



Analyzing the Heat Transfer Rate of Nanostructures of Poly (Methyl Methacrylate) / Al₂O₃ Utilizing Molecular Dynamics Simulations

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Abstract: The main methods for preventing fires are physical, chemical, or a combination of the two. One of the main thermophysical characteristics that connect the chemical structure is thermal diffusivity. The relationship between heat transport as well as heat resistance has been thoroughly established in the literature. Heat transmission can also be connected to various fire-retardant characteristics, like maximal heat release or time to ignite, which rank among the most crucial factors in defining the potential fire danger of a specific material. The thermal stability, as well as fire-retardant qualities of polymers, are enhanced by metal oxides. In the present investigation, simulations of molecular dynamics constructed using the single atom approach was used to examine the consequence of Al₂O₃ nanoparticles on thermal transfer of isotactic polymethyl methacrylate. Capacity, density, and thermal transfer were studied in the 300-700 K range to examine the heat transfer rate of poly (methyl methacrylate) besides poly (methyl methacrylate)/Al₂O₃ nanocomposite. It is possible to calculate heat capacity using fluctuating characteristics. Conductivity was calculated through a non-equilibrium modeling simulation using Fourier's law. The thermal diffusivity of the poly (methyl methacrylate) with the thermal conductivity is increased by over ten times by the alumina nanoparticles, which also enhances the T_g by around 10 K. The results show that the Al₂O₃ nanoparticles increase a transition temperature of glass; conductivity, in addition diffusivity of the poly (methyl methacrylate) while decreasing the heat capacity.

Keywords: Dynamics, Fourier's law, metal, heat, simulation

1. Introduction

The improvement of material fire resistance is a serious concern. To control and mitigate the fire's detrimental effects, a thorough examination of the fire's behavior and operational procedures is required. A lot of effort has been made to comprehend the underlying mechanisms and behaviors better. Chemical, physical, or a combination of these methods are used in flame retardancy processes. The behavior of fire is significantly influenced by chemical qualities like thermal stability or physical characteristics. One of these, thermal diffusivity, is essential for forecasting the flammability attribute [1,2].

Thermal diffusivity is the capacity of a material to transmit heat instead of absorbing it. As a result, heat is transferred through a material more quickly the higher the thermal diffusivity. Therefore, the pace at which a specific material decomposes can be physically influenced by the thermal diffusivity [3,4]. Recent research has shown that increasing thermal diffusivity mostly lengthens the time it takes for ignition to occur while reducing the peak and

overall rates of heat release. The two most important parameters of a particular substance in the assessment of its potential danger of fire are found to be the maximum heat rare release as well as overall heat release. Therefore, as thermal diffusivity is raised, flammability is decreased [5,6].

Furniture, computers, appliances, and specialized industrial parts are just a few of the many products and materials manufactured of polymer that is employed in these products. The benefits of polymers are their simplicity in production, small size, high voltage breakdown, strength, and resistance to corrosion [7,8]. Their low price is, however, their biggest advantage. Meanwhile, it is acknowledged that polymers' heat resistance is both a critical property and a challenging problem. An enhancement in the fire-resulting effect of polymer materials is therefore highly desirable when it comes to the fire resistance capabilities of polymers. As a result, a solution must be developed to lessen the risks through the development of novel, sophisticated materials with superior combustibility properties [9].

Recent research has demonstrated that reinforcements like metal oxides can improve the thermal durability of polymers while reducing their flammability. According to earlier studies, a metal oxide's predominant fire retardancy mechanism is primarily linked to its physical characteristics rather than its chemical composition. For examples, TiO₂, Al₂O₃, and other metal dioxide nanoparticles have a large ability to alter the thermal breakdown of a polymer [10]. We concentrate on investigating poly methyl methacrylate as the host matrix in this research. Due to its many beneficial qualities, the thermoplastic polymer poly (methyl methacrylate) is widely employed in a variety of applications. However, its primary flaw is that, with a limiting oxygen value of 18, it is extremely flammable. The following literature review describes how metal oxide fillers enhance the flammability of poly methyl methacrylate [11,12].

In order to better comprehend of the elements influencing the properties of polymer-metal oxide nanocomposites, researchers have extensively looked into the effects of specific material variables on thermal conductivity and properties. Al₂O₃, TiO₂, and boehmite fillers have all been studied by Friederich *et al.* [13] at varied loading contents. It has been shown that the duration of ignition improves by around 25 % in terms of different weight fractions regardless of the type of reinforcement utilized, of the additives. Additionally, peak heating rate is reduced by almost 50 % of the total at 15-20 weight % of the same fillers, per the same experiment. Utilizing alumina at a 15 wt.% concentration efficiently reduces the overall heat emission by about 30%. Iron oxide and titanium dioxide fillers both increase thermal stability by around 70°C and lower peak heat rate, according to Laachachi's [14] analysis of their effects. With an increase in the amount of both fillers, the peak heat rare rate falls and the overall burn time rises.

A molecular modeling simulation is a useful tool for researching polymer behavior. While there are some molecular modeling simulations on thermal decomposition as well as thermal degradation for polyethylene, polypropylene, and poly(isobutylene). To our knowledge, no similar computations for heat transfer using molecular dynamics exist for poly-a-methyl styrene and other materials [15,16].

Molecular modeling simulations will be used to examine how adding metal oxides can increase a polymer's ability to withstand fire. To do this, we compute the heat conductivities of poly (methyl methacrylate) as well as poly (methyl methacrylate)/Al₂O₃ nanocomposite and investigate the effects of the Al₂O₃ nanoparticles on the poly (methyl methacrylate).

2. Molecular Dynamics Simulation Setup and Materials

All molecular simulations had been carried out on Large-Scale-(Atomic/Molecular)-Massively- Parallel-Simulator [LsA/MMPS] thru a focus on materials characterization. A system was composed of three linear isotactic polymethyl methacrylate chains with a degree of polymerization of 100 surrounding an aluminum oxide nanoparticle (10% weight Al₂O₃) with a radius of 7Å, at the middle of the simulation cubic. J. Scott *et al.*[17] proposed the structure of the polymethyl methacrylate monomer. The structure of aluminum oxide is extracted from the Chichagov [18] crystallographic database. After being created in (Fortran 95), the poly (methyl methacrylate) conformations with a random algorithm and the Al₂O₃ structure had been bring in as data input into the [LsA/MMPS].

The simulations were carried out with a periodical boundary condition in three dimensions. To speed up computation, in a unified atom design; so, every carbon is clustered while utilizing its bound hydrogen. To use the force field equations in the [LsA/MMPS], some adjustments had to be performed. Interface potential (U) is described through a following equation:

$$U = \sum_{bonds} k_r (r - r_0)^2 + \sum_{angles} k_\theta (\theta - \theta_0)^2 + \sum_{torsions} \sum_{i=1} (V_n \cos n\phi) + \sum_{improper\ torsions} (K_1 (\theta - \theta_0) + K_2 (\theta - \theta_0)^2) + \sum \frac{A}{r^{12}} - \frac{C}{r^6} \quad (1)$$

The bond-stretching energy (equation 2); (*r*) is length of the bond, and (*r*₀) length of the bond at equilibrium. The energy of angular bending (equation 3); (*θ*) is the bend angle and (*θ*₀) is the bond's equilibrium angle. The energies of dihedral torsion (equation 4) and incorrect torsion (equation 5); *φ* is the diagonal torsion angle ; while *θ*, *θ*₀ are equal to total of three close bending-angles. Between two unbonded atoms or molecules, the Lennard-Jones energy (equation 6).

$$\sum_{bonds} k_r (r - r_0)^2 \tag{2}$$

$$\sum_{angles} k_\theta (\theta - \theta_0)^2 \tag{3}$$

$$\sum_{torsions} \sum_{i=1} (V_n \cos n\phi) \tag{4}$$

$$\sum_{improper\ torsions} (K_1(\theta - \theta_0) + K_2(\theta - \theta_0)^2) \tag{5}$$

$$\sum \frac{A}{r^{12}} - \frac{C}{r^6} \tag{6}$$

The poly (methyl methacrylate)/Al₂O₃ nanocomposite's interaction potential included both binding plus non-binding potentials. The interaction between the carbonyl group (C=O) and ester oxygen of the poly (methyl methacrylate) and the aluminum is defined by the binding potential. The relationship between the carbons in poly (methyl methacrylate) and the aluminum is described by the non-binding potential.

$$U_b = A \exp(-2\lambda(z_i - z_b)) - B \exp(-\lambda(z_i - z_b)) + C\lambda^2(z_i - z_b)^2 \exp(-\lambda(z_i - z_b))$$

$$U_{ab} = \frac{2}{3} \pi \sigma_i \epsilon_i \rho \left[\frac{2}{15} \left(\frac{\sigma_i}{z_i}\right)^9 - \left(\frac{\sigma_i}{z_i}\right)^3 + \frac{2}{3} \sqrt{\frac{5}{2}} \right] \tag{7}$$

Where z_i shows the separation of atom i from the surface of the aluminum. (A, B) a standard Morse potential; C is the activation energy. Between the aluminum atoms in the substrate as well as the non-binding Poly (methyl methacrylate) atoms, the Lennard-Jones constants are $\sigma_i \epsilon_i$; while ρ is the density of aluminum atoms.

It is noteworthy that, despite the fact that Shaffer and Chakraborty's stated potential was given for the unified atom, there weren't any potential interactions with hydrogen in Poly (methyl methacrylate) [19,20]. The potential was increased to Al₂O₃ by assuming that the interface between the O₂ in Al₂O₃ and Poly (methyl methacrylate) could have been described as the averaged nonbinding interface of Aluminum through Poly (methyl methacrylate). Drabold and colleagues [21] conducted the initial investigation into polymer metal oxide adhesion. They discovered that connections between alumina and poly (methyl methacrylate) atoms are quite weak, but interactions between aluminum atoms and the carbon and hydrogen in Poly (methyl methacrylate) are also very weak.

The postulated interatomic interactions via Streitz et.al [22] for the Al₂O₃ potential that has an embedded atom V_{EAM} besides an electrostatic component V_{ES} .

$$V_{EAM} = \sum_i F_i[\rho_i] + \sum_{i<j} \varphi_{ij}(r_{ij})$$

$$\rho_i(r) = \sum_{i=j} \xi_j e^{-\beta(ij-r_j^*)} \tag{8}$$

$$F_i(\rho_i) = -A_i \sqrt{\frac{\rho_i}{\xi_i}}$$

$$\varphi_{ij}(r) = 2B_{ij} e^{\frac{\beta_{ij}}{2}(r-r_{ij}^*)} - C_{ij} [1 + \alpha(r - r_{ij}^*)] e^{-\alpha(r-r_{ij}^*)} \tag{9}$$

Where $F_i(\rho_i)$ shows how much energy is needed; ρ_i ; $\varphi_{ij}(r)$ represented the pair-wise interaction. when the interatomic distance is tiny, $\varphi_{ij}(r)$ it becomes strongly repulsive. Electric charges on atoms are accounted for by the electrostatic component, which is described as:

$$V_{ES} = \sum_i v_i(q_i) + \frac{1}{2} v_{ij}(r_{ij}; q_i; q_j)$$

$$v_i(q_i) = v_i(0) + \chi_i^0 q_i + \frac{1}{2} J_i^0 q_i^2$$

$$v_{ij}(r_{ij}; q_i; q_j) = \int d^3 r_1 \int d^3 r_2 \rho_i(r_1; q_i) \rho_j(r_2; q_j) / r_{12} \tag{10}$$

3. Condition of Equilibrium

In the simulation box at T=700K, the three polymer chains were initially constructed around a sphere with the same diameter as an Al₂O₃ nanoparticle, the diameter was assumed to be zero. In the empty place where the nanoparticle would be introduced, the polymer chains could shift. A wall potential was built around the area to prevent this. The Okada team's [23] poly (methyl methacrylate) potential's average Leonard Jones parameters were used to calculate the wall potential's parameters. The conjugate gradient method was used to reduce the initial system's overall potential energy. After then, the polymer chains were given time to settle. In earlier research [24], the polymer's equilibration was described. The Al₂O₃ nanoparticle was subsequently introduced to the cavity, then after 2 ns, both system and the NPT ensemble were in equilibrium. The system was then cooled at a rate of 10K/5ns from 300 to 700 K.

4. Results and Discussion

4.1 The Nanostructures Density

Fig. 1 displays, as a function of temperature ramp, the density (ρ) of a poly (methyl methacrylate) structure as well as a poly (methyl methacrylate)/Al₂O₃ nanocomposite. It is evident that the slope of the curve changes. It is believed that a transition temperature of glass (T_g) is a point at which the slope of the curve suddenly changes. Physical properties of a polymer shift above T_g from rubbery to glassy state below T_g . Density as well as T_g of poly (methyl methacrylate)/Al₂O₃ nanocomposite is higher than those of the poly (methacrylate) alone, as shown in Figure 1. In comparison to the poly (methyl methacrylate)/ Al₂O₃ nanocomposite, Fig. 1 demonstrates an increase in T_g of roughly 10 K.

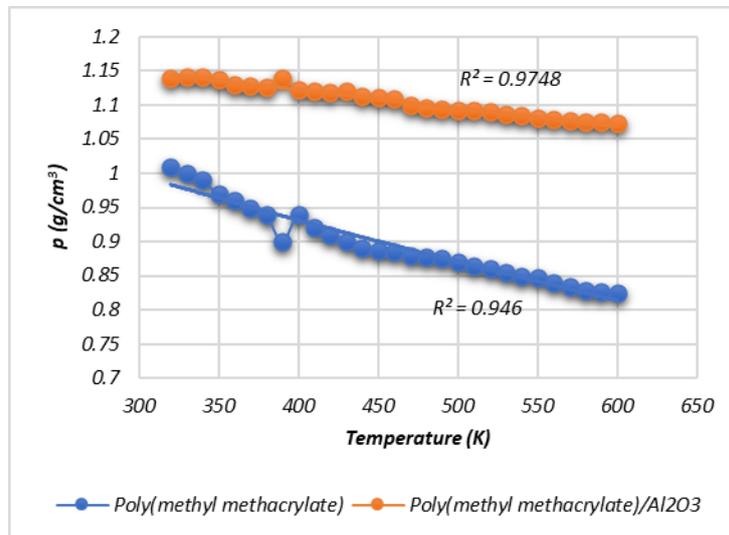


Fig. 1 - Relationship between temperature and the density of poly (methyl methacrylate) plus poly (methyl methacrylate) / Al₂O₃

4.2 Heat Conductivity

The equilibrium molecular dynamic and non-equilibrium molecular dynamics methodologies are the two approaches using molecular dynamics to figure out the thermal conductivity of T_c . In this research, the heat conductivity of the poly (methyl methacrylate) and Al₂O₃/poly (methyl methacrylate) nanocomposite was examined using an equilibrium molecular dynamic simulation using Fourier's law [25,26]. Our simulation system had been divided into multiple slabs over its whole length, with two slabs at either end housing the hot and cold regions, respectively. The temperature distribution was then obtained by fitting the linear temperature area using the least squares approach. Calculations for the thermal conductivity (k) include:

$$k = -\frac{J_q}{dT/dy} \quad (11)$$

where J_q is the heat flux determined by the following expression: in directional temperature distribution inside the unit cell, dT/dy is the steady temperature gradient and k is the thermal conductivity.

$$J_q = \frac{E}{2A_{cross-section}} \tag{12}$$

The T_C versus temperature graphs for the poly (methyl methacrylate) and poly (methyl methacrylate)/ Al_2O_3 nanocomposite is shown in Fig. 2. Heat conductivity of poly (methyl methacrylate) is observed to increase with temperature up to the T_g , but it decreases above that temperature T_g . This is because air has a low thermal conductivity and the free volume rises at temperatures over the critical point T_g . The experiments [27,28] are in good agreement with the thermal conductivity's temperature-dependent behavior.

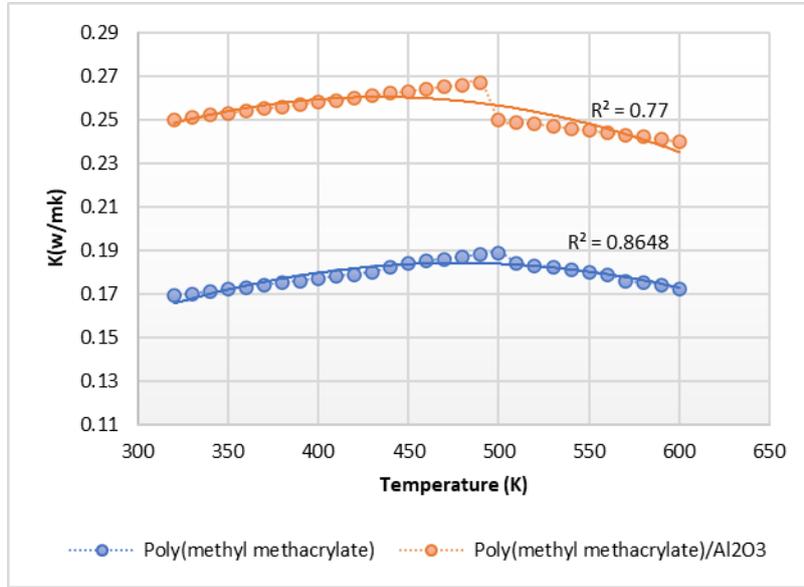


Fig. 2 - Relationship between the conductivity of poly (methyl methacrylate) as well as poly (methyl methacrylate)/ Al_2O_3

Despite having a relatively high conductivity sideways a single chain, polymers' bulk thermal conductivity is quite poor because to phonon scattering at and thermal contact resistance at chains ends [29,30]. Further off-putting factors include entangled chains, in addition even voids that performance as a scattering phonon location. In relation to temperature, Fig. 2 compares the thermophysical properties of poly (methyl methacrylate) as well as poly (methyl methacrylate)/ Al_2O_3 . The comparison shows that the T_C of the polymer rises when the Al_2O_3 nanoparticle is added, which is in line with the results of the experiment [13].

Although the results from simulation and experiment are consistent, some variations in the value of the T_C for the poly (methyl methacrylate)/ Al_2O_3 nanocomposite are still seen. These variations are caused by the voids that the addition of the nanoparticles created. The aggregation of nanoparticles in particular cities and cavities may be caused by other sources [31,32].

4.3 Thermal Capacity

The features of the fluctuations [33,34] as illustrated in Equations. 7 and 8, respectively, can be utilized to calculate the specific heat capacity at constant pressure (C_p) or volume (C_v).

$$C_{v=}\overline{C}_V = \frac{\overline{E^2 - E_i^2}}{K_B T^2} \tag{13}$$

$$C_{p=}\overline{C}_P = \frac{\overline{H^2 - H_i^2}}{K_B T^2} \tag{14}$$

Where E denotes the system's internal energy and H its enthalpy. A polymeric system's heat fluctuates before T_g and after it cools from the molten state. Consequently, T_g can be calculated using the variation in capacity with regard to temperature. It is remarkable that a transition occurs across a wide-ranging of temperature rather than just at one. T_g is equal to a temperature at an aforementioned region center.

Fig. 3 displays a calculated simulated capacity for poly (methyl methacrylate). As is evident, there is a discernible increase in the heat capacity around the poly (methyl methacrylate) and poly (methyl methacrylate)/Al₂O₃ nanocomposite T_g. Observed variations exist despite the results of the simulation and the experiment being in good agreement [35,36]. These differences from the experimental results include greater T_g values, a wider transition temperature range, and a narrower difference in thermal inertia between the glass as well as liquid phases. The poly (methyl methacrylate)/Al₂O₃ system also has a lower capacity as well as a smaller alteration in capacity between a liquid as well as a glass states, when the results for Poly (methyl methacrylate), as well as poly (methyl methacrylate) systems, are compared. The increase in heat capacity during the glass transition may be due to the need for more energy to generate a volume required for waves including vibrations with higher amplitudes [37,38].

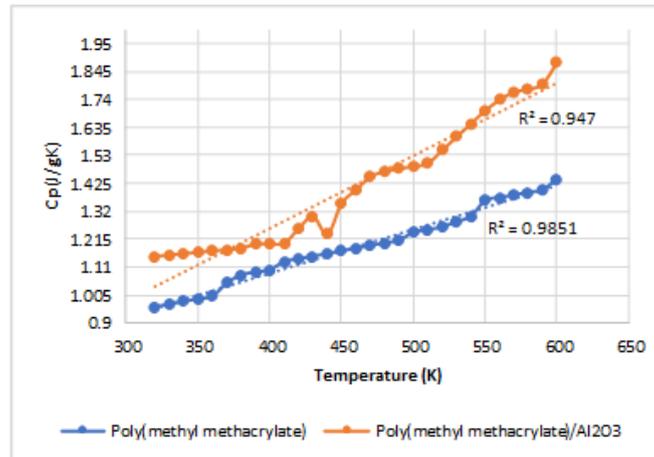


Fig. 3 - Heat capacity as a function of temperature

4.4 Diffusivity of Heat

The heat transfer can be determined using equation 15. Because of this, it is possible to determine the thermal diffusivity in this investigation by calculating the thermal conductivity, heat capacity, in addition density.

$$\alpha = \frac{K}{C_P \rho} \tag{15}$$

Fig. 4 depicts the thermal transfer versus temperature of poly (methyl methacrylate) in addition poly (methyl methacrylate)/Al₂O₃ nanocomposite. The results show that as temperature rises, heat transfer decreases, and thermal transfer of poly (methyl methacrylate)/Al₂O₃ nanocomposite is greater than thermal transfer of poly (methyl methacrylate). The change in thermal transfer during glass transition is most probable caused by changes in capacity in addition density of the heat [39,40].

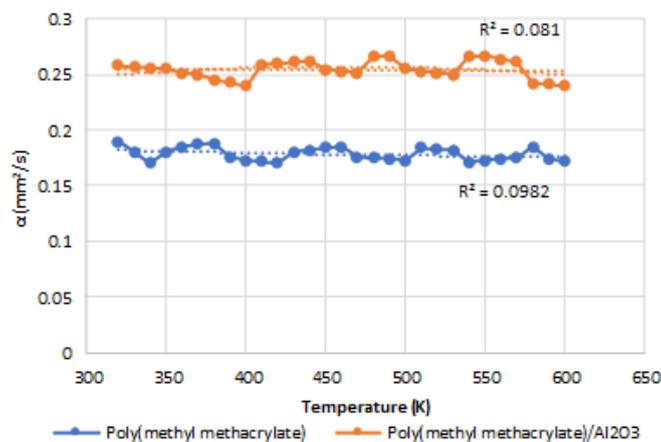


Fig. 4 - Temperature-dependent thermal transfer of poly (methyl methacrylate) as well as poly (methyl methacrylate)/Al₂O₃

5. Conclusion

The relationship between thermal diffusivity and thermal stability has been demonstrated in the scientific literature. Additionally, it may be connected to some fire-retardant characteristics like total heat release, time-to-ignition, as well as peak heat release, which are the most crucial factors when evaluating a material's potential fire risk. The flame-retardant, as well as thermal stability properties of polymers, are improved by oxides, one of the most promising flame-retardant additives.

In this research, the influence of Al₂O₃ nanoparticles on the rate of heat transfer of the polymer is investigated using simulations of molecular dynamics. By calculating specific heat, density, and thermal transfer in the range of 300-700 K, the transfer heat of poly (methyl methacrylate) as well as poly (methyl methacrylate)/Al₂O₃ had been computed. Findings indicate that the heat capacity is reduced by the alumina nanoparticles. The 10% drop in heat capacity in the rubbery state is greater than the 4% reduction in the glassy state. The heat capacity-temperature curve's trend is consistent with the experimental data, although the heat capacity amount is lower and the T_g is higher by around 50 K than what is found in the experimental results.

The thermal diffusivity of the poly (methyl methacrylate) with the thermal conductivity is increased by over ten times by the alumina nanoparticles, which also enhances the T_g by around 10 K.

The rate of cooling, polymer molecular weight, as well as the incorporation of responsive force fields into simulations, is additional crucial variables that should be examined in further research in order to more thoroughly examine the generalizability and utility of the current molecular dynamics approaches in the perseverance of thermophysical behavior, especially the thermal diffusivity.

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