

Adhesive Analysis Using Molecular Dynamics Simulations

Introduction

Recent years have seen a shift towards the use of resin (polymeric material) as a material for structural components of vehicles such as airplanes and automobiles with the aim of reducing weight. As welding cannot join these resins and various inorganic materials, including iron, light metals and ceramics, the number of opportunities for the use of adhesives is expanding.

Automobiles, for example, contain components of various types and sizes, from large parts such as car bodies and powertrain components to small parts such as electrical components. This diversification of materials and parts has presented a number of challenges in terms of bonding with adhesives. For this reason, we have been implementing multifaceted analytical methods^{1, 2)} to provide tailored solutions to issues faced by our customers.

However, even in 2021, it is not easy for adhesive manufacturers like ourselves to have a complete understanding of the phenomena surrounding adhesion. Some of the many areas that are still not fully understood include bonding mechanisms, deterioration mechanisms, adhesive bonding compatibility prediction and inspection methods. As a result, product design often relies on empirical knowledge.

As part of our efforts to explore a product design approach that is distinct from our empirical knowledge, we have also commenced studies based on molecular simulations. As a proof of concept, this article introduces some examples of our work based on using molecular dynamics simulations to understand phenomena relating to adhesion, including bond strength prediction and the effect of surface contaminants.

Table of Contents

Introduction.....	1	5. Adhesion to Oily Surfaces.....	4
1. Molecular Simulations and Adhesives ...	2	6. Interfacial Segregation of Specific	
2. Solubility Prediction.....	2	Chemical Structure.....	5
3. Mechanisms For Increased Elasticity in		7. Gas (Water Vapor) Permeation	6
Cured Adhesives	2	Closing	8
4. Bond Strength Prediction	4		

1. Molecular Simulations and Adhesives

The main areas in which computer simulations are used can be divided into electronic state level, molecular and atomic level, mesoscopic and continuum level simulations³. The main focus of this article is molecular and atomic level simulations. The examples covered were performed using molecular dynamics (MD) calculations with timescales ranging from picoseconds to tens of nanoseconds and box sizes ranging from several angstroms to tens of nanometers.

MD calculations relating to adhesion have appeared in academic papers and similar publications since about 2010. In recent years, examples such as the calculation of solubility parameters and the characteristics of crosslinking resins have been included on the websites of software manufacturers⁴⁻⁶. As a result, this method of calculation has become more familiar, even to companies that have mainly used experiments, including ThreeBond.

Based on the order in which they occur during the use of adhesives, adhesion-related phenomena include “wetting” when the adhesive is applied to the adherend, curing and associated shrinkage of reactive adhesives, and thermal stress (shrinkage) associated with cooling after curing in the case of heat-curable adhesives. In addition there are a range of processes, such as stress and deterioration, that occur during actual use after bonding. In summary, there are a large number of parameters that can affect the strength of a part⁷. It could be said that this is why the product design of actual components is often performed empirically by looking at the overall strength and durability of parts.

When designing adhesives, however, there are innumerable combinations of resin materials to be prescribed, and the number of combinations is expanding rapidly. While there is demand to predict results based on some form of data before proceeding to experiments, the present reliance on experience in many cases remains a challenge.

Molecular simulations provide one potential approach to solving this issue. While current general-purpose computers can only perform calculations covering an extremely limited timescale and box size, MD calculations may be an effective tool that enables users to visualize phenomena virtually and obtain prediction data.

In addition, confirmation that the physical characteristics of the cured adhesive are consistent with those obtained through MD calculations can be considered an important method of confirming the feasibility of adhesive designs.

As examples of our current work using MD calculations, this article covers instances of solubility prediction, mechanisms for increased elasticity in cured adhesives, bond strength prediction, adhesion to oily surfaces, interfacial segregation of specific chemical structures and gas (water vapor) permeation.

Materials Studio Forcite from Dassault Systèmes K.K. was used for MD calculations, while COMPASSII and III were used for the force field.

2. Solubility Prediction

Adhesives are compounds of multiple resins. As a result, the solubility of these resins is an important consideration. In addition, acrylic adhesives are often designed in consideration of the solubility of the adhesive and the adherend. For this reason, emphasis has been placed on solubility parameter (SP) values, which are an index of intermolecular affinity. SP values are substance-specific values defined as the square-root of the cohesive energy density of the substance. Values with closer SP values have higher affinity with each other, meaning that they are more soluble or more suitable for use as an adherend. SP values are generally estimated using the group contribution method, however, a calculation method using MD when there is no available data on existing similar compounds has also been established⁸. Using this method, we calculated the SP value of solvent molecules and compared the results to the values in existing literature⁹ (Fig. 1). As a result of cost-saving during calculations, some slight discrepancies were observed. However, even the largest deviations were within 10% of the measured values and these values can be considered sufficient for predictive purposes. These calculations are mainly used for applications such as increasing efficiency in the design of acrylic adhesives.

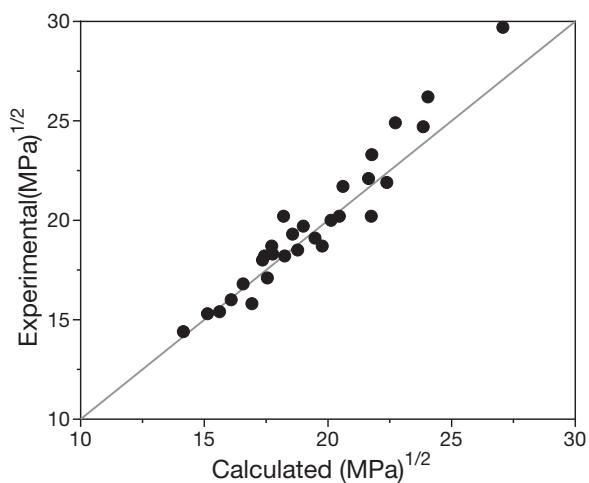


Fig. 1 Comparison of Organic Solvent SP values Calculated Using MD with Measured Values

3. Mechanisms For Increased Elasticity in Cured Adhesives

This section describes the use of simulations to perform studies relating to the curing properties of epoxy resins.

Epoxy resins containing phenyl glycidyl ethers (Fig.2) have been shown to be tougher and more elastic than other

epoxy resins¹⁰. This differs from the conventional method of adding rubber or a similar flexible molecular structure into cured epoxy resin for the purposes of toughening the resin. This is also specific in that the added epoxy resin is monofunctional. Believing that understanding the reason behind this may prove useful in future adhesive design, MD calculations were used to analyze the cause.

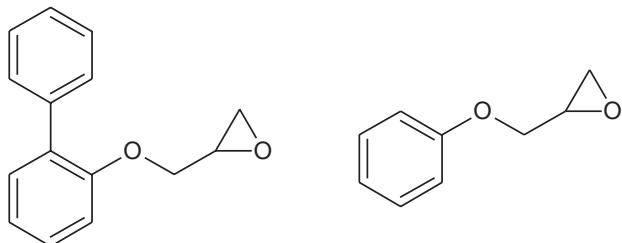


Fig. 2 Examples of Phenyl Glycidyl Ether Chemical Structure

In this case, MD was used to represent the cured adhesive and the elastic modulus was calculated based on this deformation simulation. In order to obtain the physical characteristics of a cured epoxy resin through simulation, the polymerization reaction with the amine compound, which acts as the curing agent, must first be calculated. However, MD cannot be used to calculate chemical reactions. Therefore, the atoms relating to the reaction were designated in advance and the bonds were rearranged (made to react) when they came within a set distance^{11, 12}. In addition to distance, this methodology also uses the reaction probability k , which takes activation energy into consideration, to determine whether bonds are rearranged (Formula 1). When the value of k is larger than the random number $p(0, 1)$, a reaction is made to occur. When it is smaller, no reaction is made to occur. In addition, kinetic energy equivalent to the heat of formation is added to molecules that have undergone reactions in order to promote reactions. By repeating this process, a cured epoxy resin model was obtained.

$$\text{Formula 1: } k = A \exp(-Ea/RT)$$

A: Acceleration factor, Ea: Activation energy,
R: Gas constant, T: Temperature

When the density, elastic modulus, and glass transition temperature of this cured material model were compared with experimental values, an appropriate correlation was observed. The glass transition temperature comparison is shown as an example (Fig. 3). The temperature of the inflection point estimated through calculation was approximately consistent with that of measurement data obtained through thermomechanical analysis (TMA). This confirms the appropriateness of the model.

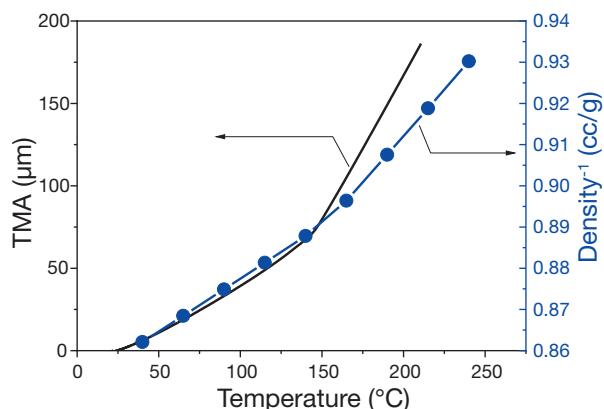


Fig. 3 Comparison of Glass Transition Temperatures (Temperature Sweep of Reciprocal of Density) Calculated Using MD and Measurement Data (TMA)

In addition, the radial distribution function of the functional group, the stress distribution under an applied load and the free volume when different concentrations and types of phenyl glycidyl ether are added were calculated. Their correlation with the elastic modulus was then examined. As a result, it was observed that the elastic modulus improves as the free volume ratio inside the simulated cell decreases (Fig. 4).

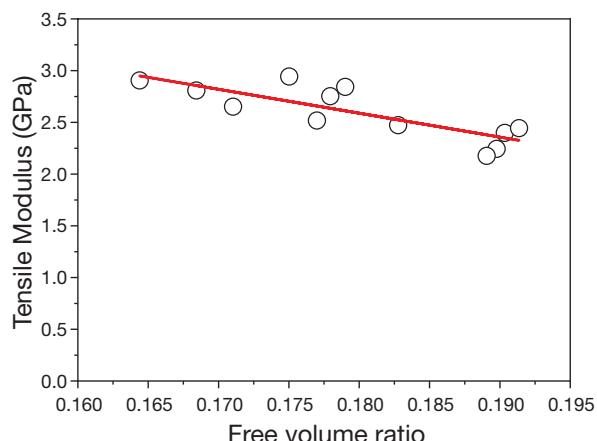


Fig. 4 Relationship Between Free Volume and Elastic Modulus When Different Concentrations and Types of Phenyl Glycidyl Ether are Added

In other words, this suggested that when a phenyl glycidyl ether is added to a system containing a standard epoxy resin and an amine compound, it acts in a similar manner to an antiplasticizer by packing the free volume and improving the elastic modulus. It has been reported that adding an antiplasticizer to epoxy resin increases the elastic modulus, improves toughness and reduces water absorption¹³. It appears that a similar phenomenon was observed on this occasion.

We believe that molecular simulation can also be applied to building hypotheses with regards to the relationship between the composition of adhesives and their physical properties, as is shown by this example.

4. Bond Strength Prediction

This section describes bond strength prediction.

Following on from section 3, it describes an epoxy resin containing a phenyl glycidyl ether. It has been reported that this formulation improves bond strength in addition to improving bulk toughness and elasticity¹⁴⁾.

Molecular simulations were performed in order to investigate whether the improvement in bond strength could be confirmed through this method. Due to the limited box size that can be covered by MD calculations on general-purpose computers, these calculations were performed for an adhesive surface approximately 4 to 5 nm along each side. The results have been included in this article because a trend towards improved bond strength was observed.

A simulation cell in which an epoxy monomer and an amine monomer are mixed were stacked onto alumina and structural relaxation was performed. The curing simulation described above was then carried out. Then, the temperature of the cell was lowered to room temperature and the curing shrinkage and heat shrinkage were calculated. Deformation calculations were performed on the obtained model in order to examine the stress-strain characteristics.

The area under the resulting stress-strain curve (Fig. 5) was used to evaluate the bond strength on this occasion. The calculated relationship between bond strength and the concentration of added phenyl glycidyl ether is shown in Fig. 6. The results were consistent with experimental results, as the amount of phenyl glycidylether increased, the bond strength increased.

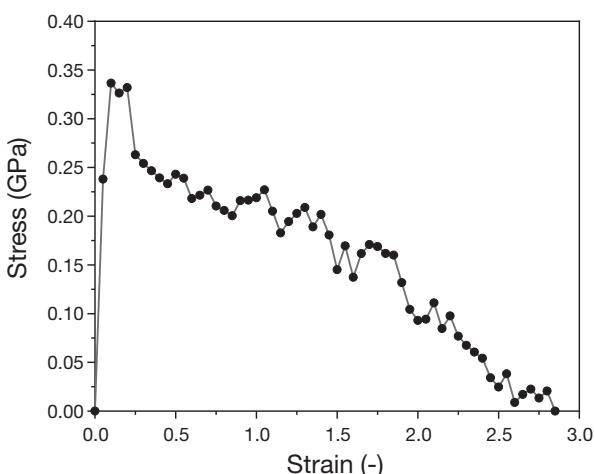


Fig. 5 Epoxy Resin Stress-Strain Curve Calculated Using MD

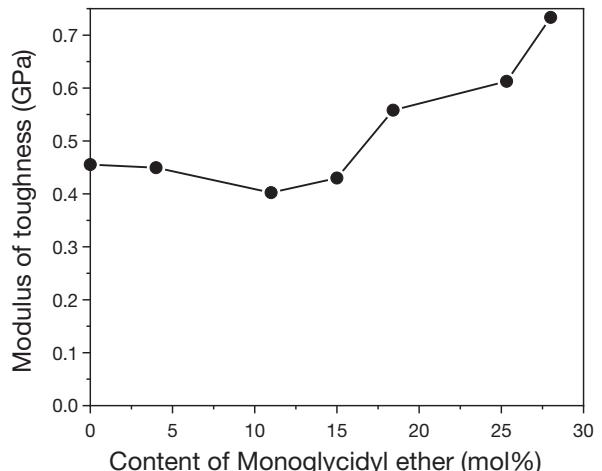


Fig. 6 Relationship between Bond Strength and Concentration of Added Phenyl Glycidyl Ether Calculated Using MD

In addition, MD simulation calculation limitations apply not only to the box size, but also to time. Consequently, the displacement per unit time may become a strain rate equivalent to or higher than the actual impact load and there may be no impurities on the surface of the adherend, resulting in a higher absolute value than in reality. For this reason, the evaluation of bond strength is considered to be a relative evaluation. Even so, there have been cases in which these bond strength evaluation results have been implemented in FEM as the bond strength between the filler and matrix resin for multiscale simulations and future applications can be expected¹⁵⁾.

5. Adhesion to Oily Surfaces

This section describes how the same simulation used above to predict bond strength has been applied to the visualization of bond failure when foreign matter such as oil is present on the surface of the adherend. The simulation cell was created using the same process as above, with the exception that oil molecules were placed on the surface of the alumina. Snapshots of the bond failure are shown in Fig. 7. The visualization shows cracks forming around the oil, which is shown in green, before failure occurs. At this time, the stress-strain curves at the time of failure were calculated for cases where the molecules of the oil and adhesive were prevented from diffusing into one another and cases where they were allowed to diffuse for a certain period of time (Fig. 8). Looking at the stress-strain curves, it can be seen

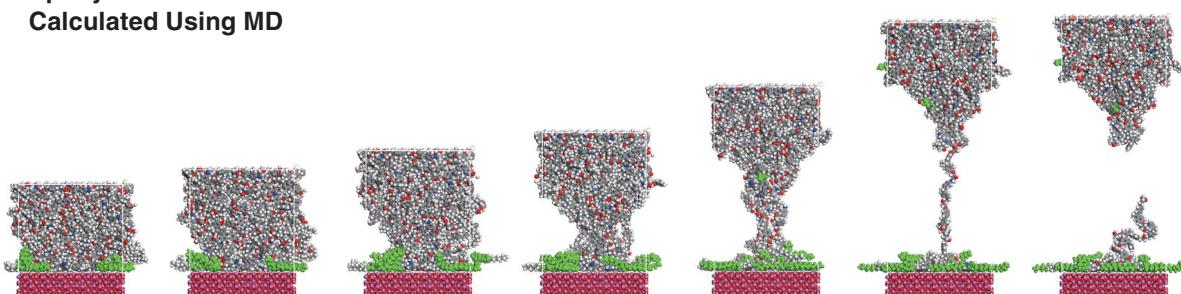


Fig. 7 Snapshots of Bond Failure Simulation

that when the oil and adhesive were allowed to diffuse for a certain period of time (Oil_Mix), the area under the curve is larger and the amount energy required for failure to occur is larger than when diffusion was not allowed to occur (Oil_Non_Mix). In other words, these result can be said to reinforce the deduction that the influence of oil on the surface of an adherend can be reduced by mixing the oil with the adhesive. Interfacial phenomena such as adhesion to oily surfaces are difficult to observe directly and empirical understanding has generally been based on indirect experimental data. Looking at such phenomena from a different perspective through simulation has the potential to enable the certainty of this understanding to be further investigated.

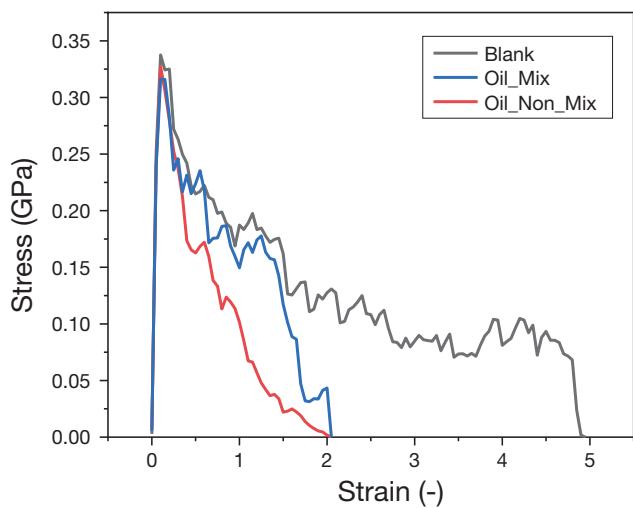


Fig. 8 Simulated Stress-strain Curves for Different Oily Surfaces

6. Interfacial Segregation of Specific Chemical Structures

This section describes the interfacial segregation of specific chemical structures. There has been a case in which MD calculation was used to examine the amine segregation mechanism at the interface when an epoxy resin and amine compound were cured on a copper substrate^[6]. We used the same method to examine how the functional groups near an alumina interface change when resin is cured in a compound system with modified silicone containing methoxy groups and a silane coupling agent.

First, a model in which modified silicone (Fig. 9) and a silane coupling agent (Fig. 10) are mixed was created and layered onto alumina. Relaxation calculations were then performed. The methoxysilane curing reaction was then performed using the same method as for the MD calculation in section 3, and changes in the segregation of functional groups that occurred around the interface when curing took place were examined.

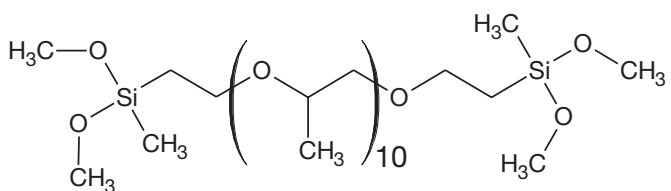


Fig. 9 Chemical Structure of Modified Silicone Used in Simulation

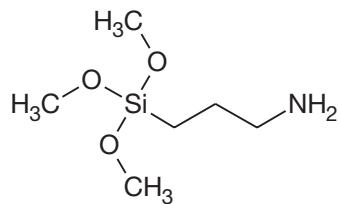


Fig. 10 Chemical Structure of Silane Coupling Agent Used in Simulation

The results showed that there was confirmed segregation of terminal methoxysilane moieties of the modified silicone and amino groups from the silane coupling agent at the alumina interface when the relaxation calculation is performed with the resin on the alumina, even after a relatively short relaxation calculation where the density is not stable to a significant degree (Fig. 11). The figure shows a model in which resin is placed on alumina. The model has been rotated 90° to the right, and is arranged so that the graph positions correspond to those of the model. In addition, although it is not in the model, the calculation was set with additional alumina to the right of the model. This is why the same segregation can be observed at the left and right ends of the graph.

It was found that the segregation of methyl groups increased as the curing reaction progressed. This is the reason for the enlarged peaks at the right-hand side of Fig. 12 and Fig. 11. This suggests the presence of polypropylene glycol methyl groups aligned towards the interface. On the other hand, no change in the amount of amino groups near the interface were observed, even when the curing reaction occurred. In other words, it can be seen that there is a continued presence of the silane coupling agent containing an amino group near the interface even when a curing reaction occurs. (Fig. 13)

Although not shown in the graph, the amount of methoxysilane segregation at the interface decreases as the reaction progresses. This may be because methoxy groups are consumed by the reaction.

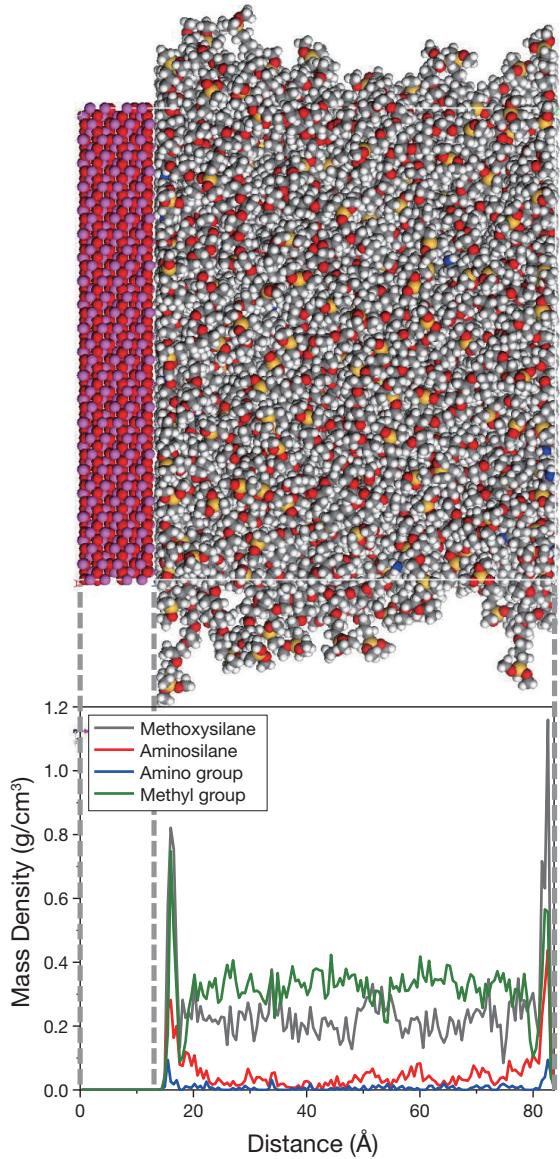


Fig. 11 Molecular Model of Modified Silicone Containing Methoxy Groups and Silane Coupling Agent Layered on Alumina and Relaxed, and the Functional Group Density Distribution at That Time

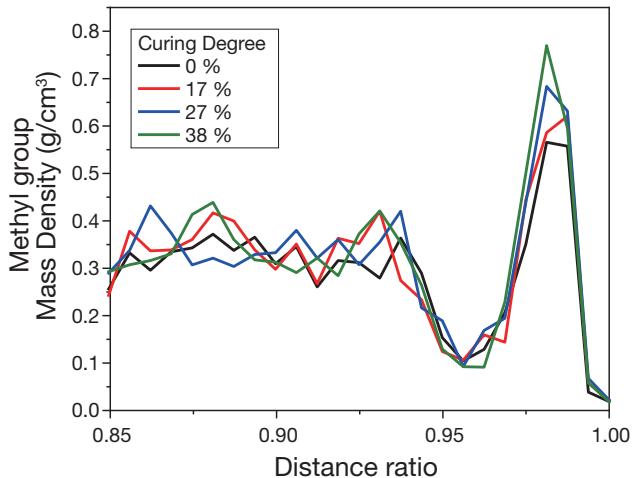


Fig. 12 Changes in Segregation Behavior due to Curing Reaction of Methyl Groups near Interface

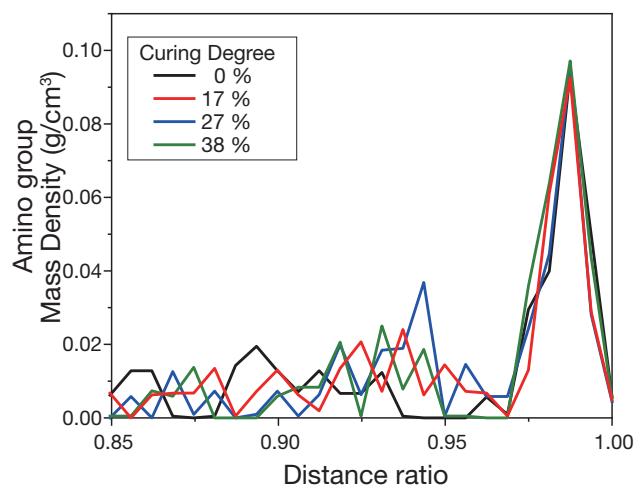


Fig. 13 Changes in Segregation Behavior due to Curing Reaction of Amino Groups near Interface

It can be envisioned that measurement of the actual segregation at this type of interface could be performed with a combination of readings obtained through means such as X-ray photoelectron spectroscopy (XPS), sum-frequency generation (SFG) and electron microscopy (TEM and SEM), however, we believe that considering these phenomenon by adding the information obtained from the simulation will lead to a better understanding of adhesion.

7. Gas (Water Vapor) Permeation

Moving on from the calculations related to direct adhesion covered so far, this section describes gas permeation simulations. The purpose of this work is to predict the gas barrier properties of sealants and to consider to deterioration mechanism due to water.

Our company produces sealants for gaskets for automobile engines, LCDs and organic EL for electronic components. These products must have liquid and gas barrier properties.

Therefore, there was a need for simulations that could be applied to the design of these products. In particular, it was believed that the screening of resin raw materials for use in products could be simplified if the permeation of gases such as helium and hydrogen, which must be measured using special equipment, could be predicted using simulations.

Water vapor permeation simulations are also being explored for applications relating to the deterioration of adhesion moisture resistance in addition to uses relating to barrier properties. In other words, in addition to the permeation of water vapor into the cured adhesive, the intention in future is to also examine the arrival of water vapor at the adhesive interface and the resulting deterioration of adhesion.

A method for calculating the diffusion coefficient of gas inside a polymer using MD had already been established^[17].

Under this method, gas molecules are placed inside the model in advance. The mean square displacement over time is found and the diffusion coefficient is then calculated from this slope. When applied to gas permeation, however, this method does not take solubility into account, including the dependence of molecular transfer on solubility to the material surface and internal diffusibility¹⁸⁾. This time, the possibility of using simulations to create a prediction that includes solubility and diffusion was examined.

While distinct from gas permeation, there has been an example of using MD calculations to examine the mechanisms of the molecular level water transport and ion rejection of an osmosis membrane when saltwater is used to produce pure water¹⁹⁾. In this case, a polymer membrane was placed between a saltwater layer and a pure water layer. The difference in concentration was then used as the driving force to calculate the water permeation of the polymer.

Using this as a reference, we placed a layer of acrylic resin cured by radical polymerization between a gas layer and a vacuum layer. The gas permeation was then calculated using the difference in gas pressure as the driving force (Fig. 14). The example featured in this article covers permeation between water and helium.

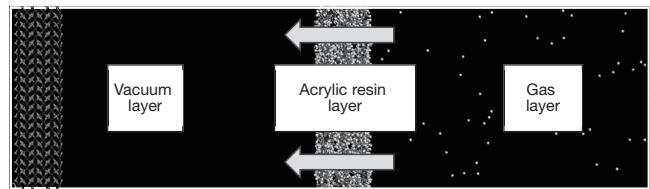


Fig. 14 Overview of Calculated Simulation Cell

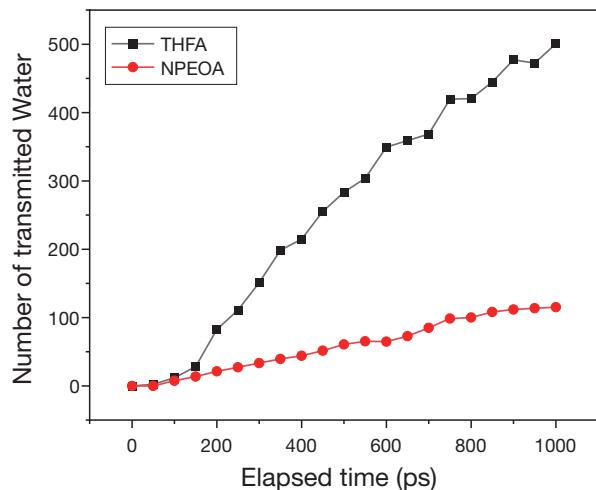


Fig. 15 Simulation Results Showing Water Molecule Permeation Over Time

The cured material model was based on a model in which tetrahydrofurfuryl acrylate (THFA), dimethylolethylene tricyclodecane diacrylate (DCPA) and a polymerization initiator are mixed at a molar ratio of 30:1:1. A cured material model was then created using the same method described in section 3, with the acrylate changed to a nonyl phenol ethoxylate ($n = 1$) acrylate (NPEOA). Fig. 15 shows a plot of the number of water molecules permeating the acrylic resin layer over time. The temperature of the system is set to 300°C with high-pressure water, enabling results to be obtained in a short time. Quantitative evaluation is not possible due to the change in the pressure difference, which is acting as the driving force. However, relative evaluation between acrylic monomers is possible. Although this article presents a simple comparison between two types of acrylic monomer, it was found that the order of permeability of different monomers can be predicted effectively compared to tests for the determination of water vapor transmission rate (JIS K 7129-2), including with other monomers. In addition, the order of the results when MD calculations were performed for a longer time at 60°C was the same as those at 300°C.

For helium permeation, MD calculation was performed using the same method at 25°C and 10 atm. The results shown in Fig. 16 were obtained by comparing the same monomers as for water molecule permeation.

While this is also a relative comparison, differences in gas permeability derived from the chemical structure of the monomer can be predicted. Referring to this type of data when designing adhesives and sealants can be expected to improve development efficiency. It also has potential applications in confirming the feasibility of designs.

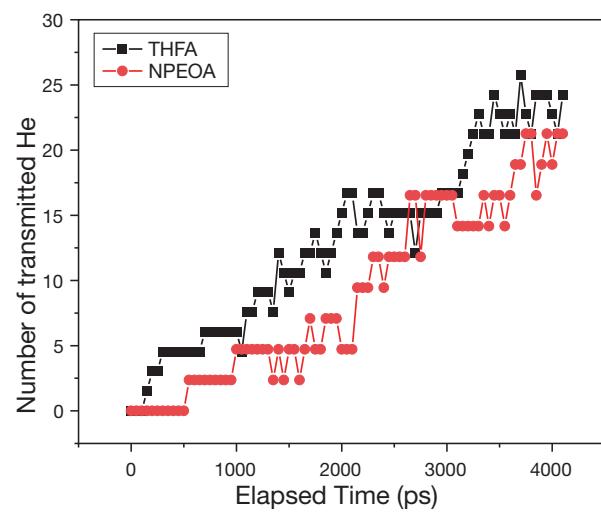


Fig. 16 Simulation Results Showing Helium Atom Permeation Over Time

Closing

This article covers several examples of the use of molecular simulation in studies designed to further understanding of phenomena related to adhesion. Although simulation technology remains in the trial and error stage, the potential for simulation to be used in combination with results from experiments to complement their respective deficiencies and build understanding of the phenomena being studied has been demonstrated.

In future, we intend to continue to utilize our existing analytical methods and combine them with simulations as appropriate to help solve our customers' problems, improve development speed, and create hypotheses.

Adhesion is an esoteric area of study that requires an interdisciplinary understanding of concepts ranging from surface chemistry, polymer physics, and fracture mechanics to the interface and bulk phenomena predicted by the simulations in this article. We continue to achieve consistent results in this field as we proceed with research and development based on input from large numbers of users, suppliers, academic societies and university professors. We would like to thank all involved parties for their support, and we will strive to continue driving development in the field of adhesion.

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