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Bonding of urethane reactants to aluminum surface

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Reaction mechanism of urethane components (phenyl isocyanate and isopropanol) on Al hydroxide surface was studied using molecular modeling, and compared with real systems by measurement of electrochemical potential and optical observation. Charge of the phenyl isocyanate was concentrated on N and O atoms, implying that the reaction of the phenyl isocyanate on substances takes place through these atoms. Due to low energy difference between the lowest unoccupied molecular orbital (LUMO) of the phenyl isocyanate and the highest occupied molecular orbital (HOMO) of Al hydroxide, it was found that the mixture of phenyl isocyanate and alcohol segregates to the Al surface. Heat of formation for the reaction steps of the phenyl isocyanate on the Al hydroxide cluster is negatively larger than that of the isopropanol-Al interaction. Variation of electrochemical potential of Al surface in the urethane reactants was measured. As a result, it was found that the phenyl isocyanate rapidly reacted with the Al surface, and the reaction products were observed after drying. An optical micrograph of the Al sample held in the isopropanol was very similar to that for a bare Al surface. Evolution of bubbles on the Al surface was expected to be H_2O formed by the formation of hydrogen bonding between the urethane and the hydroxyl groups bound on the Al surface.

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1. Introduction

Polyurethanes have been widely used as adhesive in industry such as automotive and roofing products due to their capability of rapid chemical reaction between —NCO terminal group and solid substrate that contains extractable hydrogen atoms. Most of metal forms a monolayer of bound water on their surfaces. The adhesives are usually applied as —NCO terminated prepolymer, diisocyanate with reactive —NCO terminal groups or polyurethane having free isocyanate group. It has been shown that the adhesion of polyurethanes and its derivatives to solid substrates using isocyanate significantly improve bond strength and other mechanical properties [1, 2]. Through a study about kinetics of reaction between phenyl isocyanate and various types of alcohol, the correlation of the structure of alcohols with reaction rate was also revealed [3]. However, exact reaction mechanism between the urethane mixture and metal surface has not been well established.

Adhesion of polyurethane to a solid substrate can be achieved by two mechanisms [4–7]. Firstly, a polar urethane backbone attracts to a polar solid surface at which a hydroxyl layer usually forms, due to the dissociation of water molecules in air. The second is that isocyanate end groups of polymer chains chemically react with the solid surface. The latter is plausible only for polymers containing excessive —NCO groups. The bonding of polyurethane to a solid substrate is based on the interaction between —NCO, —NHCOO functional groups and hydroxyl groups on the substrate surface. Thus, phenyl isocyanate and isopropanol were selected to the study of bonding mechanism of polyurethane to a metal surface. An Al that is typically used as a facing material to polyurethane was chosen as a solid substrate. The present study describes fundamental information on the reaction mechanism of the interface between urethane reactant mixtures and the Al. In order to examine the nature of the interface, and what molecules and/or parts of molecules preferentially segregate to the interfacial region, an electrochemical test and subsequent optical observation for the by-products between the urethane reactants and the Al surface were performed. The experimental results have been compared to data through molecular modeling. A semi-empirical MNDO method

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was used to calculate heat of formation and molecular orbitals of phenyl isocyanate mixed with isopropanol against the Al.

2. Experimental

2.1. Materials

An approximately 1000 Å thick Al film, sputtered on Si wafer, was prepared as the substrate, and the Al forms the hydroxide monolayer from dissociative water in air. Small organic chemicals such as isopropanol (Aldrich) and phenyl isocyatate (Aldrich) were selected as urethane reactants. The phenyl isocyanate was distilled using a column equipped with a vacuum pump. The Al surface was cleaned with an acetone, and dried in air. The urethane solution was prepared by mixing of phenyl isocyanate and isopropanol (1:1 molar ratio).

2.2. Electrochemical and optical observations

A potentiostat was utilized to measure the electrochemical potential of Al surface as a working electrode. The Al substrates were immersed in phenyl isocyanate, isopropanol and urethane, kept at 16°C, respectively. A Standard Calomel Electrode (SCE) was used as a reference electrode and graphite as a counter electrode. The variation of the potential was measured as a function of immersion period.

After the variation of the electrochemical potential of the Al surface is maintained at a constant value, the samples were taken out and dried in the air. Since the urethane was solidified during measuring the potential, the potential of the Al surface in the urethane was measured before the completion of the solidification. The Al surfaces were observed under an optical microscope to examine whether the reaction products were remained.

2.3. Molecular modeling procedure

The extraction of thermodynamic and molecular orbital data became possible through quantum chemical calculations using various softwares which provide molecular orbital such as highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) including thermodynamic data; heat of formation (ΔH_f), heat capacity, entropy etc. [9]. Semi-empirical method, such as Modified Neglect of Diatomic Overlap (MNDO), is useful for modeling of the bonding and reaction mechanism of organic functional materials to surfaces and interface. The MNDO provides quick results for multiple bonds compared to the other methods, i.e., complete neglect of differential overlap (CNDO) and modified intermediate neglect of differential overlap (MINDO) [10]. Therefore, a geometrical optimization was carried out using the MNDO semi-empirical method using GAUSSIAN 94 program (Gaussian, Inc. Pittsburgh, 1994). Bond angles and lengths for the initial organic structures were built using MOLDA (Department of Chemistry, Hiroshima University, Japan) and CHEM-3D (CambridgeSoft Corporation, Cambridge, MA). Heat of formation, charge distribution, and molecular orbital data for phenyl isocyanate, isopropanol, urethane, and Al hydroxide cluster as a substrate top surface were calculated after the geometrical optimization. Since most of metal surfaces are adsorbed by water molecules in air, the consideration of Al hydroxide cluster as a top surface monolayer is appropriate to study the reaction mechanism between organic molecules and Al surface. All thermodynamic and molecular orbital data were calculated at room temperature and one atmosphere.

3. Results and discussion

The variation of electrochemical potential does not only represent the existence of surface film formed by interaction between liquid and metal, but it also implies whether the film sustains. The electrochemical test is very appropriate to study the reaction mechanism between liquid substances and metal surface. The measurement of the potential for metal surface as a function of immersion period provides how fast the surface film forms. This test was performed on the Al films, sputtered on Si wafer, immersed in the phenyl isocyanate, isopropanol, and urethane. Fig. 1 shows the variation of the potential for the Al surface immersed in the urethane reactants. The phenyl isocyanate rapidly reacts with the Al surface, followed by being constant potential in three minutes. A fast chemical reaction of the phenylisocyanate with outermost hydroxyl layer of the Al surface took place. The increase of the electrochemical potential indicates the film formation at the Al surface, due to a reaction between the phenyl isocyanate and the Al substrate. The potential was most likely maintained even after further immersion, implying that the formed film is not broken. Apparently, the film formed from the chemical reaction between NCO and Al hydroxide surface is stable. The isopropanol slowly reacts with the Al film surface. Even though the electrochemical potential significantly fluctuates during the initial immersion period, the potential, in overall, increases with time. It turns out that the repetitious breakdown and formation of the surface film was caused by

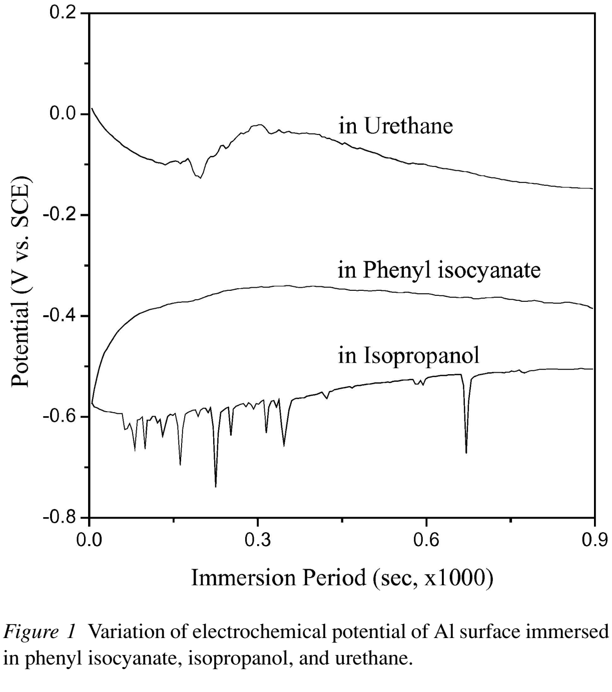


Figure 1 Variation of electrochemical potential of Al surface immersed in phenyl isocyanate, isopropanol, and urethane.

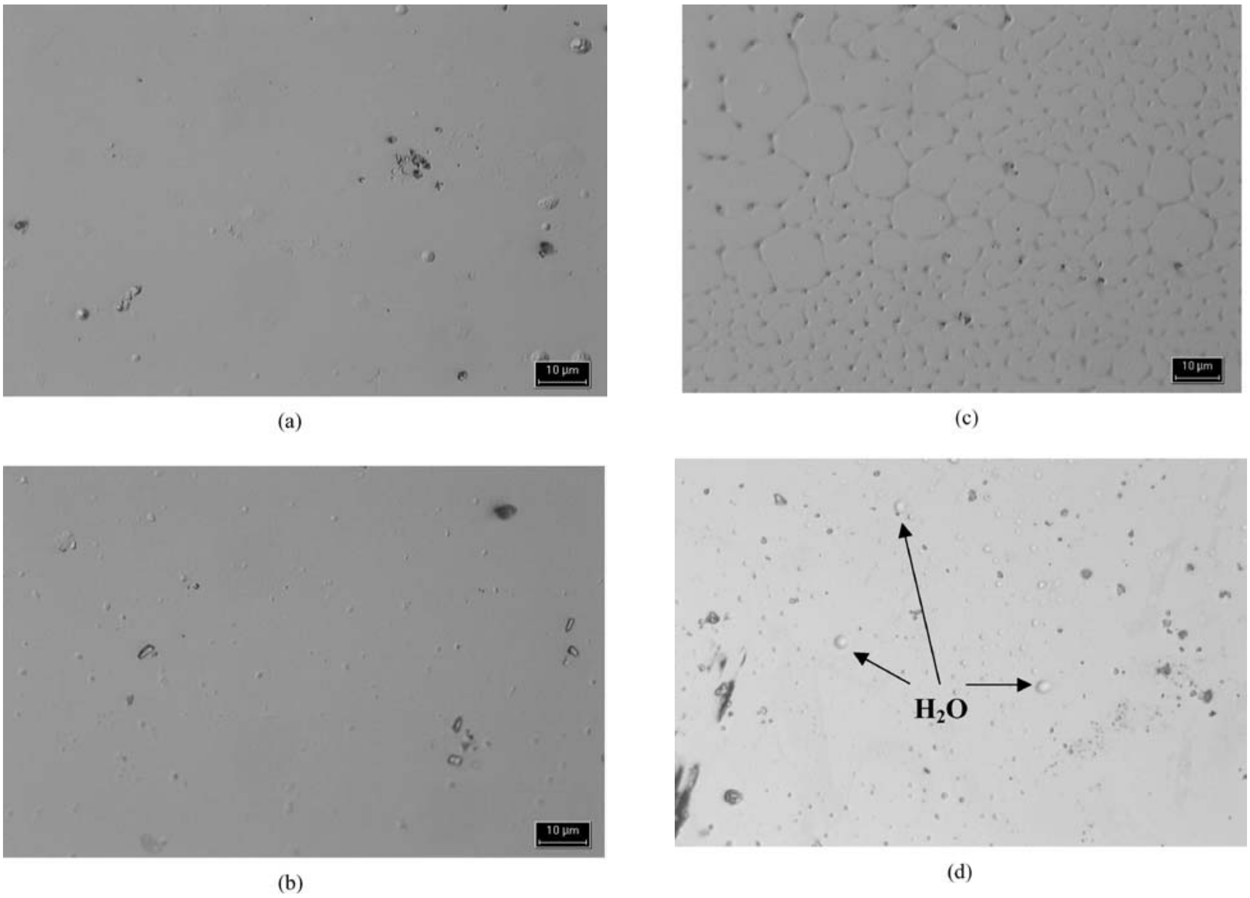

(a) (c) (b) (d)

Figure 2 Optical micrographs for Al surface immersed in urethane reactants. A bare Al (a) shows the similar surface image to one (b) immersed in isopropanol. A reaction product appears for Al substrate (c) immersed in phenyl isocyanate, while bubbles was found on Al samples immersed in urethane.

unstable interaction between the isopropanol and the Al surface. One wonders if the film is formed, and can be sustained even at drying, since the reaction between isopropanol and Al surface is accomplished by hydrogen bonding. The persisting ability of the film is discussed in the part of optical observation. A formation of film on the Al, held in the urethane, was relatively unstable during entire immersion period; the Al surface is initially corroded, the film is formed, and then the film is slowly broken. This phenomenon is not understood, but the generation of gas bubbles at the Al surface may have led to this change of the electrochemical potential.

The Al samples immersed in the urethane reactants to measure the variation of the electrochemical potential were dried in air, and their surfaces were observed under an optical microscope. An optical micrograph for an Al surface that was not immersed in the chemicals was shown in Fig. 2a. The bare Al surface shows very similar image to one immersed in the isopropanol as displayed in Fig. 2b. Volatilization of the isopropanol, adsorbed to the Al surface during immersion, occurred during drying in air. The reaction products were not found even in the Al samples, held in the isopropanol for 3 and 5 days. It turns out that the alcohol weakly attracts to the Al surface. This corresponds to the modeling result, discussed in the later part, in such a way that the heat of formation for overall reaction steps is close to zero, and thus, the reaction negligibly proceeds. Meanwhile, a by-product appeared on the Al surface immersed in the phenyl isocyanate (see Fig. 2c). It results from the interaction between NCO— and Al hydroxide clusters, as expected from the electrochemical test. The surface film was sustained even after drying in air, since the reaction between—NCO and Al hydroxide surface chemically proceeded. The formation of the honeycomb morphology is not understood. It is presumed that the morphology relates to grain boundaries of the Al surface and/or surface tension of the film. Although there was an attempt to investigate the composition of the film only, indistinguishable peaks from a FT-IR appeared. However, it is expected that the surface film would be composed of the urethane linkages. This is shown in molecular modeling section. From an optical micrograph of the Al surface held in the urethane (Fig. 2d), the bubbles were found. The randomly distributed droplets were trapped underneath the surface film. The evolution of the bubbles is examined through the following molecular modeling studies.

The molecular modeling was carried out to confirm above experimental results, and further, to suggest exact reaction mechanism between urethane reactants and Al surface. Geometrical optimization under the minimum energy state was performed on the each chemical and Al hydroxide cluster using a semi-empirical MNDO method. The charge distribution map was obtained, and thermodynamic data were calculated at room temperature. The charge distribution of geometrically optimized phenyl isocyanate is shown in Fig. 3a. Electron

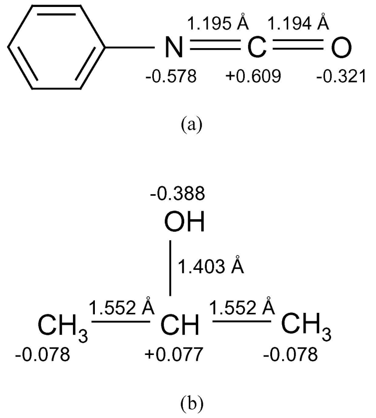


Figure 3 Charge distribution of phenyl isocyanate and isopropanol, calculated using molecular modeling. Bond angles and lengths are greatly exaggerated.

TABLE I Calculated molecular orbital energies

Materials	HOMO (eV)	LUMO (eV)
Aluminum hydroxide cluster	−0.19067	0.00704
Phenyl isocyanate	−9.042	0.029
Isopropanol	−11.242	3.288

density is concentrated on nitrogen (−0.578) and oxygen (−0.321) atoms with a net positive charge on carbon atom (+0.609). Based on the charge distribution map, it is evident that the reactivity of the phenyl isocyanate originates from nitrogen and oxygen atoms. Therefore, the carbon and nitrogen atoms of phenyl isocyanate tend to attract to oxygen and hydrogen atoms of the hydroxyl group on Al surface, respectively. It leads to the formation of urethane NHCOO— linkage at the Al surface. From the charge distribution of isopropanol in Fig. 3b, isopropanol should interact through hydrogen bonding with the Al hydroxide cluster. The reaction steps between the urethane reactants and the Al surface were established from this charge distribution map and molecular orbitals discussed in the following.

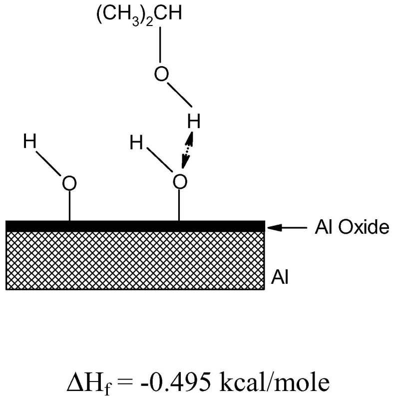


Figure 4 Reaction model through hydrogen bonding between isopropanol and Al surface bound by hydroxyl groups. Heat of formation for this reaction step is close to zero.

The energies of HOMO and LUMO for an Al hydroxide cluster, phenyl isocyanate, and isopropanol are listed in Table I. It is well known that the orbitals in most similar energy tend to mix to afford bonding interaction [8]. Therefore, the mechanistic pathway was predicted by the molecular orbital calculations based on the LUMO of the urethane reactants and the HOMO of the Al hydroxide cluster. The charge should transfer from the LUMO of the urethane substances to the HOMO of the Al surface covered with the hydroxide clusters. The energy difference (0.220 eV) between the HOMO of Al hydroxide cluster and the LUMO of phenyl isocyanate is lower than the corresponding interaction (3.479 eV) between the HOMO of Al hydroxide surface and the LUMO of isopropanol. Consequently, the phenyl isocyanate preferably segregates near the Al surface with the formation of urethane linkage faster than the isopropanol, if two raw chemicals are put together onto the Al surface.

The heat of formation for the possible reaction paths was calculated to examine by-products between urethane reactants and Al surface. The reaction steps were suggested from the charge map and molecular orbital energies of each chemical. The heat of formation for all of the reactions is obtained in Fig. 4 through Fig. 6. Isopropanol attaches to the OH groups bound to a native Al oxide surface, resulting from hydrogen bonding between a hydrogen atom of the isopropanol and an oxygen atom of the hydroxide cluster surface (Fig. 4). This reaction, however, may negligibly proceed, because the calculated heat of formation (−0.495 kcal/mole) is close to zero. This corresponds to the microscopic result that did not show a reaction product at the Al surface. It is evident that the volatilization of the adsorbed isopropanol took place during drying, due to

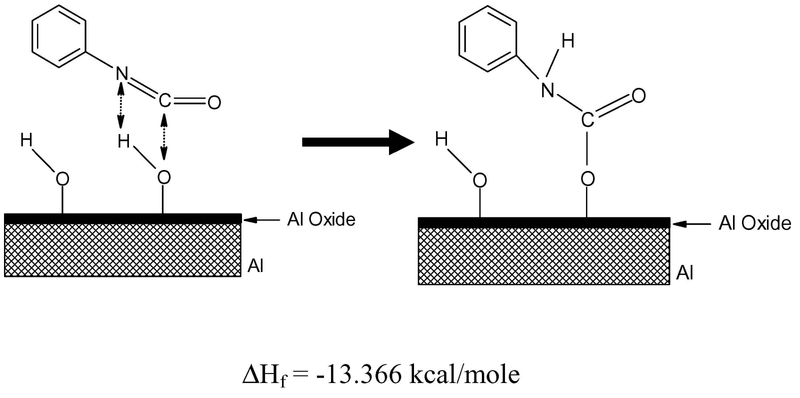
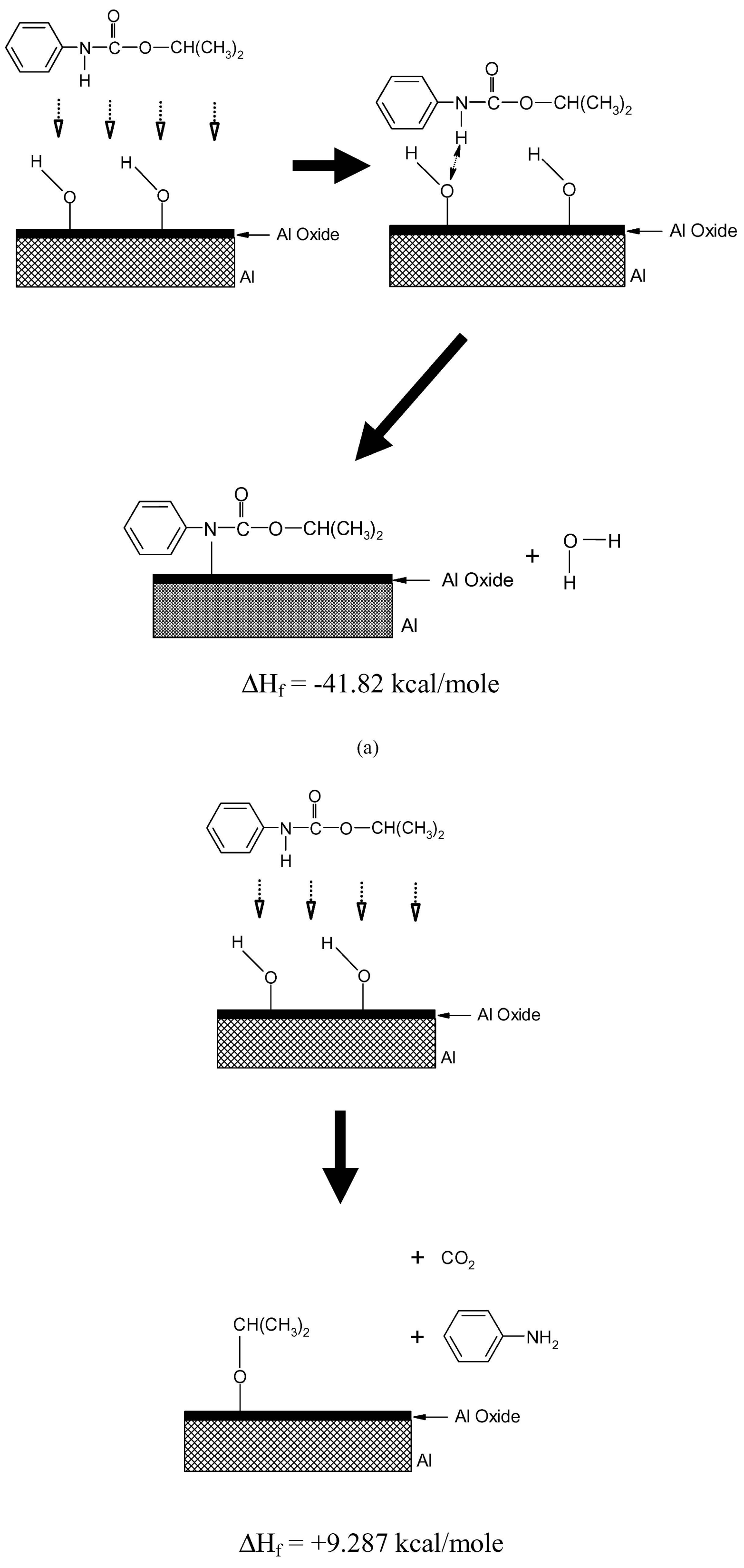


Figure 5 Reaction model through chemical bonding between phenyl isocyanate and Al surface covered with dissociative water molecules. In the final stage, urethane linkage is generated at the Al surface.



(a)

(b)

Figure 6 Reaction model through hydrogen bonding between urethane functional group and Al surface adsorbed with hydroxyl groups. Reaction (a) provides a water molecule as a by-product, while reaction (b) evolves amine and CO_2 gas.

the high vapor pressure of the isopropanol capable of breaking the hydrogen bonding attracted to the Al surface. This resulted in the absence of the reaction product between the isopropanol and the Al hydroxyl surface.

Phenyl isocyanate interacts with the Al hydroxide surface through the formation of hydrogen bonding (Fig. 5). Subsequent reaction does not lead to the extraction of hydrogen atom from hydroxyl group bound at the Al surface, but it also causes the interaction between the carbon atom of —NCO and the oxygen atom of the hydroxide surface. The reaction ends up with the generation of urethane linkage at the Al surface. Based upon the negative ΔH_f (-13.366 kcal/mole) for the reaction step in Fig. 5, it is clear that the phenyl isocyanate should react with the Al surface consisted of hydroxide top surface. This confirms the optical micrograph obtained from the Al sample immersed in the phenyl isocyanate, in such a way that honeycomb morphology was formed as the by-product. It is obvious that this chemical segregated onto the Al surface.

The reaction step of a urethane with the Al hydroxide cluster was modeled as two types, based upon ref. 11. As shown in Fig. 6a, the hydrogen atom in —NHCOO interacts with the oxygen atom of the Al hydroxide surface, followed by the evolution of H_2O molecule in further reaction. Another possible reaction step of urethanes and Al hydroxide produces amine and CO2 (see Fig. 6b). The preference of two reactions was estimated by the calculation of ΔH_f. The reaction step that evolves the H_2O ($\Delta H_f = -41.820$ kcal/mole) is more favorable than the reaction step producing amine and CO_2 ($\Delta H_f = +9.287$ kcal/mole); the first reaction thermodynamically proceeds. Based on the thermodynamic calculation through the molecular modeling, the bubbles are most likely condensed water molecules.

4. Conclusions

The interaction between urethane reactants, such as phenyl isocyanate and isopropanol, and Al hydroxide clusters has been studied using electrochemical test and molecular modeling. Both the electrochemical test and the optical observation showed that —NCO favorably reacts with Al hydroxide, providing the surface film. The attraction of —NHCOO— to the Al hydroxide evolved the bubbles. Based upon the molecular modeling, it was determined that the trapped droplets are H_2O bubbles. It was found that the reaction between the phenyl isocyanate and the Al hydroxyl surface had a greater negative heat of formation and a smaller energy difference between the LUMO and HOMO than those for the corresponding reaction of the isopropanol with the Al hydroxide cluster. Hence, charge should transfer from the Al hydroxide covered with OH groups into an atom of the phenyl isocyanate —NCO group. Consequently, the molecular orbitals and the thermodynamic evaluation of reaction steps in terms of the heat of formation, calculated by molecular modeling, correspond to the two adhesion mechanisms between the polyurethane and a solid substrate. That is, the hard segments of polyurethane, composed of urethane and/or isocyanate groups, would get together with the solid surface covered with OH group. Furthermore, the —NCO terminated polyurethane may strongly bond to the metal surface. It gives a guide how to synthesize polymer when the better adhesion to metal surface is needed.

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