Structure analysis of a buried interface between organic and porous inorganic layers using spin-contrast-variation neutron reflectivity

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This work demonstrates the advantage of spin-contrast-variation neutron reflectivity (NR) for the structure analysis of a buried interface in a bilayer film comprising organic and inorganic layers of acrylic urethane resin and methylated silica (MePDS), derived from methyl-group-substituted perhydro-polysilazane. As the proton polarization $P_H$ changed from 0 to ±24%, the NR curve of the bilayer film varied significantly. These NR curves were not reproduced using global fitting with a standard bilayer model. The oscillation in the NR curve at $P_H = 0%$ was shifted slightly and non-negligibly from the fitting curve using the best-fit structure parameters for the curve at $P_H = 0%$. It was found from the shift of the oscillation that the density of the MePDS layer decreased within several nanometres of the interface, but the resin did not permeate the low-density MePDS layer.

1. Introduction

Nano-ordered organic–inorganic composite materials, known as hybrid materials, which consist of a molecular-level dispersion of organic and inorganic components, have been attracting attention for their use in high-functionality materials. The high degree of control over the composition and nanostructure of the materials results in improved mechanical, thermal, electrical, optical and chemical properties compared with the organic or inorganic materials alone (Srivastava, 2013).

The nanostructure analysis of the interface between the organic and inorganic components is important in the development of hybrid materials because strong coupling between these components is essential for achieving functionality. For example, small voids between the polymer and SiO$_2$ or SiC nanocomposites for power electronics devices reduce discharge endurance (Tanaka et al., 2004, 2005). Chemical bridging between rubber and silica in car tires is essential to increase elasticity and decrease inner friction (Sengloyluan et al., 2014). Systematic investigation of structure–property relationships will greatly advance the development of hybrid materials.

Neutron reflectivity (NR) and X-ray reflectivity (XR) are promising techniques that nondestructively measure the structure of buried interfaces between organic and inorganic layers in a multilayer film. NR has an advantage over XR for...
measuring buried interfaces because of the higher transmission of neutron beams (Russell, 1990; Stoev & Sakurai, 2020). Since the number of structure parameters of multilayer films is too large to determine the structure of the buried interface using a single NR curve, several contrast variation techniques, such as deuterium contrast variation (Crowley et al., 1991; Heinrich, 2016), magnetic contrast variation (Majkrzak & Berk, 1999), combined NR and XR (Nelson, 2006), and resonant XR (Wang et al., 2007) have been developed. However, these techniques have various limitations.

To overcome these limitations, we recently applied spin-contrast-variation (SCV) – which has been used for small-angle neutron scattering (SANS) – to NR (Kumada et al., 2019). SCV relies on the large variation of the coherent polarized neutron scattering length of a proton ($b_H$) as a function of the proton polarization ($P_H$) against the neutron spin direction (Knop et al., 1989, 1991).

$$b_H(P_H) = (-0.374 + 1.456P_H) \times 10^{-12} \text{ cm}. \quad (1)$$

Thus, as $P_H$ increases, the scattering length density (SLD) – the sum of the scattering length of atoms in a unit volume – of each layer of a multilayer film increases proportionally with the proton number density (Knop et al., 1991; Sears, 1992; Brandrup et al., 1999). The variation of SLD results in the variation of the NR curve. Multiple structure parameters of the multilayer films are determined by the $P_H$-dependent multiple NR curves.

We have developed methylated silica (MePDS) derived from methyl-group-substituted perhydropolysilazane (Me-PHPS) as a primer coating material for use between inorganic and organic materials (Niizeki et al., 2016; Akutsu et al., 2018). To prevent peeling and cracking due to thermal expansion and contraction of organic components, MePDS was made more flexible than conventional perhydropolysilazane (PHPS)-derived silica (PDS) by the partial substitution of oxygen (which bridges neighboring Si atoms via an Si—O—Si bond) with a methyl group. In addition, because the methyl group is hydrophobic, it is expected that MePDS will bind to organic resins more strongly than PDS.

SCV is good for the structure analysis of composite materials composed of high- and low-hydrogen-content layers, such as organic and inorganic materials. Generally, the SLD of organic materials varies with $P_H$ much more than that of inorganic materials because the number density of hydrogen in organic materials is much higher than that of inorganic materials. Thus, the scattering intensity, which is proportional to the square of the difference in their SLDs, varies greatly as a function of $P_H$. We previously used SCV for SANS measurements of the assembled structure of silica nanoparticles in model systems for car tires (Noda et al., 2016). In this study, we applied SCV-NR to the structure analysis of the buried interface between acrylic urethane resin and MePDS in a bilayer film. We demonstrate that SCV-NR is also useful for the structure analysis of organic–inorganic hybrid materials.

2. Experiment

2.1. Sample

The sample was a bilayer film of acrylic urethane resin on MePDS. The MePDS layer was prepared by spin-coating a mixture of 3% PHPS (AZ Electronic Materials Co. Ltd, Tokyo, Japan) and 1% Me-PHPS (Akutsu et al., 2018) in xylene. After a 25 × 25 × 1 mm single-crystal Si substrate was covered with the solution, it was rotated at a speed of 6000 r min$^{-1}$ for 60 s using a spin-coater (MS-A150, Mikasa Co. Ltd, Tokyo, Japan) and allowed to stand for 1 week at room temperature. The acrylic urethane resin was composed of acrylic polyol and polyisocyanate [Utanal (L) Clear, Ohashi Chemical Industries Ltd, Osaka, Japan]. A thinner (No. 7400), composed of toluene, methanol and ethyl acetate, was doped with 3.3 mM 4-methacryloyloxy-2,2,6,6-tetramethylpiperidine 1-oxyl free radical (TEMPO methacrylate, Aldrich, 730297) as a polarizing agent beforehand. Within a few minutes of the main resin, curing agent (M-60) and thinner being mixed at a volume ratio of 4:1:45, the solution was spin-coated on the MePDS-coated Si substrate at a speed of 6000 r min$^{-1}$ for 60 s. The film was then cured at 60°C for 12 h. The thinner evaporated, and thus the concentration of the polarizing agent in the resin increased to 34 mM. Elemental analysis of the MePDS powder was conducted at the Center of Instrumental Analysis, Ibaraki University. Calculated for CH$_3$.25O2.75N0.25Si: C, 10.10; H, 2.76; N, 2.94. Found: C, 9.99; H, 3.33; N, 2.69.

2.2. Proton polarization

The protons in the film samples were polarized using dynamic nuclear polarization (DNP), in which the nuclear spins are hyperpolarized by polarization transfer from electron spins in the polarizing agent to the nuclear spins (Wenekebach, 2016). In this study, instead of the cryogen-free apparatus used in the previous SCV-NR measurements (Kumada et al., 2018, 2019), we used conventional cryogen-filled DNP apparatus (Kumada et al., 2009) for the SCV-NR measurements because we expected that higher $P_H$ can be obtained due to the higher cooling power. The DNP apparatus comprised a horizontal-field superconducting Helmholtz coil magnet (JMTC-3.5T/50/SP, JASTEC, Tokyo, Japan) and a cryostat, microwave devices and a proton NMR circuit. The sample in the cryostat was cooled to 1.2 K by pumping liquid helium with a serially connected dry pump (NeoDry60E, Kashiya, Tokyo, Japan) and two booster pumps (SMB-C06 and SMB-C25, Shinko Seiki, Kobe, Japan). The sample was irradiated with microwaves with a frequency of 94 GHz from a Gunn oscillator (VCO-10-9415-10RI, VCSS, Rancho Palos Verdes, CA) and an amplifier (AMP-10-01300, Millitech, Northampton, MA) at 3.3 T to transfer polarization from electrons in the free radicals to protons. Because the number of protons in the film sample was too small to observe an NMR signal, we monitored the dynamically polarized proton signals of a 33 mM 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO)-doped polystyrene reference sample, which was set 17 mm above the film sample, to tune the magnetic field and microwave frequency and power.
2.3. NR measurement

The SCV-NR measurements were performed by placing the DNP apparatus in the SHARAKU polarized neutron reflectometer (BL17) of the Materials and Life Science Experimental Facility (MLF) at the Japan Proton Accelerator Research Complex (J-PARC) (Takeda et al., 2012; Akutsu-Suyama et al., 2020). Pulsed neutrons with the wavelength ($\lambda$) range 0.24–0.88 nm were polarized up to 98.5% using a polarizing Fe/Si supermirror, and then the film samples on the Si substrates were irradiated at incident angles $\theta = 0.3, 0.9$ and $2.7^\circ$ from the free-surface side. The spot size of the neutron beam was 20 mm high and 15 mm wide and was maintained by adjusting the slit width every time $\theta$ was changed. The unpolarized neutron reflectivity (UNR) curve was measured using unpolarized neutron beams and the unpolarized sample, whereas the polarized NR curves were measured using polarized neutrons and the proton-polarized sample. The polarization of the incident neutrons was inverted in parallel and perpendicular to the proton polarization every 30 s to measure the positively polarized neutron reflectivity (PNR) and negatively polarized reflectivity (NNR) curves almost simultaneously. All the NR measurements were carried out at 1.2 K in liquid helium. The NR curves were analyzed using the Motofit program (Nelson, 2006).

3. Results and analysis

3.1. Results

The symbols in Fig. 1 show the UNR, PNR and NNR curves of the film sample as a function of the magnitude of the scattering vector $Q$, where

$$Q = 4\pi \sin \theta/\lambda. \tag{2}$$

The oscillations with periods of 0.1 and 0.03 nm$^{-1}$ are related to the thicknesses of the MePDS and resin layers, respectively. The reflectivities of the PNR and NNR curves are much higher than that of the UNR curve over the whole $Q$ range. The critical $Q$ value of the total reflection of the PNR curve is much higher than that of the UNR and NNR curves, indicating that total reflection occurs at the resin layer in the PNR curve, but at the Si substrate in the UNR and NNR curves (see Section 3.2 for details). The visibility of the oscillation – which corresponds to the oscillation amplitude in the logarithmic graph – of the NNR curve is higher than that of the UNR curve, but that of the PNR curve is lower. This result suggests that, as $P_H$ increases, the reflection amplitudes at specific surfaces or interfaces become higher than those at the others. The intensity of the background electronic noise signal – observed as a plateau at the high-$Q$ limit – of the PNR and NNR curves is twice as large as that of the UNR curve. Because the intensity of the incident polarized neutron beam is approximately half that of the unpolarized beam, the intensity of the background signal normalized by the incident beam intensity of the PNR and NNR curves becomes larger than that of the UNR curve.

3.2. Analysis using the standard model

The solid lines in Fig. 1 show the global fitting curves using a standard bilayer model. The inset shows the SLD profiles used for the fitting of the UNR, PNR and NNR curves with a common set of structure parameters and $P_H$-dependent SLDs for the resin $(\rho_0^r, \rho_+^r, \rho_-^r)$ and for MePDS $(\rho_0^s, \rho_+^s, \rho_-^s)$, which are restricted to the calculated SLD $\rho_i(P_H)$:

$$\rho_i^0 = \rho_i(0), \tag{3}$$

$$\rho_i^+ = \rho_i(+P_{\text{DNP}}). \tag{4}$$

Figure 1

SCV-NR curves of the resin-on-MePDS bilayer film. Solid lines show the best-fit simulation curves using the standard bilayer model with SLD profiles in the inset. The structure parameters used for the fitting are shown in Table S1 of the supporting information.
where $P_{\text{DNP}}$ is the absolute value of proton polarization of the polarized sample. We stress that $P_{\text{H}}$ in the MePDS layer is the same as that in the resin layer because $P_{\text{H}}$ in organic materials is homogenized up to the micrometre length scale due to spin-diffusion under our DNP conditions (Miura et al., 2021). $\rho_i(P_{\text{H}})$ is obtained by substituting the density $d_i$, elemental composition $N_i$, coherent polarized-neutron scattering length $b_i$ and mass $m_j$ of element $j$ in resin ($i = r$) and MePDS ($i = s$) into

$$
\rho_i(P_{\text{H}}) = d_i N_i b_i (P_{\text{H}}) + \sum_j d_j N_j b_j,$$

and then finding the other SLDs and structure parameters.

Fig. 2 shows the best-fit SLDs, $\rho_i(P_{\text{H}})$ and $\rho_i(P_{\text{DNP}})$, which are obtained using $d_r = 1.30\, \text{g cm}^{-3}$ and $d_s = 1.30\, \text{g cm}^{-3}$, respectively. $P_{\text{DNP}} = 24\%$ was also determined by substituting $\rho_i^+$ into equation (4). $d_i$ is close to the densities of the main components of the resin, poly(methyl methacrylate) ($1.2\, \text{g cm}^{-3}$) and poly(urethanes) ($1.1-1.5\, \text{g cm}^{-3}$) (Brandrup et al., 1999), whereas $d_i$ is much smaller than the density of silica ($2.65\, \text{g cm}^{-3}$) because nano- and micropore networks are generated in polymer-derived ceramics (Wilhelm et al., 2005; Konegger et al., 2016, 2021; Akutsu et al., 2018). The porosity of spin-coated PDS is estimated to be 40% from the ratio in SLD between PDS and bulk silica (Akutsu et al., 2018), and thus that of MePDS is expected to be comparable.

The fitting curves reproduce the UNR and PNR curves, but not the NNR curve. The phase of the oscillation with a period of $0.1\, \text{nm}^{-1}$ in the NNR curve is shifted from that in the simulation using the best-fit structure parameters for the UNR curve. The oscillation is caused by the interference of reflected neutrons from the resin–MePDS interface and Si substrate. The distance between them is determined to be $64\, \text{nm}$ from the analysis of the UNR curve but $66\, \text{nm}$ from the NNR curve.

3.3. Analysis using the permeation model

Because the standard model uses a Gaussian smearing function to characterize the roughness and diffuseness of surfaces and interfaces, it cannot represent asymmetric roughness and diffuseness across an interface (Mizusawa et al., 2003). The fitting assumes that, from the MePDS layer to the resin layer across the interface, the pore network and MePDS are substituted for the resin at the same ratio [Fig. 3(a)]. If the resin permeates the pores of the MePDS layer, the porosity in the permeated volume will be lower than that in the MePDS layer [Fig. 3(b)]. We searched for the best-fit parameter using a

\[ \rho_i^+ = \rho_i (-P_{\text{DNP}}), \]
\[ \rho_i^0 = \rho_i (0), \]
\[ \rho_i^+ = \rho_i (+P_{\text{DNP}}), \]
\[ \rho_i^- = \rho_i (-P_{\text{DNP}}). \]
permeation model, which has a resin-permeated low-porosity MePDS sublayer (permeated sublayer) between the resin and MePDS layers. However, the deviation in the oscillation phase between the NNR curve and its fitting is worse than that in the standard model (not shown). This result indicates that the resin does not permeate into the pore network of the MePDS layer.

3.4. Analysis using the density gradient model

The density of a spin-coated PDS film within a few nanometres of the surface is lower than that inside the film (Akutsu-Suyama et al., 2020). Thus, a similar density gradient is expected to occur near the interface of the MePDS layer of the film sample. The solid lines in Fig. 4 show the global fitting of the UNR, PNR and NNR curves with the model in which the resin does not permeate the MePDS layer, and the density of the MePDS layer gradually decreases by 35% within 2.5 nm of the interface [Fig. 3(c)]. In other words, the porosity in the density gradient is higher than that inside the MePDS layer.

The fitting curves reproduce all the UNR, PNR and NNR curves, including the phase of the oscillation, much better than those in Fig. 1. Because the increase in SLD at the resin–MePDS interface (blue arrow in the inset) is much larger than that at the density gradient in the negatively polarized sample, the reflection amplitude at the interface is much larger. Thus, oscillation periods in the NNR curves are determined by the distances from the free surface and Si substrate to the interface. In contrast, because the increase in SLD at the density gradient (black arrow in the inset) is larger than that at the interface in the unpolarized sample, the reflection amplitude at the density gradient is larger. Thus, the oscillation period in the UNR curve is determined by the distances to the density gradient rather than to the interface. The thickness of the density gradient from the interface is determined to be 2.5 nm from the difference in the oscillation period between the NNR and UNR curves.

4. Discussion

This fitting result reveals that, although the porosity near the interface of the MePDS layer is higher than that inside, the resin does not permeate the pore network. Because the resin and curing agent were mixed before the spin-coating, they polymerized before permeation and the polymer was probably too large to permeate the pore network of the MePDS layer. This is not desirable for manufacturing hybrid materials because a smaller contact area between the resin and MePDS results in a higher risk of detachment. To decrease the risk, we propose that the pore network near the interface is permeated with the resin and curing agent successively before spin-coating of the resin layer. If the resin and curing agent permeate successively, they will polymerize in the pore network [Fig. 3(b)], and the polymer chains that extend from the pore will be entangled with those in the resin layer.

The advantage of the SCV-NR technique is that multiple NR curves can be obtained from a single sample with a single beam source. We used SCV-NR to discriminate between the reflected neutrons from the interface itself and the density gradient near the interface. However, other contrast variation techniques would struggle to discriminate between these two reflections. For example, if we observed such a small difference in oscillation period between multiple NR curves from multiple partially deuterated samples in deuterium-contrast-variation measurements, we could suspect that the difference arose from the structural reproducibility between samples. It would be more difficult to compare XR and NR curves than to compare SCV-NR curves because the coherent length of beams and optical layouts of the XR and NR
measurements, which determine properties including resolution and experimental error, are different for these curves. Magnetic contrast variation cannot vary contrast between non-magnetic layers. Resonant soft X-ray reflectivity (RSoXR) may be able to discriminate, because both RSoXR and SCV-NR change the contrast using a single sample and a single beam source. SCV-NR controls $b_H$ with polarizing protons, whereas RSoXR controls the scattering lengths of carbon and heavier elements by tuning the soft X-ray energy close to the absorption edges of light atoms (Wang et al., 2007). We should recognize the advantages of SCV-NR and other contrast variation techniques, such as RSoXR, for the structure analyses of buried interfaces.

Currently, doping of nonvolatile polarizing agents is the key point of SCV-NR measurements. We use TEMPO methacrylate rather than TEMPO, which is generally used for polarization of bulk samples, because TEMPO methacrylate does not vaporize from the surface of the nanometre-thick film samples at room temperature. However, it does vaporize when the sample is annealed at higher temperatures. To overcome this problem, we are developing a technique to dope vaporized TEMPO methacrylate and/or other TEMPO derivatives into polymer samples at higher temperatures. The vaporizing doping technique was established for TEMPO (Bunyatova, 1995) but not for TEMPO methacrylate and other derivatives due to their lower volatility and larger molecular size. Such improvements of the doping will extend the applicability of the SCV-NR technique to a wider variety of samples.

5. Conclusions

We used SCV-NR for the structure analysis of the interface between acrylic urethane resin and MePDS layers in a thin film. The UNR, PNR and NNR curves of the film were not reproduced by the global fitting with a standard bilayer model. In particular, the phase of the oscillation with a period of approximately 0.1 nm$^{-1}$ in the NNR curve was slightly but non-negligibly shifted from that of the simulation curve using the best-fit structure parameters for the UNR curve. A model assuming the permeation of the resin into the pore network of the MePDS layer resulted in worse fitting, that is, a larger shift in the oscillation phase. In contrast, the three NR curves were globally fitted with a model in which the MePDS layer density gradually decreased by 35% within 2.5 nm of the interface and the porosity increase was complementary. This fitting result revealed that, although a larger pore volume was generated near the MePDS layer interface, the resin did not permeate the pore network. Such structural information at the interface is important for the development of hybrid materials. We aim to establish the SCV-NR technique as a tool in quality management.

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