Enhanced Mechanical Properties of Polymer Nanocomposites Using Dopamine-Modified Polymers at Nanoparticle Surfaces in Very Low Molecular Weight Polymers

Na Kyung Kwon, † Hyunhong Kim, † Im Kyung Han, † Tae Joo Shin, ‡ Hyun-Wook Lee, ‡ Jongnam Park, * † ‡ † and So Youn Kim * † ‡

†School of Energy and Chemical Engineering and ‡UNIST Central Research Facilities and School of Natural Science, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulsan 44919, Republic of Korea

Supporting Information

ABSTRACT: While incorporation of nanoparticles in a polymer matrix generally enhances the physical properties, effective control of the nanoparticle/polymer interface is often challenging. Here, we report a dramatic enhancement of the mechanical properties of polymer nanocomposites (PNCs) using a simple physical grafting method. The PNC consists of low molecular weight poly(ethylene glycol) (PEG) and silica nanoparticles whose surfaces are modified with dopamine-modified PEG (DOPA-mPEG) brush polymers. With DOPA-mPEG grafting, the nanoparticle surface can be readily altered, and the shear modulus of the PNC is increased by a factor of $10^3$ at an appropriate surface grafting density. The detailed microstructure and mechanical properties are examined with small-angle X-ray scattering (SAXS) and oscillatory rheometry experiments. The attractive interactions between particles induced by DOPA-mPEG grafting dramatically improve the mechanical properties of PNCs even in an unentangled polymer matrix, which shows a much higher shear modulus than that of a highly entangled polymer matrix.

While nanoparticles (NPs) are frequently incorporated into polymer matrix to enhance the mechanical, electrical, and rheological properties, controlling the interface of NP/polymer matrix is often challenging because of the intrinsic incompatibility between particle and polymer. Numerous studies have been dedicated to understanding the NP/polymer interactions at the interface and resulting NP dispersions, and have found that physical/chemical grafting of polymer onto NPs can effectively tune particle interactions, where grafting density, size, and morphology of NPs and polymer molecular weights (MWs) are key parameters.

Chemical grafting of polymers onto NPs seemed to be the most effective method to ensure a favorable interaction between NPs and polymers; however, it generally requires complicated synthesis and purifications, increasing the number of processing steps. Physical grafting can be an alternative; however, it is relatively weak, unstable and often difficult.

In polymer nanocomposites (PNCs), the use of high MW polymer is generally preferred because polymer entanglements improve the mechanical property of PNCs. While high MW polymers with entanglements may provide good adsorption stability onto NPs, the good dispersity and resulting enhanced properties are not always guaranteed because the increasing MW can drive additional bridging or depletion aggregation. Furthermore, the dramatic increase of viscosity with MW significantly decreases processability.

In this Letter, we investigate the microstructure and rheological properties of low MW PNC, where the dopamine-modified, brush-type polymer was employed as a physical grafting agent. Dopamine molecules are well-known to adsorb on many substrates via strong H-bonding, readily modifying the surface properties. Here we found that a simple physical grafting of dopamine-modified methylated poly(ethylene glycol) (DOPA-mPEG) polymer onto silica NPs can dramatically improve the mechanical properties of low MW PNCs. The detailed microstructure and rheological information on PNCs was obtained with small-angle X-ray scattering (SAXS) and oscillatory rheometry experiments, while the surface coverage density, $\sigma$, of dopamine-modified polymers was systematically varied.

Our study revealed that the grafted dopamine-modified polymer can (i) increase the effective volume of NPs, (ii) bring strong interactions between grafted and matrix polymer at the interface, and thus, (iii) create networked superstructures. These combined effects tremendously increased the modulus of low MW PNC comparable to that of high MW PNCs.

Received: June 27, 2018
Accepted: July 20, 2018
DOPA-mPEG grafted silica NPs were first prepared by mixing DOPA-mPEG with silica NPs in aqueous solutions with vigorous stirring for several hours, where \( \sigma \) of DOPA-mPEG was controlled by changing the mixing ratio. Then, PNCs were prepared by adding the necessary amount of PEG (average \( M_w = 400 \) g/mol), followed by annealing at 70 °C in a vacuum oven for 2 days. The particle diameter, \( D_t \), was around 35 nm and the particle volume fraction, \( \phi_v \), was varied from 0 to 0.48. More experimental details are provided in the Supporting Information (SI).

Figure 1a shows the surface chemistry of bare and DOPA-mPEG grafted silica NPs. The grafting of DOPA-mPEG on silica surfaces was confirmed by TGA (Figure S2) and FT-IR results (Figure S3), and we found DOPA-mPEG was strongly grafted on silica via H-bonding between catechol groups of DOPA-mPEG and silanol groups of silica surfaces with \( \sim 2 \) nm of thickness (Figure S4).\(^{24,25}\) In Figure 1b, the monolayer\(^{21}\) of mPEG was controlled by changing the mixing ratio. Then, more experimental details are provided in the Supporting Information (SI).

Figure 1. (a) Surface chemical structures of silica NPs without (top) and with (bottom) DOPA-mPEG grafting. (b) Adsorption isotherm for DOPA-mPEG on silica NPs (left y-axis, black squares) and the surface coverage rate, \( r_s \) (right y-axis, red triangles). The fitting curve is drawn from the experimental results.

Figure 2. Experimental scattering intensity, \( I(qD) \), of silica NPs in PNCs are plotted as a function of normalized wavevector, \( qD \), with varying \( r_s \) of DOPA-mPEG at (a) \( \phi_v = 0.07 \), (b) 0.17, and (c) 0.38. Insets are the corresponding structure factor, \( S(qD) \). (d) The change of the first peak positions, \( q^*D \), is plotted with \( r_s \) for different \( \phi_v \). All samples were measured at 75 °C.

Particle microstructure and dispersion stability in polymer matrix. The details of the SAXS analysis are found in the SI.

At \( \phi_v = 0.07 \), no substantial change of particle structures was found with DOPA-mPEG grafting; all scattering intensities resemble the particle form factor, \( P(qD) \), shown in Figure 2a, and thus, the structure factors, \( S(qD) \), approach unity, as shown in the inset.

At \( \phi_v = 0.17 \), NPs without DOPA-mPEG were well-dispersed without aggregation showing the first order peak at \( qD \sim 4.5 \). As \( r_s \) increases, particles were gradually less ordered and aggregated, as indicated by the peak disappearance and upturns at low \( qD \).\(^{26-28}\)

At higher \( \phi_v \) of 0.38, particle dispersions with DOPA-mPEG grafting abruptly changed and showed aggregated. Noting the position of the first peaks indicates the average center-to-center distance of particles, the change in position of the first peak to \( qD \sim 7 \) implies that particles came into contact and aggregated with increasing \( r_s \). To capture the particle aggregation with DOPA-mPEG grafting, the positions of the first peaks are plotted for different \( \phi_v \) in Figure 2d. While the DOPA-mPEG grafting had no impact on particle dispersion at low \( \phi_v \), the shift in \( qD^* \) implies that DOPA-mPEG grafting makes particles more attractive, bringing them in contact, and its effect is more significant at higher \( \phi_v \).

The abrupt change of particle microstructures with DOPA-mPEG grafting also influences the physical properties of PNCs. To explore the effect of DOPA-mPEG grafting on mechanical properties, the complex shear modulus, \( G^* \), is measured in the linear viscoelastic regime with frequency sweep at 0.1% strain, as shown in Figure 3. \( G^* \) is defined as \( G^* = G' + iG'' \), where \( G' \) and \( G'' \) are the storage and loss shear modulus, respectively.\(^{29}\)

When \( \phi_v = 0.07 \), where the surface-to-surface distance between NPs is far apart (about 40 nm), no change of modulus is observed, as shown in Figure S5, consistent with the scattering result.

When \( \phi_v = 0.17 \), where the surface-to-surface distance between NPs decreases to about 16 nm, a rapid modulus decrease
increased entropic repulsion. All frequency-dependent stretching of grafted chains, which could result in slight reduction in $10 \text{ Pa}$ and a liquid-to-glass transition occurs. With full grafting, the modulus enhancement is observed much more easily. Despite partial grafting, $G^*$ increases to $3000 \text{ Pa}$, 105 times higher than that of bare NP PNC. The values of $k$ are plotted as a function of particle volume fraction for $\phi_c < 0.05$ and fitted to the equation in Figure 4.

At higher particle loadings such as $\phi_c = 0.38$, the modulus enhancement is observed much more easily. Despite partial grafting ($r_g = 0.16$), $G^*$ is more than $10^2$ times greater than that of bare PNCs ($r_g = 0$). However, at larger $r_g (>0.51)$, a slight reduction in $G^*$ was found, possibly due to the crowding and stretching of grafted chains, which could result in increased entropic repulsion. All frequency-dependent $G'$ and $G''$ behavior with varying $r_g$ is provided in Figure S6b.

In principle, the mechanical properties of PNC can be enhanced with adding inorganic NPs (fillers), while the degree of enhancement can be dependent on the nature of particle—polymer interactions. Therefore, we suspect that the modulus enhancement can be derived from increased effective volume of particles with DOPA-mPEG grafting. Due to the Newtonian behavior of unentangled PEG melts and the large particle-to-polymer size ratio, the effective particle volume, $\phi_{\text{eff}}$, can be estimated with the intrinsic viscosity in the dilute particle limit. The low shear viscosity of PNC at low $\phi_c$ was measured and fitted to the equation $\eta_{\alpha,0} = 1 + 2.5k\phi_c + B(k\phi_c)^2$, where $\eta_{\alpha,0}$ is the relative shear viscosity close to the zero-shear rate and $k$ is the particle intrinsic viscosity factor; thus, $\phi_{\text{eff}}$ is defined as $k\phi_c$ and $B$ is the pair-interaction coefficient. At low $\phi_c$, $B$ can be neglected, and thus, $k$ can be estimated as $k = (\eta_{\alpha,0} - 1)/2.5\phi_c$.

$r_g$ increases from 0 to 0.51, $k$ increases from 1.18 to 1.47, suggesting an increase of $\phi_{\text{eff}}$ with DOPA-mPEG by 25%. While the increase of $k$ confirms a thicker layer of DOPA-mPEG grafting than mere PEG chains, the degree of increment is not sufficient to explain the dramatic change of particle microstructures and modulus enhancement. For example, the effective particle radius is only larger by 1.6 nm at $r_g = 0.51$, increasing $\phi_c$ by 25% over bare NPs. If DOPA-mPEG grafting on silica surface merely increased the effective volume of NPs, $G^*$ of PNC at $\phi_c = 0.17$ with $r_g = 0.51$ ($\phi_{\text{eff}} = 0.21$) would have a modulus equivalent to PNC at $\phi_c = 0.21$ without DOPA-mPEG grafting. However, we found that PNC without DOPA-mPEG remains liquid-like even up $\phi_c = 0.28$ (Figure S7), whereas PNC at $\phi_c = 0.17$ with $r_g = 0.51$ with DOPA-mPEG shows solid-like behavior at most frequencies. Thus, the increased effective volume of particles cannot be enough to explain the large modulus enhancement.

Based on the scattering structure results, we predict that grafting DOPA-mPEG on the silica surface induces particle agglomeration, possibly creating percolating networks, which results in dramatic reinforcement of the polymer matrix. DOPA-mPEG chains can attract each other because of their internal ability to H-bond, thus, residual DOPA-mPEG in bulk and on NPs induces additional attractions for NPs. Indeed, the networked superstructure of PNCs with DOPA-mPEG grafting is found in Figure S8.

To reveal the origin of mechanical property enhancement and detailed interfacial structures between grafted DOPA-mPEG and matrix polymer, strain-induced structure deformation was observed with strain sweep experiments, as shown in Figure 5.
First at $\phi_c = 0.17$ (Figure 5a), up to $r_\sigma = 0.32$, a general liquid-like strain dependency is found ($G' \sim \gamma^{-2}$ and $G'' \sim \gamma^{-1}$), and strain-dependency is gradually decreased with increasing $r_\sigma$ (Figure S9a). At high coverage ($r_\sigma > 0.50$), the formed agglomerations exhibited linear viscoelastic response at low strain with the significant modulus enhancement and became nonlinear at high strain, implying a weak glass structure.33,34

At higher $\phi_c$ of 0.38 (Figure 5b), the effect of DOPA-mPEG grafting was greater because grafted chains can interact each other in a shorter distance. First, the plateau modulus was elevated by 3 orders of magnitude, resulting from the percolated particle agglomeration.35 The degree of modulus elevation is indeed exceptional considering the low MW of the polymer matrix. Second, two yield strains were observed. The first yield strain was associated with initial distortion of particle microstructure, which occurs when glassy networks are deformed and does not change with $r_\sigma$.33 However, the second yield and an intermediate strain softening regime only existed in DOPA-mPEG grafted PNCs. It is also noteworthy that even though the second yielding is a typical characteristic of entangled PNC, it is observed with a relatively low $\phi_c$ and unentangled polymers. Furthermore, its effective particle volume fraction is $\phi_{eff} = 0.384$ for $r_\sigma = 0.16$, still well below the random close packing particle volume fraction of 0.64.37,38

Thus, the unique existence of second yield was considered to be associated with grafting-induced particle aggregations. When particles are close enough, the grafted DOPA-mPEGs can mediate entanglements by intrinsic attractions; thus, even short matrix chains are also trapped, bringing particles in contact.26,35 While Baeeza et al. showed that bridging aggregations with entangled polymers is critical to increase mechanical strength of PNC, aggregations with low MW PNC was not reported.39 The breakage of this association requires strong strain, around 280%, independent of $r_\sigma$ and a slight strain hardening was observed with a localized $G''$ maximum at the second yield (Figure S9b). This was caused by increased internal stress due to stretching during the disentanglement between grafted DOPA-mPEGs and trapped polymers before they are separated.26,35

One considers that increasing composition ratio of DOPA-mPEG simply alters the physical properties of PNC irrespective of whether or not it is grafted. For comparison, we prepared another type of PNC with DOPA-mPEG where DOPA-mPEG is mixed later, so it is expected to remain in bulk. When the DOPA-mPEG is in bulk, not at the particle interface, the modulus and its texture are rather similar to that of PNC with bare NPs over a year (Figure S10). Therefore, the enhanced shear modulus and existence of two-step yielding can be regarded as arising from the grafted DOPA-mPEG mediated aggregations near particle interfaces. The proposed microstructure of PNCs with and without DOPA-mPEG is drawn in Scheme 1.

In conclusion, we showed that the state of particle dispersion of PNCs can be readily controlled with simple polymer-grafted NPs. The appropriate level of polymer-grafting can provide the ability to control the interparticle and grafted-matrix polymer interactions such that attractive grafted polymer chains can mediate liquid-to-solid transitions and particle agglomerations forming glassy superstructures, resulting in dramatic modulus enhancement. We note that Jouault et al. employed adsorbed block copolymers as an effective control of interparticle interactions and unlike the current research, particle agglomeration was found at low adsorption density. In addition, the agglomeration was produced with high MW polymer and did not yield a homogeneous gel-like network.40 Akcora et al. reported formation of superstructures with spherical polymer-grafted NPs;41 however, this remarkable improvements (more than 10^5 times) was not reported at low...
MW without entanglements. Furthermore, the modulus enhancement of low MW PNC found in this study is even comparable to that of highly entangled PNCs. It is interesting to note that our observations are in agreement with the computational prediction by Hattemer et al.,18 which explains the modulus enhancement of PNCs via high affinity between grafted/host matrix chains and shear distortion effects caused by grafted polymer.

DOPA-mPEG grafting provides a new strategy for controlling intrinsic particle interactions, and the ability to change the mechanical property of PNCs with low MW polymers can greatly extend the PNC’s processability. Finally, we emphasize that a detailed understanding of interfacial structures of polymer chains can always provide more opportunity to explore the micro- and macroscopic structures and properties of polymeric materials, including PNCs.

**REFERENCES**


