

Tuning the Electrically Conductive Network of Grafted Nanoparticles in Polymer Nanocomposites by the Shear Field

Luo Yan-Long, Duan Xiao-Hui, Li Bin, Chen Xian-Ling, Gao Yang-Yang, Zhang Li-Qun

Cite this article as:

Luo Yan-Long, Duan Xiao-Hui, Li Bin, Chen Xian-Ling, Gao Yang-Yang, Zhang Li-Qun. Tuning the Electrically Conductive Network of Grafted Nanoparticles in Polymer Nanocomposites by the Shear Field[J]. *Chinese J. Polym. Sci.*, 2020, 38(12): 1-9. doi: 10.1007/s10118-020-2467-x

View online: <https://doi.org/10.1007/s10118-020-2467-x>

Articles you may be interested in

Electrically Conductive and Flame Retardant Graphene/Brominated Polystyrene/Maleic Anhydride Grafted High Density Polyethylene Nanocomposites with Satisfactory Mechanical Properties

Chinese J. Polym. Sci. 2019, 37(5): 509 <https://doi.org/10.1007/s10118-019-2220-5>

Water Soluble Amino Grafted Silicon Nanoparticles and Their Use in Polymer Solar Cells

Chinese J. Polym. Sci. 2014, 32(4): 395 <https://doi.org/10.1007/s10118-014-1415-z>

POLYMER NETWORKS BY MOLECULAR DYNAMICS SIMULATION: FORMATION, THERMAL, STRUCTURAL AND MECHANICAL PROPERTIES

Chinese J. Polym. Sci. 2013, 31(1): 21 <https://doi.org/10.1007/s10118-013-1209-8>

细乳液聚合制备接枝纳米粒子及其在聚合物基体中的空间分布调控

Tuning Spatial Distribution of Polystyrene-grafted Silica Nanoparticles in Different Polymer Matrices

高分子学报. 2016(11): 1546 <https://doi.org/10.11777/j.issn1000-3304.2016.16081>

水溶液中管状带电纳米颗粒跨膜运输的分子动力学模拟

MOLECULAR DYNAMICS SIMULATION OF THE TRANSPORT OF CHARGED TUBE-LIKE NANOPARTICLES THROUGH A FLUIDIC CHANNEL

高分子学报. 2013(12): 1561 <https://doi.org/10.3724/SP.J.1105.2013.13144>

导电聚合物PEDOT在有机溶剂中的分散性研究

Dispersion of Electrically Conductive Polymer PEDOT in Organic Solvents

高分子学报. 2014(11): 1532 <https://doi.org/10.11777/j.issn1000-3304.2014.14094>

Tuning the Electrically Conductive Network of Grafted Nanoparticles in Polymer Nanocomposites by the Shear Field

Yan-Long Luo^{a,b}, Xiao-Hui Duan^{b,c}, Bin Li^d, Xian-Ling Chen^a, Yang-Yang Gao^{b,c*}, and Li-Qun Zhang^{b,c}

^a College of Science, Nanjing Forestry University, Nanjing 210037, China

^b Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, China

^c State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China

^d School of Chemical Engineering and Technology, Sun Yat-sen University, Zhuhai 519082, China

Electronic Supplementary Information

Abstract Controlling the formation of the conductive network in the polymer nanocomposites (PNCs) is very meaningful to enhance their electrical property. In this work, we investigated the effect of grafted nanoparticles (NPs) on the conductive probability of PNCs in the quiescent state as well as under the shear field via a coarse-grained molecular dynamics simulation. It is found that the smallest percolation threshold is realized at the moderate grafting density, the moderate length of grafted chains or the moderate interaction between grafted chains and free chains. Corresponding to it, the dispersion state of NPs varies from the contact aggregation to the uniform dispersion. By analyzing the connection mode among NPs, the probability of NPs which connect three other ones reaches the maximum value at their moderate dispersion state which is responsible for the optimal conductive probability. In addition, the main cluster size is characterized to better understand the conductive network which is consistent with the percolation threshold. It is interesting to find that the percolation threshold is smaller under the shear field than under the quiescent state. The shear field induces more NPs which connect three other ones. This benefits the formation of the new conductive network. Meanwhile, the anisotropy of the conductive probability is reduced with increasing the grafting density. In summary, this work provides a clear picture on how the conductive network of grafted NPs evolves under the shear field.

Keywords Conductive network; Grafted nanoparticles; Molecular dynamics simulation

Citation: Luo, Y. L.; Duan, X. H.; Li, B.; Chen, X. L.; Gao, Y. Y.; Zhang, L. Q. Tuning the electrically conductive network of grafted nanoparticles in polymer nanocomposites by the shear field. *Chinese J. Polym. Sci.* <https://doi.org/10.1007/s10118-020-2467-x>

INTRODUCTION

Filling a nonconductive polymer matrix with conductive nanoparticles (NPs) (such as carbon nanotubes (CNT), carbon black (CB), and graphite) can significantly improve its electrical properties.^[1–3] However, the NPs tend to form the aggregation to reach the minimize surface energy which is the main cause for the low electrical conductivity of polymer nanocomposites (PNCs). The percolation threshold of PNCs, where the conductive network is formed, is desired to be as low as possible from the application viewpoint. Otherwise, a large number of conductive NPs in the polymer matrix are detrimental to the other physical properties such as the transparency, the flexibility, and the adhesive strength.^[4–6] Therefore, it is important to control the formation of the conductive network to obtain PNCs with the excellent performance, which, however still remains a challenging problem.

Generally, the conductive behavior of PNCs is dependent

on the spatial distribution and structure of NPs in the matrix which depends on their interaction, size, shape, alignment, and so on. Currently, intensive work has aimed to establish the methods for controlling the formation of the conductive network which hopes to obtain the highly conductive PNCs. For example, the surface modification of NPs can enhance their miscibility with polymers, thereby enhancing the electrical conductivity of PNCs.^[7] In addition, CNTs with the large aspect ratio are favorable to reduce the percolation threshold, where their relationship can be predicted by the analytical percolation models.^[8] Compared with CBs and graphene, CNTs can form a percolating network at a lower volume fraction in a polypropylene matrix, which is attributed to their shape.^[9] The spatial distribution of NPs can be tuned by the grafting density, the length of grafted chains, and the free chains so as to optimize the electrical conductivity.^[10–13] The poor dispersion or overdispersion of NPs is harmful to the formation of the conductive network whose relationship needs to be clarified. The shear field can induce the translation, rotation and bending of NPs which is another effective method for tuning the conductive network. Accompanied by it, the anisotropy of the electrical conductivity appears. It is

* Corresponding author, E-mail: gaoyy@mail.buct.edu.cn

Received May 12, 2020; Accepted June 1, 2020; Published online August 11, 2020

reported that the conductive network will be broken down under the shear field, which increases the percolation threshold for the partially aggregated NPs.^[14,15] However, the shear-induced agglomeration of NPs rebuilds the conductive path and reduces the percolation threshold for the dispersed ones.^[16] Interestingly, the electrical conductivity of PNCs is nearly independent of the initial dispersion state of NPs, which indicates the dominant effect of the shear field.^[17] The experimental techniques are incapable of intuitively characterizing the conductive network in response to the shear field. On the contrary, computer simulation has an obvious advantage in analyzing their evolution process *in situ*, which provides the access to the study of conductivity behavior. By adopting molecular dynamics simulation, the percolation threshold of PNCs is reduced with increasing the polymer-NP interaction, which is attributed to the tightly formed conductive network sandwiched *via* one polymer layer.^[18] In addition, the percolation threshold follows an exponential relationship with the aspect ratio of fibers *via* a Monte Carlo model.^[19] Meanwhile, the aspect ratio of CNTs plays a more important role in building the conductive network than the tunneling barrier height.^[20,21] The rod NPs can build the conductive network at a lower volume fraction than the sphere NPs and the sheet NPs under condition that they have the same size.^[22,23] Based on a developed percolation network model, the effect of the CNT structural distortion on the electrical conductivity has been analyzed by tuning the temperature.^[24] The dispersion state and phase behavior of grafted nanofillers have been systemically investigated by the theory and model, which conversely will influence the conductivity.^[25–28] The original conductive network is broken down under the shear field, which affects the electrical conductivity. Then, a new one will be formed, which depends on the CNT aspect ratio and the shear rate.^[29–31] It is interesting to observe the breakage of the conductive network induced by the CNT aggregation when the shear rate exceeds a critical value.^[32] Furthermore, a simple model is proposed to calculate the electrical conductivity of PNCs, which takes the interphase thickness and tunneling distance between CNTs into consideration.^[33]

Based on the above work, the aggregation of nanoparticles (NPs) is the main limitation for enhancing the electrical conductivity, which can be inhibited by grafting the chains on their surface. The spatial distribution of NPs has been analyzed and attributed to a competition between the matrix-induced depletion attraction between NPs and the steric stabilization provided by grafted chains. However, their relationship with the conductive probability is still unclear and deserves to be further investigated, especially under the shear field. Thus, in this work a coarse-grain model is adopted to understand how the conductivity probability of PNCs is regulated by tuning the grafting density and the length of the grafted chains in the quiescent state as well as under the shear field. By characterizing the connection mode among the NPs and the cluster size, the dependence of the conductive probability on the grafting density and the length of grafted chains is clarified, which can aid to understand the mechanism. Last, the effect of the miscibility between grafted chains and free chains on the conductive probability is discussed.

MODEL AND SIMULATION METHODS

In our simulations, a coarse-grained model is adopted to study the polymer-grafted spherical NPs filled PNCs. The bead-spring model is adopted to model both free chains and grafted chains whose chemical properties are identical in most cases. Each free chain is composed of thirty beads while the number of beads in one grafted chain L_g ranges from 1 to 7. The grafting density Σ_g is defined by $N_g/\pi D_n^2$ where N_g represents the number of grafted chains and D_n means the diameter of NPs. It is noted that the numbers of free chains and grafted chains are varied for different systems while the total number of beads is fixed to be 24000. Two symbols σ and m are adopted to stand for the diameter and mass of a polymer bead, respectively.^[21,34] There are five types of Lennard-Jones (LJ) beads in the simulation, which are shown in Table SI (in the electronic supplementary information, ESI). In order to fix the grafted chains on the surface of NPs, the NP core is modeled as a solid sphere with 96 virtual points, which can be found in our previously published work.^[35] Each virtual surface point is bonded with neighboring ones and the NP core which can fix the shape of the virtual surfaces during the whole simulation. The grafted chains which are bonded with NPs through the grafting sites and the virtual surface points are not free to rotate around the NPs surface. It is noted that the grafting site is one end reactive bead of grafted chains. The virtual surface points occupy no space but just act as the functional groups on the NPs in practice. The diameter of NPs ($D_n = 4\sigma$) is four times of that of a polymer bead (σ). Although the short chains are shorter than real polymer chains, they can exhibit the static characteristic behaviors of long chains well.^[36] Each bond in this model corresponds to 3–6 covalent bonds in a realistic polymer chain when mapping the coarse-grained model to a real polymer.

Here, the modified Lennard-Jones (LJ) potential is employed to model all the non-bonded interactions, as following

$$U_{ij}(r) = \begin{cases} 4\varepsilon_{ij} \left[\left(\frac{\sigma}{r - r_{EV}} \right)^{12} - \left(\frac{\sigma}{r - r_{EV}} \right)^6 \right] + C & r - r_{EV} < r_{cutoff} \\ 0 & r - r_{EV} \geq r_{cutoff} \end{cases} \quad (1)$$

where ε_{ij} is the pair interaction energy parameter, r is the distance between center of mass of two interaction sites and σ is the characteristic size. r_{cutoff} stands for the distance ($r - r_{EV}$) at which the interaction is truncated and shifted so that the energy is zero. C is a constant to guarantee that the potential energy is continuous everywhere. r_{EV} stands for the effect of the excluded volume of different interaction sites. For polymer-NP and NP-NP interactions, r_{EV} is set to be 1.5σ and 3.0σ respectively. For polymer-polymer interactions, r_{EV} becomes zero. In our systems, the interactions ε_{ij} (ε_{pp} , ε_{np} , ε_{nn}) are set to be 1.0. ε_{pp} , ε_{np} , and ε_{nn} denote the polymer-polymer interaction, polymer-NP interaction, and the NP-NP interaction, respectively. The cutoff distance is set to be 2.5σ . The LJ parameters for all types of interactions are listed in Table SII (in ESI).

Here, a stiff harmonic potential is employed to stand for the bonded interaction between the adjacent beads including both polymer chains and NPs, which is given by

$$E_{bond} = \frac{1}{2}K(r - r_0)^2 \quad (2)$$

where $K = 2000\varepsilon/\sigma^2$ and $r_0 = 1.0\sigma$ can guarantee a certain

stiffness of the bonds while avoiding high-frequency modes and chain crossing. r_0 of the virtual surface point-virtual surface point bond and virtual surface point-NP core bond is set to be 1.0σ and 2.5σ , respectively. It is noted that the harmonic potential is proved to be efficient in modeling polymer systems.^[37–39]

Since it is not our aim to study a specific polymer chain, all parameters are simplified by setting the mass m and the diameter σ to be unit, namely all the simulated quantities are dimensionless. Similar to our previous work,^[21,34,35] all the free chains, grafted chains, and NPs are first put into a large simulation box without overlap. Such initial structures are further equilibrated under the NPT ensemble for 20000τ (τ is the reduced time unit) with the temperature and pressure fixed at $T^* = 1.0$ and $P^* = 0.0$ by using the Nose-Hoover temperature thermostat and pressure barostat. Then the systems are further equilibrated at $T^* = 5.0$ for 20000τ to ensure that each free chain has moved at least $2R_g$. Next, the systems are gradually cooled down to $T^* = 1.0$ by reducing T^* by 0.02 every 250τ . Afterwards, the end-grafting reaction begins under the NVT ensemble. A covalent bond between the grafting sites and the virtual surface point is formed if their distance is less than 0.5σ as described by the stiff harmonic potential in Eq. (2) with $r_0 = 0.0$. It is noted that the one-to-one bonded reaction is allowed. Last, the obtained systems are further equilibrated under the NVT ensemble with $T^* = 1.0$ for 20000τ . The number density of polymer beads reaches nearly 0.85, which means the density of polymer melts. The glass transition temperature of our system is about 0.4–0.5, which is below the simulated temperature $T^* = 1.0$. After that, the structure and dynamics data are collected for ensemble average. Periodic boundary conditions are adopted in all three directions to eliminate edge effects. The equations of motion are integrated by using the velocity-Verlet algorithm with a time step $\delta t = 0.001$. All simulations have been performed by using the large-scale atomic/molecular massively parallel simulator (LAMMPS).^[40]

The electrical properties of PNCs closely depend on the conductive network. Thus, to determine whether the conductive network is formed, a criterion is used to check whether any two NPs are connected. It is reported that any two carbon black fillers can be connected once their gap is less than 10 nm (the tunneling distance (TD)) according to the field emission theory.^[41] Meanwhile, the diameters of carbon black fillers are usually about 25–40 nm as denoted by one NP in the simulation.^[42,43] The selected ratio of the NP diameter (4.0σ) to monomer size (1.0σ) can in general represent polymer nanocomposites in our simulation^[44,45] and is suitable for achieving relatively quick equilibration of the simulations. Following the real systems, the maximum gap between any two connected NPs ranges from 1.0σ to 1.6σ in our model. Here, the uniform value 1.5σ is selected as the TD for conductive connection. It is noted that TD will affect the percolation threshold while it does not change the trend of the results. The method for calculating the conductive probability can be found in ESI.^[21,23] More than 100000 equilibrated configurations are collected to perform the data analysis. The time interval between two continuous frames is 10τ . At last, we counted the number of configurations where the network

is percolated in the three-dimensional directions or in one direction. The conductive probability Λ , $\Lambda_{||}$, and $\Lambda_{\perp}$ are used to represent the probability of forming the conductive network in the three-dimensional directions, parallel to the shear field direction, and perpendicular to the shear direction, respectively.

RESULTS AND DISCUSSION

Conductive Properties of PNCs

Grafting density

When NPs are grafted with chains, they can provide steric repulsion between NPs.^[12,46] Thus, the grafted chains can exert a crucial effect on the dispersion state of NPs, which will affect the electrical property of PNCs. In this section, we investigated the effect of grafting density Σ_g on the conductive probability Λ of PNCs by fixing the length of grafted chain ($L_g = 3$). The details of the simulated systems (1–8) can be referred to the Table SIII (in ESI). As shown in Fig. 1, the conductive probability Λ first changes slowly at a low volume fraction of NPs (ϕ). Then a quick increase of Λ is observed near the percolation threshold which is known as the percolation phenomenon. Meanwhile, the percolation threshold ϕ_c is defined as ϕ at $\Lambda = 0.5$ ^[47] as presented in Fig. 2. It presents that ϕ_c first decreases and then increases with Σ_g and reaches the minimum value at the moderate $\Sigma_g = 0.3$. To better interpret it, the coordination number is adopted to denote the dispersion state of NPs, which is defined as the average number of NPs around every NP within the distance of 5.5σ . From Fig. 2, the coordination number gradually decreases with increasing Σ_g , which reflects their gradually uniform dispersion. Because of the self-attractive interaction, the ungrafted NPs form the direct contact aggregation at $\Sigma_g = 0$. Thus, the conductive network is not formed in the matrix which leads to $\Lambda = 0$. The aggregation of NPs is attributed to the depletion effect that results in a fully entropic attraction between them according to the previous theories^[48,49] and experiments.^[11,12] Then, grafted chains on the NPs repel other NPs apart with increasing Σ_g , which breaks the aggregation down. As a result, NPs gradually disperse into the matrix, leading to the transition of their dispersion state from the contact aggregation to the relatively uniform dispersion.

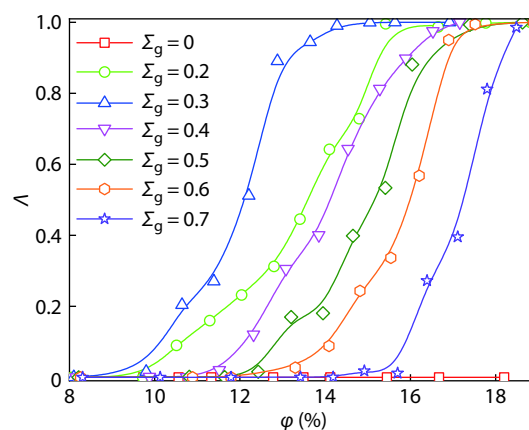


Fig. 1 Conductive probability Λ as a function of the nanoparticle volume fraction ϕ for different grafting density Σ_g ($T^* = 1.0$, $\dot{\gamma} = 0.0$).

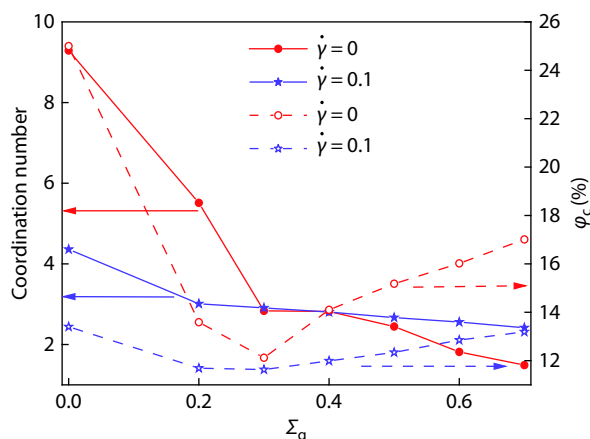


Fig. 2 The coordination number (left axis) and percolation threshold ϕ_c (right axis) with respect to the grafting density Σ_g at the shear rate $\dot{\gamma} = 0.0$ and 0.1 ($T^* = 1.0$).

This favors the connection among NPs and the formation of the conductive network, which reduces ϕ_c . However, too many grafted chains reduce the connection probability among NPs with a further increase of Σ_g . Thus, more NPs are broken away from the conductive network to form relatively small and loose clusters or isolated NPs, thus increasing ϕ_c . Therefore, the lowest percolation threshold ϕ_c is realized at the moderate Σ_g . Furthermore, the formation of the conductive network is closely related to the connection mode among NPs. Here, the number of the nearest neighbor NPs surrounding one NP at a separation closer than 5.5σ is analyzed and denoted by N_{num} . This stands for the average number of NPs when each NP connects. The change of the probability distribution P_N of N_{num} with Σ_g is presented in Fig. 3 at $\phi = 13.7\%$. The results clearly reflect that N_{num} at the maximum P_N gradually decreases from 6 to 1 while P_N at $N_{\text{num}} = 0.0$ (denoted by the number of isolated NP) increases with Σ_g . This reflects the gradual dispersion of NPs into the matrix. In general, we speculated that each NP should connect 3 other NPs to effectively form the conductive network. If each NP connects 0–2 or more than 4 other NPs, the NPs are isolated or aggregated, which is

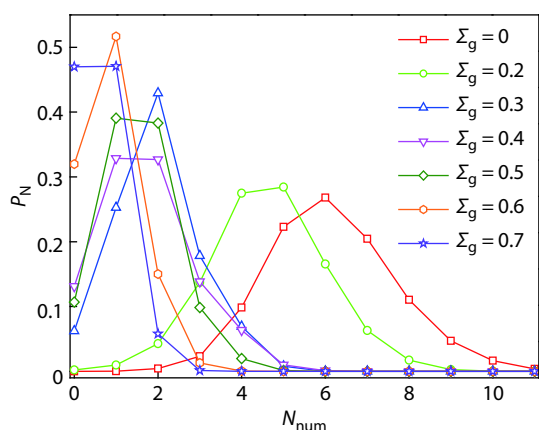


Fig. 3 The probability distribution P_N of the nearest neighbor nanoparticles (NP) surrounding one NP at a separation closer than 5.5σ (N_{num}) for different grafting density Σ_g ($T^* = 1.0$, $\dot{\gamma} = 0.0$).

unfavorable to form the conductive network. As shown in Fig. S1 (in ESI), P_N at $N_{\text{num}} = 3$ exhibits a first increase from 0.023 to 0.178 and then a decrease to 0.0015 with Σ_g and reaches the maximum value at the moderate $\Sigma_g = 0.3$. This is consistent with ϕ_c . Furthermore, the main cluster size C_n (the number of NPs within the biggest cluster) is characterized to analyze the conductive network. It is noted that λ correlates with C_n but is not directly proportional to it. As shown in Fig. 4(a), it is found that C_n first increases and then decreases with Σ_g in the percolation region, consistent with λ . It is noted that even though C_n is large at $\Sigma_g = 0.0$ (not shown), the isolated aggregation cannot form the conductive network. Fig. 4(b) presents some representative snapshots of the main cluster (red beads) to observe the conductive network for different Σ_g at $\phi = 13.7\%$. It is observed that the direct contact aggregation of NPs leads to the non-conductivity at $\Sigma_g = 0.0$. Then, NPs gradually disperse and are connected with each other to form a continuous conductive network with increasing $\Sigma_g \leq 0.3$ as reflected by more red NPs. However, the uniform dispersion of NPs results in the isolated ones with a further increase of Σ_g which cannot span the systems. These results are consistent with ϕ_c . In summary, the dispersion state of NPs varies from the contact aggregation to the uniform dispersion state with Σ_g . However, the percolation threshold of PNCs reaches the minimum value at the moderate $\Sigma_g = 0.3$.

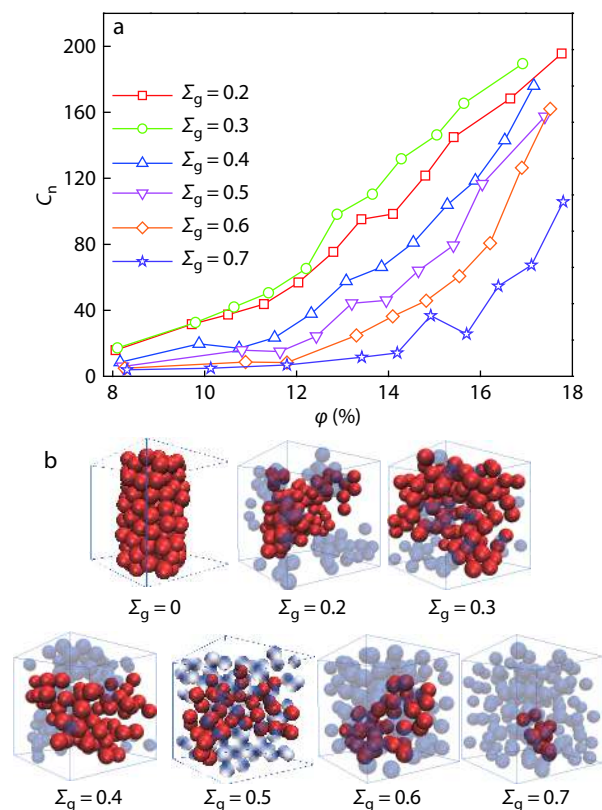


Fig. 4 (a) Change of the main cluster size C_n as a function of the nanoparticle (NP) volume fraction ϕ at different grafting density Σ_g . (b) Some snapshots of NPs with different Σ_g where the polymer chains are neglected for clarity at $\phi = 13.7\%$. The red spheres denote the NPs within the main cluster while the blue spheres represent the other NPs ($T^* = 1.0$, $\dot{\gamma} = 0.0$).

Length of grafted chains

It is reported that the length of grafted chain (L_g) is another deterministic factor to influence the dispersion behavior of NPs, which may affect the conductive property.^[11,12] Thus, we present the result how L_g changes the conductive probability in this section. L_g is chosen to be 0, 1, 3, 5, and 7 by fixing $\Sigma_g = 0.3$ where φ_c is the lowest. The details of the simulated systems (1, 9–12) can be found in Table SIII (in ESI). The dependence of λ on φ is shown in Fig. 5 for different L_g . It is found that the percolation threshold φ_c first decreases and then increases with L_g and reaches the minimum at the moderate $L_g = 1$. Similarly, the probability distribution P_N of the N_{num} is analyzed with L_g as presented in Fig. 6(a). N_{num} at the maximum P_N declines from 6 to 1 while P_N at $N_{\text{num}} = 0.0$ increases with the L_g which reflects the gradual dispersion of NPs. Meanwhile, the P_N at $N_{\text{num}} = 3$ first rises from 0.023 to 0.21 and then declines to 0.039 with L_g . It reaches the maximum value at the moderate $L_g = 1$ which is consistent with φ_c . Then, the main cluster size C_n is calculated for different L_g to better understand the conductive network in Fig. 6(b). It is observed that C_n presents a monotonous decrease with the increase of L_g which is consistent with φ_c . These can be further proved by some representative snapshots of the main cluster (red beads) for different L_g at $\varphi = 13.7\%$ in Fig. S2 (in ESI). In summary, the moderate dispersion of NPs is beneficial to connecting the other NPs to form the conductive network and reduce φ_c . However, the contact aggregation or the over-dispersion of NPs has adverse effects in forming the conductive network, which leads to the minimum φ_c at the moderate $L_g = 1$.

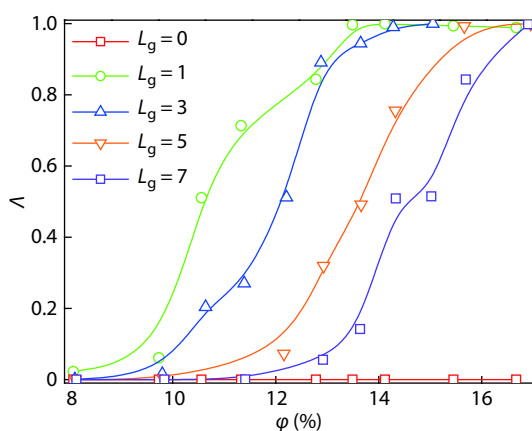


Fig. 5 Conductive probability λ as a function of the nanoparticle volume fraction φ for different lengths of grafted chains L_g ($T^* = 1.0$, $\dot{\gamma} = 0.0$).

Interaction strength between grafted chains and free chains

If the chemical property between grafted chains and free chains is different, their miscibility will change the dispersion state of NPs and further affect the conductive network. In this section, the interaction ε_{gf} between grafted chains and free chains varies from 0.1, 1.0, to 3.0 (namely from weakly repulsive to strongly attractive). The details of the simulation systems (13–15) are shown in Table SIII (in ESI). The dependence of λ on ε_{gf} is presented in Fig. 7, which indicates that φ_c first

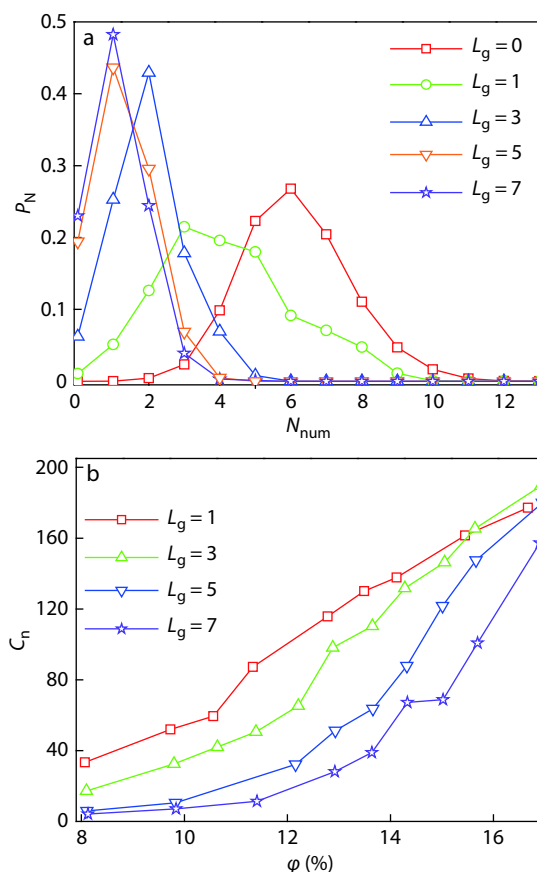


Fig. 6 (a) The probability distribution P_N of the nearest neighbor nanoparticles (NP) surrounding one NP at a separation closer than 5.5σ (N_{num}) for different lengths of grafted chains L_g . (b) Change of the main cluster size C_n as a function of the NP volume fraction φ ($T^* = 1.0$, $\dot{\gamma} = 0.0$).

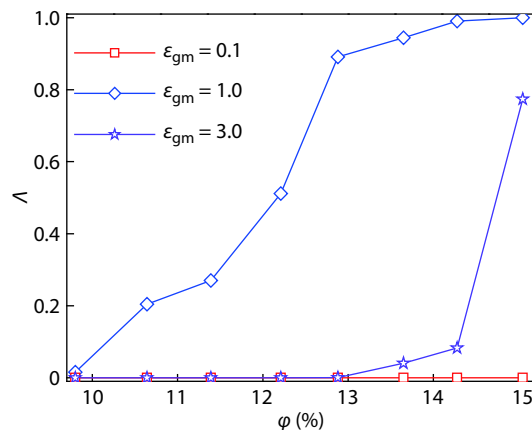


Fig. 7 Conductive probability λ as a function of the nanoparticle volume fraction φ for different interaction strength between grafted chains and free chains ε_{gf} ($T^* = 1.0$, $\dot{\gamma} = 0.0$).

decreases and then increases with ε_{gf} . It reaches the minimum value at the mediate $\varepsilon_{gf} = 1.0$. Then, P_N of N_{num} is calculated for different ε_{gf} to understand this result in Fig. S3(a) (in ESI). It is found that P_N at $N_{\text{num}} = 3$ first rises from 0.11 to 0.23 and then declines to 0.02 with ε_{gf} . The maximum P_N appears at the

moderate $\varepsilon_{gf} = 1.0$, which is consistent with φ_c . Then, Fig. S3(b) (in ESI) presents the change of C_n with ε_{gf} showing that C_n gradually decreases with ε_{gf} . Furthermore, the snapshots of NPs are shown in Fig. 8 for different ε_{gf} to observe the conductive network. With the increase of the ε_{gf} , the main cluster size (the red beads) shows a continuous decrease. The phase separation between polymer and NPs appears at $\varepsilon_{gf} = 0.1$ and leads to the non-conductivity. Then, an improved dispersion of NPs induces their connection with other NPs to form the conductive network with increasing the ε_{gf} and reduces the φ_c .

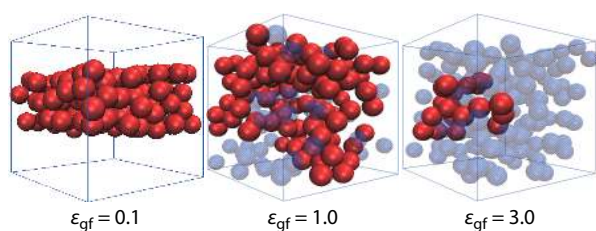


Fig. 8 Some snapshots of NPs with different interaction strength between grafted chains and free chains ε_{gf} where the polymer chains are neglected for clarity at $\varphi = 13.7\%$. The red spheres denote the NPs within the main cluster while the blue spheres represent the other NPs ($T^* = 1.0$, $\dot{\gamma} = 0.0$).

However, the overdispersion of NPs induces their large distance with a further increase of ε_{gf} , which is harmful to the conductive network. Thus, an increase in φ_c is observed. In summary, the percolation threshold reaches the a minimum value at the moderate ε_{gf} .

Shear field

It is noted that PNCs will undergo strong shear deformation in the manufacturing process, which affects the conductive network. Thus, it is necessary to clarify how the shear field affects the conductive probability for different Σ_g . Here, a non-equilibrium molecular dynamics simulation of a continuously strained system is performed with the SLLOD algorithm.^[50] The SLLOD equations of motion are implemented with the compatible Lees-Edwards “sliding brick” boundary conditions,^[51] wherein two opposing periodic images are incrementally moved in opposite directions consistent with the applied shear rate. The shear field is exerted on the simulation box by moving the top xy plane along the x direction. Fig. 9 presents Λ , $\Lambda_{||}$ and $\Lambda_{\perp}$ as a function of φ for different Σ_g at the shear rate $\dot{\gamma} = 0.1$. From Fig. 9(a), the percolation threshold φ_c first decreases and then increases with Σ_g the same as shown in Fig. 2. It is noted that φ_c is smaller at $\dot{\gamma} = 0.1$ than that at $\dot{\gamma} = 0.0$, which reflects the high conductive probability at $\dot{\gamma} = 0.1$. To explain it, we first turned to $\Lambda_{||}$ and $\Lambda_{\perp}$ in Figs. 9(b) and 9(c) which determine Λ . As shown in Fig. S4 (in ESI), φ_c of $\Lambda_{||}$ exhibits an increase with the Σ_g . This is because the grafted chains on NPs induce their separation in large distance and thus break the conductive network along the shear direction. Meanwhile, φ_c of $\Lambda_{\perp}$ first decreases and then increases with Σ_g . The aggregation of NPs breaks the conductive network perpendicular to the shear direction at $\Sigma_g = 0.0$, which is still is not overcome by the shear field. Meanwhile, the difference of the φ_c for $\Lambda_{||}$ and $\Lambda_{\perp}$ is reduced with the increase of Σ_g which reflects the small anisotropy of the conductive probability. Furthermore, we

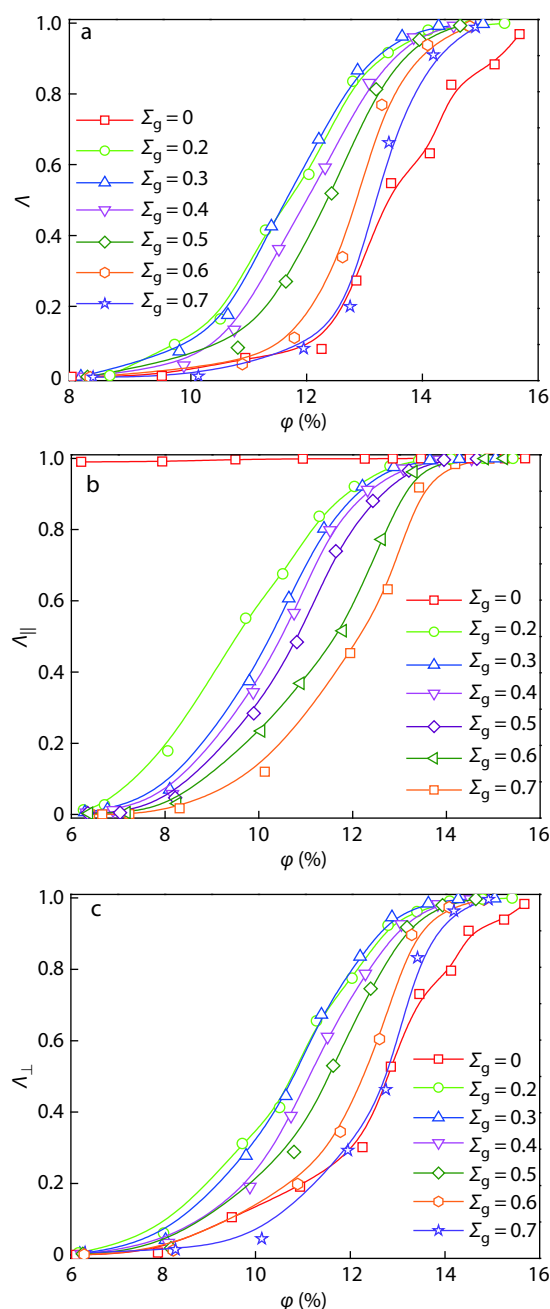


Fig. 9 (a) Conductive probability Λ , (b) $\Lambda_{||}$ parallel to the shear direction, and (c) $\Lambda_{\perp}$ perpendicular to the shear direction as a function of the nanoparticle volume fraction φ for different grafting density Σ_g ($T^* = 1.0$, $\dot{\gamma} = 0.1$).

calculated P_N of N_{num} for different Σ_g at $\dot{\gamma} = 0.1$ in Fig. 10. P_N at $N_{num} = 3$ first rises from 0.18 to 0.23 and then declines to 0.04 with Σ_g at $\dot{\gamma} = 0.1$, and is consistent with the φ_c . Compared with that at $\dot{\gamma} = 0.0$ in Fig. S1 (in ESI), the higher P_N at $N_{num} = 3$ indicates the easier formation of the conductive network at $\dot{\gamma} = 0.1$ and thus reduces the φ_c . Meanwhile, the difference of P_N for $N_{num} = 3$ at $\dot{\gamma} = 0.0$ and 0.1 is smaller for $\Sigma_g = 0.3$ than for the others which is roughly responsible for their similar φ_c . Then, the main cluster size C_n is calculated to reflect the conductive network in Fig. 11. The results indicate

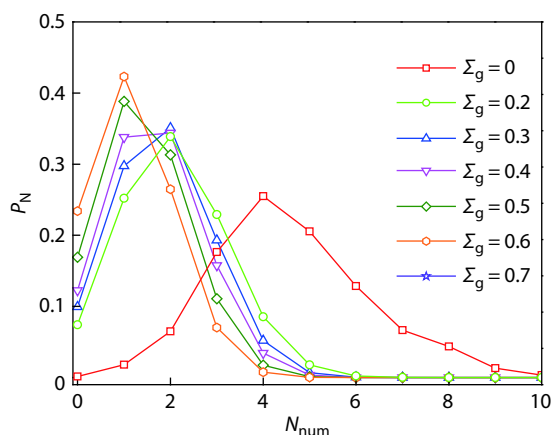


Fig. 10 The probability distribution P_N of the nearest neighbor nanoparticles (NP) surrounding one NP at a separation closer than $5.5\sigma(N_{\text{num}})$ for different grafting density Σ_g ($T^* = 1.0$, $\dot{\gamma} = 0.1$).

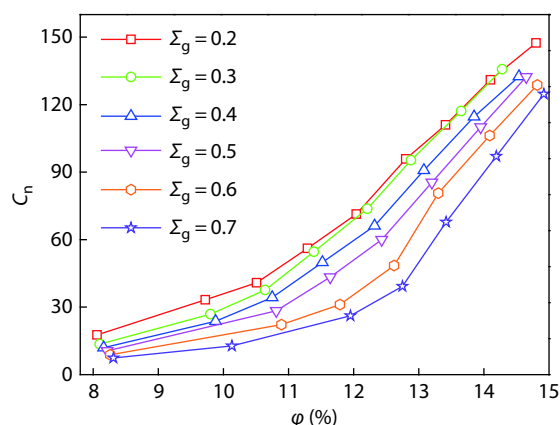


Fig. 11 Change of the main cluster size C_n as a function of the nanoparticle (NP) volume fraction ϕ for different grafting density Σ_g ($T^* = 1.0$, $\dot{\gamma} = 0.1$).

that C_n is gradually reduced with the increases of $\Sigma_g \geq 0.2$, which is consistent with ϕ_c . This can be further proved by the snapshots of some typical systems at $\dot{\gamma} = 0.1$ in Fig. S5 (in ESI). In summary, the number of NPs that connect three other ones increases under the shear field, which helps to form the conductive network and reduces the ϕ_c .

Discussion

If mapping the coarse-grained model to real polymers, the interaction parameter ϵ is set to be about 2.5–4.0 kJ·mol^{−1} for different polymers, thus $\epsilon_{\text{gf}} = 1.0$ –3.0 (in units of ϵ) is about 2.5–12.0 kJ·mol^{−1}. The persistence length varies between 0.35 and 0.76 nm for real polymers^[52] while it is about 0.676σ for the coarse-grained model, which means that σ is roughly 1 nm. Thus, a grafting density of $\Sigma_g = 0.7$ corresponds to 0.7 chains per nm², which is within the experimental range.^[12,53] Furthermore, the diffusion coefficient D of NPs is about $2.12 \times 10^{-4} \tau^{-1}$ while the shear rate $\dot{\gamma}$ is $0.1 \tau^{-1}$ in the simulation, higher than that in the real physical experiments. As a result, the Peclet number ($Pe = \frac{\dot{\gamma}}{D}$) about 470 is roughly comparable with the experimental value.^[54] Thus, our simulation results are roughly within the range of the real experiments.

In this work, we mainly investigated the effect of polymer-grafted NPs on the conductive probability in the quiescent state and under the shear field. The percolation threshold varies from 10% to 30% in the CBs filled PNCs in experiments,^[1,14,55,56] which can be compared to the simulated value from 12.1% to 17% for different Σ_g (except $\Sigma_g = 0.0$). However, the quantitative comparison between them should be very careful in view of the following three aspects. (1) Considering the limited simulation length scale, the adopted NP size (4 nm) in the simulation is much smaller than the CB size (25–50 nm) in experiments. (2) CBs intend to form the aggregation. Thus, both the surface modification of CBs and the shear field will be applied to disperse them into the matrix. Unfortunately, CBs will reaggregate when the shear field is removed. Thus, the dispersion state of CBs is always not in the thermodynamic equilibrium state in experiments while it reaches the thermodynamic equilibrium in the simulation. (3) The conductive probability is used to qualitatively reflect the electrical conductivity in our simulation, but not quantitatively. It just varies from 0.0 to 1.0 (one order of magnitude) which depends on the tunneling distance. However, the electrical conductivity changes more than 10 orders of magnitude near the percolation threshold in experiments. It is noted that the effects of grafted chains and free chains between NPs are different on blocking the flow of current from one NP to another. Especially, for NPs grafted with long and dense chains, the grafted chains break the filler structure and reduce their inherent conductivity. However, it is not considered in our model. Furthermore, it is reported that too many grafted chains on the nanofillers prevent the formation of the electrical conductive path in the polylactide matrix, which is consistent with our results.^[57] In total, our simulation can clearly reflect the experiments and thus provides a further understanding of the conductive network formed by grafted NPs under the shear field.

CONCLUSIONS

By adopting the coarse-grained molecular dynamics simulation, we focused on how the grafted nanoparticles (NPs) affect the conductive probability of polymer nanocomposites (PNCs) in the quiescent state as well as under the shear field. The dispersion state of NPs varies from the contact aggregation to the uniform dispersion with the grafting density, the length of grafted chains as well as the interaction between grafted chains and free chains. Corresponding to it, the probability of NPs which connect three other ones first increases and then decreases and reaches the maximum value at their moderate dispersion state. The connection mode among NPs has a close relationship with the conductive network (namely the main cluster size). These are responsible for the smallest percolation threshold which optimizes the conductive probability. Interestingly, compared with that in the quiescent state, the percolation threshold is reduced under the shear field, which reflects the higher conductive probability. The aggregation structure of NPs is broken down at the low grafting density while more NPs connect three other ones at high grafting density and thus help to form the new conductive network. In addition, the high grafting density reduces the anisotropy of the conductive probability. In summary, this work presents that the

grafted chains and the shear field can be used to effectively tune the conductive network in the PNCs.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-020-2467-x>.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 51973012, 21704003, and 51903122), National 973 Basic Research Program of China (No. 2015CB654704), the Foundation for Innovative Research Groups of the NSF of China (No. 51521062). The authors acknowledge the National Supercomputer Center in Guangzhou, Lvliao, and Shenzhen.

REFERENCES

- Zhang, Q.; Wang, J.; Zhang, B. Y.; Guo, B. H.; Yu, J.; Guo, Z. X. Improved electrical conductivity of polymer/carbon black composites by simultaneous dispersion and interaction-induced network assembly. *Compos. Sci. Technol.* **2019**, *179*, 106–114.
- Mutiso, R. M.; Winey, K. I. Electrical properties of polymer nanocomposites containing rod-like nanofillers. *Prog. Polym. Sci.* **2015**, *40*, 63–84.
- Alig, I.; Pötschke, P.; Lellinger, D.; Skipa, T.; Pegel, S.; Kasaliwal, G. R.; Villmow, T. Establishment, morphology and properties of carbon nanotube networks in polymer melts. *Polymer* **2012**, *53*, 4–28.
- Yang, X.; He, W.; Wang, S.; Zhou, G.; Tang, Y. Preparation and properties of a novel electrically conductive adhesive using a composite of silver nanorods, silver nanoparticles, and modified epoxy resin. *J. Mater. Sci. Mater. Electron.* **2012**, *23*, 108–114.
- Nagai, T.; Aoki, N.; Ochiai, Y.; Hoshino, K. Electric conductivity-tunable transparent flexible nanowire-filled polymer composites: orientation control of nanowires in a magnetic field. *ACS Appl. Mater. Interfaces* **2011**, *3*, 2341–2348.
- Lyons, P. E.; De, S.; Elias, J.; Schamel, M.; Philippe, L.; Bellew, A. T.; Boland, J. J.; Coleman, J. N. High-performance transparent conductors from networks of gold nanowires. *J. Phys. Chem. Lett.* **2011**, *2*, 3058–3062.
- Bréchet, Y.; Cavaillé, J. Y.; Chabert, E.; Chazeau, L.; Dendievel, R.; Flandin, L.; Gauthier, C. Polymer based nanocomposites: effect of filler-filler and filler-matrix interactions. *Adv. Eng. Mater.* **2001**, *3*, 571–577.
- White, S. I.; Mutiso, R. M.; Vora, P. M.; Jahnke, D.; Hsu, S.; Kikkawa, J. M.; Li, J.; Fischer, J. E.; Winey, K. I. Electrical percolation behavior in silver nanowire-polystyrene composites: simulation and experiment. *Adv. Funct. Mater.* **2010**, *20*, 2709–2716.
- Li, Y.; Zhu, J.; Wei, S.; Ryu, J.; Wang, Q.; Sun, L.; Guo, Z. Poly(propylene) nanocomposites containing various carbon nanostructures. *Macromol. Chem. Phys.* **2011**, *212*, 2429–2438.
- Srivastava, S.; Agarwal, P.; Archer, L. A. Tethered nanoparticle-polymer composites: phase stability and curvature. *Langmuir* **2012**, *28*, 6276–6281.
- Chevigny, C.; Dalmas, F.; Di Cola, E.; Gigmès, D.; Bertin, D.; Boué, F.; Jestin, J. Polymer-grafted-nanoparticles nanocomposites: dispersion, grafted chain conformation, and rheological behavior. *Macromolecules* **2011**, *44*, 122–133.
- Kumar, S. K.; Jouault, N.; Benicewicz, B.; Neely, T. Nanocomposites with polymer grafted nanoparticles. *Macromolecules* **2013**, *46*, 3199–3214.
- Kumar, S. K.; Benicewicz, B. C.; Vaia, R. A.; Winey, K. I. 50th Anniversary perspective: are polymer nanocomposites practical for applications? *Macromolecules* **2017**, *50*, 714–731.
- Liu, X.; Krücker, J.; Zheng, G.; Schubert, D. W. Mapping the electrical conductivity of poly(methyl methacrylate)/carbon black composites prior to and after shear. *ACS Appl. Mater. Interfaces* **2013**, *5*, 8857–8860.
- Liu, X.; Krücker, J.; Zheng, G.; Schubert, D. W. Electrical conductivity behaviour of sheared poly(methyl methacrylate)/carbon black composites. *Compos. Sci. Technol.* **2014**, *100*, 99–104.
- Skipa, T.; Lellinger, D.; Böhm, W.; Saphiannikova, M.; Alig, I. Influence of shear deformation on carbon nanotube networks in polycarbonate melts: interplay between build-up and destruction of agglomerates. *Polymer* **2010**, *51*, 201–210.
- Bauhofer, W.; Schulz, S. C.; Eken, A. E.; Skipa, T.; Lellinger, D.; Alig, I.; Tozzi, E. J.; Klingenberg, D. J. Shear-controlled electrical conductivity of carbon nanotubes networks suspended in low and high molecular weight liquids. *Polymer* **2010**, *51*, 5024–5027.
- Gao, Y.; Cao, D.; Liu, J.; Shen, J.; Wu, Y.; Zhang, L. Molecular dynamics simulation of the conductivity mechanism of nanorod filled polymer nanocomposites. *Phys. Chem. Chem. Phys.* **2015**, *17*, 22959–22968.
- Ma, H. M.; Gao, X. L. A three-dimensional Monte Carlo model for electrically conductive polymer matrix composites filled with curved fibers. *Polymer* **2008**, *49*, 4230–4238.
- Bao, W. S.; Meguid, S. A.; Zhu, Z. H.; Pan, Y.; Weng, G. J. Effect of carbon nanotube geometry upon tunneling assisted electrical network in nanocomposites. *J. Appl. Phys.* **2013**, *113*, 234313.
- Duan, X.; Zhang, H.; Liu, J.; Gao, Y.; Zhao, X.; Zhang, L. Optimizing the electrical conductivity of polymer nanocomposites under the shear field by hybrid fillers: insights from molecular dynamics simulation. *Polymer* **2019**, *168*, 138–145.
- Kwon, S.; Cho, H. W.; Gwon, G.; Kim, H.; Sung, B. J. Effects of shape and flexibility of conductive fillers in nanocomposites on percolating network formation and electrical conductivity. *Phys. Rev. E* **2016**, *93*, 032501.
- Gao, Y.; Qu, F.; Wang, W.; Li, F.; Zhao, X.; Zhang, L. Increasing the electrical conductivity of polymer nanocomposites under the external field by tuning nanofiller shape. *Compos. Sci. Technol.* **2019**, *176*, 37–45.
- Gong, S.; Wang, Y.; Xiao, Z.; Li, Z.; Wang, Z. X.; Lei, R. S.; Zhu, Z. H. Effect of temperature on the electrical property of epoxy composites with carbon nanotube. *Compos. Sci. Technol.* **2017**, *149*, 48–54.
- Pryamitsyn, V.; Ganesan, V.; Panagiotopoulos, A. Z.; Liu, H.; Kumar, S. K. Modeling the anisotropic self-assembly of spherical polymer-grafted nanoparticles. *J. Chem. Phys.* **2009**, *131*, 221102.
- Jayaraman, A.; Schweizer, K. S. Effective interactions and self-Assembly of hybrid polymer grafted nanoparticles in a homopolymer matrix. *Macromolecules* **2009**, *42*, 8423–8434.
- Akcora, P.; Liu, H.; Kumar, S. K.; Moll, J.; Li, Y.; Benicewicz, B. C.; Schädler, L. S.; Acehan, D.; Panagiotopoulos, A. Z.; Pryamitsyn, V.; Ganesan, V.; Ilavsky, J.; Thiyagarajan, P.; Colby, R. H.; Douglas, J. F. Anisotropic self-assembly of spherical polymer-grafted nanoparticles. *Nat. Mater.* **2009**, *8*, 354–359.
- Harton, S. E.; Kumar, S. K. Mean-field theoretical analysis of brush-coated nanoparticle dispersion in polymer matrices. *J. Polym. Sci., Part B: Polym. Phys.* **2008**, *46*, 351–358.
- Eken, A. E.; Tozzi, E. J.; Klingenberg, D. J.; Bauhofer, W. Combined effects of nanotube aspect ratio and shear rate on the carbon nanotube/polymer composites. *Polymer* **2012**, *53*, 4493–4500.

- 30 Eken, A. E.; Tozzi, E. J.; Klingenberg, D. J.; Bauhofer, W. A simulation study on the effects of shear flow on the microstructure and electrical properties of carbon nanotube/polymer composites. *Polymer* **2011**, *52*, 5178–5185.
- 31 Gao, Y.; Cao, D.; Wu, Y.; Liu, J.; Zhang, L. Destruction and recovery of a nanorod conductive network in polymer nanocomposites via molecular dynamics simulation. *Soft Matter* **2016**, *12*, 3074–3083.
- 32 Kwon, G.; Heo, Y.; Shin, K.; Sung, B. J. Electrical percolation networks of carbon nanotubes in a shear flow. *Phys. Rev. E* **2012**, *85*, 011143.
- 33 Zare, Y.; Rhee, K. Y. A simple model for electrical conductivity of polymer carbon nanotubes nanocomposites assuming the filler properties, interphase dimension, network level, interfacial tension and tunneling distance. *Compos. Sci. Technol.* **2018**, *155*, 252–260.
- 34 Zhang, H.; Li, H.; Hu, F.; Wang, W.; Zhao, X.; Gao, Y.; Zhang, L. Cavitation, crazing and bond scission in chemically cross-linked polymer nanocomposites. *Soft Matter* **2019**, *15*, 9195–9204.
- 35 Hu, F.; Nie, Y.; Li, F.; Liu, J.; Gao, Y.; Wang, W.; Zhang, L. Molecular dynamics simulation study of the fracture properties of polymer nanocomposites filled with grafted nanoparticles. *Phys. Chem. Chem. Phys.* **2019**, *21*, 11320–11328.
- 36 Golmohammadi, N.; Boland-Hemmat, M.; Barahmand, S.; Eslami, H. Coarse-grained molecular dynamics simulations of poly(ethylene terephthalate). *J. Chem. Phys.* **2020**, *152*, 114901.
- 37 Chao, H.; Riggleman, R. A. Effect of particle size and grafting density on the mechanical properties of polymer nanocomposites. *Polymer* **2013**, *54*, 5222–5229.
- 38 Raos, G.; Moreno, M.; Elli, S. Computational experiments on filled rubber viscoelasticity: what is the role of particle-particle Interactions? *Macromolecules* **2006**, *39*, 6744–6751.
- 39 Srinivas, G.; Discher, D. E.; Klein, M. L. Self-assembly and properties of diblock copolymers by coarse-grain molecular dynamics. *Nat. Mater.* **2004**, *3*, 638–644.
- 40 Plimpton, S. Fast parallel algorithms for short-range molecular dynamics. *J. Comput. Phys.* **1995**, *117*, 1–19.
- 41 van Beek, L. K. H.; van Pul, B. I. C. F. Internal field emission in carbon black-loaded natural rubber vulcanizates. *J. Appl. Polym. Sci.* **1962**, *6*, 651–655.
- 42 Cao, Q.; Song, Y.; Tan, Y.; Zheng, Q. Conductive and viscoelastic behaviors of carbon black filled polystyrene during annealing. *Carbon* **2010**, *48*, 4268–4275.
- 43 Sisk, B. C.; Lewis, N. S. Vapor sensing using polymer/carbon black composites in the percolative conduction regime. *Langmuir* **2006**, *22*, 7928–7935.
- 44 Smith, G. D.; Bedrov, D. Dispersing nanoparticles in a polymer matrix: are long, dense polymer tethers really necessary? *Langmuir* **2009**, *25*, 11239–11243.
- 45 Smith, J. S.; Bedrov, D.; Smith, G. D. A molecular dynamics simulation study of nanoparticle interactions in a model polymer-nanoparticle composite. *Compos. Sci. Technol.* **2003**, *63*, 1599–1605.
- 46 Moll, J. F.; Akcora, P.; Rungta, A.; Gong, S.; Colby, R. H.; Benicewicz, B. C.; Kumar, S. K. Mechanical reinforcement in polymer melts filled with polymer grafted nanoparticles. *Macromolecules* **2011**, *44*, 7473–7477.
- 47 Nam, S.; Cho, H. W.; Lim, S.; Kim, D.; Kim, H.; Sung, B. J. Enhancement of electrical and thermomechanical properties of silver nanowire composites by the introduction of nonconductive nanoparticles: experiment and simulation. *ACS Nano* **2013**, *7*, 851–856.
- 48 Hooper, J. B.; Schweizer, K. S. Contact aggregation, bridging, and steric stabilization in dense polymer-particle mixtures. *Macromolecules* **2005**, *38*, 8858–8869.
- 49 Patra, T. K.; Singh, J. K. Coarse-grain molecular dynamics simulations of nanoparticle-polymer melt: dispersion vs agglomeration. *J. Chem. Phys.* **2013**, *138*, 144901.
- 50 Evans, D. J.; Morriss, G. P. Nonlinear-response theory for steady planar Couette flow. *Phys. Rev. A* **1984**, *30*, 1528–1530.
- 51 Lees, A. W.; Edwards, S. F. The computer study of transport processes under extreme conditions. *J. Phys. C: Solid State Phys.* **1972**, *5*, 1921.
- 52 Hiemenz, P. C.; Lodge, T. P. *Polymer chemistry*. CRC Press: London, New York, **2007**, p. 587.
- 53 Rungta, A.; Natarajan, B.; Neely, T.; Dukes, D.; Schadler, L. S.; Benicewicz, B. C. Grafting bimodal polymer brushes on nanoparticles using controlled radical polymerization. *Macromolecules* **2012**, *45*, 9303–9311.
- 54 Larson, R. G. *The structure and rheology of complex fluids*. Oxford University Press: New York, **1999**, p. 663.
- 55 Zhang, C.; Ma, C. A.; Wang, P.; Sumita, M. Temperature dependence of electrical resistivity for carbon black filled ultra-high molecular weight polyethylene composites prepared by hot compaction. *Carbon* **2005**, *43*, 2544–2553.
- 56 Gubbels, F.; Blacher, S.; Vanlathem, E.; Jerome, R.; Deltour, R.; Brouers, F.; Teyssie, P. Design of electrical composites: determining the role of the morphology on the electrical properties of carbon black filled polymer blends. *Macromolecules* **1995**, *28*, 1559–1566.
- 57 Yoon, J. T.; Lee, S. C.; Jeong, Y. G. Effects of grafted chain length on mechanical and electrical properties of nanocomposites containing polylactide-grafted carbon nanotubes. *Compos. Sci. Technol.* **2010**, *70*, 776–782.