Demonstrating the impact of molecular weight on the glass transition temperature of poly-methyl methacrylate using molecular dynamics simulations

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Abstract

The glass transition temperature of materials can be vital towards their applications in terms of heat and stress tolerance. The material of PMMA has been widely used on products such as plastics, glass substitutes and LED layers. This research was conducted through the method of molecular dynamics simulation for the relatively large size of the PMMA. From the simulations, results show that an increase in monomer length (molecular weight) would increase the glass transition temperature of PMMA. For all three molecular weights, the glass transition temperature could range from approximately 150 to 250 degree celsius. With determination of Tg, PMMA can be widely used under certain temperature environments with prevention of PMMA phase change.

Introduction

The research project conducted focused on the thermal properties of polymers.

PMMA is strong, tough and lightweight. It also possesses the properties to have tensile strength, flexural strength, transparency, polishability, and UV tolerance.

The material PMMA has been widely used in many industries. In the drug and the food industry, one of the most challenges faced was the poor aqueous solubility. [11] The amorphous drugs are often in a highly disordered state. Therefore, they required high molecular mobility and molecule reactivity to inherent chemical and physical instability. [1] This makes determining the PMMA glass transition temperature very important for the stability of produced drugs and foods.The properties of PMMA also makes it suitable to create a layer for LED lights. It allows the LED lights to reach its maximum light emitting potential. [19] The indispensable material has been used for various optical applications for its unsuppressed transparency and unique combination of illumination.With the high tolerance to Ultraviolet lights, PMMA offers high translucency and even light distribution, making the results better than standard plastic at a lower lighting capacity. Acrylic PMMA have been widely distributed in museums and galleries for protecting artworks from photography. [2]

There have been many interesting properties of PMMA that can make it a suitable material for many applications. PMMA possesses free rotating methyl groups which prevents the polymer chains packing closely. Therefore, it has been widely used in the industry of plastics for its tough and rigid properties. In addition, PMMA has been used for LED layers for its perfect transmission of visible light and stability after exposure to long term ultraviolet radiation. With these properties, PMMA had been considered a common substitution for glass. Subsequently, determining the glass transition temperature based on conditions of PMMA would be dominant to maintain stability of PMMA.

PMMA possesses the chemical name (C5H8O2)n. It possessed a density of 1.18g/cm^3, therefore the density of the system in the simulation is also adjusted to 1g/cm^3, being closest to the density of PMMA. Based on the monomer number and chain length, the molecular weight for PMMA could vary. This also makes the glass transition temperature of PMMA to vary. Thus, the determination of PMMA Tg is required for 3 different monomer lengths to testify the hypothesis.

Exploring the effect of the molecular weight of polymers on glass transition temperature. I will be monitoring the molecular weight by changing the length of the polymer chains. For each molecular weight, the glass transition temperature can also be predicted with simulations under different temperature conditions. With the density of the system recorded for each temperature, a graph can be generated to decide the glass transition temperature of one certain molecular weight. The process of getting the results will be discussed in the methods section.

The research goal consists of mainly two parts:

1. Predict glass transition temperatures (Tg) and how it could be monitored by adjusting the different temperatures
2. Investigate the effect on the molecular weight (monomer length) on the glass transition temperature under same conditions

The general decreasing pattern of the PMMA density based on increase in temperature can be predicted. At a low temperature, PMMA ensembles to a structure with more order. The motion of molecules is very slow. With an increase in temperature in the system, the system will have more thermal energy as well as kinetic energy of the molecules, including vibrational and rotational kinetic energy. Force fields are highly impacted by the change in temperature. The motion of the molecules becomes a lot quicker. With the temperature reaching polymer melt, the PMMA molecule will enter a more disordered state. The change in structure will also result in atoms moving even at a higher velocity, taking up more volume of the system. Therefore, the density of the system decreases.

After a certain temperature, the PMMA transfers into a glassy state from a solid state. The glass transition of PMMA is a rather more solid-solid transition instead of liquid-liquid transition. At the glassy state, the atoms will become more disordered with a slight increase in temperature. Therefore, the density will decrease even more than regular, resulting in a steeper slope.

Methods

IUPAC chemical name as poly(methyl 2-methylpropenoate)

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Molecular Dynamics (MD) studies how atomic coordinates evolve under given conditions. [3] With the reliance on the framework from mechanics, molecular dynamics simulates chemical and physical processes on computers.

Under an environment with limited access to laboratory equipment, Molecular dynamics would be the best approach towards finding the glass transition temperature. With simulation based on it, there will not require high cost materials as the experiment requires heating up lots of samples.

Molecular dynamics would also be an appropriate approach for PMMA specifically due to its relatively large molecular weight. This gives more stability in the movements of electrons as its movement will be limited with higher weak interaction within the larger molecules. Conversely with smaller molecules, the results will be more unstable and unreliable as electrons are easier to move around with a relatively faster velocity, making the behavior of the change in density of the system harder to predict.

Born-Oppenheimer Approximation provides a mathematical approximation on simulations relating to Molecular Dynamics. Proposed by Max Born and J. Robert Oppenheimer, BO approximation considers the molecular energy as a sum of individual terms. The equation consists following forces:

E(total) = E(electronic) + E(vibrational) + E(rotational) + E(nuclear spin)

With the consideration of the forces, a quantum chemistry approach would not be necessary for molecular dynamics simulation. Based on the force fields influenced by the movement of electrons, an observation can be made for atactic PMMA as reaching designated temperature.

The coordinates for the nucleus would be considered as fixed due to the relatively large atomic mass.

PMMA consists of 15 nuclei and 40 electrons. To obtain a certain energy level or a designated temperature, the Schrödinger equation can be used. It contains 3 × 15 = 45 nuclear + 3 × 40 = 120 electronic = 165 variables for the wave function, therefore requiring at least 165^2 = 27225 hypothetical calculation steps during computational chemistry calculation.

To determine the stability of the amorphous systems, the glass transition temperature (Tg) of various polymers can be observed. Unlike most other phase transitions (1st order), the glass transition temperature is a second order transition. This is due to the system not going through an abrupt change in the volume. Instead, the amorphous system changes the heat capacity going from solid state and rubbery state. Heat is not transferred. The glassy state is high viscous and brittle, while the rubbery state is less viscous and more mobile. Thus, achieving a rubbery state could also improve solubility of materials.

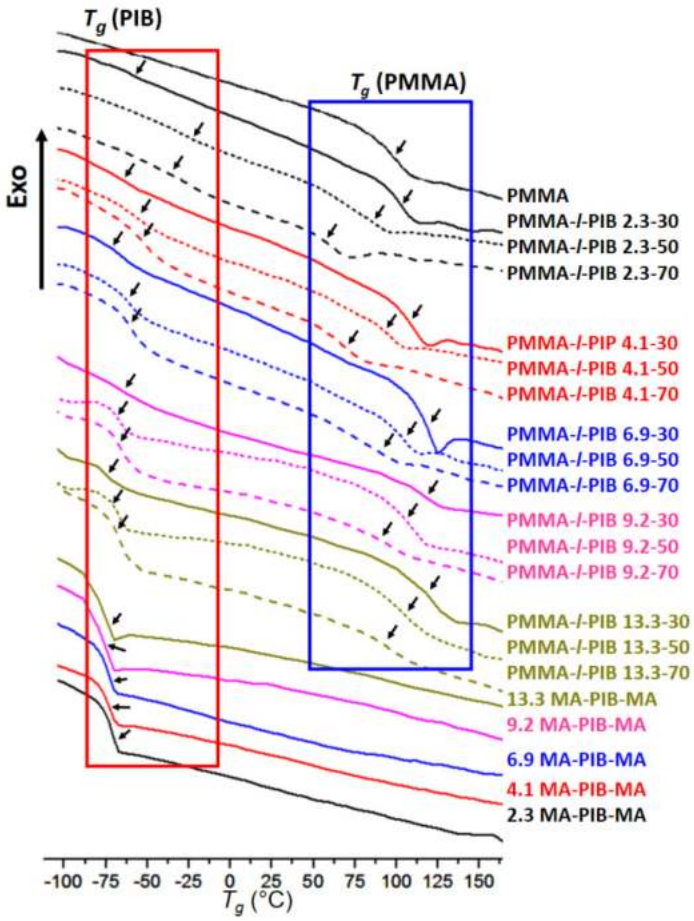

Figure 1. [20]
Glass transition temperatures (*Tg*) of the poly(methyl methacrylate)-*l*-polyisobutylene (PMMA-*l*-PIB) conetworks as a function of composition (the lines represent the *Tg* of the methacrylate-telechelic polyisobutylenes (MA-PIB-MA) macromolecular cross-linkers and the poly(methyl methacrylate) (PMMA) homopolymer, and the inflection points as *Tg* values are indicated by arrows).

In this simulation, I focused mainly on Atactic PMMA for more randomness of the orientation. Atactic PMMA would be ideal for this experiment as different conditions relating to the orientation of long length PMMA would apply in real life application.

For the parameters of the simulation, configurational bias Monte Carlo (CBMC) and Molecular Dynamic simulations are combined to improve sample efficiency, producing a more accurate result.

The density for this simulation is set to be 1g/cm^3, which is closest to the density of PMMA (1.13g/cm^3). The simulation is also conducted under NPT condition, as pressure is fixed at 1 atm. Therefore without taking into consideration pressure, the density can be observed with the increase of temperature.

Temperature of each simulation ranges from 15 to 275 degree celsius, with a 10K difference in between. The 10K difference is determined due to the error and efficiency of the simulation. The wide range is required to generate a more complete and comprehensive graph indicating two clearly different slopes.

The time step for each simulation is determined at 1fs, as it will lead to more accurate data. However, the efficiency of simulation certainly decreased. Similarly, the number of molecular steps is determined at 30,000. This means more steps are taken into consideration when generating a density vs time graph based on a certain designated temperature, leaving more room for the system to equalize. With a density relatively closer to the stable environment under high temperature, the results would become more accurate.

After each of the simulations are complete, the files regarding the density of PMMA vs. Time data could be saved. With these data, the last three points of density are taken and recorded into the graph. This is because the last three points are generally the density that the system is equalizing to. After that with more time steps, the density is not likely to change significantly.

With an average value taken for the last three densities recorded, the other two trials for the certain temperature will also go through the same steps. As the average density of three trials

for each of the temperatures is taken, a graph can be generated based on density (in g/cm^3) vs. temperature (degree celsius with increments of 10 ranging from 15 to 275).

The flory-fox equation determines the glass transition temperature. It requires some variables including Mn (average molecular weight per mole) and K constant (determined by the free volume present in the polymer sample. Based on the maximum glass transition temperature that can be reached (Tg infinity), Tg can be calculated. Monitoring the polymer length can cause an effect on the Mn value, thus affecting glass transition temperature.
The numerical value of PDI (polydispersity index) ranges from 0.0 (for a perfectly uniform sample with respect to the particle size) to 1.0 (for a highly polydisperse sample with multiple particle size populations). The Mn value for the flory-fox equation can be derived from the PDI index for polymers. It was affected by the particle size of polymers.

Therefore, looking into the PDI index can be a method to determine the differences between glass transition temperature of various materials. (polymers)

Based on the previous theory from the flory-fox equation on free volume, a graph of specific volume (cc/g) vs. temperature (K) can be plotted. A major difference in two slopes can be observed as the temperature increases. The first slope (flatter) identifies as the solid state (glass) where solubility is limited. The other slope (steep) will represent the rubbery state with a high solubility due to the disorder of the molecule system. The point of transition between the two slopes can be determined as the glass transition temperature (Tg).

The previous steps have to be repeated for various times with monitoring the length of the polymer. With the data of Tg collected, another graph can be plotted for Tg vs. polymer length (# of monomers per chain). This should show the relationship between the polymer length and the glass transition temperature. The plan is to collect data with the same method for both atactic polypropylene and Polystyrene. With analysis on their structures, we might be able to find out the factors affecting their glass transition temperature.

Results and discussion

By analyzing the Tg plot for n=30 (Figure 2), a clear indication of slope change can be observed at 100.24 degrees Celsius. The temperature value at that certain point indicates that at 100.24 degrees Celsius, the structure of PMMA is going through a phase change into a glassy structure.

For some graphs, higher temperature might result in some deviation from predicted results. The plots on the graph tend to fluctuate more than lower temperature plots. For higher temperatures,

the motion of the atoms in the monomer fluctuates faster causing more variability in the structure. It will take more time to relax the structure. Therefore, they are more likely to react more vigorously than predicted causing more deviation.

With only 1 trial taken into consideration, more fluctuation can be more clearly observed. There will be more errors in the simulations as the results are not always accurate with only one trial. However, this problem can be simply solved by adding more trials. With up to 3 trials, the errors in each trial tend to balance out. The results for the three trials are a lot less fluctuating, creating a graph with two clearly indicated slopes based on the plots. The plots are also clearly closer to each other with less error.

For the early stages of simulation, the results can only generate one slope. No notable changes in slope can be observed. We predicted that this is because the glass transition temperature has not been reached. With an increase in range of temperature focusing on higher temperatures, a change in the slope of the graph can be clearly identified.

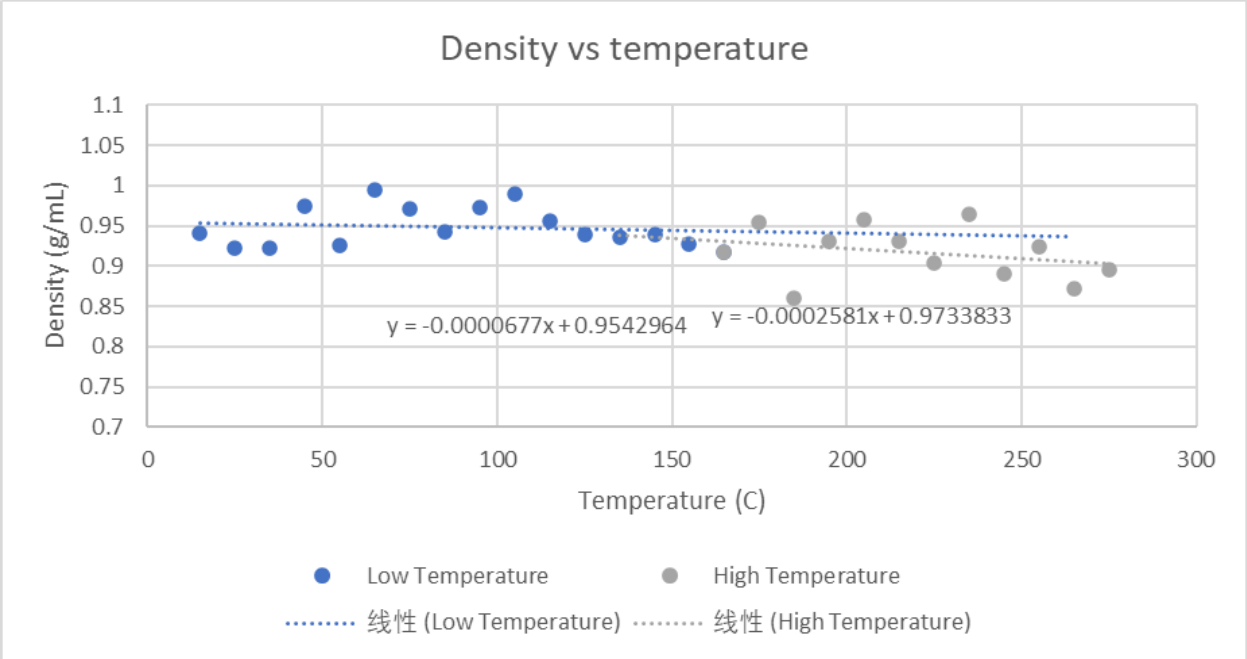

Figure 2. Tg plot for n=30

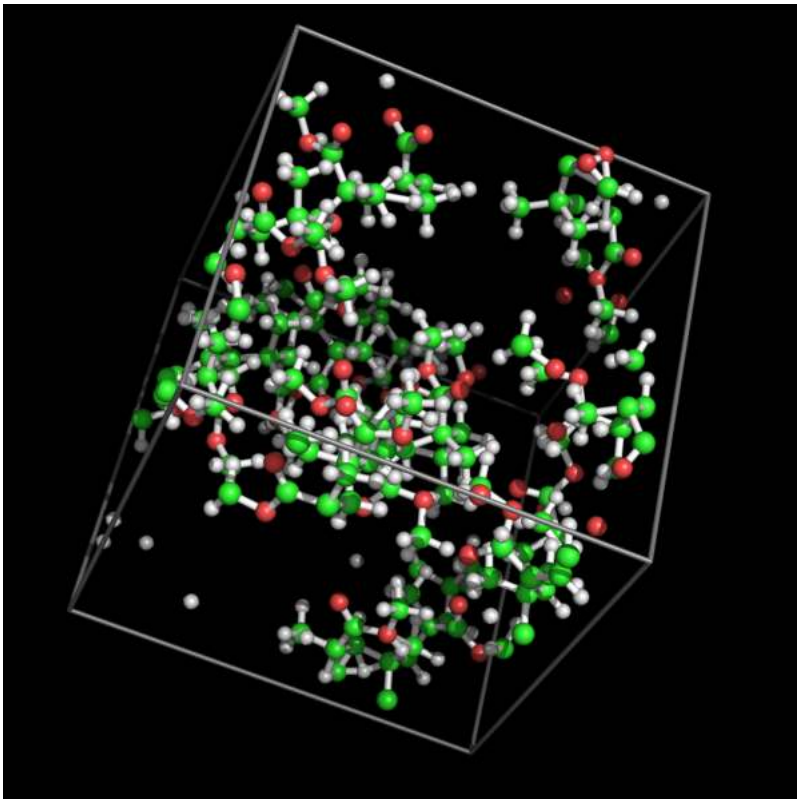

Figure 3. N=30 Structure at 528K

Comparing the Tg plot of n=30 with n=40 and n=50, it can be clearly seen that n=50 possessed a higher point of intersection for two slopes than n=40 or n=30. The glass transition temperature can be observed as following:

N=30: Molecular Weight = 3003.47g, Tg = 373.39K
N=40: Molecular Weight = 4004.63g, Tg = 381.23K
N=50: Molecular Weight = 5005.79g, Tg = 430.62K

Based on this pattern, it can be observed that with increasing polymer length (monomer number), the glass transition temperature also increases. This is because a longer chain of molecules will possess higher weak interaction. It will also be more tangled up and form a more ordered glass structure. Therefore, it requires more energy for the atoms to fluctuate and become mobile. With the more interaction, a higher kinetic energy is also required to break down the molecule transitioning into the glassy state. Therefore, there will be a higher energy barrier to overcome, requiring more thermal energy and a higher temperature for glass transition.

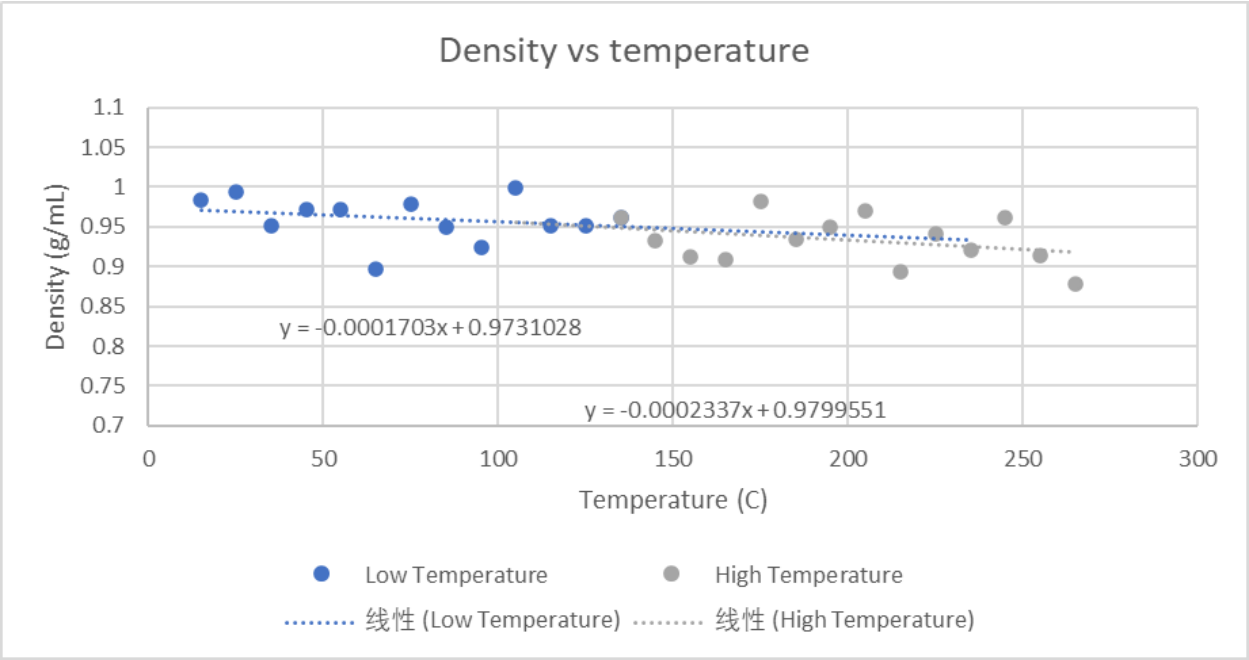

Figure 4. Tg plot for n=40

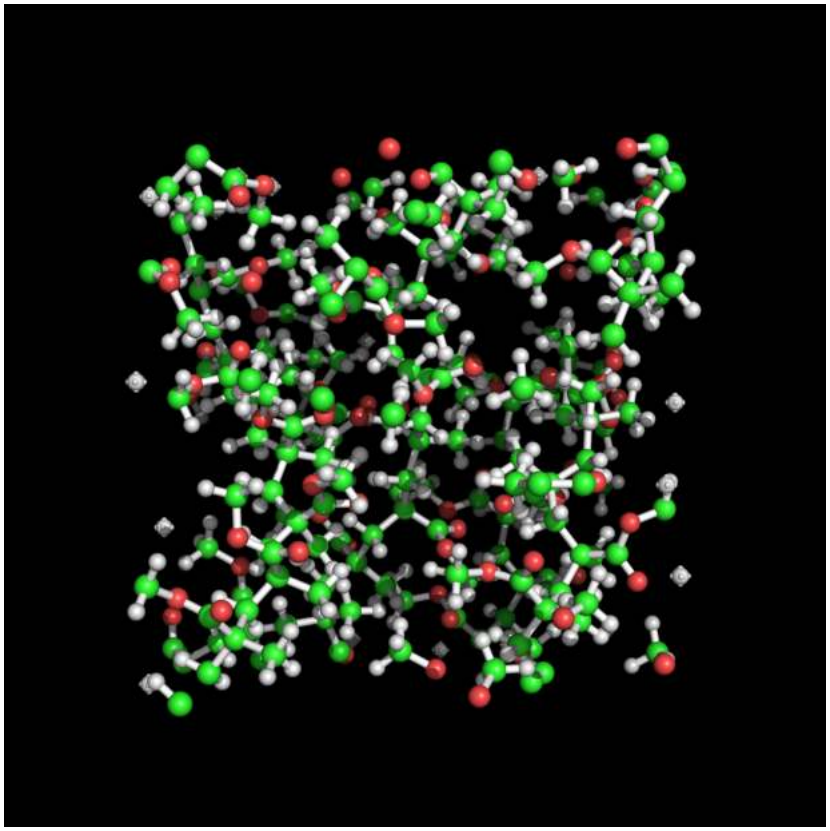

Figure 5. N=40 Structure at 528K

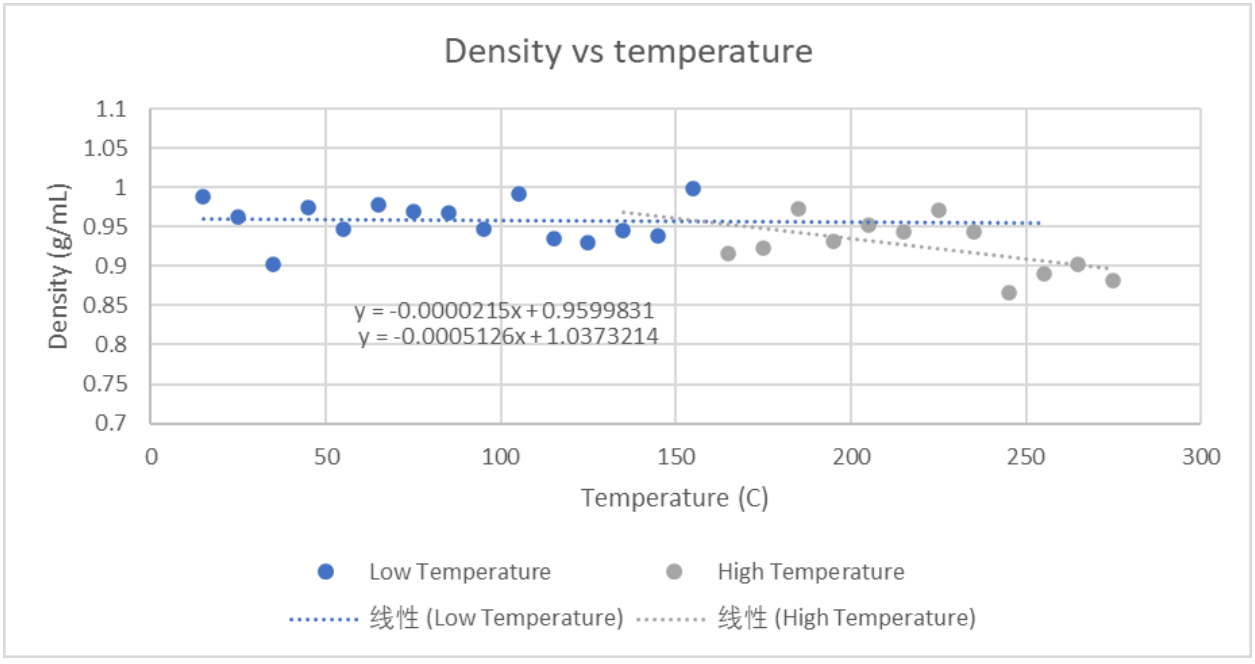

Figure 6. Tg plot for n=50

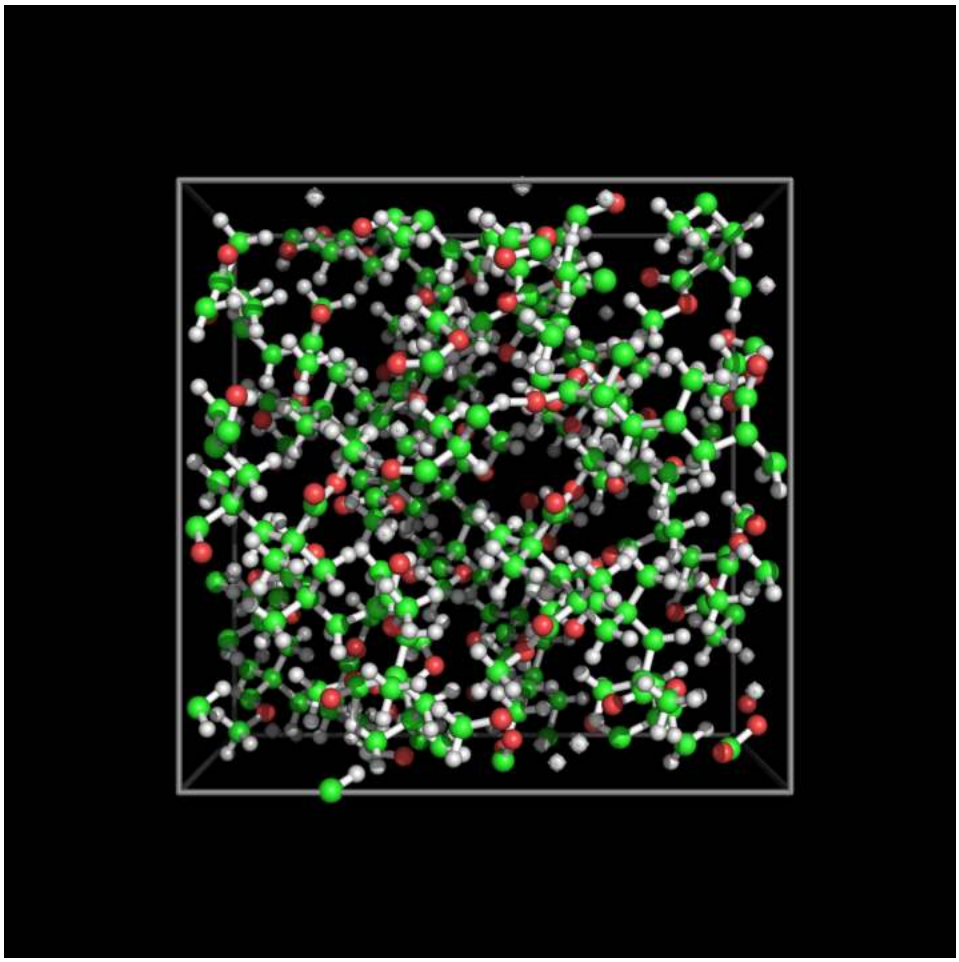

Figure 7. N=50 Structure at 528K

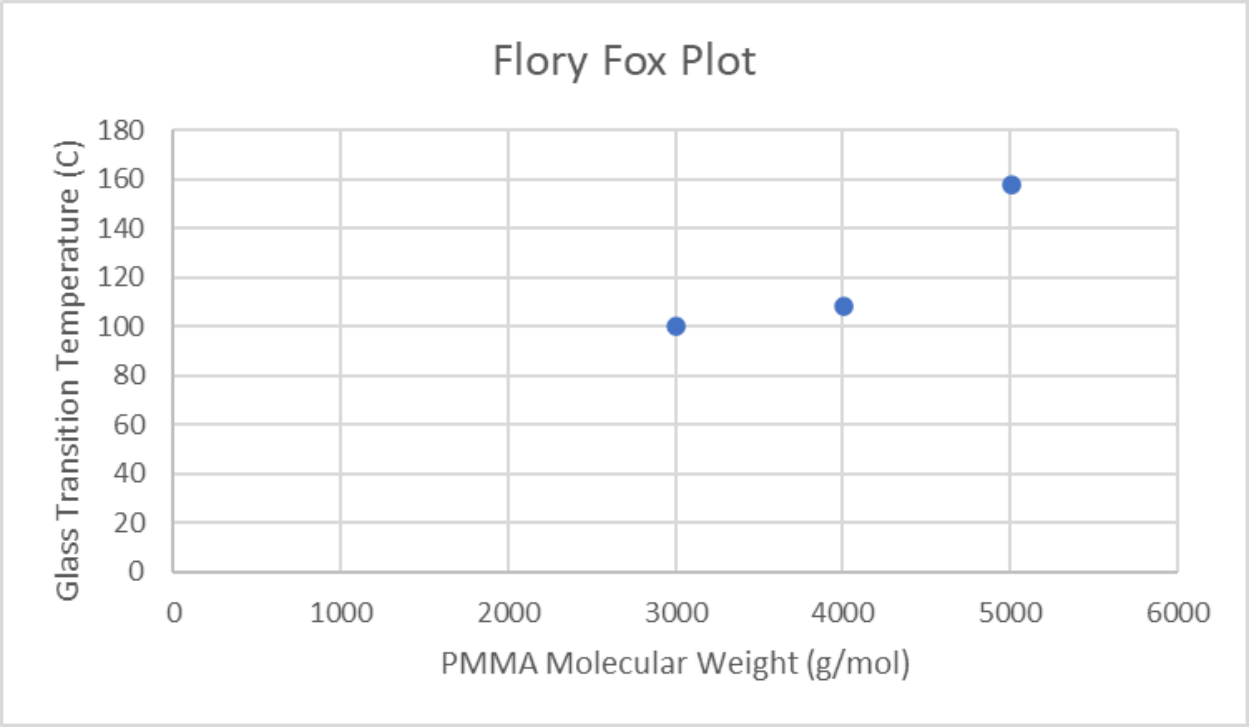

Figure 8: Glass transition temperature vs. polymer length

The relationship between Tg and molecular weight can be determined linearly based on the data in figure 8. However, according to other research results, data are graphed at a pattern of increasing value while concave down.

For the simulation conducted in this research paper, only low molecular weight is used to determine glass transition temperature. According to other results, low molecular weight below 10000 g forms a linear relationship, while higher molecular weight above 10,000 forms an increasing concave down relationship.[18] As this research hasn't reached that high temperature, only a linear relationship can be observed.

Standard PMMA possesses parameters of Tg infinity at 135 degree celsius and the constant K at 1.4 x 10^5 Cg/mol. [18]

This indicates that the glass transition temperature should be at a maximum of 135 degree celsius. With a higher temperature, it represents that the simulation is overestimating the Tg value. A prediction of the overestimation is caused by the lack of sufficient MD steps and high time steps for the system to reach the equilibrium density of each designated temperature, as the data is taken without getting to the decreasing steps of the density of the system.

Conclusion

The errors for this experiment resulting in a glass transition temperature greater than Tg infinity can be ignored under some certain circumstances. For example, when observing the general pattern of glass transition temperature relationship to molecular weight, or comparing the Tg value with another material, these deviations can be ignored. Despite a decrease in accuracy of results, simulation provides a quicker alternative pathway to get results without experimenting. The efficiency of simulation can be accounted for when considering benefits of molecular dynamics simulation.

With determining the glass transition based on polymer length, applications of PMMA can be benefited with a more detailed molecular weight provided to reach certain melting points. The melting of PMMA can also be prevented based on the environment's temperature, leading to more sustainable and effective products made based on PMMA.

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7. Author links open overlay panelPaul N. Patrone a b 1, a, b, 1, c, AbstractThe composites industry is increasingly using molecular dynamics (MD) simulations to inform its materials development decisions. As a result, Li, C., Fan, H. B., Yu, S., Soni, N. J., Sirk, T. W., Pathria, R., Christensen, S., Engineering, I. C. M., Dienstfrey, A., Donth, E.,

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15. Author links open overlay panelMajid Hadipeykani, AbstractA molecular dynamics simulation study is performed to predict the glass transition temperature (Tg) and the volumetric coefficient of thermal expansion (CTE) of thermoset polymer based nanocomposite reinforced by carbon nanotube (CNT). An atomist, QuaresiminM., ThostensonE.T., AlipourP., TackJ.L., KarbasifarB., RuhaniB., JavadzadeganA., FanH.B., GojnyF.H., CiL., Hernández-PérezA., ShenJ., BandyopadhyayA., LiC., SunH., DuanW.H., MahboobM., … AghadavoudiF. (2020, January 2). *A molecular dynamics simulation of the glass transition temperature and volumetric thermal expansion coefficient of thermoset polymer based epoxy nanocomposite reinforced by CNT: A statistical study*. Physica A: Statistical Mechanics and its Applications. https://www.sciencedirect.com/science/article/abs/pii/S0378437119322113?via%3Dihub

16. Author links open overlay panelMaryam Mohammadi a, a, b, c, AbstractThe glass transition temperature (Tg) governs the mechanical and physical performances of polymeric materials and thus their ultimate applications. Although an extensive body of research has focused on the study and determination of the Tg, Samith, V. D., Huang, M., Rask, M. B., Knapek, M., Wood, C. D., Sun, W., Silalai, N., Thirunarayanan, S., Hughes, D., Hodge, I. M., Shell, M. S., Binder, K., Soldera, A., Subramanian, V., … Moynihan, C. (2017, March 30). *The glass transition temperature of PMMA: A molecular dynamics study and comparison of various determination methods*. European Polymer Journal. https://www.sciencedirect.com/science/article/abs/pii/S001430571631237X
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