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THE INFLUENCE OF SUBSTRATE SURFACE ENERGY ON THE ADHESION COMPATIBILITY OF EPOXY ADHESIVE USING MOLECULAR SIMULATION TOOL

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ABSTRACT

The utilization of structural adhesive onto aluminium oxide (Al_2O_3), aluminium (Al) and polyvinyl chloride (PVC) can be remarkably observed in much industrial application such as aerospace, automotive, electronics and medical. Due to the abundant prominent properties exhibited by epoxy resin, the relevancy of opting for it as adhesive agent in the aforementioned industry is believed to be highly beneficial. However, the feasibility of implementing the idea is still not clear. It was the objective of this study to shed light on those aspects which are lacking in literature. In this study, Materials Studio 6.0 will be utilized to model and simulate the compatibility and adhesion strength of epoxy resin with three different substrates i.e. Al_2O_3, Al and PVC. Simulation consist of molecular dynamics (MD) and molecular mechanics (MM) reveal the significant influence that each substrate gives in promoting the adhesion compatibility within the epoxy-substrate system. The computed result has shown significant agreement upon the experimental data in which the epoxy resin is most compatible with Al_2O_3, followed by Al and lastly with PVC.

Keywords: substrate material, epoxy resin, simulation, adhesion strength, adhesion compatibility.

INTRODUCTION

Upon the discovery of structural adhesive, man has set their eyes on its fascination and has widely been used in various engineering fields such as aerospace, electronics, medical, oil and gas, optical as well as automotive. Among the structural adhesives available in the market, epoxy resin is without doubt the most used for their distinguished properties. Having introduced commercially in 1950, the utilization of epoxy resin has grown steadily since. Compared to alternative resins, cured epoxy systems are renowned to have outstanding adhesion to a broad range of substrates and reinforcing materials [1-2]. Epoxy resin can be formulated into low viscosity systems which "cure" (i.e. eventually harden after forming cross-links throughout the surfaces substrate) at room temperature with a minimal shrinkage during curing [3]. However, the temperature for curing to occur actually depends on the formulation of the epoxy adhesive [3]. In fact, when correctly formulated and cured, epoxy resins exhibit an excellent combination of mechanical properties and chemical resistance towards environmental agents [4].

In industry, the prominent properties exhibited by epoxy resin when being used as adhesive agent has enabled its usage in various activities namely bonding, sealing, coating, potting and encapsulation. For instance, in the aerospace and automotive industry, extensive utilization of structural adhesive can be observed during its application onto aluminium oxide (Al_2O_3) substrate [5]. In addition to that, the usage of structural adhesive in providing protective shield for aluminium (Al) core Printed Circuit Board (PCB) in electronics industry is also worth to be noted [6]. Apart from engineering field, another notable implementation of structural adhesive was discovered in the medical field for which having important application especially onto polyvinyl chloride (PVC) based appliances [7].

Due to the abundant prominent properties exhibited by epoxy resin, the relevancy of opting for it as adhesive agent in industrial application is believed to be highly beneficial. Since that adhesion concept emerge from the fact that there are forces of attraction acting in all intermolecular level of materials, this force can be referred to as van der Waals forces [4]. However, the assessment of the resulted adhesion reaction from the aforementioned theory requires complex experimental approach [8-9]. Therefore, an in depth analysis using Biovia Materials Studio 6.0 is believed to not only reduce experimental cost, but also assist in accelerating the investigation with minimal time consumption.

SIMULATION METHODOLOGY

A. Model preparation for epoxy resin and substrate materials

The study commences by developing the modelled geometry of polymeric epoxy resin as well as the substrate surfaces; Al_2O_3, Al and PVC. The monomer structure of diglycidyl ether of bisphenol A (DGEBA) which was portrayed in Figure-1 was drawn in the Materials Studio software prior to conducting any simulation procedure. In this study, DGEBA was chosen to represent epoxy resin due to its establishment in being the most versatile resin base during the polymerization of epoxy resin [2].

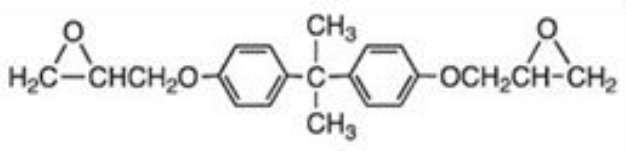


Figure-1. Chemical structure of DGEBA epoxy resin.

B. Analytical and crystallization of substrates

The modelled substrate surfaces of Al_2O_3 and Al was subjected to morphology simulation to obtain their relevant active surfaces. A force field called condensed phase optimized molecular potential for atomistic simulation studies (COMPASS) was utilized to perform molecular mechanics (MM) and 500 steps of geometry optimization simulation along with the incorporation of smart minimizer function in Forcite modules. To further obtained a reasonable 3D structure from the previously 2D cleaved surface, a Supercell of Al_2O_3 and Al was then established with a preset parameter i.e. v=3 and u=3 before being added to a Vacuum Slab structure.

On the other hand, the polymerised structure from the monomer of PVC which is vinyl chloride was subjected to a similar sets of geometric optimization as well as MM simulation after undergoing a sets of homopolymerisation procedure consisting of 20 repeating chain. After a reasonable amorphous structure within the framework of confined layer was obtained, an MD simulation later takes place with 5000 steps for which allows the relaxation of materials' central unit system as well as eliminating overlapping and unsolicited close contacts [2,10].

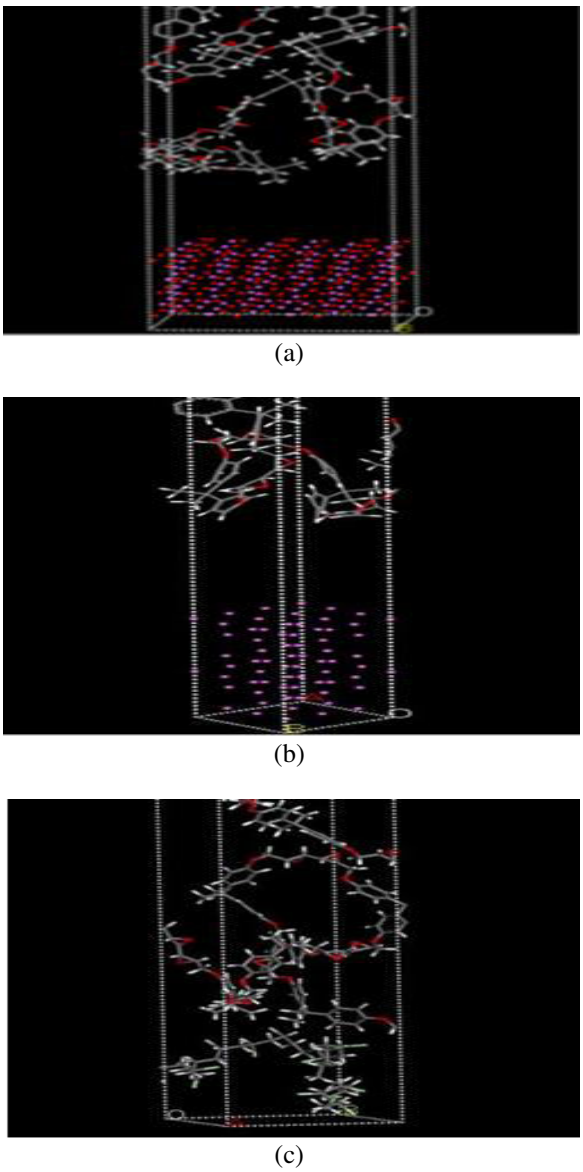
C. Polymer and classical simulation of epoxy resin

Simulation of COMPASS-based MM and geometry optimization similar to substrate surface was subjected to the drawn monomer of epoxy resin. The incorporation of COMPASS forcefield into the simulation framework has enable the consideration of non-bonded interaction energy i.e. Van der Waals forces [11]. Before placing the neutralized monomer into an embedded Amorphous Cell module, the monomer of epoxy resin was polymerized by using Random Copolymer module with 20 repeating units.

Prior to simulating the epoxy resin reaction with substrate surfaces, the copolymer of epoxy resin was first undergo MD simulation at constant temperature and constant volume condition i.e. NVT at 300 K along with Nosé ensemble thermostat for 100 ps and 1.0 fs of time step.

D. Analytical and crystallization of substrates

During the final stage of this project, the aforementioned well-minimized structure of epoxy resin as well as substrates (i.e. Al_2O_3, Al and PVC) was subjected to Layer modules for which will enable the adhesion process to takes place in the proceeding steps of this simulation. The generated configuration of epoxy substrate system are portrayed in Figure-2.



(a) (b) (c)

Figure 2. Epoxy-substrate system of: (a) Epoxy/Al_2O_3 (b) Epoxy/Al (c) Epoxy/PVC.

COMPASS force filed was then employed in Forcite module to further optimize the geometry by 10000 steps for the epoxy substrate system. The final simulation of adhesion force was being conducted through MD simulation which involves the incorporation of Nosé ensemble thermostat in NVT at 300K based procedure. Since that COMPASS forcefield was used, the calculation of MD simulation will also include van der Waals forces interaction and subsequently resulted in an output which enables the evaluation of epoxy-substrate energy compatibility by using Dupré equation (1).

$$\Delta E_{adhesion} = \Delta E_{total} + (E_1 + E_2) \quad (1)$$

Where;

E_{total} is the total energy of the epoxy-substrate system after interaction while E_1 and E_2 is single point

energy of the substrate and epoxy adhesive separated in vacuum, respectively.

Subsequently, the assessment of adhesion strength was determined through the Morse potential relation portrayed in equation (2). Prior to use this relation, a single point energy analysis for tensile and compressive condition was performed. During this procedure, an assumption that detachment only occur at the interface between epoxy substrate and not within the epoxy adhesive was made. Such assumption was made following the result of a study performed by Tsiafis [12]. The aforementioned tensile and compressive condition was performed by varying the Δr in perpendicular direction to the substrate surface from -0.5 to 2.0 Å. While D_e and α are binding energy and relative constant of a system, respectively.

$$E = D_e(1 - e^{-\alpha\Delta r})^2 \quad (2)$$

The obtain curve from the plotting of Morse potential was then subjected to differentiation by Δr for which will generate a force-distance curve of the epoxy-substrate system [2, 13]. Such procedure can be represented by equation (3).

$$F = \frac{\delta E_{adhesion}}{\delta \Delta r} \quad (3)$$

From the generated force-distance curve, the evaluation of adhesion strength in terms of tensile and compressive condition can be made by utilizing equation (4). The adhesion strength can be said to depend on the maximum value, F_{max} recorded in the previous force-distance curve as well as θ, which resembles the density of interaction site on substrate surfaces (i.e. Al_2O_3, Al and PVC).

$$S_{adhesion} = F_{max}\theta \quad (4)$$

RESULTS AND DISCUSSIONS

A. Polymeric epoxy resin equilibrium

In this study, the justification in determining whether the modelled epoxy resin system possessed the same properties as those of real polymeric resin was done by monitoring the specific volume of it over an entire different temperature simulation approach. The resulted data from this strategic procedure is the glass transition temperature (T_g) [14, 15].

Such procedure involves a gentle heating technique of the previously optimized structure from 250 K to 600 K, at a 100 ps step of NPT simulation. Subsequently, the specific volume of the system was measured during the next entire course of cooling down process to 250 K by 50 K steps. The variation recorded in the specific volume of the polymeric epoxy resin system have been plotted in Figure-3.

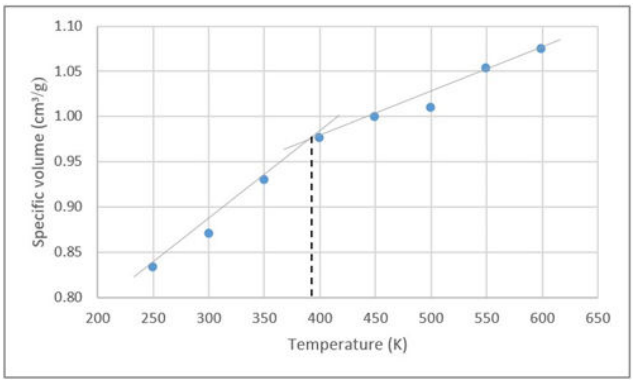
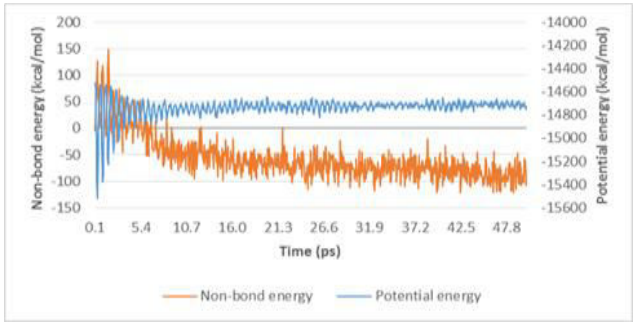


Figure-3. Specific volume against temperature for modelled epoxy resin.

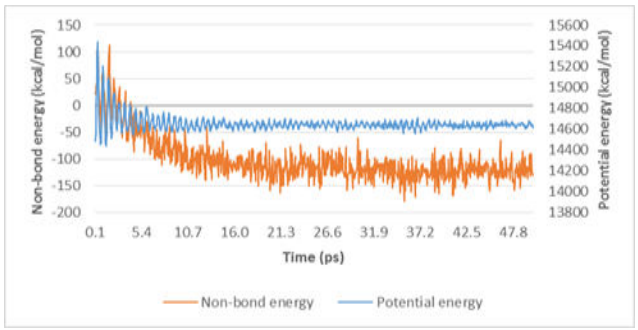
As illustrated in this figure, there is an abrupt changes of the slope curve from 250 K to 400 K. This is because during these temperature range, the calculated slope curve is 0.94581 x 10^{-3} cm³/gK while at temperature of 450 K to 600 K, the slope curve is 0.50179 x 10-3 cm³/gK. When the curve is subsequently extrapolated, the intersection of them was recorded to be at 398 K, which resemble the Tg of the modelled epoxy resin. The obtained Tg was in a good agreement with experimental data for which having a Tg of 402 K [16, 17].

B. Modelled structure of epoxy-substrate system

The simulated epoxy-substrate system are said to have reached their equilibrium state from the obtained data on energy (non-bonded and potential energy) in the MD simulation. As shown in Figure-4, the interface model of Al_2O_3/Resin, Al/Resin and PVC/Resin reached the balance at 37 ps, 26 ps and 21 ps, respectively. A significant reduction in the total energy from the non-bond perspective of the polymer and substrate can be observed once the MD simulation started. According to Golzar [18], such decrease in the energy value also shows that the derived approach in this study has finally succeed in producing an ideal model for which possessed similar properties to experimental work



(a)



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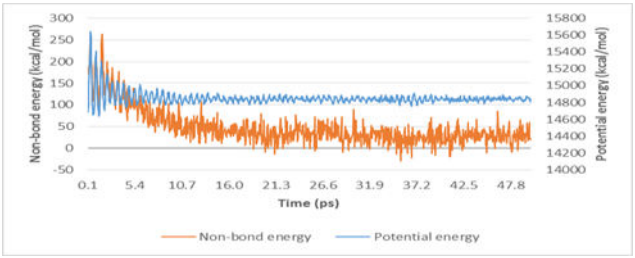


(c)

Figure-4. Potential and non-bonded energy of: (a) Epoxy/Al_2O_3 (b) Epoxy/Al (c) Epoxy/PVC.

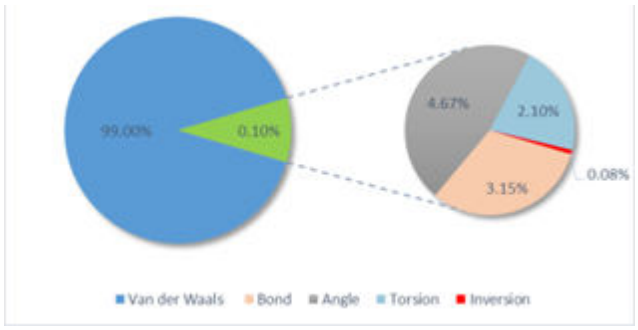
C. Computation of energy compatibility

Prior to obtain the data on each energy component, the generated result was then utilized in the computation of final adhesion energy, $\Delta E_{adhesion}$. As documented in Table-1, the computed adhesion energy for all epoxy/substrate system is negative for which depict the possibility of adhesion reaction within the epoxy and substrate interface. The computed $\Delta E_{adhesion}$ for Epoxy/Al_2O_3, Epoxy/Al and Epoxy/PVC are -203.2 kcal/mol, -42.46 kcal/mol and -24.13 kca/mol, respectively. From the result, it can be seen that epoxy resin possessed the highest compatibility with Al_2O_3, followed by Al and lastly, PVC. This result demonstrate the possibility of opting for epoxy resin as the adhesive agent for all the aforesaid substrates.

Table-1. Energy computation for adhesion compatibility of epoxy/substrate system.

Epoxy (kcal/mol)	Epoxy/Al_2O_3	Epoxy/Al	Epoxy/PVC
Etotal	11.85 x 10^9	46.35 x 10^3	14.72 x 10^3
E_1	11.85 x 10^9	28.82 x 10^3	-87.93
E_2	14.93 x 10^3	17.58 x 10^3	14.83 x 10^3
$\Delta E_{adhesion}$	-203.20	-42.46	-24.13

From the analysis of Figure-5, the percentage of Van der Waals force recorded during the computation of E_{total} for Epoxy/Al_2O_3, Epoxy/Al and Epoxy/PVC are 99%, 64.04% and 0.06%, respectively. This result shows a significant relation with the energy compatibility of epoxy/substrate system i.e. Δ $E_{adhesion}$. This is because, when the percentage of Van der Waals force in the system increases, the computed $\Delta E_{adhesion}$ increases as well.



(a)

(b)

(c)

Figure-5. Energy component from the computation of E_{total}: (a) Epoxy/Al_2O_3 (b) Epoxy/Al (c) Epoxy/PVC.

D. Durability of adhesion strength

During industrial application, the modelled epoxy/substrate structure will undergo various types of stresses such as tensile, compressive, shear, cleavage and peel. In the interest of assessing the durability of the modelled epoxy/substrate system, a condition of which involve tensile and compressive stress has been chosen in this study. Such condition was chosen based on the analysis on several literatures of which they discovered that the most significant force experienced by their modelled adhesive-substrate system are tensile and compressive [2, 19].

The obtained plot of energy against distance curve from the simulated tensile and compressive condition are shown in Figure-6. Subsequently, the generated force against distance curve from the derivation of the previously plotted energy-distance data by Morse potential is then shown in Figure-7.

From the generated force-distance curve, the evaluation of adhesion strength in terms of tensile and compressive condition can be further deduce by utilizing equation (4). The adhesion strength can be said to depend on the maximum value, Fmax recorded in the previous force-distance curve as well as θ, which resembles the density of interaction site on substrate surface. From all of the above simulation results, Table-2 depict the summarization obtained regarding the durability of adhesion strength for Epoxy/Al_2O_3, Epoxy/Al and Epoxy/PVC system.

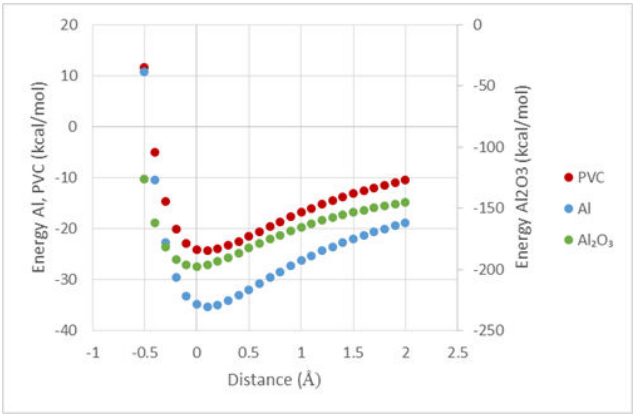


Figure-6. Energy vs. distance plot of epoxy/substrate system.

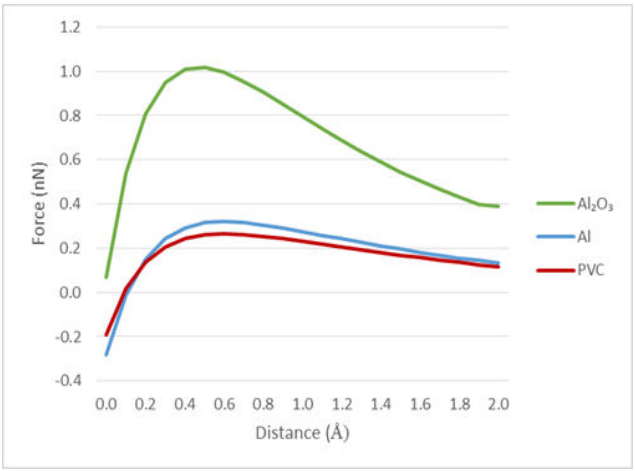


Figure-7. Force vs. distance curve of epoxy/substrate system.

Table-2. Results of adhesion durability from molecular dynamics (MD) simulation.

Model	$E_{adhesion}$ (kcal/mol)	F_{max} (nN)	Sadhesion (MPa)
Epoxy/Al_2O_3	-197.00	1.018	2.23 x 10^2
Epoxy/Al	-35.26	0.322	0.24 x 10^2
Epoxy/PVC	-24.33	0.265	0.15 x 10^2

From the result shown, Epoxy/Al_2O_3, has the highest ability to withstand tensile and compressive force, followed by Epoxy/Al, and lastly by Epoxy/PVC. The computed adhesion strength, $S_{adhesion}$ for Epoxy/Al system has shown excellent agreement with the experimental work of Tsiafis [12] in which the recorded tensile strength was 23 MPa. The detachment assumption was also validated when the recorded $S_{adhesion}$ for Epoxy/Al and Epoxy/PVC is significantly lower than the value documented by Wypych [20] i.e. 40-65 MPa. It can be concluded that detachment does not occur to the epoxy resin, but instead to the interface region between epoxy resin and substrate material.

However, the deviation obtained in the $S_{adhesion}$ for Epoxy/Al_2O_3 system was believed to be resulted from the chosen approach for which having limitation in terms of hydrogen bonding analysis. Therefore, the incorporation of hydrogen bonding in the adhesion

analysis involving systems that possess the possibility of forming hydrogen bond is definitely essential to address in future work.

CONCLUSIONS

The possibility of opting for epoxy resin as the adhesive agent for aluminium oxide (Al_2O_3), aluminium (Al) and polyvinyl chloride (PVC) has been comprehensively demonstrated through the framework of molecular dynamics (MD) and molecular mechanics (MM). The theoretical result obtained signifies a good agreement with experimental data, considering the limitation of MD simulation especially involving secondary bond adhesion component. From the results, it can observed that the most compatible substrate with epoxy resin is Al_2O_3, followed by Al and lastly by PVC. It can also be concluded that van der Waals force could facilitate the adhesion rate and thus lead to higher adhesion strength of epoxy-substrate system.

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