku University, Japan

*Author to whom correspondence should be addressed:

E-mail: rizky.ruliandini71@ui.ac.id

(Received October 17, 2019; Revised May 2, 2020; accepted May 21, 2020).

Abstract: Due to the strong Van der Waals force, agglomeration will occur to nanoparticles, which added into bio lubricant. Although some studies show that homogeneity in the mixture does not have a significant effect on lubricant behavior in friction reduction, but a more stable mixture is more expected. In experiments, the agglomeration that occurs is observed visually. The disadvantage is that this method is considered inefficient because of time-consuming. This study is aimed to assess this agglomeration phenomenon using molecular dynamics simulation methods. The simulation results show that mixtures of TMPTO with less than 0.4wt% hBN additions have a good dispersibility.

Keywords: bio lubricant, nanoparticles, agglomeration, stability, molecular dynamic simulation

1. Introduction

As with animal fat, plant oil can also be used as a lubricant. This plant oil or what we called as bio lubricants can be synthesized from plants that its seed is containing oil such as palm, canola, soybean, castor, jatropha, coconut and rice bran[1)2)3)4)]. Although it has several weaknesses, such as poor thermal and oxidative stability, poor fluid flow behavior, and had solidification at low temperature the presence of polar and non-polar regions found in bio lubricants, has made a sufficient lubrication characteristic[1)] . At present, the development of bio lubricants research has succeeded in finding various modification methods, either chemically, physically or genetically, to improve the ability of bio lubricants[5)6)]. For instance, in order to obtain a molecular structure that has better oxidative and thermal stabilities, the chemical method is employed. By transesterification, esterification, epoxidation and or homopolymerization, the chemical chain of fatty acids is modified[7)] . Furthermore, to improve the lubrication ability, some small amounts of nanoparticle which acts as a modifier friction can be added into the bio lubricant. This addition succeeded in increasing thermophysical and tribological properties such as increased thermal conductivity[8)9)10)11)] increased load-carrying ability[12)13)14)] , which resulted in less wear and friction. Nanoparticles are innovative materials that have unique characteristics which diameter ranges from 1-100nm in size. Its nano-sized make it possible to fill in the gap due to surface roughness (asperity). The character of the nanomaterial added will also produce good chemical interactions with the surface so that the tribo-films formed, and its spherical shapes will create a rolling effect[15)]. Several groups of nanomaterials that can be added to bio-lubricants are derived from sulfur[16)], phosphorus[16)] and boron groups such as CuO[17)18)], MoS2[17)], ZnO[18)], TiO2[19)] and hBN[20)21)22)]

On the other hand, working with nanoparticles is not easy, because the substances tend to form agglomeration due to strong Van der Waals force. Even some studies show that homogeneity in nanofluid mixture does not have a significant effect on lubrication behavior in friction reduction, but the unstable mixture will not exhibit a good heat transfer capability. As previous studies conducted, the agglomeration was assessed by visual observation or sedimentation method, and it was time-consuming since it needed at least 2 weeks to observe graphene oxide in poly-α-olefin lubricating oil[23)] and 55 days for TiO2 in mineral-based[24)] and 7 months for 6nm Ag in PEG-based lubricants[25)]. The fact that there is still an unrevealed phenomenon by experimental and theoretical work in the tribo-film formation mechanism made a molecular dynamics simulation method as a proper preliminary study. This study is aimed to investigate the

agglomeration phenomenon using molecular dynamic simulation methods by assessing its dispersion stability through the MSD curve and diffusion coefficient value. The same methods and parameters were also applied to defined dispersibility and stability CuO nanoclusters in alkane[26] and to reveal stability phenomenon at the early stages of SiO2 production in a colloidal solution[27].

2. Methods and computing details

Mean Square Displacement (MSD) analysis is a measure of the position deviation of a particle concerning its initial position for a certain time. MSD is a critical factor that shows the microscopic dynamics of nanoparticles that reflect the rheological nature of a nanofluid. MSD is calculated using the equation as below:

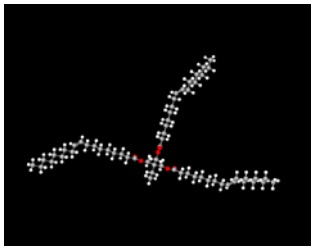
$$MSD(t) = \frac{1}{N}\left\langle \sum_{i=1}^{N} |r_i(t) - r_i(t_0)|^2 \right\rangle \qquad (1)$$

Nanoparticle's motion in a lubricant is analogous to random motion, such in Brownian motion. If the nanoparticles are randomly moving, due to gravity, the nanoparticles will move to a small concentration region. Nanoparticle's motion is analyzed by calculating its diffusion coefficient, D. In addition, D is used to analyze system aggregations and viscous regimes. Besides using the equation (2) below, the value of D can also be calculated by calculating the gradient (slope) of the MSD curve.

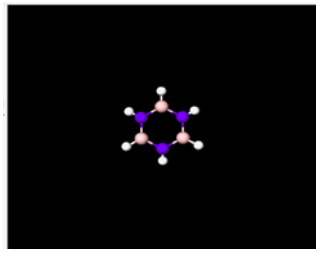
$$D = \frac{1}{6}\lim_{t\to\infty}\left(\frac{d}{dt}MSD(t)\right) \qquad (2)$$

Performing the simulation process takes several stages of initial simulation, each molecular structure of the system compiler must be separately modeled. Figure. 1(c) below is the system with replicating one molecule of TMP Trioleate/ TMPTO with 15.2 Å spacing and hBN in between so that the system occupies a space of 100Å x 80Å x 70Å. The fluid and nanoparticles are built using Moltemplate. The fluid's particle is generated using OPLSAA forcefield, whether the nanoparticles built without forcefield assigned. The next step is combining the TMPTO system with hBN molecules, which have also been replicated as much as the desired wt%. The wt% concentration chosen was as much as 0.05%, 0.1% 0.2%, 0.3%, 0.4% and 0.5%. The fluid – nanoparticles interaction will be defined by employing the 12-6 Lennard Jones (LJ) potential. Furthermore, the Lorentz – Barthelot mixing rules is also applied for cross interaction of different atoms[28]

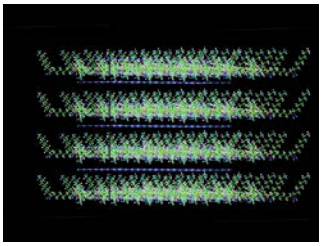
Once the nanofluid system is successfully created, the next step is to do the LAMMPS simulation to find the MSD graph and diffusion coefficient value, D. The D value is obtained from the MSD graphical gradient value, and this is needed as an indicator of the dispersion of nanoparticles in the bio lubricant. At this stage, simulation is minimized and equilibrated with the NPT ensemble. Minimization is an important step in order to have minimum energy when the system equilibrated. The time needed to minimize the system will vary greatly from 100 fs to 1000 ns depending on the complexity of the system, complex systems such as biomolecules or long-chain hydrocarbons will be required longer minimization times than systems containing water molecules. After the minimization stage is reached, the sampling can be produced.



(a)



(b)



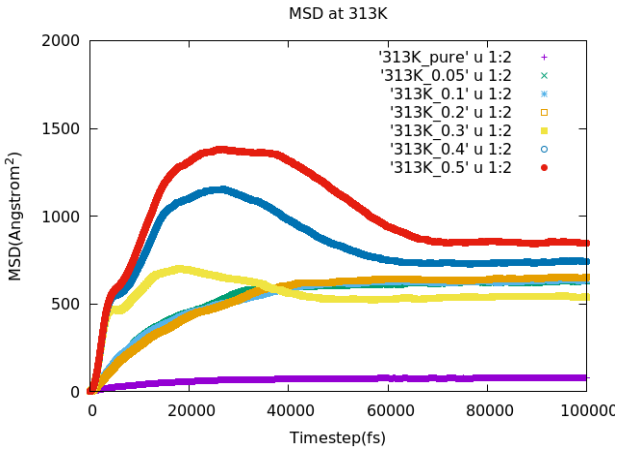
(c)

Fig. 1: (a) Structure molecule of Trimethylolpropane trioleate (TMPTO), (b) Structure molecule of hexagonal Boron Nitride (hBN), (c) Duplicated TMPTO and hBN in a 100 Å x 80Å x 70Å box

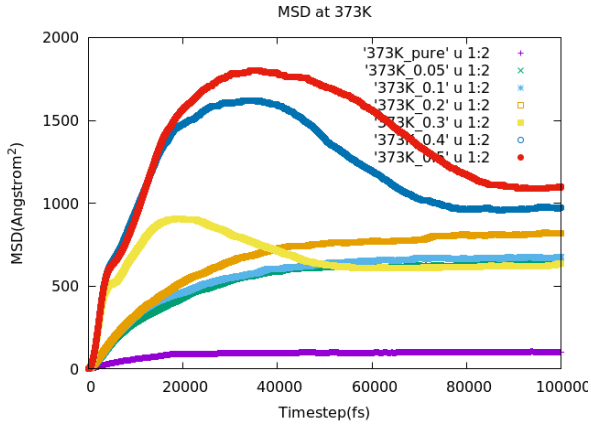
3. Result and Discussion

The most effective performance of nano lubricants is the one with long term dispersion stability of nanoparticles in suspension. With molecular dynamics simulations, we can predict its stability by interpreting the MSD curve. This method is also adopted to investigate the aggregation of graphene nanoplate in poly-α-olefin lubricating oil , graphene oxide nanosheet dispersion in

water[29] and overlapped graphene sheets in linear aliphatic hydrocarbons[30].



(a)



(b)

Fig. 2: (a) MSD graph at 313K (b) MSD graph at 373K

The hBN diffusion behavior in TMPTO fluid is shown by the MSD curves, as seen in Figure 2 above. As much as 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 wt% hBN molecules are simulated at two different temperatures 313K and 373K. Either Figure 2(a) and 2(b) showing a similar trend of motion. Referring from both graphs, 0.3, 0.4 and 0.5wt% nanoparticle hBN in suspension are moving very far from the initial position, which indicated by the fluctuated curve. Whereas, the linear curve indicating that the particles are not experiencing many position changes. Hence, we can conclude that as much as 0.05, 0.1 and 0.2wt% of hBN nanoparticles contained by TMPTO fluid is well dispersed. This result is indirectly confirmed the previous study conducted by Oztekin et al (2012) that viscosity is proportional to the concentration as well as shear thinning, which means it will increase as the concentration of additives and shear thinning increased. The agglomeration happened is indicated by shear thinning formed[29]

Diffusion coefficient or self-diffusion (D) is affected by concentration, temperature, pressure, solvent properties and diffusing chemical properties. In this case diffusion coefficient is a parameter to describe how well the rate of migration of hBN in TMPTO fluid. From Table 1. Below, we can infer that hBN nanoparticles in (TMPTO+0.3wt%), (TMPTO+0.4wt%) and (TMPTO+0.5wt%) mixture has the highest of D value. It is indicating that the more particles the more higher probability to aggregate due to higher frequency of collision between particles and yet cohesion during collision. The nanoparticles in (TMPTO+0.1wt%) and (TMPTO+0.2wt%) mixture has a quite smaller D value. It makes the (TMPTO+0.1wt%) and (TMPTO+0.2wt%) mixture has a stable dispersion than other mixtures.

Tabel 1. Diffusion coefficient

Base oil + additives	**$D_{@313K}$ ($m^2.s^{-1}$)**	**$D_{@373K}$($m^2.s^{-1}$)**
Pure TMPTO	0.00156 x 10^{-5}	0.00298 x 10^{-5}
TMPTO + 0.05%hBN	0.01120 x 10^{-5}	0.01787 x 10^{-5}
TMPTO + 0.1%hBN	0.01058 x 10^{-5}	0.01092 x 10^{-5}
TMPTO + 0.2%hBN	0.01078 x 10^{-5}	0.0202 x 10^{-5}
TMPTO + 0.3%hBN	0.02898 x 10^{-5}	0.04149 x 10^{-5}
TMPTO + 0.4%hBN	0.03446 x 10^{-5}	0.05031 x 10^{-5}
TMPTO + 0.5%hBN	0.05748 x 10^{-5}	0.06479 x 10^{-5}

4. Conclusion

This study focuses on assessing the stability of hBN nanoparticle additives in the TMP triester based biolubricant using simulation approach. The stability of hBN nanoparticles is given at 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5wt%, respectively, are assessed by looking at the pattern of distribution curve of hBN at 313K and 373K which is presented by the MSD graph. From the graph, we can conclude that the linear curve which is shown by the mixture with 0.05%, 0.1%% and 0.2% showing a better dispersibility than the mixture containing 0.3, 0.4 and 0.5wt% hBN.

In the experiment there are some procedures employed in order to enhance the stability of nano lubricants. Sometimes surfactant usage or the nanoparticle itself is modified at its surface using organic compound or silane coupling agents are used to overcome the aggregation in the mixture, so the mixture obtained is much more stable. In this simulation the substance of either surfactant or modification agents are not taken into account.

For the future simulation work, the surfactant, organic compound or silane coupling agents should take into account in order to mimic the real experiment, so the result

would be more accurate.

Acknowledgments

The publication and conference are financially supported by Ministry of Higher Education of Indonesia Government under PDUPT scheme. Also, we would like to thank Tokumasu Laboratory members because part of the work was carried out under the Collaborative Research Project of the Institute of Fluid Science, Tohoku University, Sendai, Japan.

Nomenclature

MSD	Mean square displacement
N	total number of atoms
$r_i\ (t)$	position of atom i at time t
$r_i\ (t_0)$	the initial position of the atom
D	Diffusion coefficient

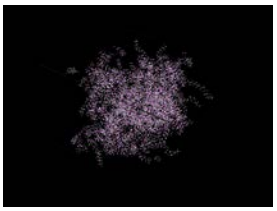
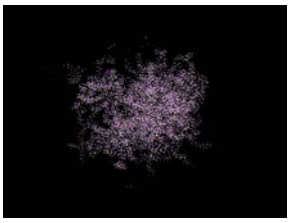
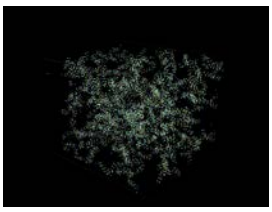
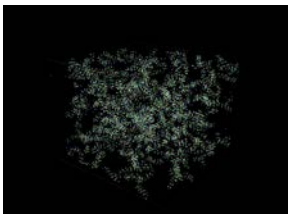
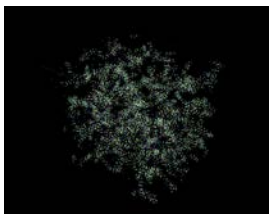
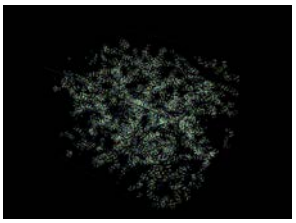
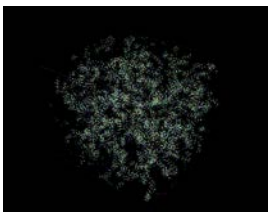
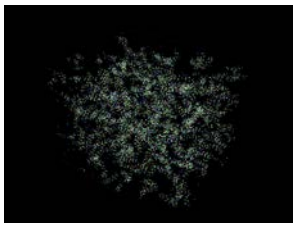
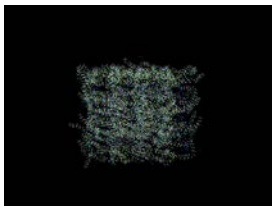
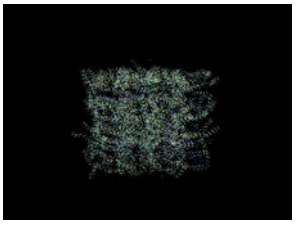
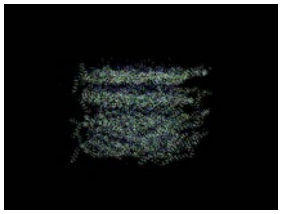
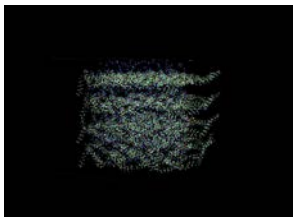
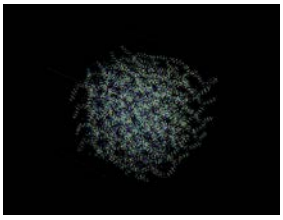
References

1) N. Talib, and E.A. Rahim, "Experimental evaluation of physicochemical properties and tapping torque of hexagonal boron nitride in modified jatropha oils-based as sustainable metalworking fluids," *J. Clean. Prod.*, (2018). doi:10.1016/j.jclepro.2017.10.061.
2) J. McNutt, and Q.S. He, "Development of biolubricants from vegetable oils via chemical modification," *J. Ind. Eng. Chem.*, (2016). doi:10.1016/j.jiec.2016.02.008.
3) N.H.A. Ameen, and E. Durak, "Study of the tribological properties the mixture of soybean oil and used (waste) frying oil fatty acid methyl ester under boundary lubrication conditions," *Renew. Energy*, (2020). doi:10.1016/j.renene.2019.06.117.
4) S.K. Tulashie, and F. Kotoka, "The potential of castor, palm kernel, and coconut oils as biolubricant base oil via chemical modification and formulation," *Therm. Sci. Eng. Prog.*, (2020). doi:10.1016/j.tsep.2020.100480.
5) I. Paryanto, T. Prakoso, B.H. Susanto, and M. Gozan, "The effect of outdoor temperature conditions and monoglyceride content on the precipitate formation of biodiesel-petrodiesel blended fuel (bxx)," *Evergreen*, (2019). doi:10.5109/2321010.
6) T.M. Panchal, A. Patel, D.D. Chauhan, M. Thomas, and J. V. Patel, "A methodological review on bio-lubricants from vegetable oil based resources," *Renew. Sustain. Energy Rev.*, (2017). doi:10.1016/j.rser.2016.11.105.
7) C.H. Chan, S.W. Tang, N.K. Mohd, W.H. Lim, S.K. Yeong, and Z. Idris, "Tribological behavior of biolubricant base stocks and additives," *Renew. Sustain. Energy Rev.*, (2018). doi:10.1016/j.rser.2018.05.024.
8) M.A. Kedzierski, R. Brignoli, K.T. Quine, and J.S. Brown, "Viscosity, density, and thermal conductivity of aluminum oxide and zinc oxide nanolubricants," *Int. J. Refrig.*, (2017). doi:10.1016/j.ijrefrig.2016.10.003.
9) Y. Hwang, H.S. Park, J.K. Lee, and W.H. Jung, "Thermal conductivity and lubrication characteristics of nanofluids," *Curr. Appl. Phys.*, (2006). doi:10.1016/j.cap.2006.01.014.
10) N.F. Azman, and S. Samion, "Dispersion stability and lubrication mechanism of nanolubricants: a review," *Int. J. Precis. Eng. Manuf. - Green Technol.*, (2019). doi:10.1007/s40684-019-00080-x.
11) V. Sridhara, and L.N. Satapathy, "Effect of nanoparticles on thermal properties enhancement in different oils-a review," *Crit. Rev. Solid State Mater. Sci.*, (2015). doi:10.1080/10408436.2015.1068159.
12) Q. Wan, Y. Jin, P. Sun, and Y. Ding, "Tribological behaviour of a lubricant oil containing boron nitride nanoparticles," in: Procedia Eng., 2015. doi:10.1016/j.proeng.2015.01.226.
13) M.I.H. Chua Abdullah, M.F. Bin Abdollah, N. Tamaldin, H. Amiruddin, and N.R.M. Nuri, "Effect of hexagonal boron nitride nanoparticles as an additive on the extreme pressure properties of engine oil," *Ind. Lubr. Tribol.*, (2016). doi:10.1108/ILT-10-2015-0157.
14) S. Ingole, A. Charanpahari, A. Kakade, S.S. Umare, D. V. Bhatt, and J. Menghani, "Tribological behavior of nano tio2 as an additive in base oil," *Wear*, (2013). doi:10.1016/j.wear.2013.01.037.
15) J.M. Liñeira del Río, M.J.G. Guimarey, M.J.P. Comuñas, E.R. López, A. Amigo, and J. Fernández, "Thermophysical and tribological properties of dispersions based on graphene and a trimethylolpropane trioleate oil," *J. Mol. Liq.*, (2018). doi:10.1016/j.molliq.2018.07.107.
16) S.M. Alves, V.S. Mello, E.A. Faria, and A.P.P. Camargo, "Nanolubricants developed from tiny cuo nanoparticles," *Tribol. Int.*, (2016). doi:10.1016/j.triboint.2016.01.050.
17) S. Shahnazar, S. Bagheri, and S.B. Abd Hamid, "Enhancing lubricant properties by nanoparticle additives," *Int. J. Hydrogen Energy*, (2016). doi:10.1016/j.ijhydene.2015.12.040.
18) M. Gulzar, H. Masjuki, M. Varman, M. Kalam, R.A. Mufti, N. Zulkifli, R. Yunus, and R. Zahid, "Improving the aw/ep ability of chemically modified palm oil by adding cuo and mos2 nanoparticles," *Tribol. Int.*, (2015). doi:10.1016/j.triboint.2015.03.035.
19) M.F. Trajano, E.I.F. Moura, K.S.B. Ribeiro, and S.M. Alves, "Study of oxide nanoparticles as additives for vegetable lubricants," *Mater. Res.*, (2014). doi:10.1590/1516-1439.228213.
20) N.W.M. Zulkifli, M.A. Kalam, H.H. Masjuki, and R. Yunus, "Experimental analysis of tribological properties of biolubricant with nanoparticle additive.,"

in: Procedia Eng., 2013. doi:10.1016/j.proeng.2013.12.161.

21) N. Talib, R.M. Nasir, and E.A. Rahim, "Tribological behaviour of modified jatropha oil by mixing hexagonal boron nitride nanoparticles as a bio-based lubricant for machining processes," *J. Clean. Prod.*, (2017). doi:10.1016/j.jclepro.2017.01.086.
22) N. Talib, and E.A. Rahim, "Performance of modified jatropha oil in combination with hexagonal boron nitride particles as a bio-based lubricant for green machining," *Tribol. Int.*, (2018). doi:10.1016/j.triboint.2017.09.016.
23) L. Wu, B. Song, L.M. Keer, and L. Gu, "Molecular dynamics investigation of graphene nanoplate diffusion behavior in poly-α-olefin lubricating oil," *Crystals*, (2018). doi:10.3390/cryst8090361.
24) M.K.A. Ali, H. Xianjun, R.F. Turkson, Z. Peng, and X. Chen, "Enhancing the thermophysical properties and tribological behaviour of engine oils using nano-lubricant additives," *RSC Adv.*, (2016). doi:10.1039/c6ra10543b.
25) H. Ghaednia, M.S. Hossain, and R.L. Jackson, "Tribological performance of silver nanoparticle–enhanced polyethylene glycol lubricants," *Tribol. Trans.*, (2016). doi:10.1080/10402004.2015.1092623.
26) A. Loya, J.L. Stair, A.R. Jafri, K. Yang, and G. Ren, "A molecular dynamic investigation of viscosity and diffusion coefficient of nanoclusters in hydrocarbon fluids," *Comput. Mater. Sci.*, **99** 242–246 (2015). doi:10.1016/j.commatsci.2014.11.051.
27) R. Gholizadeh, Y. Wang, and Y.X. Yu, "Molecular dynamics simulations of stability at the early stages of silica materials preparation," *J. Mol. Struct.*, (2017). doi:10.1016/j.molstruc.2017.03.021.
28) H.W.B. Teo, and A. Chakraborty, "Methane adsorption characteristics of hkust-1 and mil-101(cr) using gcmc (grand canonical monte carlo) simulation," *Evergreen*, (2015). doi:10.5109/1544079.
29) E.K. Goharshadi, G. Akhlamadi, and S.J. Mahdizadeh, "Investigation of graphene oxide nanosheets dispersion in water based on solubility parameters: a molecular dynamics simulation study," *RSC Adv.*, (2015). doi:10.1039/c5ra19932h.
30) S. Chen, S. Sun, C. Li, C.U. Pittman, T.E. Lacy, S. Hu, and S.R. Gwaltney, "Molecular dynamics simulations of the aggregation behaviour of overlapped graphene sheets in linear aliphatic hydrocarbons," *Mol. Simul.*, (2018). doi:10.1080/08927022.2018.1465569.

Table 2. Visualization

313 K		373 K	
TMPTO		TMPTO	
TMPTO + 0.05wt%		TMPTO + 0.05wt%	
TMPTO + 0.1wt%		TMPTO + 0.1wt%	
TMPTO + 0.2wt%		TMPTO + 0.2wt%	
TMPTO + 0.3wt%		TMPTO + 0.3wt%	
Continued TMPTO + 0.4wt%		TMPTO + 0.4wt%	
TMPTO + 0.5wt%		TMPTO + 0.5wt%