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Electronic Supplementary Information (ESI) of Evidence of chemical bonding formation at interface between epoxy polymer and isocyanate primer

Kazuhiro Sensui,^a Taishi Tarui,^a Takayuki Miyamae,^{*b} and Chiaki Sato^{*b, c}

a. Nissan Motor Co., Ltd., 1, Natsushima, Yokosuka, Kanagawa 237-8523, Japan.
b. Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan.
c. Tokyo Institute of Technology, Institute of Innovative Research, 4259-G2-20, Nagatsuta-cho, Midori-ku, Yokohama, 226-8503, Japan.

Experimental Section

Sample preparation

CaF₂ substrates with a diameter of 20 mm and thickness of 1 mm were purchased from the Pier Optics Co. Japan. To improve the adhesion between the epoxy polymer and the substrates, a 100 nm thick silica thin films were sputtered onto the calcium fluoride substrates. Chloroform solution of the precursor of the epoxy polymer was spin-coated on the silica coated substrate. After spin-coating, the films were cured at 80 °C for 18 h for the polymerization. Thicknesses of the epoxy polymers were about 200 and 2000 nm, for the SFG and ATR-IR, respectively.

0.5wt% of MDI butyl acetate solution was spin-coated on the 2000 nm thick epoxy polymer film at 3000 rpm for ATR-IR measurements.

Sum-Frequency Generation Vibrational Spectroscopy

For the SFG system, a mode-locked Nd:YAG laser (PL2231-50; EKSPLA, Lithuania) was used to generate the visible beam at 532 nm and to generate the frequency tunable infrared (IR) beam. Both the beams were irradiated to the sample surface with incident angles of 60° and 55°, respectively. The generated SFG signal was filtered with a holographic notch filter and the grating monochromator, and then detected using a photomultiplier tube. Further, the SFG spectra were collected using ssp polarization combination (s-polarized SF signal, s-polarized visible beam, and p-polarized IR beam) that scanned the IR frequency in the 1600–1800 cm⁻¹, 2200–2400 cm⁻¹, and 2750–3800 cm⁻¹ ranges. To minimize the influence of the water vapor and CO₂ absorption of the IR, the sample box was purged by the N₂ gas. The sample set up of the SFG experiments was shown in Figure S1.



Figure S1. Schematic illustration of the setup used for the SFG measurements under (a) dry condition and (b) in contacted with MDI solutions.



Figure S2. SFG spectra of epoxy polymer surface after contacting MDI solution and after rinsed by acetone. (Upper) Just after rinse by acetone. (Lower) After heated at 80 °C.