Lubricants

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Oil-Soluble Polymer Brush Grafted Nanoparticles as Effective Lubricant Additives for Friction and Wear Reduction

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Abstract: *The development of high performance lubricants has been driven by increasingly growing industrial demands and environmental concerns. Herein, we demonstrate oil-soluble polymer brush-grafted inorganic nanoparticles (hairy NPs) as highly effective lubricant additives for friction and wear reduction. A series of oil-miscible poly(lauryl methacrylate) brush-grafted silica and titania NPs were synthesized by surface-initiated atom transfer radical polymerization. These hairy NPs showed exceptional stability in poly(alphaolefin) (PAO) base oil; no change in transparency was observed after being kept at −20, 22, and 100°C for ≥55 days. High-contact stress ball-on-flat reciprocating sliding tribological tests at 100°C showed that addition of 1 wt% of hairy NPs into PAO led to significant reductions in coefficient of friction (up to ≈40%) and wear volume (up to ≈90%). The excellent lubricating properties of hairy NPs were further elucidated by the characterization of the tribofilm formed on the flat. These hairy NPs represent a new type of lubricating oil additives with high efficiency in friction and wear reduction.*

Lubricants play an indispensable role in enhancing the durability and efficiency of automotive engines and industrial machinery. Fully formulated engine lubricants are composed of a base oil, such as polyalphaolefin (PAO), and a variety of additives including anti-wear (AW) agents, friction reducers, antioxidants, detergents, and viscosity index improvers.[1] The most common AW and friction reduction agent is zinc dialkyldithiophosphate (ZDDP).[2] Although widely used, it has been reported that ZDDP may cause damage to the catalysts in catalytic converters, and the sulfur emission from ZDDP also raises an environmental concern.[1b] Despite progress in the lubricant industry, as evidenced by the increasingly longer intervals for engine oil changes for vehicles, the sheer ubiquity of these systems means that even a small increase in lubricant performance could save a huge amount of energy because of the large number of vehicles on the road. This prospect, coupled with increased consideration of environmental protection, drives the pursuit of more efficient and environmentally benign lubricant additives. Nanoparticles (NPs) have been suggested to have good potential as effective lubricant additives for reducing friction and wear,[3–6] and various NPs have been evaluated, including metals,[3] metal oxides,[4] and metal sulfides.[5] Spherical NPs can behave like rolling elements at local asperities and create, along with base oils, load-bearing films between rubbing solids, reducing surface-to-surface contact and thus decreasing interfacial friction. Moreover, NPs can be physically pressed by the mechanical load onto the contact area to form tribofilms, protecting the rubbing surfaces. To realize tribological benefits, the NPs must be well dispersed in base oils, forming homogeneous dispersions that exhibit long-term stabilities. While various methods have been employed to disperse NPs in base oils, achieving the full potential of NPs as lubricant additives remains a great challenge.

Polymer brush-grafted NPs, also called hairy NPs, consist of a core (inorganic, metallic, or polymeric) and a layer of polymer chains densely tethered by one end by a covalent bond on the core's surface.[7] Among various intriguing properties of hairy NPs, their impressive dispersibility in good solvents are especially noteworthy. The favorable enthalpic interactions between polymer brushes and solvents and the entropic steric repulsions among hairy NPs impart superior solubility and stability in good solvents. Furthermore, polymer brushes have been shown to exhibit excellent lubrication properties.[8] Nevertheless, the tremendous potential of hairy NPs as additives for lubricating oils has not yet been explored. Herein, we report that oil-soluble hairy NPs are highly effective lubricant additives for friction and wear reduction, while exhibiting exceptional long-term stability in PAO.

To demonstrate this concept, we first synthesized poly(lauryl methacrylate) (PLMA) brushes from initiator-functionalized, 23.8 nm silica NPs (Scheme 1) by surface-initiated atom transfer radical polymerization (SI-ATRP). PLMA is known to be soluble in PAO.[1a,8e] The initiator silica NPs were prepared by immobilizing a monochlorosilane-terminated ATRP initiator onto the surface of silica NPs.[9a,10] To better control the SI-ATRP and facilitate the characterization of the grafted chains, we added a free initiator, ethyl 2-bromoisobutyrate (EBiB), into the polymerization mixtures. Many researchers have reported that the molecular weights and polydispersities of the grafted polymers on NPs are essentially identical to those of the free polymers formed from the free initiators.[7e,g,9a] Four PLMA hairy silica NP samples with differing molecular weights were made and purified.[10] The corresponding free polymers were analyzed by size

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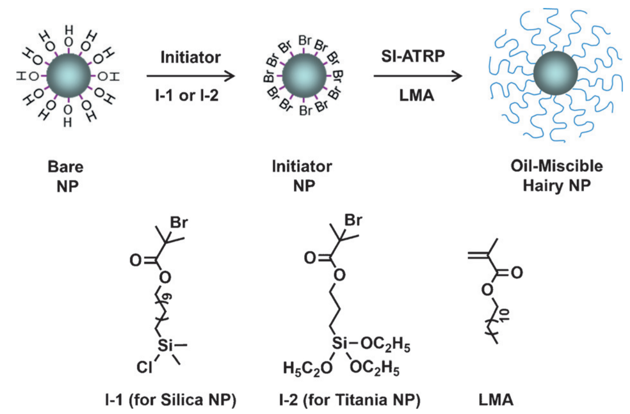

Scheme 1. Synthesis of oil-soluble poly(lauryl methacrylate) (PLMA) brush-grafted silica and titania NPs by surface-initiated atom transfer radical polymerization (SI-ATRP).

exclusion chromatography (SEC) relative to polystyrene standards, and the number-average molecular weights ($M_{n,SEC}$) were 38.0, 21.7, 11.8, and 4.1 kDa, respectively, with polydispersity indices (PDIs) of < 1.15 (Table 1). Thermogravimetric analysis (TGA) indicated that the weight retention at 800 °C of hairy NPs decreased with increasing brush molecular weight.[10] Transmission electron microscopy (TEM) study of hairy silica NPs cast from their dispersions in $CHCl_3$, a good solvent for PLMA, revealed that the hairy NPs self-assembled into close-packed patterns, and the interparticle distance decreased with decreasing brush molecular weight (Figure 1 A–D). By using degrees of polymerization (DPs),[10] TGA data, and NP size, the grafting densities of four samples were calculated and found to be in the range of 0.67–0.72 chains/nm^2 (Table 1). If we assume that the grafted polymer chains form a uniform brush film around the core NP in the dry state, the film thickness was calculated to be 14.1, 10.2, 7.9, and 1.6 nm, respectively, for the four hairy silica NP samples.

Table 1: Characterization data for PLMA brush-grafted silica and titania NPs and corresponding free polymers.

Hairy NPs[a]	DP	$M_{n,SEC}$ [kDa][c]	PDI[c]	Grafting density σ [chains nm^{-2}][d]
HNP-SiO_2-38.0k	117[b]	38.0	1.09	0.70
HNP-SiO_2-21.7k	66[b]	21.7	1.10	0.72
HNP-SiO_2-11.8k	31[b]	11.8	1.13	0.72
HNP-SiO_2-4.1k	5[b]	4.1	1.14	0.67
HNP-TiO_2-21.5k	66[e]	21.5	1.10	1.27[e]
HNP-TiO_2-16.2k	57[b]	16.2	1.12	0.83
HNP-TiO_2-8.1k	22[b]	8.1	1.16	0.80

[a] HNP = hairy NPs; the $M_{n,SEC}$ is appended to the end of the sample name. [b] The degree of polymerization (DP) was calculated using the monomer conversion and the molar ratio of monomer to the sum of free and surface initiators. [c] The $M_{n,SEC}$ and polydispersity index (PDI) were obtained by SEC relative to polystyrene standards. [d] The grafting densities of polymer brushes were calculated by using TGA data, DPs, and the core NP size (23.8 nm for SiO_2 NPs from TEM and 15 nm for TiO_2 NPs from the manufacturer). [e] Considering the similar molecular weights from SEC for HNP-SiO_2-21.7k and HNP-TiO_2-21.5k, the DP = 66 of HNP-SiO_2-21.7k was used in the calculation of the grafting density of HNP-TiO_2-21.5k.

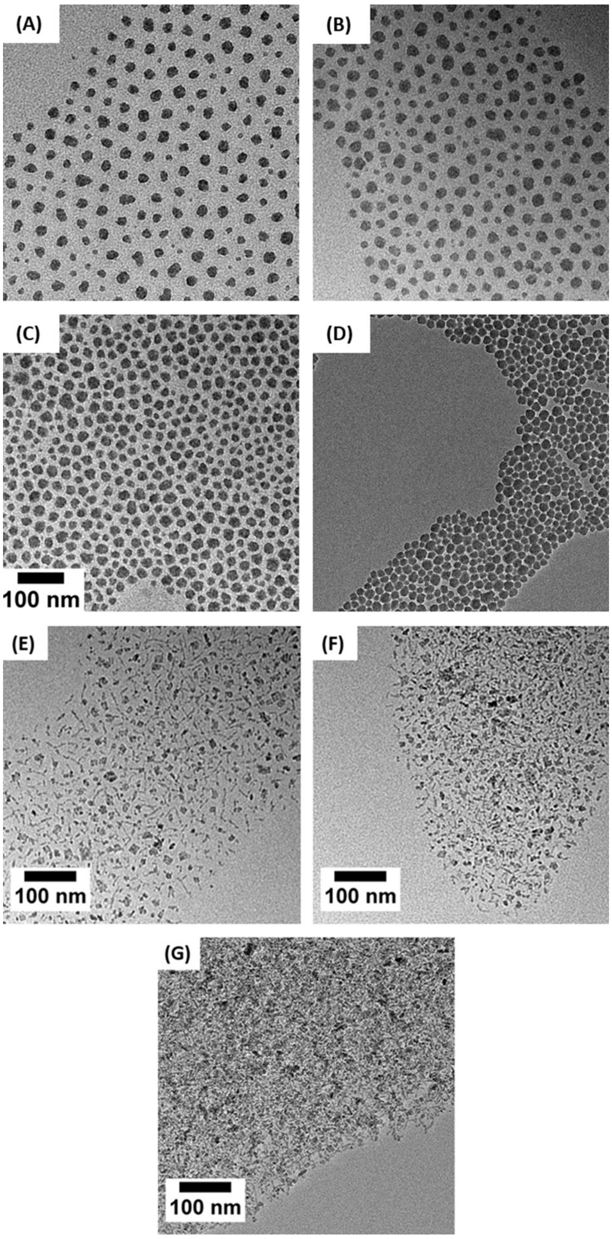

Figure 1. Bright-field TEM images of PLMA brush-grafted silica NPs with $M_{n,SEC}$ of 38.0 kDa (A), 21.7 kDa (B), 11.8 kDa (C), and 4.1 kDa (D), and PLMA brush-grafted titania NPs with $M_{n,SEC}$ of 21.5 kDa (E), 16.2 kDa (F), and 8.1 kDa (G). The scale bars for A, B, C, and D are the same. The hairy NPs were cast onto carbon-coated, copper TEM grids from dispersions in a good solvent ($CHCl_3$ for hairy silica NPs and THF for hairy TiO_2 NPs) with a concentration of 4 mg mL^{-1}.

All four batches of the hairy silica NPs could be well dispersed by ultrasonication in a lubricating base oil, PAO Spectrasyn^{TM} 4 (Exxon-Mobile), forming completely transparent dispersions as if no NPs were present. To examine the stability of hairy silica NPs in PAO, three 1 wt % PAO dispersions of HNP-SiO_2-4.1k were kept at −20 °C, 22 °C, and 100 °C, respectively. The dispersions stayed clear and no change in transparency was observed after 55 days (Figure 2 A,B), demonstrating the superior stability of these hairy NPs in PAO.

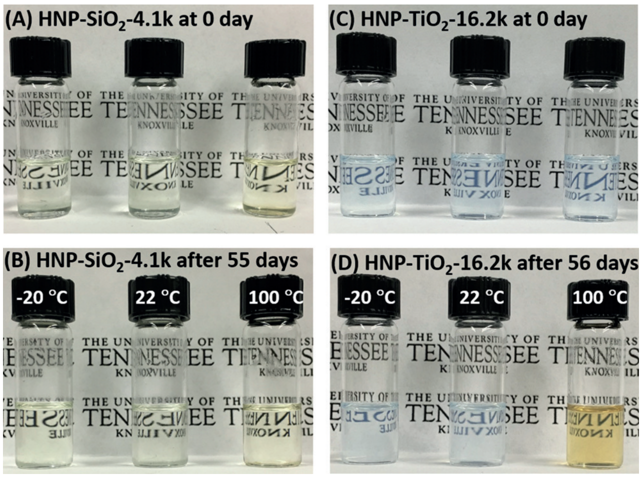

Figure 2. Photos of 1 wt% dispersions of HNP-SiO$_2$-4.1k in PAO in the initial state (A) and after being kept at −20, 22, 100 °C for 55 days (B), and 1 wt% dispersions of HNP-TiO$_2$-16.2k in PAO in the initial state (C) and after being kept at −20, 22, 100 °C for 56 days (D).

The lubricating performances of 1 wt% PAO dispersions of four hairy silica NP samples were evaluated using a Plint TE-77 tribo-tester in a ball-on-flat (52100 steel ball against CL35 cast iron flat) reciprocating configuration at 100 °C. The normal load was 100 N, the oscillation frequency was 10 Hz with 10 mm stroke, and the sliding distance was 1000 m. Two repeat tests were carried out for each lubricant and averaged. The wear volumes were measured using a Wyko NT9100 optical profilometer after each tribological test. The results are summarized in Figure 3 and Table 2. For neat PAO, the coefficient of friction (COF) started below 0.08, but rapidly increased to above 0.14, indicating that scuffing occurred.[11] The base oil exhibited some recovery from this "wear-in" process, reaching a COF of 0.11 at 115 m, from which a gradual increase to 0.14 was observed over the testing period. The addition of 1 wt% of hairy silica NPs into the PAO greatly improved the lubricating performance: for HNP-SiO$_2$-38.0k, the COF was noticeably lower than that of neat PAO over the entire sliding experiment, approaching 0.12 at 1000 m. The addition of 1 wt% HNP-SiO$_2$-21.7k had a similar effect on COF, with a slightly lower value of 0.11 at 1000 m. The use of lower molecular weight samples, HNP-SiO$_2$-11.8k and -4.1k, showed a marked improvement in COF even over their higher molecular weight analogues, with values lower throughout the testing range and the final COFs around 0.10 at 1000 m; HNP-SiO$_2$-4.1k performed slightly better in the beginning and at the end of the testing with the COF at 1000 m reduced by ≈30% compared with neat PAO. Overall, there appears to be a general trend that with decreasing brush molecular weight, the friction reduction increases. In addition, all of the samples showed a marked decrease in wear volume (Table 2), partially owing to the prevention of scuffing at the beginning of the tribological test.

Table 2: Wear volumes for both balls and flats from tribological tests.

Lubricant Sample	Wear Volume Flat ($\times10^7$ μm^3)	Wear Volume Ball ($\times10^7$ μm^3)
PAO	112.99	0.786
PAO + 1 wt% PLMA	19.08	0.059
PAO + 1 wt% HNP-SiO$_2$-38.0k	15.20	0.091
PAO + 1 wt% HNP-SiO$_2$-21.7k	16.48	0.157
PAO + 1 wt% HNP-SiO$_2$-11.8k	17.48	0.035
PAO + 1 wt% HNP-SiO$_2$-4.1k	8.12	0.052
PAO + 1 wt% HNP-TiO$_2$-21.5k	14.60	0.066
PAO + 1 wt% HNP-TiO$_2$-16.2k	8.17	0.065
PAO + 1 wt% HNP-TiO$_2$-8.1k	9.50	0.027

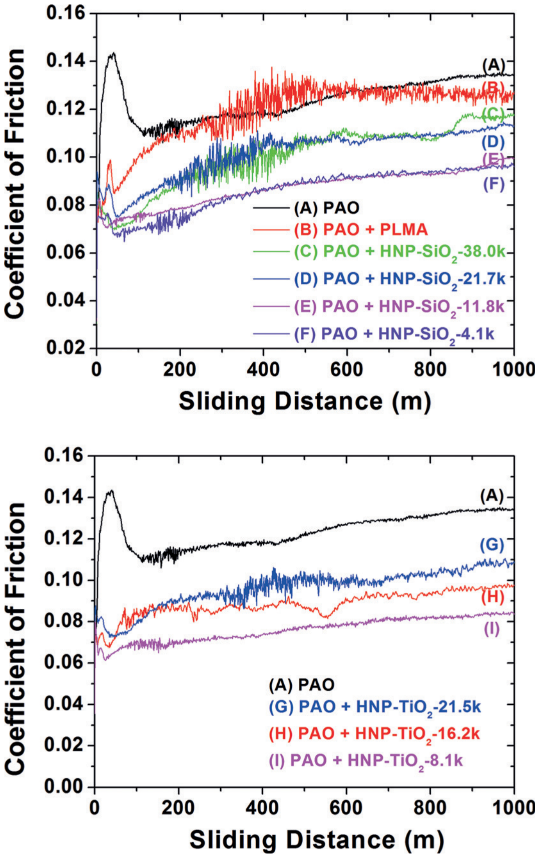

Figure 3. Friction curves for PAO SpectraSyn^{TM} 4 (A), PAO containing 1 wt% of free PLMA with a $M_{n,SEC}$ of 38.0 kDa (B), HNP-SiO$_2$-38.0k (C), HNP-SiO$_2$-21.7k (D), HNP-SiO$_2$-11.8k (E), HNP-SiO$_2$-4.1k (F), HNP-TiO$_2$-21.5k (G), HNP-TiO$_2$-16.2k (H), and HNP-TiO$_2$-8.1k (I). The tribological tests were performed using a Plint TE-77 tribo-tester at 100 °C under a point contact load of 100 N for a sliding distance of 1000 m.

Free polymer PLMA with a $M_{n,SEC}$ of 38.0 kDa was tested for comparison with hairy silica NPs. As shown in Figure 3, the 1 wt% solution of free PLMA in PAO performed similarly to neat PAO for the most part of the sliding, with slightly better performance in the beginning and the end of the experiment. Note that scuffing was not observed for the PAO lubricants additized with 1 wt% of either free PLMA or hairy NPs, likely owing to the electrostatic interactions between the polar ester groups of PLMA and the positively charged metallic surface, which help reduce direct metal–metal asperity contact-induced adhesion to prevent micro-welding or scuffing. Because the 1 wt% solution of free PLMA in PAO contained more polymer than any of the tested hairy NP-additized PAO lubricants, it can be inferred that a substantial portion of the benefit of blending hairy NPs into PAO stems from the inorganic NPs, though it is unclear if the polymer brush lubrication mechanism operates here owing to the much harsher conditions used compared with those typical for brush lubrication studies.[8] This is further bolstered by the apparent superiority of lower molecular weight samples in friction reduction, which is likely a result of their high number density of NPs at 1 wt %. To investigate the concentration effect of hairy silica NPs on lubrication performance, tribological tests were carried out using three additional dispersions of HNP-SiO_2-21.7k in PAO with concentrations of 0.25, 2.0, and 4.0 wt %. The COF was observed to decrease with increasing NP concentration, but there was a limit; the 4.0 wt % lubricant performed only slightly better than the 2.0 wt % sample.[10] Note that at 2.0 wt % HNP-SiO_2-21.7k performed similarly to HNP-SiO_2-11.8k and -4.1k.

Given these results, the inorganic NP core itself appears to play a critical role in friction reduction. To further demonstrate the potential of hairy NPs as additives for lubricating oils and to confirm the observed molecular weight effect, we synthesized PLMA brush-grafted TiO_2 NPs and studied their tribological properties. Note that TiO_2 NPs have previously been explored as a lubricant additive.[4a,6c,12] Anatase TiO_2 NPs with a size of 15 nm were functionalized with a triethoxysilane-terminated ATRP initiator.[10,9b] Three PLMA brush-grafted TiO_2 NP samples with $M_{n,SEC}$ values of 21.5, 16.2, and 8.1 kDa were made by SI-ATRP. Figure 1 E–G shows the TEM images of the three hairy TiO_2 NP samples cast from THF dispersions. In contrast to nearly spherical SiO_2 NPs, TiO_2 NPs were irregular in shape with the presence of plate- and rod-like nanostructures. Like the hairy silica NPs, the interparticle distance from TEM decreased and the weight retention at 800 °C of hairy titania NPs from TGA increased with decreasing brush molecular weight.[10] The characterization data for hairy TiO_2 NP samples and the corresponding free polymers are summarized in Table 1. To gain an idea about the brush grafting densities, we assumed that the TiO_2 NPs were spherical with a size of 15 nm, the size from the manufacturer, and calculated the grafting densities, which were in the range of 0.80–1.27 chains/nm^2. We also note here that the ^1H NMR spectra of hairy TiO_2 NPs and the free PLMA in $CDCl_3$ were essentially identical,[10] which clearly demonstrated the high mobility of the grafted chains in a good solvent.

All of the hairy TiO_2 NPs could be well dispersed in PAO and form stable dispersions as hairy silica NPs. To study the stability in PAO, HNP-TiO_2-16.2k was selected and three 1 wt % dispersions in PAO were made (Figure 2 C). The slightly white color might be caused by the higher refractive index of anatase TiO_2 NPs ($n_D = 2.488$ in contrast to 1.460 for silica). As for HNP-SiO_2-4.1k, the three dispersions were kept at −20, 22, and 100 °C, respectively. After 56 days there were no changes in transparency observed, except the appearance of a slightly yellow color for the dispersion kept at 100 °C, which was likely due to the oxidation of the residual ATRP Cu/ligand complex in the hairy NPs.

The tribological properties of 1 wt % hairy TiO_2 NPs in PAO were investigated using the same tribo-test as that for hairy silica NPs. All of the hairy TiO_2-additized PAO lubricants exhibited lower COFs in the entire sliding processes compared with neat PAO, and there was a clear trend that the COF decreased with decreasing brush molecular weight (Figure 3 G–I). At the end of sliding (1000 m), the COFs of PAO lubricants containing 1 wt % of HNP-TiO_2-21.5k, -16.2k, and -8.1k were 0.11, 0.10, and 0.08, respectively, in contrast to 0.14 for neat PAO. A ≈40 % reduction in friction was observed for the lowest molecular weight sample, demonstrating the exceptional lubricating performance of these TiO_2 NPs. The COF reduction appeared to be larger than that of hairy SiO_2 NPs at similar molecular weights, which could be caused by the differences in brush grafting density, the size, shape, number, and chemical composition of core NPs. Like the addition of 1 wt % hairy silica NPs, the wear was also reduced significantly (Table 2); >90 % reductions in wear volumes of iron flats were observed for the two lower molecular weight hairy TiO_2 nanoparticle samples. We note here that HNP-TiO_2-16.2k and HNP-SiO_2-4.1k performed comparably to the commercially used ZDDP and amine-phosphate antiwear agents,[10,14c] and more encouragingly HNP-TiO_2-8.1k exhibited better friction behavior than both of the commercial ones.[10,14c]

The observed friction and wear reductions for hairy NP-additized PAO lubricants are believed to result from the function of NPs at the interfacial zone between the two rubbing surfaces and the formation of tribofilms. To characterize the tribofilm, we used the focused ion beam (FIB) technique to lift out a small, thin cross-section from the wear scar on the iron flat tested with the PAO lubricant containing 1 wt % HNP-SiO_2-4.1k and examined the area near the surface zone with TEM. As shown in Figure 4 A, a 200–400 nm thick tribofilm can be clearly seen between the cast iron substrate and the carbon layer (for protecting the surface during the FIB process). A closer examination revealed that the tribofilm is an amorphous matrix embedded with small nanocrystals (Figure 4 B). Interestingly, both the thickness and morphology of the NP-formed tribofilm are similar to the tribofilms formed by organic AW additives such as ZDDPs[2] or ionic liquids.[13] Energy-dispersive X-ray spectroscopy (EDS) analysis showed that the tribofilm contained high concentrations of silicon, iron, and oxygen. We believe that under the rather harsh tribological testing conditions (a point contact load of 100 N at 100 °C), complex mechano-chemical

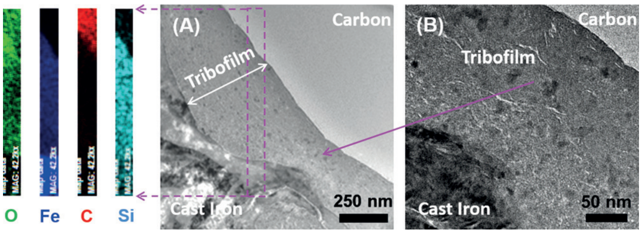

Figure 4. A) Transmission electron micropscopy (TEM) micrograph of the cross-section of the wear scar on the cast iron flat tested with 1 wt % HNP-SiO_2-4.1k-additized PAO. The element mapping data of Si, C, Fe, and O of the selected area are shown on the left. The cross-section TEM sample was prepared using the focused ion beam (FIB) technique. B) Higher magnification TEM image of the area of the tribofilm pointed to by the arrow.

reactions, which involved hairy NPs, occurred, producing a nanostructured tribofilm on the wear track. Such a dynamic, self-healing tribofilm provided a protective boundary for the underneath material, thereby preventing scuffing and reducing friction and wear.[14]

In summary, we synthesized a series of oil-soluble polymer brush-grafted SiO_2 and TiO_2 NPs by SI-ATRP and demonstrated that they are a promising class of friction- and wear-reduction additives for lubricating oils. The hairy NPs can be well dispersed in PAO and exhibited exceptional stability at both low and high temperatures with no changes in transparency for ≥ 55 days. Significant reductions in both COF and wear were observed with the addition of 1 wt% hairy NPs in PAO. We believe that using oil-miscible polymer brushes to functionalize inorganic NPs makes it possible to achieve the full potential of NPs as lubricant additives for friction and wear reduction, opening up opportunities to further improve durability and efficiency.

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Keywords: friction reduction · lubricant additives · nanoparticles · polymer brushes · polymerization

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