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Probing surface and interfacial molecular structures of a rubbery adhesion promoter using sum frequency generation vibrational spectroscopy

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ABSTRACT

The molecular structures of an adhesion promoter, polybutadiene-modified epoxy (PBME) rubber at surfaces and buried interfaces with gold (Au) were studied using sum frequency generation (SFG) vibrational spectroscopy. The SFG spectra showed that the soft butadiene part of PBME can segregate to the surfaces and buried interfaces in two base formulations. This is consistent with its application as an adhesion promoter. For the first time, the orientation of the segregated vinyl methylene groups of PBME at the surface and buried interface was evaluated. We found that the vinyl methylene groups at the surface were highly tilted and twisted by quantitative analysis; while the vinyl methylene groups at the buried Au interface were highly tilted by qualitative estimation. Furthermore, this study confirms that the sandwiched-face-down experimental setup can be employed to study the buried interfaces. This could be developed into a standard way to probe the buried interfaces between the commercialized resins and metal substrates.

1. Introduction

Adhesion promoters are a type of key ingredients in many engineering materials, such as paints, coatings, and encapsulants, or as base materials for adhesives. The high performance of adhesion promoters depends on the ability of integrating matrix materials with substrates like metals, glasses, or plastics, etc. Although an adhesion promoter and its matrix material are chemically miscible, the segregation of the adhesion promoter to the substrate surface generally occurs when the matrix keeps in contact with the substrate, leading to the desirable chemical or/and physical interaction towards the substrate. So it is very important to study how an adhesion promoter adheres to the substrate since the properties of the two integrated phases — matrix and substrate like chemical composition, thermal and mechanical properties are not necessarily similar. Numerous studies have been done to understand the formation of such interfaces based on X-ray photoelectron spectroscopy (XPS) [1–5], scanning electron microscopy (SEM) [6–9], infrared spectroscopy (IR) [10–12] and surface enhanced Raman spectroscopy (SERS) [13–15], etc. It is generally accepted that the formation of such interfaces is a complex process depending on the sample pretreatment, curing process, and even post-treatment. Nonetheless, the interfacial microscopic structures with respect to the chemical or physical interactions accumulated at the interface have to be directly associated with the interfacial properties [3,12,16,17]. It is therefore of great significance to probe the molecular-level interfacial structures for the purpose of understanding the formation mechanism of the interface. In order to probe such a buried interface in situ, a non-destructive and interface-sensitive technique is needed which should have the ability to reach the buried interface. In the nearest decades, the second-order nonlinear optical technique, sum frequency generation vibrational spectroscopy has been proved to be a powerful technique to probe the molecular-level structures at the surfaces and interfaces [18–25]. Under the electric dipole approximation, the materials with inversion symmetry do not generate any SFG resonant signals; while at the surfaces or interfaces, the inversion symmetry is necessarily broken and the generated SFG resonant signals with different polarization combinations can be used to analyze the surface or interfacial molecular information like segregation, orientation, and orientation distribution [26]. We ourselves developed several methodologies to probe the buried polymer/metal interfaces using polymethylmethacrylate (PMMA)/silver (Ag), polymethacrylate (PMA)/Ag, and polyethyl methacrylate (PEMA)/Ag as model systems [27–29]. We also prove that for amorphous polymer thin films with thicknesses of ~100 nm, the bulk contribution could be neglected for the reflection mode [29], which is consistent with the already reported results [30,31]. Recently, we have focused on studying the polybutadiene-modified epoxy (PBME) rubber, which has proved to be an effective adhesion promoter or a key ingredient for adhesives towards the noble metal interfaces. In this paper, we report our study on the surface and interfacial molecular structures of PBME and two base formulations containing PBME. We prove that our previously developed experimental setup [28] can be used to

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study the interfacial molecular structures between commercial resins and metal substrates. The detected polar-ordered molecular structures of PBME at surfaces and interfaces were discussed.

2. Experimental section

2.1. Materials

Polybutadiene-modified epoxy resin (PBME, Nippon Petrochemicals Co., Ltd.) was provided with courtesy by Henkel Electronics, Co., Ltd. One of the curing agents, bisphenol-A (BPA, 99%) was purchased from Sigma-Aldrich Co. The other curing agent, 4,4′-diaminodiphenyl methane (DDM, 98%), was purchased from the Aladdin Reagent Database, Inc. as well as the catalyst — imidazole (IMD, 99.5%). All the materials were used without further treatment. The epoxy equivalent weight (EEW, corresponding to the weight of resin in grams which contains one-mole-equivalent of epoxide groups) of PBME was 230 measured by a titration method. The chemical formulas of PBME, BPA, DDM and IMD and the pictorial reactions during the curing process [32,33] were shown in Fig. 1. The Au substrates were prepared by sputtering 200-nm layers of Au onto the clean glass slides by an ion sputter coater (JS-1600, Beijing Hetong Chuangye Technology Co., Ltd.). Before that, a 10-nm layer of nickel (Ni) was sputtered onto the glass slides to promote the adhesion between Au and glass slides. PBME, BPA, and DDM were dissolved in the mixed chloroform/ethanol (v:v = 1:1) solution to prepare the sample films. Since without the curing agents, PBME itself cannot cure, the stoichiometrically equivalent PBME and curing agents were also mixed in the chloroform/ethanol solution to prepare the sample films for the curing process. For PBME/BPA, the weight ratio is 2:1; for PBME/BPA/DDM, the weight ratio is 4:1:1. There were two types of sample films for the SFG experiments (see Fig. 2). For Type I, the solutions were directly cast onto the silica windows to form sample films and heated at 40 °C for hours to remove the solvents. For Type II, a gold (Au) substrate was directly attached to the surface of a sample film already prepared on the silica window, leading to a sandwiched silica/sample/Au geometry, as illustrated by our previous publication [28]. The thicknesses for all the films studied in this paper were controlled ~100 nm. In this paper, curing of the sample films (Type I and Type II) was run at 150 °C for two hours. With respect to Type II, after curing, a sandwiched sample film was tightly bound to the silica window and the Au substrate, which was suitable for the SFG experiment.

2.2. SFG spectroscopy

Our infrared-visible SFG system is a custom-designed Ekspla SFG spectrometer (EKSPLA, Lithuania) based on a Nd:YAG laser. The 532-nm-wavelength visible beam was generated by frequency-doubling the fundamental output pulses of ~30 ps pulse width with wavelength of 1064 nm. The tunable IR beam was generated from an optical parametric generation/amplification and difference frequency generation system based on BBO and $AgGaS_2$ crystals. The visible and tunable IR beams were overlapped on the sample surface with incident angles of 60° and 55° respectively. Both beams were focused on the sample surface with diameters of ~0.5 mm. Photodiodes were used to monitor the visible beam and IR beam powers by detecting parts of reflections from focus lenses. The sum frequency signal was collected by a monochromatic spectrograph. The SFG spectra as a function of the input IR frequency (wavenumber cm^{-1}) were thus normalized by the powers of the input laser beams. In this study, a face-up experimental geometry was used to collect the sample surface spectra (Type I samples); while a face-down experimental setup with a sandwiched geometry (Type II samples) that we developed previously [28] was used to collect the buried interfacial spectra of our samples with Au. The two SFG experimental geometries were shown in Fig. 2.

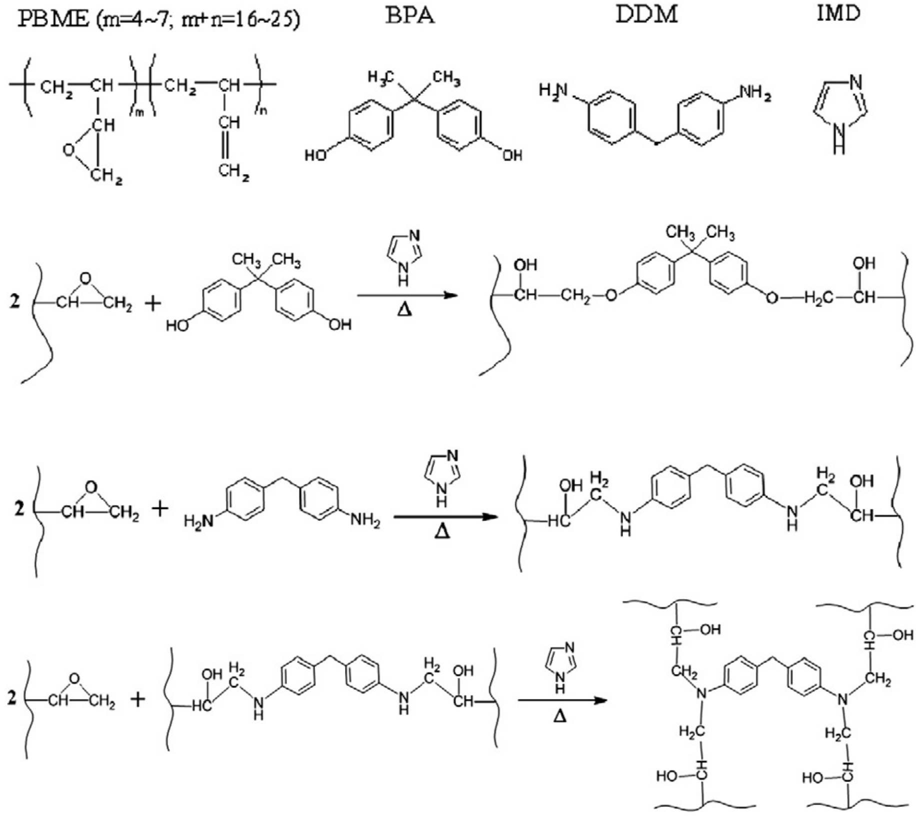

Fig. 1. Chemical formulas of the materials and the pictorial curing reactions involved in this study.