Theoretical Studies of Adhesive Interactions between Silica Surface and Polymers

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<div align="center">論 文 内 容 の 要 旨</div>

Adhesion technology is widely used in various industries, such as construction, automotive, aerospace, sports equipment, and electronics, due to its lightness, mechanical strength, and insulation properties. Adhesion technology has been advancing day by day, and a lot of experimental-based research has been conducted for various applications. However, the principles underlying it are not fully understood, due to its complexity. In other words, the theory of adhesion is still in its infancy, leaving the possibility for new research. General introduction of this thesis is given in Chapter 1.

In Chapter 2, the molecular mechanism of the adhesion between silica surface and epoxy resin under atmospheric conditions is investigated by using periodic density-functional-theory (DFT) calculations. Slab models of the adhesion interface were built by integrating a fragment of epoxy resin and hydroxylated (0 0 1) surface of α-cristobalite in the presence of adsorbed water molecules (Figure 1a). Effects of adsorbed water on the adhesion interaction are evaluated on the basis of geometry-optimized structures, adhesion energies, and forces (Figure 1b). Calculated results demonstrate that adsorbed water molecules significantly reduce both the adhesion energies and forces of the silica surface–epoxy resin interface. The reduction of adhesion properties can be associated with structural deformation of water molecules confined in the tight space between the adhesive and adherend as well as structural flexibility of the hydrogen-bonding network in the interfacial region during detachment of the epoxy resin from the hydrophilic silica surface.
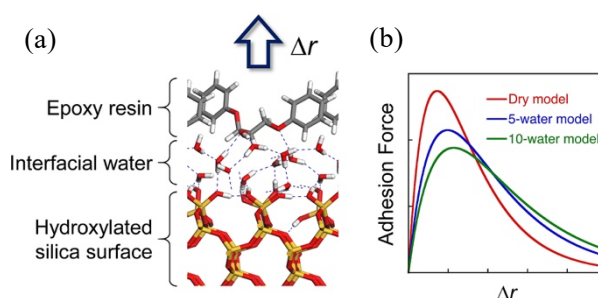

Figure 1. (a) Epoxy/water/silica adhesive interface and (b) Force–displacement curves.

In Chapter 3, we report the energy decomposition of the interfacial interaction energy (ΔE_{int}) between epoxy resin and silica surface using pair interaction energy decomposition analysis (PIEDA), which can divide ΔE_{int} into four components: electrostatic (ΔE_{es}), exchange repulsion (ΔE_{ex}), charge-transfer (ΔE_{ct}), and dispersion (ΔE_{disp}) energies. Our previous study showed that the synergistic effects of ΔE_{es} and ΔE_{disp} are essential at the interface between hydrophilic surfaces and an epoxy resin fragment. The present study is designed to confirm that the synergistic effects can be maintained in the interface model with the epoxy resin layer consists of 20 epoxy monomers on the hydrophilic silica surface. The layer model also shows that 3.6 Å

region of the epoxy layer from the silica surface accounts for more than 99% of ΔE_{int}. The 20 epoxy molecules in the layer are investigated individually to closely correlate the four energy components for each epoxy molecule with their structural features. As a result, most of the ΔE_{disp} ratios of the 20 epoxy molecules are controlled by the magnitude relation between ΔE_{es} and ΔE_{ex} rather than ΔE_{disp}. These energies are significantly related to either H-bonding interaction or OH/π interaction.

In Chapter 4, the work proposes a unified approach to predict glass transition temperatures (T_gs) of linear homo/hetero-polymers and cross-linked epoxy resins by machine-learning approaches based on descriptors of reagents undergoing polymerization, represented in a formal way such as to encompass all the three scenarios: linear homo- and heteropolymers, plus reticulated heteropolymers. In silico design and data analysis (ISIDA) fragment counts with special status given to the "marked atoms" participating in the polymerization process were combined using "mixture" strategies to generate the final polymer descriptors. Three predictive models based on support vector regression (SVR) are discussed here. After reproducing results of Katritzky *et al.* with a local model applicable only to linear homo/hetero-polymers, an epoxy resin-specific model applicable to both linear and reticulated forms was built. Eventually, the general model applicable to all these families was constructed. In 12 × repeated 3-fold cross-validation challenges, it displayed the highest accuracy of $Q^2 = 0.920$, RMSE = 34.3 K over the training set of 270 polymers (Figure 2a), and $R^2 = 0.779$, RMSE 35.9 K for an external test set of 119 polymers. Generative topographic mapping (GTM) analysis produced a 2D map of "polymer chemical space", highlighting the various classes of polymers included in the study and their relationship with respect to T_g values (Figure 2b).

Figure 2. (a) Plot of predicted T_g values versus experimental T_g values and (b) the GTM map with T_g landscape and representative polymer structures.

General conclusions are summarized in Chapter 5. This thesis explains how the epoxy resin adheres to the silica surface at the molecular level with first-principle calculations. It also shows the way how to create T_g prediction models of linear homo/hetero-polymers and cross-linked epoxy resins via chemoinformatics approaches. Curing agents of the epoxy resin, dynamic behavior of polymers, or heating rate in T_g measurement have not yet been incorporated into our work. However, our work provides a useful guidance for the future development of comput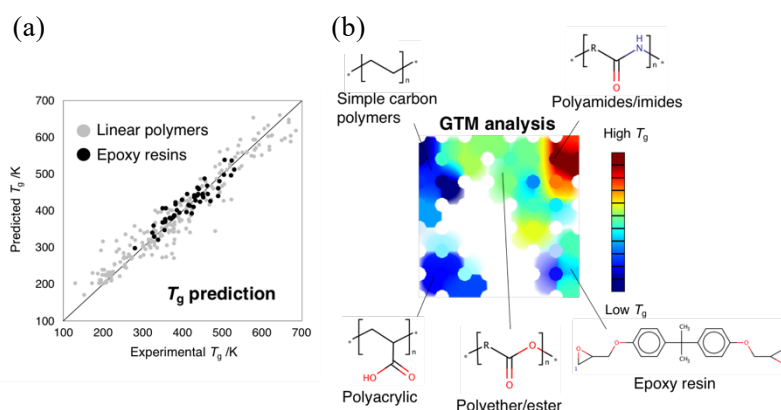ational approaches in the field of polymer chemistry.