Effects of Humidity on Aggregation Structure at Epoxy / Metal Interface

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1. Introduction

Diffusion of water into the polymer structures can influence the structure and properties of the polymers. The absorbed water is believed to degrade the strength and properties of the polymers and hence it is important to study how it affects the thermal and mechanical properties of the polymers. For example, in the field of adhesion which attracts attention as a structural material, epoxy resins are considered to be hardy polymers capable of withstanding deleterious conditions for considerable times. As such, they are much used as adhesives, matrices for composite materials, encapsulating agents, etc. However, extended exposure to water (or water vapor) can lead to damage, and much work has been devoted to better understanding of the mechanisms involved. The transport properties of water have been studied on epoxy–amine networks in relation with the polymer structure. The water diffusion has already been studied in the several literatures principally considering the specific interactions between the water molecules and the polar groups of the networks. The chemical structure is then a fundamental parameter, and in that way, the polar groups concentration and the composition of the reactive system are the main parameters. However, to guarantee the safety of adhesives, we have to ensure the mechanical strength between adhesive and substrates. In this situation, concentration of water molecules to adhesive / substrate interface should be important. Recently, we demonstrated a simple but efficient strategy for creating ultrathin protective coating for versatile and practically useful structural metal/alloy substrates. We also revealed the interfacial aggregation structure of ultrathin protective coating by using neutron reflectivity (NR, SOFIA at BL-16). (RSC Advances 5, 15977 (2015).) Then, in this study, to promote our research to the next stage, we apply one of the most depth sensitive techniques, NR, to adhesive layer so that we can give a better understanding of relation between adhesion and interfacial structure. Additionally, to investigate the interfacial structure using bulk sate is very important in the field of adhesion. Here, we have established a method to clearly evaluate the structural change of the pseudo bulk state adhesive and the adherend interface so far thanks to past and present progressive approved proposals by MLF. However, the interfacial concentration of water molecules could not be sufficiently studied. Therefore, we evaluated the interfacial aggregation structure between metal adherend and bulk epoxy adhesive by NR.

2. Experiment

In our experiment, we found that the 60-nm metal (Copper) layer is effective to elucidate the interfacial aggregation structure between adhesive and metal, therefore "Adhesive / Metal(Cu, Al, Au) / Substrate(Si)" geometries are prepared. The existence of this Copper layer enables us to detect the interfacial information no matter how thick the adhesive layer is. As adherend layers, Al and Cu are used. In case of Cu adherend, Cu is directly deposited onto thick silicon blocks with a size of 40 × 40 × 7 mm. On the other hand, in case of Al adherend, Al is deposited onto thick silicon blocks with Cu surface layer. Figure 1 shows the variety of multi-layer substrates. The thickness of the metal layer is controlled to be approximately ca. 60 nm which is appropriate for NR measurements. Then, as adhesives, epoxy films are coated on the top of metal layers mentioned above. To evaluate the intrinsic interfacial structures of adhesive/metal system, samples are aged in deuterium oxide (D_2O) for a given temperature and time, which is sufficiently enough to induce contrast change by sorption of liquids. Density profiles of the films along the direction normal to the surface in contact with D_2O are examined by NR.

3. Results

Figure 2 shows the neutron reflectivity curves for Cu/Si, epoxy/Cu/Si and D2O/epoxy/Cu/Si systems, respectively. Despite the fact that the thickness of the epoxy resin was thicker than 50 μm, clear fringes were observed in the reflectivity curves (blue and red symbols). Furthermore, since the shape of the fringes are clearly different from the case of the Cu/Si system, it can be said that the data reflects the aggregation structure of the epoxy resin layer. Even when epoxy/Cu/Si and D_2O/epoxy/Cu/Si are compared, the shape of the reflectivity curve also changed. This means that, by bringing the adhesive layer of the epoxy resin into contact with deuterated water, water molecules diffuse to the vicinity of the interface with the Cu covered substrate. Moreover, in the system contact with water, the fringe in the high q region became unclear compared with dry environment. Therefore, despite a thick film, it is considered that water molecules concentrate near the interface with metal and the density profile of the epoxy adhesive gradually changed.

4. Conclusion

It is considered that the aggregated structure of thick adhesive layer near the interface with metal could be clarified based on the NR measurement. As a result, it is possible to accurately evaluate the effect of water content under actual conditions. We are currently conducting more precise analysis, and if additional experiments are needed we are going to apply for next machine time and we are going to publish more details in the near future.

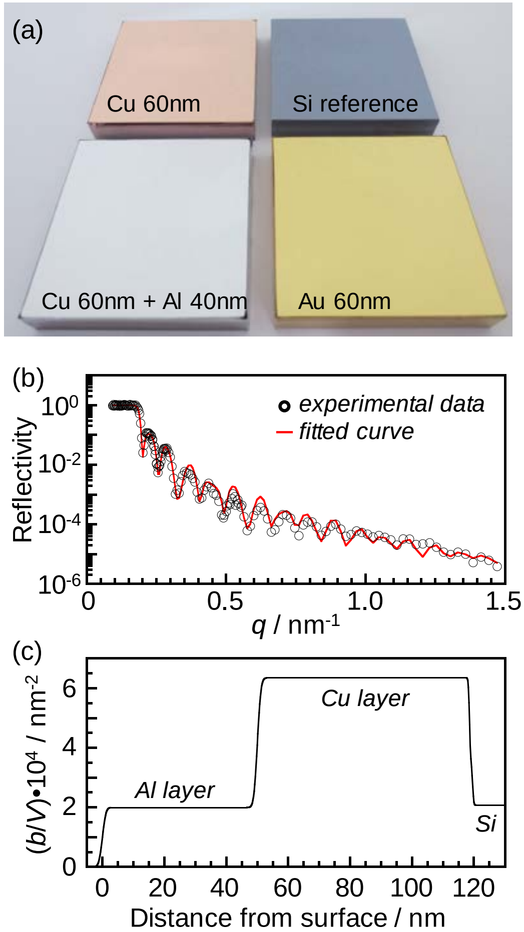

Figure 2. (a) Photo images for metal covered Si wafers. (b) Neutron reflectivity for (Al/Cu) bilayer on Si wafer. Open symbols depict experimental data, and solid line is reflectivity calculated based on the model scattering length density profiles in panel (c).

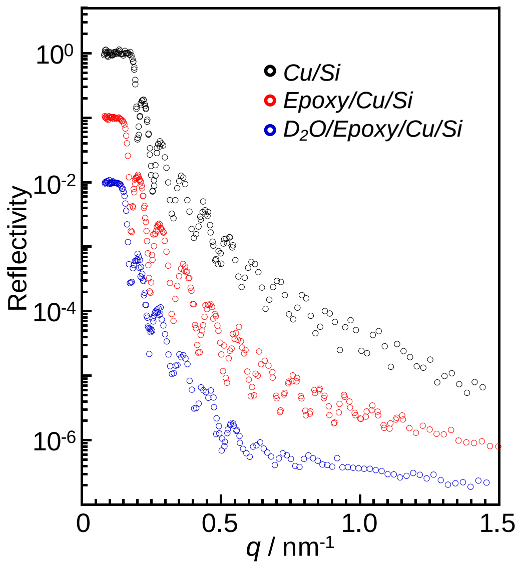

Figure 2. Neutron reflectivity for Cu layer, epoxy/Cu on Si wafer. Open symbols depict experimental data, and blue symbols measure in D_2O.