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분자동역학 모사를 이용한 고강도, 저발열 고분자 복합재료 설계 및 연구

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Study and Design of High Strength and Low Heat Generation Polymer Composites by Molecular Dynamics Simulation

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Abstract: The molecular dynamics simulation was used to study and design a polymer composites system with excellent mechanical strength and less heat generation in a dynamic process. A series of system factors such as filler loading, surface modification onto filler, and network of cross-linking filler particles on mechanical and heat generation of polymer composites are systematically considered. It is found that the surface grafting onto fillers can restrain the heat generation of polymer composite in the dynamic process, while it shows less effect on the mechanical property. A network of cross-linking filler particles can be fabricated by a combination of grafting chains onto fillers. By filling such a network into the polymer, the mechanical and heat generation properties of polymer composites are significantly improved. Simulation results can help experimental fabrication of polymer composites with excellent mechanical and heat generation properties.

Keywords: molecular dynamics simulation, polymer composite, surface modification, cross-linking network.

Introduction

Inorganic fillers are important to physical properties of polymer composites, such as carbon blacks are added into rubber to enhance the mechanical properties of rubber products.[1-3] However, for elastomer materials those undergo high-frequency dynamic repeating deformation, inorganic fillers may increase the heat generation in dynamic process owing to the friction between fillers and polymers.[4] Such as, Kucherskii and collaborators found that the rubber composites with carbon black as fillers show stronger rigidity during the stretching process, and increased heat generation during the relative sliding process.[5] As is well known, heat flux will damage the mechanical and aging properties of polymer materials.

Surface modification on fillers may be an effective way to restrain heat generation in polymer composites. Theoretically, people predicted that surface treatment onto fillers will improve the dispersion of filler particles in composites.[6] Obviously, surface modification may improve affinity between fillers and polymers and so make a good dispersion of fillers in composites, which will reduce the friction between fillers. Liu and collaborators carried out molecular dynamics simulations on polymer composites, they found that surface grafting onto nanoparticles can improve its dispersion, with the increasing of grafting density and length, the Payne effect reduces accordingly.[7] Researchers have developed many experimental technologies to surface modify filler particles, such as, surface grafting polymer chains,[8,9] plasma treatment,[10-12] *in situ* modification and sol-gel method etc.[13-16] These surface modifications onto fillers improved tensile strength and elongation at break of polymer composite. However, previous researching reports less data on heat generation of polymer composites in

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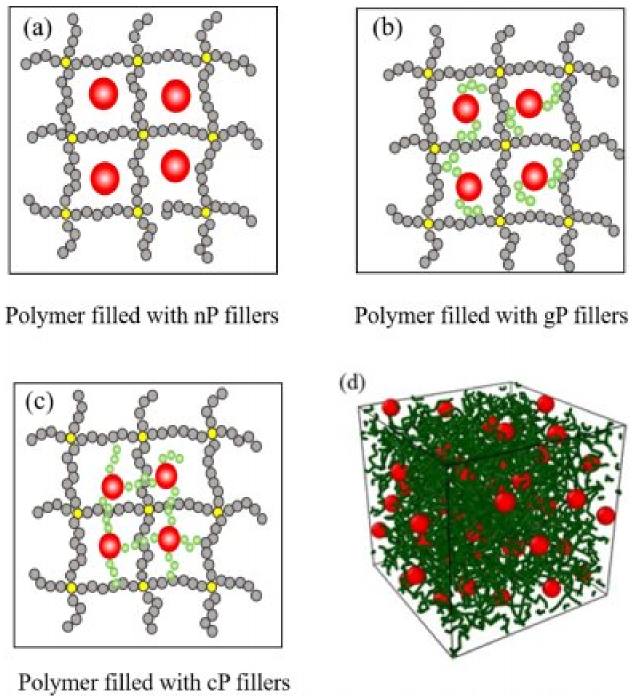
the dynamic process. It is hard to determine the effect of surface modification on heat generation of polymer composites.

In this theoretic study, we carried out molecular dynamic simulation on polymer composites. By constructing cross-linking polymer models and surface modified filler particles, we studied the effect of surface modification on mechanical property of polymer composites and heat generation during dynamic process. To make polymer composites with strong mechanical strength and less heat generation we built a cross-linking network of modified fillers and make such network penetrate into the network of polymer chains. Our simulation results are illuminating to experimental researching.

Models and Methods

We performed classical molecular dynamics simulation methods to study the polymer composites. The polymer chain is represented by a bead spring model developed by Kremer and Grest,[17] individual beads are connected by a finite expandable nonlinear elastic (FENE) potential.[18] Interaction between nonbonding beads are represented by expended Lennard-Jones potential. To distinguish coarse-grained beads of filler and polymer segment, we set the diameter of polymer and grafted chain beads are σ and mass of them to be m respectively, while the diameter and mass of filler beads are 4σ and $64m$ respectively. Due to the dimensionless units setting, m and σ are 1 in the simulation. Liu *et al*. once performed molecular dynamic simulation on polymer composites, and their simulation results are reasonable and accordant to experimental observation. In this study, we set up the parameters which are the same in reference.[19] We constructed a three-dimensional polymer network and each lattice of the polymer network is composed of 10 polymer beads. The cross-linking degree of such network is calculated as number of cross-linking beads over number of polymer beads, which is 6.43% for all composites. Filler particles are imposed into the polymer networks. Filling degree represented by n is defined as $n=N/M$, where N is the total number of filler beads and M is the total number of polymer beads, keep the number of filler beads and polymer beads unchanged to make the filling degree equal in different systems. We considered three kinds of filler particles in the simulation as shown in Scheme 1, those are (a) native particle (nP) without surface modification; (b) surface grafted particle (gP) whose surface is grafted with polymer beads; (c) a network of particles (cP) by cross-linking grafting chain at surfaces of adjacent particles.



Scheme 1. Simulation models of polymer composites: (a) polymer filled with nP fillers; (b) polymer filled with gP fillers; (c) polymer filled with cP fillers; (d) a typical snapshot of filled polymer composites.

NPT ensemble and periodic boundaries were employed in simulation. The simulated temperature is fixed at $T^*=1.0$ and the pressure is fixed at $P^*=0$ through the Nose-Hoover hot bath. The system are fully equilibrated (more than 10^7 cycles). The model was equilibrated and then stretched at strain ratio of 327% ($\varepsilon_{max}=3.27$) at NVT ensemble to get stress-strain curves of polymer composites. The stress σ is calculated as the same with that in reference.[19] To calculate heat generation of polymer composites during cyclic deformation, we imposed cyclically tensile loading processes at strain ratio of 20% ($\varepsilon_{max}=0.2$) for equilibrated composites, which will produce a hysteresis loop of loading and unloading stress-strain curves. The area of hysteresis loop of stress-strain curves is calculated to represent the energy loss during dynamic process, which will be released in the form of heat in the experiment and correspond to the heat generation of polymer composites during dynamic process. More simulation details are consistent with those in reference.[19] The simulation process was implemented using a large-scale atom/molecule integrated parallel simulator (LAMMPS) developed by Sandia National Laboratory.[20]

Results and Discussion

Effect of Filling on Temperature of Glass Transition (T_g) of Composite Materials. To simulate a polymer composite, system temperature must be higher than T_g of polymer composites. We equilibrate composites model with a cooling rate of $5\times10^{-4}/\tau$ to gradually decrease temperature recording the variation of composites density. The T_g value of composites is estimated from the break point of linear variation of composites' density. For polymer composites filled with three kinds of filler particles (nP, gP and cP, respectively), the T_g values of them are about 0.55, as shown in Figure 1. In the following simulation, we set the system temperature at 1 to ensure the system being a rubber state.

Effect of Filler Loading on Mechanical and Heat Generation of Polymer Composites. Firstly, we compared the effect of different fillers on mechanical and heat generation of polymer composites. We imposed three types of fillers with the same filling degree into a cross-linked polymer matrix respectively. For grafted particles (gP), there are six chain segments symmetrically grafted onto the surface of a native particle, each chain segment is composed of three beads. Grafting chain segments between the nearest adjacent gP are furtherly combined to form a cross-linked particles (cP) network involved in the polymer network. As shown in Figure 2 and 3, the mechanical strength of all polymer composites are improved correspondingly by filling degree increasing from 0.5% to 1.34%. In Figure 2, the mechanical strength of polymer composites filled with grafted particles (gP) are slightly less than those filled with native particles (nP). This is because in our simulation model grafting of polymer beads decreases filling content of composites in somewhat. It is worth to be noted that, in Figure 3 polymer composites filled with cP network exhibit excellent mechanical strength than those filled with nP. This means, the network of cP may effectively strengthen the polymer matrix in comparison with gP does. The same as in reference,[19] the mechanic strength of polymer

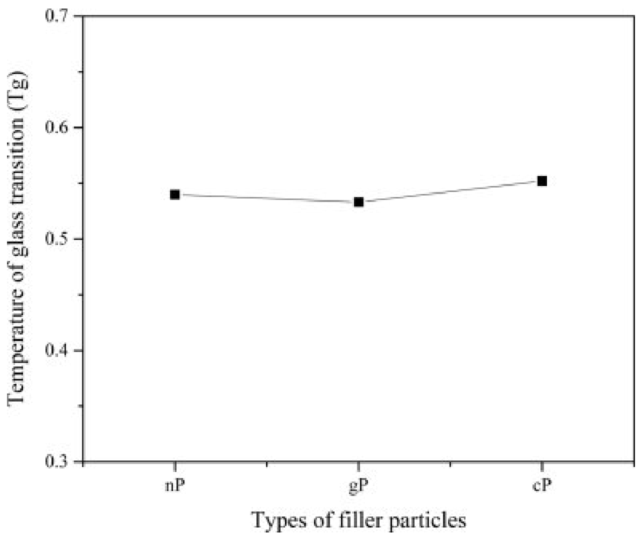


Figure 1. Temperature of glass transition (T_g) of polymer composites filled with different types of filler particles (nP, gP and cP, respectively). Filling degree is 1.34%.

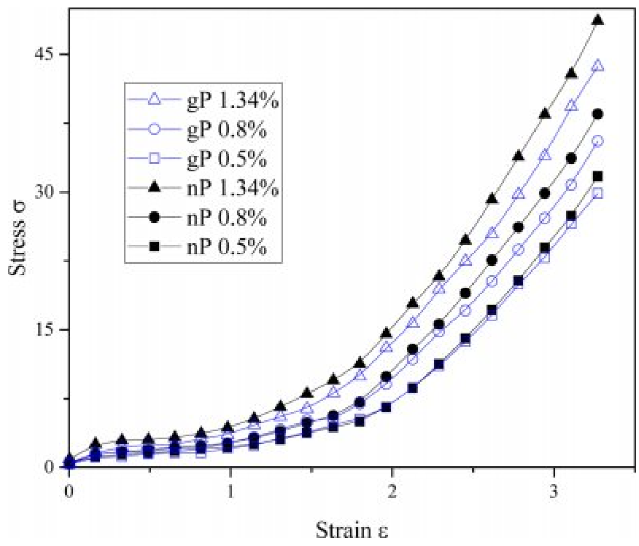


Figure 2. Effect of filling degree on the mechanical properties of grafted particle and primary particle filled rubber composites.

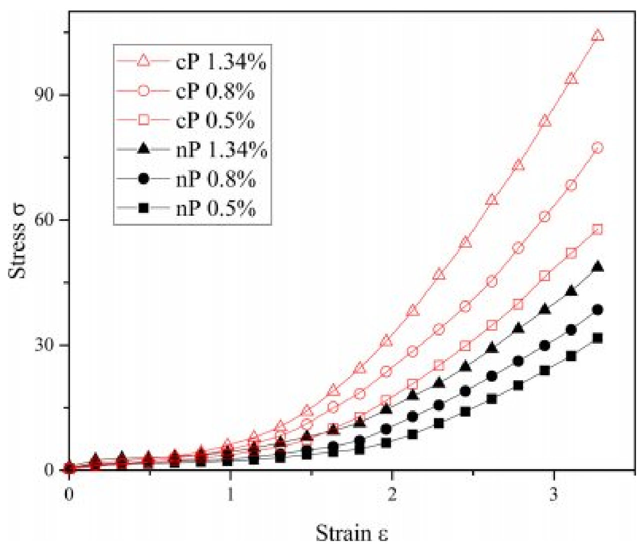


Figure 3. Effect of filling degree on mechanical properties of network of particles and primary filled rubber composites.

composites are enhanced with the increase of fillers.

To study the effect of filler loading on heat generation, we calculated the area of a hysteresis loop of loading and unloading stress-strain curves as shown in Figure 4. To avoid the random error, the area values are averaged with at least 19 hysteresis loops of loading and unloading stress-strain curves, those are shown in Figure 5. It is obviously, the area values increase along with increasing of filling degree for all polymer composites, while those of polymer composites filled with gP and cP are lower than that filled with nP. This means surface grafting may effectively decrease heat generation of polymer composites during dynamic process. Considering the excellent mechanical strength of polymer composites filled with cP network as shown in Figure 3, it is worthy to study the effect of cP network on mechanical and heat generation properties in deep.

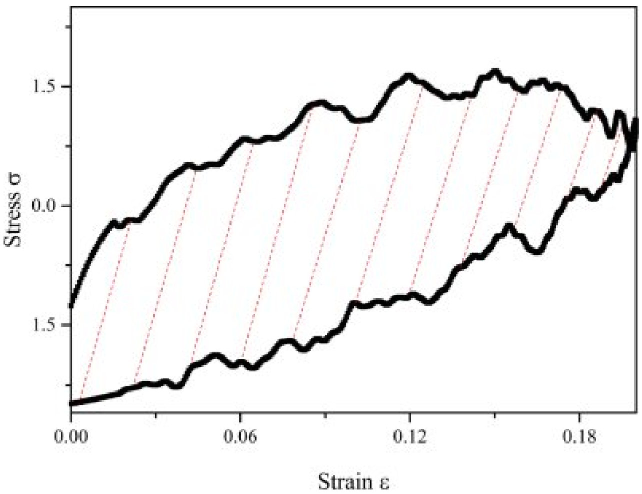


Figure 4. Hysteresis loop of loading and unloading stress-strain curves.

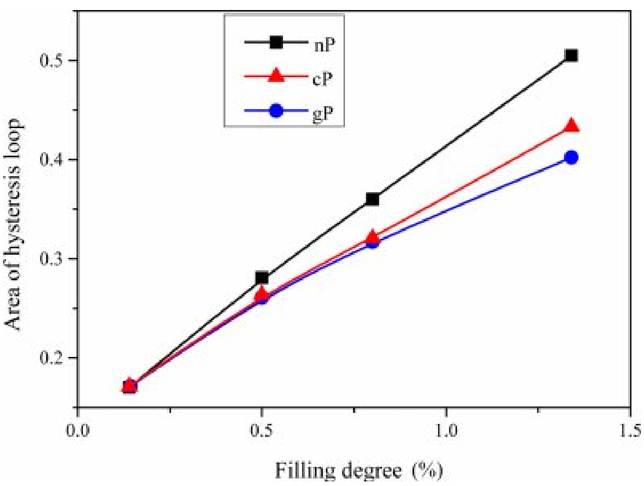


Figure 5. Effect of different filler loading on the grafted particle, network of particles and primary particle systems to hysteresis area.

Effect of cP Network on Mechanical and Heat Generation Properties of Polymer Composites. As discussed above, the cP network may effectively strengthen polymer composites, at the same time restrain the heat generation during dynamic process. We considered different grafting chain length in cP network to find out the reason of network structure on affecting mechanical and heat generation properties. Grafting chain

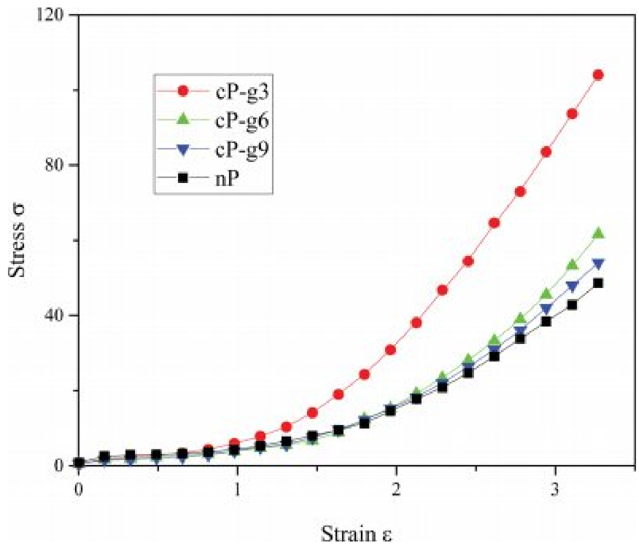


Figure 6. Effect of graft chain length on the grafted particle and network of particles to the mechanical properties.

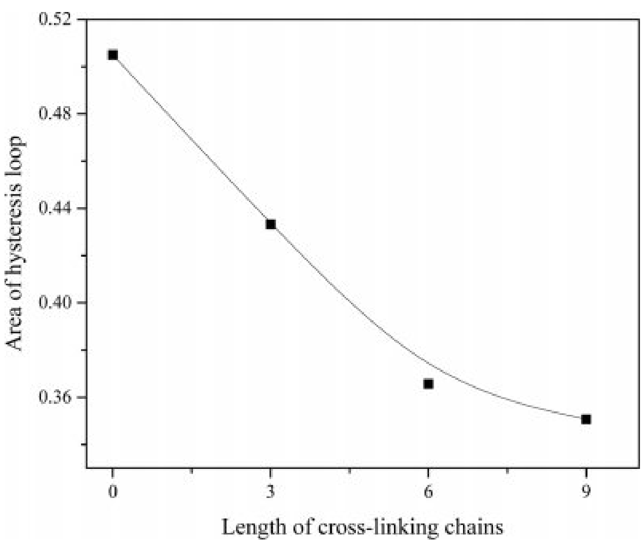


Figure 7. Effect of graft chain length on the network of particles to hysteresis area

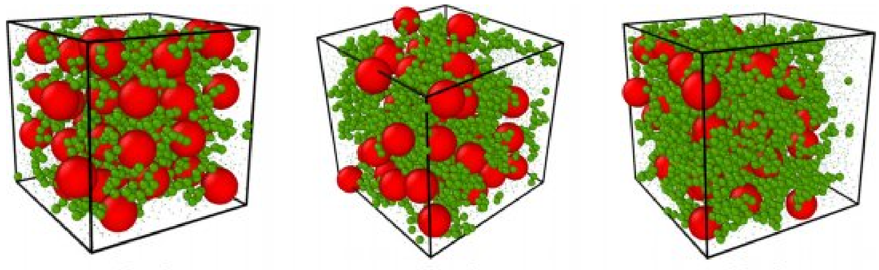


Figure 8. Snapshots of polymer composites filled with grafting chains with lengths to be 3 beads (nP-g3), 6 beads (nP-g6) and 9 beads (nP-g9), respectively.

lengths onto the particle surfaces are varied from 3 beads to 9 beads. The stress-strain curves can be found in Figure 6. With increasing of grafting chain lengths, the strength of polymer composites reduces rapidly. In Figure 7 the area of the hysteresis loop of stress-strain curves of polymer composites reduced along with the increasing of grafting chain lengths. We think this is because surface grafting chains covered the particles from each other, and so reduced the interaction between filler particles. As a result, the filler particles interact predominantly with polymer chains, which reduce the heat generation from friction of fillers as shown in Figure 6. In cases the grafting chain length is rather short, such as 3 beads in Figure 6, the network of cP is rather intensive, which can effectively strengthen the polymer matrix. For better illustration, the snapshots of the coating status of different grafting chain lengths on the filler are shown in Figure 8. Note that the polymer chains are represented by olive points to avoid obscuring the nanoparticles, the red spheres denote the fillers, the green spheres denote graft chains. These snapshots also intuitively display that the longer the graft chain is, the more the filler surface is coated.

Conclusions

The effects of three different types of filler particles on the mechanical and heat generation properties of polymer composites were studied by molecular dynamics simulation. The results show that the surface modification onto filler particles can reduce the friction between filler particles, and so to restrain the heat generation of polymer composites in dynamic process. A moderate cross-linked filler particles network may effectively strength polymer matrix. To design an ideal network of cross-linked filler particles in polymer composites can make a polymer material with wonderful mechanical and heat generation properties.

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References

1. Z. H. Tang, L. Q. Zhang, W. J. Feng, B. H. Guo, F. Liu, and D. Jia, *Macromolecules*, **47**, 8863 (2014).
2. S. J. Park, J. Y. Kang, and S. K. Hong, *Polym. Korea*, **29**, 151 (2005).
3. C. Nah and B.W. Jo, *Polym. Korea*, **23**, 271 (1999).
4. A. I. Medalia, *Rubber Chem. Technol*., **64**, 481 (1991).
5. A. M. Kucherskii, *Polym. Test.*, **24**, 733 (2005).
6. T. V. M. Ndoro, E. Voyiatzis, A. Ghanbari, D. N. Theodorou, M. C Böhm, and F. Müller-Plathe, *Macromolecules*, **44**, 2316 (2011).
7. J. X. Shen, J. Liu, Y. Y. Gao, D. P. Cao, and L. Q. Zhang, *Langmuir*, **27**, 15213 (2011).
8. C. Mahoney, C. M. Hui, S. Majumdar, Z. Y. Wang, J. A. Malen, M. N. Tchoul, and K. Matyjaszewski, *Polymer*, **93**, 72 (2016).
9. M. Mahmoudian, E. Nozad, and M. Hosseinzadeh, *Polym. Korea*, **42**, 434 (2018).
10. S. J. Park, K. S. Cho, and S. K. Ryu, *Carbon*, **41**, 1437 (2003).
11. Y. Q. Tan, L. J Fang, J. L Xiao, and Q. Zheng, *Polym. Chem.*, **4**, 2939 (2013).
12. I. J. Jang, J. H. Jeong, and J. W. Jeong, *Polym. Korea*, **41**, 741 (2017).
13. X. Ye, M. Tian, and L. Q. Zhang, *J. Appl. Polym. Sci.*, **124**, 927 (2012).
14. Q. Li, X. Li, S. H. Jang, D. H. Lee, Y. Fan, and U. R. Cho, *Polym. Korea*, **41**, 1027 (2017).
15. J. Kim, H. Im, J. Han, and J. Kim, *Polym. Korea*, **36**, 22 (2012).
16. I. A. Rahman and V. Padavettan, *J. Nanomater.*, **2012**, 132424 (2012).
17. K. Kremer and G. S Grest, *J. Chem. Phys.*, **92**, 5057 (1990).
18. M. Kröger, *Phys. Rep.*, **390**, 453 (2004).
19. J. Liu, S. Z. Wu, L. Q. Zhang, W. C Wang, and D. P. Cao, *Phys. Chem. Chem. Phys.*, **13**, 518 (2011).
20. S. Plimpton, *J. Comput. Phys.*, **117**, 1 (1995).