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폴리이소프렌-폴리스티렌 복합재료의 분자 동력학 연구: 공간 보완 거동

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Molecular Dynamics Study of Polyisoprene-polystyrene Composites: Spatial Complementary Behaviour

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Abstract: Various additives have been applied to adjust the properties of rubber in the tire industry. As an important environmental waste, plastic is a potential additive to be added to rubber to blend aiming at forming abrasive and deformation resistance elastomers. However, the molecular details remain unclear, especially for their assembly structure. Using all-atom molecular dynamics simulations, we have studied the assembly structures and processes of polyisoprene and polystyrene complex, focusing on the spatial complementary behavior. The simulation results indicate that polyisoprene and polystyrene can form tight entangled structure. The polyisoprene can adjust their conformations to fill up the cavity generated from polystyrene self-aggregation. The formed cross-linked and spatial polystyrene complementary structures can improve the plasticity and abrasive resistance, which is superiority in tire design. Our results provide an important understanding of the rubber application and tire industry and give a possible idea to deal with abandoned plastics.

Keywords: tire industry, polyisoprene-polystyrene composites, assembly structure, spatial complementary behavior.

Introduction

The amount of car has been expanding rapidly since the beginning of the 20th century, which is projected to increase to 1500 million by 2050. The spectacular expansion of car usage has inevitably increased the number of car accidents, with millions of people are suffering from the severe injuries every year.[1] Many reasons can lead to car accidents,[2,3] such as driver careless and vehicle defects. Among important vehicle defects, tire defect has become a serious problem.[4] Tire defects can generate from two main reasons, including physical damage and thermal damage, both often occurring in high-speed driving.

Rubber, a polymer material, is the most important and the largest portion of the tire. Previous studies indicate that rubbers can undergo the deformation if existing external deformation force and stress.[5,6] Experiencing long-time driving, the tire may abrade and generate irreversible deformation, which will increase the risk of car accident. Thus, increasing the abrasive and deformation resistance of rubber need further study.

Several additives have been selected to improve performance, such as abrasive and deformation resistance. These additives contain nanoparticles[7-12] and polymers.[13,14] Plastic, such as polystyrene (PS), is a long-chain structure same as rubber. Plastic is easily synthesized and even can be obtained from environmental waste, thus some researchers focus on using plastic to adjust the properties of rubber. Rheological properties like shear viscosity, shear modulus, die swell, and extrudate surface have been monitored for numerous thermoplastic elastomeric systems over the years.[15-19] For example, Banerjee *et al.* have investigated the interaction parameter of polyamide 6/ fluoroelastomer blends through rheological measurement by estimating the interfacial tension between the dispersed rubber

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phase and the continuous matrix of thermoplastic.[20] As we know, structure determines the properties, but no study paid attention to the structure of the rubber and plastic mixture.

In this study, we have studied the assembly structures and processes of polyisoprene (PP) and PS complex by all-atom molecular dynamics simulations. The simulation results indicate that PP and PS can form tight entangled structure, with PP adjusting their conformations to fill up the cavity of PS self-aggregation. Depending on the adding ratio, adding PS can slightly increase the gyration and increase the density of the complex. The formed cross-linked and spatial complementary structures decrease the molecular diffusion and can potentially improve the plasticity and abrasive resistance.

Methods

Gromos force field[21] was selected to simulate the assemble process of PP and PS and obtain final molecular structures, which has been widely used in polymer simulations. The models of PP and PS were generated by using ATB tool (Figure 1 (a), (b)).[22] Each PP and PS both contain 40 repeated units. The system setup included 20 PP molecules and PS molecules with different number, varying from 0 to 20. Both PP and PS monomers were inserted randomly into the box (Figure 1(c)). Period boundary conditions were applied in all three dimensions. The system energy was firstly minimized using the steepest descent algorithm, and then followed by 1 ns simulation under NVT ensemble condition using conjugate gradient algorithm. Isotropic Berendsen barostat was used with a coupling constant of $\tau_P = 4$ ps. The compressibility was 5×10^{-5} bar^{-1}. The time step of simulations was 10 fs, and the neighbor list was updated every 10 steps. The temperature was maintained at 298.15 K by v-rescale temperature coupling. Simulations in NPT ensembles lasted until up to the equilibrium state. All simulations were performed using GROMACS 4.6.7.[23] Snapshots were rendered by VMD.[24]

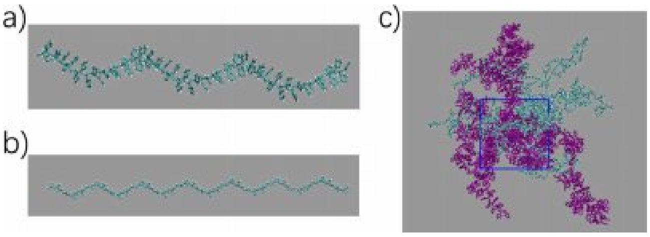

Figure 1. Models for our simulations: (a) polystyrene; (b) polyisoprene; (c) initial mixed system.

Results and Discussion

Structure Characterization of PP and PS Assembly. To testify our models of PP and PS, we have added extra simulations to calculate the glass transition temperature for PP and PS. The system was prepared with the chains in a stretched configuration. The system was firstly relaxed in melt at 540 K, and then cooled down to 300 K (PS) and 120 K (PP) with a constant colling rate of 0.01 K/ps. The glass transition temperature of PP and PS are 217 K and 406 K, respectively (Figure S1). The values agree well with the glass transition temperatures in previous researches,[25,26] thus our models are appropriate. Four different mixed ratios of PP and PS were performed to finish the assembly, experiencing 50 ns NPT equilibrium. From Figure S2, the potential energy of different mixed ratios all finally reaches a plateau. Final assembly structure was shown in Figure 2. For the pure PP system, initial discrete PP finally formed an aggregation state (Figure 2(a)), corresponding to a high peak of radial distribution function at 0.2 nm (Figure 2(f)). While adding PS into the system, PP and

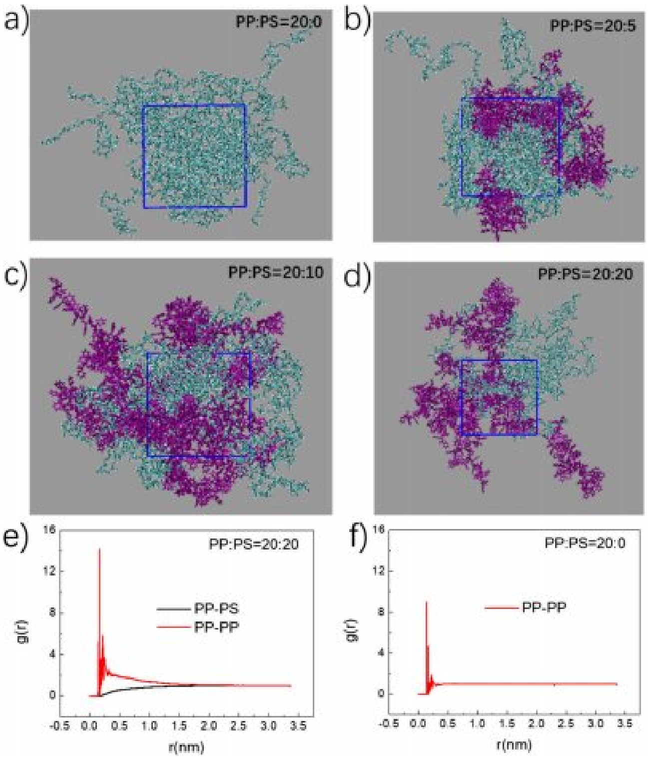

Figure 2. Characterizations of assembly structures. Final snapshots of PP-PS complex of different mixed ratios for PP:PS=20:0 (a); 20:5 (b); 20:10 (c); 20:20 (d). Radial distribution function of PP-PS and PP-PP for PP:PS=20:20 (e); 20:0 (f).

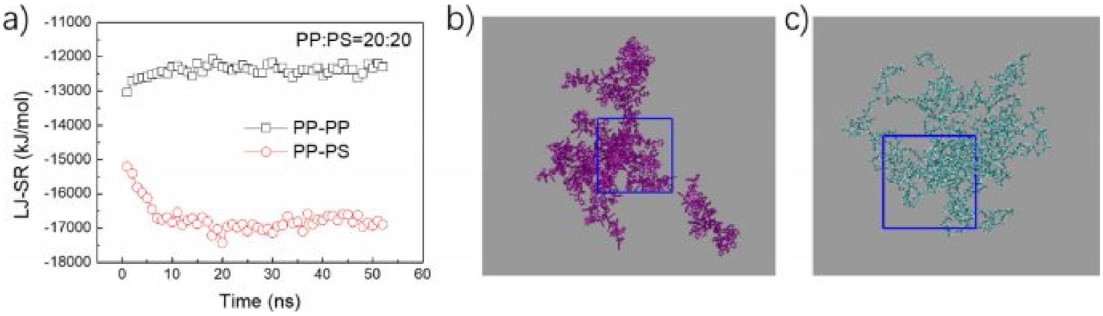

Figure 3. (a) Time evolutions of LJ potential energy for PP-PP and PP-PS. Stable conformations of PS (b); PP (c). The mixed ratio is 20:20.

PS can first assemble into aggregation *via* cross-linking (Figure 2(b)-(d)). The peak at 0.2 nm for PP - PP contact increases especially for the ratio of 20:20 (Figure 2(e) and Figure S3). This means PS assembly can make PP themselves contact more tightly. LJ interaction energy for PS-PP and PP-PP were shown in Figure 3(a) and Figure S4. PP-PP interaction decreases while the PS-PP interaction increases. This means additional PS molecules can contact the PP aggregation and finally form mixed assembly structures. The separated PP and PS assemblies were shown in the Figure 3(b) and 3(c), which exhibit amorphous structures. This indicates that PS and PP can form irregular cross-linking structures. The cross-linking degree is dependent on the adding ratio of PS. A higher adding ratio can make more PS contact the PP. If no extra PS was added into rubber, the interaction of PP-PP just kept at a stable level.

Adding Ratio of PS Mediated Density and Diffusion Variation of PP and PS Assembly. From the above analysis, PP and PS finally formed crossing-linking structures. With the increase of adding ratio, the density of complex increases gradually. If the adding ratio is smaller than 33.3%, the density increases linearly. However, continuous adding PS cannot increase the density always *via* linear relation. Adding PS up to the ratio of 20:20, the density is only a little higher than the ratio of 20:10, because nearly all of the cavities of PP aggregation were filled by the PS (Figure 4 and Figure S5).

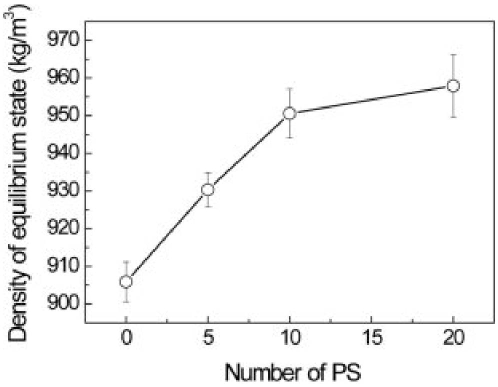

Figure 4. Density of equilibrium state for different mixed ratios.

The gyration radius of different systems were calculated and shown in Figure 5. For the pure PP system, the final gyration radius of single PP was 2.8 nm. After adding PS molecules, the gyration radius increases to 3.1 nm, no matter what the adding ratios are. It was expected for PS that the gyration radius

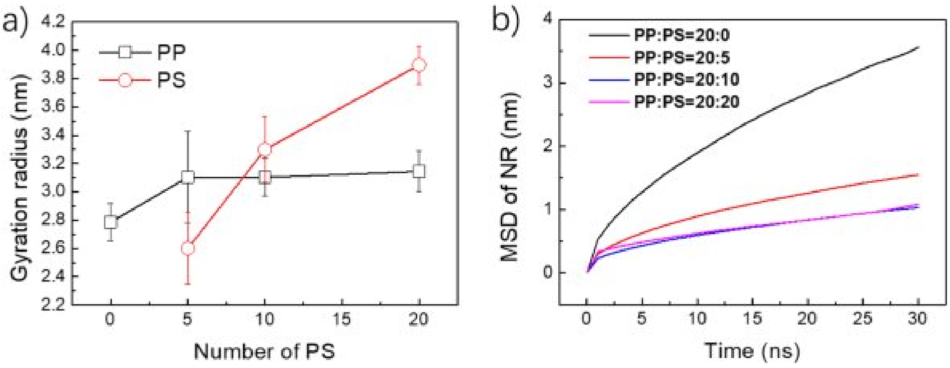

Figure 5. (a) Gyration radius of PP and PS under different mixed ratios; (b) Mean square displacement of PP for different mixed ratios.

increases with the increase of adding ratio, because the PS inserts into the PP assembly, which makes PS more amorphous. The cross-linking structure also makes the diffusion of PP decreases, from the analysis of mean square displacement (Figure 5(b)). Likewise, adding PS also can decrease the diffusion rate of the whole system, which in turn proves the crossing-linking structures (Figure S6(a), S6(b)).

Spatial Complementary Behavior of PS and PP. Comparing to experimental investigations, molecular dynamics simulations can give structure details of the molecular level. Time evolutions of typical snapshots for single PP and PS were shown in Figure 6. For PS chain, it can shrink itself to aggregation by hydrophobic and π-π interactions. But because of the steric hindrance and bending rigid, it's difficult for the long-chain to adjust itself to form a compact structure. Inevitably, there are some defects on the surface of formed aggregation, which have been labeled using the red lines (Figure 6(a)). Lacking in the π-π interactions but higher rigid, PP chain is more difficult to bend itself to form aggregation, only some local bending exists during the whole chain.

Bearing in our mind that the density increases after adding PS into PP phase, the free volume was calculated to explore the reason (Figure 7(a)). In Gromacs software, the program of free volume tries to insert a probe with a given radius into the simulations box and if the distance between the probe and any atom is less than the sums of the van der Waals radii of both atoms, the position is considered to be occupied. Relative to the whole volume, free volume decreases gradually with the ratio of PS increasing. It means that the gaps among the PP aggregation is filled with the PS chain. The molecular structure was captured and shown in Figure 7(a) and 7(b). The side chain is embedded in the surface defects of PS aggregation exactly. In the past decades, many additives have been added to PP to improve the abrasive and deformation resistance. For example, natural rubber filled with carbon black can form a higher degree of entanglement, causing higher Young's mod-

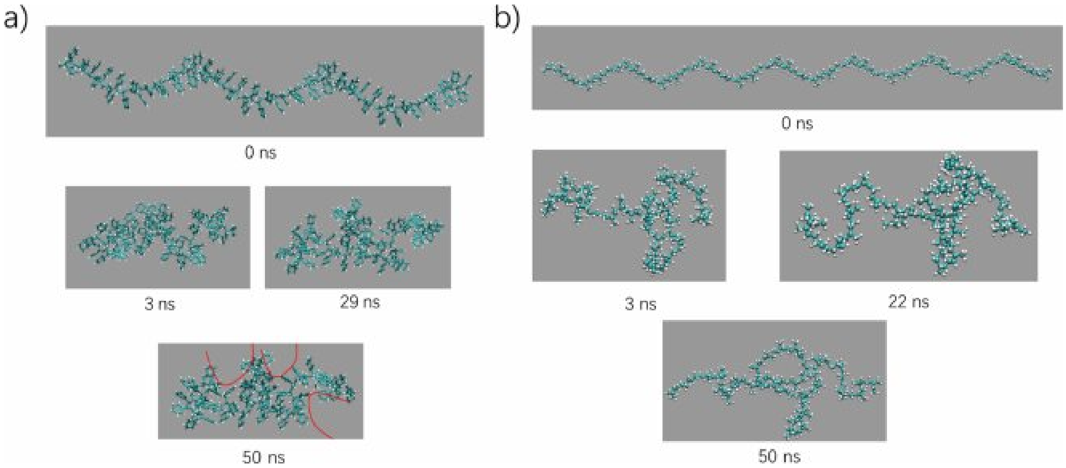

Figure 6. Time evolutions of typical snapshots depicting the conformation transformations of single PP (a); PS (b).

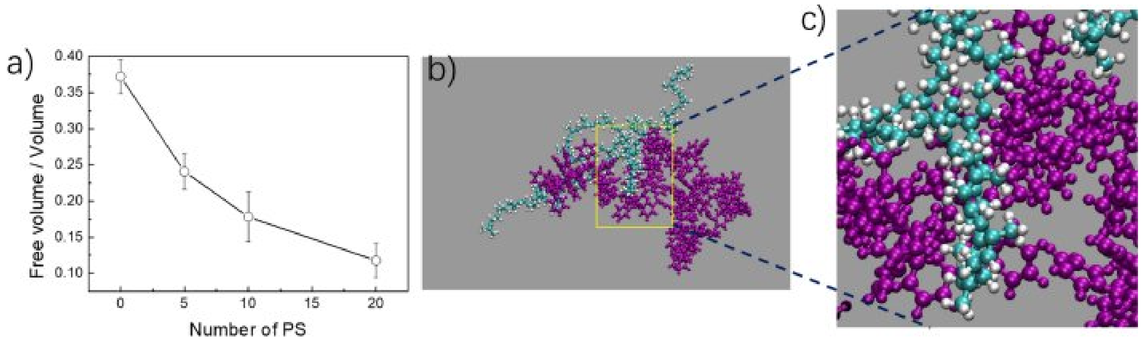

Figure 7. (a) The ratio of free volume among whole volume for different mixed systems. (b) Typical embedded structure exhibiting spatial complementary behavior. (c) Partial enlarged detail corresponding to (b).

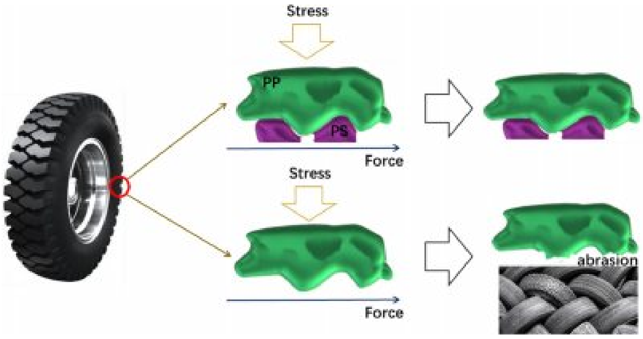

Figure 8. Sketch map of possible impact mechanism for using PP and PS mixture producing tires.

ulus and hardness.[12] Another report revealed a strong connection between the resorcinol formaldehyde latex fiber coating and the peroxide-cured rubber matrix.[13] The mechanisms of different additives are similar, both forming a complex structure of entanglement state. In our work, the complex structure of PP and PS shows a typical spatial complementary behavior, which can increase the entanglement at a very high degree, thus it will improve the abrasive and deformation resistance highly.

Effect of Spatial Complementary Behavior in Car Industry. The above simulations indicate that the spatial complementary of PP and PS can increase the cross-linking degree and decrease the surface defects. If using pure PP to produce the tire, it is easier to generate deformation while adding high shear force and stress. Also, due to the surface defects or gaps, friction between tire and road can more easily cause the tire abrasion. On the contrary, the complex of PP and PS can form a tight cross-linking structure, which may resist higher external force. Due to improving the compactness of tire, the surface of the tire can resist more stress, without increasing the intensity of pressure. In a word, adding PS is a potential solution to increase abrasive and deformation resistance. The possible impact mechanism was described in Figure 8 vividly.

Conclusions

The studies of PP and PS blends have been performed in the past years, but the molecular mechanism remains unclear. Using all-atom molecular dynamics simulations, we have studied the assembly structures and processes of PP and PS complex. The simulation results indicate that PP and PS can form a tight entangled structure. The PP can adjust their conformations to fill up the cavity generated from PS self-aggregation, which will offset the original defects. After adding PS, the density of complex increases, which is corresponding to the decrease of free volume. Besides, the diffusion rate for PP decreases apparently because some chains of PP are inserted into PS aggregations. The formed cross-linked and spatial complementary structures can improve the plasticity and abrasive resistance, which is superiority in tire design.

Our results demonstrate the complementary structure of PP-PS complex, which in turn provides an important understanding for rubber application and tire industry. Besides, plastic waste has become a serious environmental problem. Using plastic as potential materials to modify the tire abrasive resistance may be an effective solution to deal with dumped plastic. Although our results reveal the spatial complementary behavior of PS and PP, many problems are requiring study. For example, how do the kinds of plastic affect the PP properties? In any event, our recent results give a theoretical explanation for future PS applications in the tire industry.

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Supporting Information: The Supporting Information is available regarding the additional simulation results, including the glass transition temperature for PP and PS, time evolutions of potential energy, radial distribution function of PP-PS and PP-PP or PP:PS=20:5 and 20:10, time evolutions of LJ potential energy and density for different mixed ratios, and mean square displacement of system and PS for different mixed ratios. The materials are available via the Internet at http://journal.polymer-korea.or.kr.

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