Experimental report

Proposal:	9-12-665
Council:	10/2022
Title:	Unraveling molecular design-performance relationship in automobile tires
Research area:	Materials

This proposal is a new proposal

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Samples: silica nanoparticles

hydrogenated polybutadiene

hydrogenated polybutadiene/deuterated polybutadiene random copolymer

Instrument	Requested days	Allocated days	From	To
IN15	8	5	05/04/2023	10/04/2023
D22	1	1	06/04/2023	07/04/2023

Abstract:

The addition of fillers to rubbers is a powerful route to improving mechanical and other properties and designing next-generation engineering materials including automobile tires. There is general agreement that "bound rubber" (BR) (i.e., polymer chains physisorbed on the filler surfaces) is a critical parameter for rubber reinforcement. However, a molecular mechanism behind the "BR-induced reinforcement" is still missing in this comparatively mature field. Our previous investigations using neutron scattering/spectroscopy techniques and molecular dynamics simulations of a simplified carbon black (CB)-filled polybutadiene revealed the novel structures and dynamics of BR and the roles of the structural partitions and dynamical hierarchies in rubber reinforcement. We here expand this integrated methodology to industrially more interesting silica-reinforced rubbers. The bottleneck of silica-reinforced rubbers is the weak reinforcement effect compared to CB-filled rubbers. The comparison of the structures and dynamics of the BR between CB and silica filler surfaces through this research is a critical step toward material design insight into filled rubbers necessary for future tires.

Unraveling molecular design-performance relationship in automobile tires

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Goals. Tires are a key component of automotive supply chains and contribute greatly to vehicle safety and fuel efficiency. Carbon black (CB) filled elastomers are known as the most successful rubbers for the industry. Recently, silica (SiO_2) nanoparticles (NPs) have been paid great attention to improving the processability of rubbers and are being used as partial or even complete replacements for CB fillers in automobile tires, playing a critical role in creating environmentally "green" tires. While the property improvements achieved by the addition of inorganic nanoparticles are well understood empirically, the mechanism at the molecular level is still unclear. There is growing evidence that the bound rubber (BR) chains, either physically or chemically adsorbed on the nanoparticle surface, are responsible for the improved mechanical properties of PNCs. According to the seminal work of Simah and co-workers[1], the equilibrium bound chain on a solid surface is comprised of three distinct segment sequences: "trains" (adsorbed segments), "loops" (sequences of free segments connecting successive trains), and "tails" (non-adsorbed chain ends). A critical yet unanswered question is: "*How do the nanometer-scale topological polymer structures on the nanoparticle surface control the macroscopic mechanical properties?*" This is the question we set out to answer. A suite of neutron scattering techniques is integrated with isotope labeling to directly probe the structure of the BR chains on the nm length scale, as well as the dynamics on the time scale of up to 100 ns. In addition, coarse-grained molecular dynamics simulations are performed to complement the experimental results and to further resolve details that are not accessible experimentally. The results are then correlated with the resulting mechanical properties.

Experimental. Spherical SiO_2 filler (with an average diameter of 112 ± 8 nm, Nippon Shokubai) and monodisperse hydrogenated PB (hPB, $M_w = 45.1$ kg/mol, $M_w/M_n = 1.08$, 1,4 addition = 80 %, "hPB50k", Sumitomo Rubber), and deuterated PB (dPB, $M_w = 50$ kg/mol, $M_w/M_n = 1.08$, 1,4 addition = 80 %, "dPB50k", Polymer Sources Inc.) were used. Since the interaction between SiO_2 and PB is much weaker than that between CB and PB, bis(3-triethoxysilylpropyl)disulfide (SI266, $(C_2H_5O)_3Si(CH_2)_3S_2(CH_2)_3(C_2H_5O)_3Si$, the density of 1.08 g/ml, Evonik) was used as the silane coupling agent. The BR layer on the surface of the spherical SiO_2 filler (hereafter referred to as "BR-coated SiO_2 filler") was prepared by solvent leaching. The details have been described elsewhere[2, 3]. The filler loading was adjusted to a volume fraction of 20 %, which is below the percolation threshold (≈ 30 %), so that the effect of polymer bridges between adjacent fillers can be ruled out. The thickness of the BR (without the matrix) was estimated to be 5.4 nm based on a TGA experiment. In addition, given that the neutron scattering length density (SLD_N) of SiO_2 ($SLD_{N,SiO2} = 3.2 \times 10^{-4}$ nm^{-2}) falls between the hPB ($SLD_{N,hPB} = 0.4 \times 10^{-4}$ nm^{-2}) and dPB ($SLD_{N,dPB} = 6.5 \times 10^{-4}$ nm^{-2}), contrast-matched neutron experiments with a hPB/dPB random copolymer as the matrix are ideal. For the purpose of this study, a hPB/dPB random
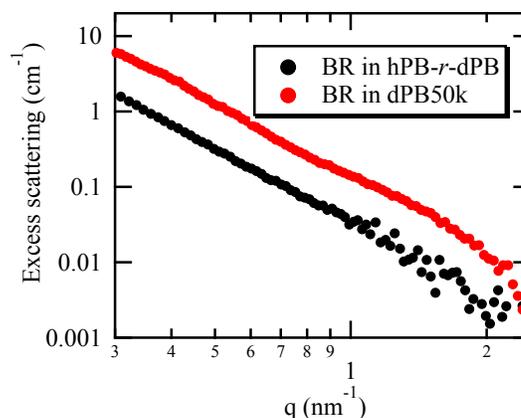

Figure 1. Comparison of the excess scattering of the BR-coated SiO_2 in the different matrices at 50 °C after the corrections.

copolymer (M_n=49.3 kg/mol, M_w/M_n= 1.04, 1,4 addition = 94 %, the composition of hPB/dPB =53/47 (by weight)) was synthesized in collaboration with the Jülich Centre for Neutron Science Deuteration Program. SANS experiments were performed at the NCNR, NIST for the BR-coated SiO_2 in dPB50k matrix and at the Institut Laue Langevin (ILL) for the BR-coated SiO_2 in the hPB-r-dPB matrix. We also prepared the SiO_2 filler (containing SI266, but without a hydrogenated BR layer) embedded in dPB50k or hPB-r-dPB with a volume fraction of 20 % (referred to as "SiO_2 in dPB50k" and "SiO_2 in hPB-r-dPB") as controls (*i.e.*, background). The temperature of the sample was systematically varied from 25 °C to 150 °C. NSE measurements were performed on the CHRNS-NSE instrument at the NCNR for the BR-coated SiO_2 in dPB50k and the IN15 beamline at the ILL for the BR-coated SiO_2 in hPB-r-dPB. The measurements were performed at the four q values of 0.8 nm^{-1}, 1.1 nm^{-1}, 1.5 nm^{-1}, and 2.0 nm^{-1}. The Fourier time domain was investigated up to 100 ns at the NCNR and ILL.

Figure 2. Comparison of $S(q,t)/S(q,0)$ for the BR-coated SiO_2 in the different matrices at the given two q values and 150 ºC.

Results. Figure 1 shows the excess scattering of the BR-coated SiO_2 in the two different matrices at 50 °C after the background corrections. The SANS profile for the contrast-matched system (i.e., hPB-r-dPB as the matrix) was found to be identical to that of the non-contrast-matched sample (i.e., dPB50k as the matrix), with the exception of the scattering intensity, which was found to be about three times weaker than that of the non-contrast-matched sample. **Figure 2** shows the $S(q,t)/S(q,0)$ for the non-contrast-matched sample (i.e., dPB50k as the matrix) is in good agreement with that of the contrast-matched sample (i.e., hPB-r-dPB as the matrix). It should be emphasized that $S(q,t)/S(q,0)$ for the contrast-matched sample is noisy due to the lower scattering contrast, as shown in **Figure 1**, and high incoherent scattering signals. Therefore, it is reasonable to conclude that the cross-term contributions due to the contrast mismatch[4] are minimal for the non-contrast-matched sample. Since neutron backscattering (NBS) mainly probes the hydrogen atom motions, the non-contrast-matched sample is more suitable to study the BR dynamics. Consequently, we used the SANS, NBS, and NSE data for the non-contrast-matched sample for detailed data analysis.

Our integrated experimental-computational study reveals the following findings on the interfacial structures and dynamics of the chemisorbed BR on the SiO_2 surface in the melt[5]: (i) the BR consists of two components (*i.e.*, loops and tails) with their fractions on the SI266 monolayer. There is no inner layer of less than 1 nm thick, which does not allow the penetration of matrix chains and has been identified in the physisorbed BR chains on the CB surface[3]; (ii) the loops, the minority
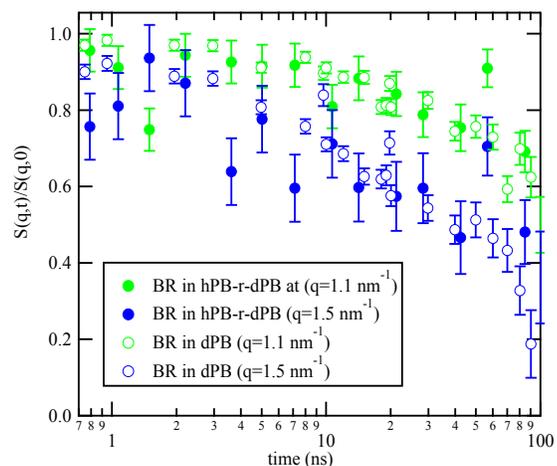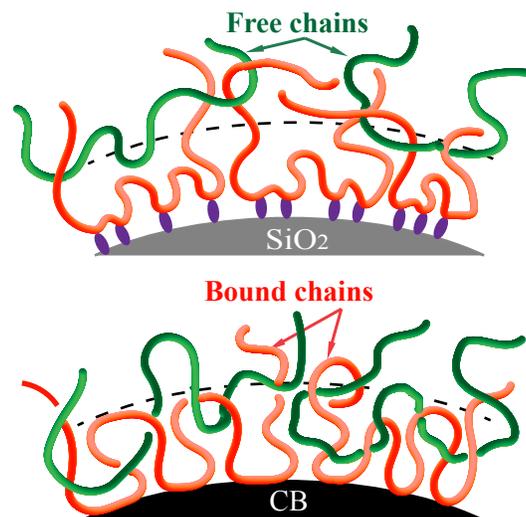

Figure 3. Schematic chain conformations of the bound rubber (BR) on the SiO_2 (top) and CB (bottom). The BR chains are shown in red. The purple elongated circles correspond to the SCA molecules, and free chains in a polymer matrix are shown in green. Note that there are trains (an immobile fraction of the BR chains) strongly adsorbed on the CB surface.

of the BR, exist mostly in the vicinity of the SiO$_2$ surface; (iii) the tails, the majority of the BR, extend into the matrix and interdigitate with the matrix chains. Further comparisons with the BR on the CB surfaces reveal the following similarities in the interfacial structures and dynamics of the loops and tails: (iv) the average segmental dynamics of the loops and tails on the SiO$_2$ and CB surfaces remain unchanged; (v) the tails on both the SiO$_2$ and CB surfaces extend into the matrix to a similar extent and interdigitate with the matrix chains. However, as summarized in **Figure 3**, the results also reveal the remarkable difference: (vi) the average loop size on the SiO$_2$ surface is much shorter than that on the CB surface, and the grafting density of the loops on the SiO$_2$ surface is about 7 times higher than that on the CB surface. As a result, such small and dense loops on the SiO$_2$ surface prevent interdigitation with the matrix polymer chains. Combined with the macroscopic mechanical analysis, we conclude that the large, uncrowded loops on the filler surface facilitate the interdigitation with the matrix polymer chains, thereby establishing a strong connectivity between the matrix and filler via BR, leading to stronger and more flexible material performance.

References
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