Supplementary Information (SI)

Buried interfacial structures in cellulose-reinforced styrene–butadiene rubber composites probed by sum-frequency generation spectroscopy

Tatsuki Abe,[a*] Ryosuke Ozawa,[b] Tomofumi Maekawa,[b] Yuta Tsuji,[c] Satoru Yamamoto,[a] and Keiji Tanaka[a,d*]

[a] Centre for Polymer Interface and Molecular Adhesion Science, Kyushu University, Fukuoka 819-0395, Japan

[b] Sustainable Polymers Laboratory, Asahi Kasei Corporation, Kanagawa 210-0863, Japan

[c] Faculty of Engineering Sciences, Kyushu University, Kasuga 816-8580, Japan

[d] Department of Applied Chemistry, Kyushu University, Fukuoka 819-0395, Japan

To whom correspondence should be addressed:

t-abe@cstf.kyushu-u.ac.jp (T.A.)

k-tanaka@cstf.kyushu-u.ac.jp (K.T.)

SFG spectra of PMMA at different tilt angles. To examine how the sample installation angle (θ) affects the elimination of SFG signals originating from the surface and the substrate interface, SFG spectroscopy was conducted on a 200 nm-thick film of poly(methyl methacrylate) (PMMA; M_n = 300k; PDI = 1.05; T_g = 403 K), a representative amorphous polymer. The film was prepared by spin-coating a toluene solution of PMMA onto a quartz substrate, followed by thermal annealing at 433 K for 24 h under vacuum. SFG measurements were then taken at different values of θ. Figure S1 shows the SFG spectra of the PMMA thin film obtained at θ = 0° and 9°. At θ = 0°, peaks corresponding to the symmetric and antisymmetric C-H stretching of CH_2 groups, and the symmetric C-H stretching of OCH_3 groups were observed at 2,912, 2,942, and 2,955 cm^{-1}, respectively.[S1] In contrast, no SFG signals were detected when the sample was measured at θ = 9°, suggesting that the SFG signals generated at the surface and the substrate interface were effectively deflected away from the detector under the tilted geometry.

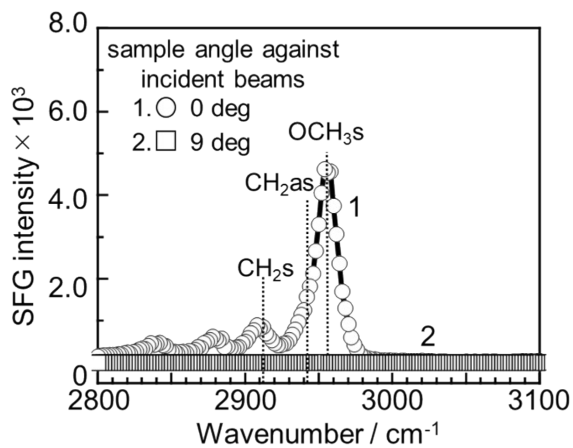

Figure S1. SFG spectra of a PMMA thin film measured at θ = 0° and 9°.

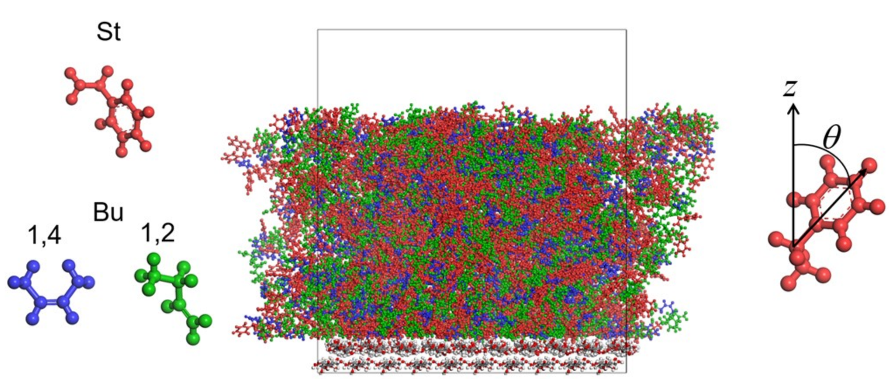

Figure S2. MD Simulation model and definition of the phenyl orientation angle.

Phenyl group orientation analysis by MD simulation. Figure S2 shows the MD simulation model and the definition of the phenyl orientation angle. The angle was defined as that between a vector lying in the phenyl ring plane and the z-axis (surface normal of the CNF surface). It was calculated from atomic coordinates obtained from the MD trajectories. Phenyl groups within 1 nm of the CNF surface were selected for the analysis. The frequency distribution was plotted at 10° intervals, as shown in Figure 5.

CNF dispersion analysis by visible transmittance. The transmittance of the kneaded SBR/CNF composite sheets used for the SFG measurements in Figure 4 was also evaluated using a U-4100 spectrophotometer (Hitachi High-Technologies Co., Tokyo, Japan). Figure S3 shows the visible-light transmittance spectra of the SBR6/CNF, SBR12/CNF, and SBR25/CNF sheets as a function of wavelength. Despite their similar thicknesses, the transmittance of the SBR25/CNF sheet was markedly higher than that of the SBR6/CNF and SBR12/CNF sheets, likely due to reduced light scattering. This result indicates improved CNF dispersibility in the SBR25 matrix. Better dispersion increases the effective interfacial area between the SBR matrix and CNF, which may also contribute to the stronger SFG response observed in Figure 4.

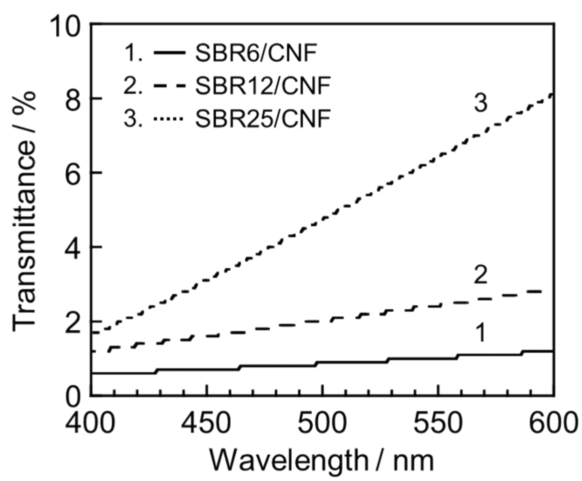

Figure S3. Transmittance of the kneaded SBR/CNF sheets with varying St content.

References

S1. Y. Tateishi, N. Kai, H. Noguchi, K. Uosaki, T. Nagamura and K. Tanaka, *Polym. Chem.*, 2010, **1**, 303–311.