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Mesoscale dynamic simulation on phase separation between plasticizer and binder in NEPE propellants

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ABSTRACT

It has been found that phase separation between polymer binder and small molecular plasticizer has an important effect on the properties of nitrate ester plasticized polyether (NEPE) propellants. However, the phase separation mechanism and factors of influencing the phase separation have not been clarified yet. To shed some light on this issue, a simple and novel method, that is Dissipative Particle Dynamics (DPD) mesoscale simulation, was used to study the influence of temperature and chains length on the phase separation behavior between binder and plasticizer. The results indicated that the temperature is the key factor in controlling the moving speed of molecules in NEPE propellants system. While the interaction between binder and plasticizer plays an important role on the phase separation. With temperature decreasing, the phase separation takes place later and the extent of phase separation is higher. Within a range, when the length of polymer chains is larger, the occurrence of phase separation is earlier. However, for long chains system, the phase separation is less completely than that of the short chains system when the process reaches equilibrium.

1. Introduction

Nitrate ester plasticized polyether (NEPE) propellants are a type of high-energetic composite solid propellants which use polyether such as polyethylene glycol (PEG) or ethylene oxide–tetrahydrofuran co-polyether, as polymer binder and use mixed nitrate (usually using nitroglycerin and 1,2,4-butanetriol trinitrate) as plasticizer. Large amount of solid particles (aluminum powder, octogen, ammonium perchlorate, etc.) is filled in the propellants. The mass ratio of plasticizer and preformed polymer can reach 4.0. Since the solubility parameters of nitrate and binder are very near [1,2], the two kinds of materials can mixed very well, so the phase separation will not happen at normal and high temperatures. However, at low temperature, some experiments showed [3], when the mass ratio of plasticizer and polymer is less than 2.8, the PEG chains will crystallize which means that the phase separation between binder and plasticizer takes place. The experimental evidences indicated that the properties of the propellants, such as the low temperature mechanical properties, impact sensitivity, friction sensitivity, combustion rate, etc. changed apparently with the occurrence of the phase separation. In other words, the phase separation has an important effect on the properties of NEPE propellants. However, the phase separation mechanism and the influence factors have not been clarified yet [4,5]. This may attribute to the short history of NEPE propellants [6], which has not been known very systematically. Another reason may be that the study on phase separation at low temperature is not easy to carry out experimentally [7].

In the present article, we studied the phase separation of macromolecular binder and small molecular plasticizer using mesoscale simulation method of Dissipative Particle Dynamics (DPD). The objective is to investigate how the temperature and chains length affect the phase separation behavior.

2. Simulation system and characterization of phase separation

2.1. Simulation system

DPD is a relatively new mesoscale simulation method [8,9], wherein the system is represented by a set of (N) discrete particles of equal mass (m) placed in a three-dimensional (3D) simulation box. The DPD particles interact pairwise, and are subject to repulsive conservative forces, dissipative forces, and random forces associated with interactions with surrounding particles within a specified cutoff radius. Recent studies showed that DPD is feasible in simulation of a system with phase separation [10–17].

The present work adopted the model systems of our previous studies [18,19]. Therefore most of the parameters are the same as

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those in previous works. For instance the simulation box contains 48 000 particles in $20 \times 20 \times 20$ cubes and the system has the same density $\rho = 6$ (each cube contained 6 particles). The parameters of the conservative forces, $\prod_{ij}$, between the same kinds of particles ($i = j$), were 12.5. The time step δ_t was 0.02 and the parameter of random force ξ was 3. To prevent the binder chains from crossing the simulation box, which would lead to wrong results, the bounced wall boundary condition was adopted in the present study [20–22]. Frozen particles were used to represent the wall and the density of wall particles was 6. The frozen particles interacted as normal particles, but had a fixed position and velocity. The repulsive force from the wall particles was big so as to bounce the inner binder and plasticizer particles back, in other words, the $\prod_{ij}$ between the wall particles and inner particles were set as 80 rather than 12.5 in order to produce bouncing force. The thickness of the wall was 2. The frozen positions of the wall particles in these methods intrinsically invoked ordering of particles in the vicinity of the wall, causing density fluctuations and affecting the fluid behavior near the wall. However, since the present article studied not the flow near the wall but the phase separation in whole system, so it should be realized that such phenomena near the wall should not be influential on the problems we aimed at.

The binder particles (red) were connected with Fraenkel springs into chains in order to simulate the behavior of polymer chains [23,24]. The parameter of the spring was 0.1. The free particles (blue) represented the small molecular plasticizer. According to the ratio of binder and plasticizer in NEPE propellants [3,25], the present simulation system adopts 1:2.6 as the ratio of red particles to blue ones. Although large amount of solid particles was filled in real NEPE propellants, the phase separation the article focused on was happened between binder and plasticizer, so the simulation system did not include the solid particle phase in order to simplify the simulation process. Considering the peculiarity of the phase separation will not happen at normal and high temperatures, referencing the results of experiments [1,2] and our previous study [18,19], the parameter $\prod_{ij}$ between red and blue particles was set to 10 at beginning.

2.2. Characterization of phase separation

In simulation, the process of phase separation can be observed directly by recording the history of morphology changing of the system. However, there is no suitable method to characterize the phase separation quantitatively [26–29]. We noticed that when the phase separation happened between the binder and plasticizer, the binder would congregate in the center of the system while the plasticizer would get together far from the center, which is also a normal rule of phase separation between polymer and solvent [30]. Through trial and error the present study designed a method as shown in Fig. 1 to characterize the phase separation in the present simulation system. The method included two spherical shells or tori: the inner was *a* and the outer was *b*. Both the size and position of the two spherical shells could be changed in need. In the present study the size of spherical shell *a* was $2 \le r_a \le 3$ while spherical shell *b* was $5 \le r_b \le 6$. The two spherical shells were fictive in simulation system and were used only to track the number changing of blue particles in system during the process of phase separation. When phase separation occurred, the chains would aggregate in the system center since they were entangled each other and the free particles would be piled out to the part near the box wall. Then the number of blue particles in spherical shell *a* would decrease while in spherical shell *b* would increase. Therefore, the changes of blue particles' number in the two spherical shells could simply show the evolvement of phase separation.

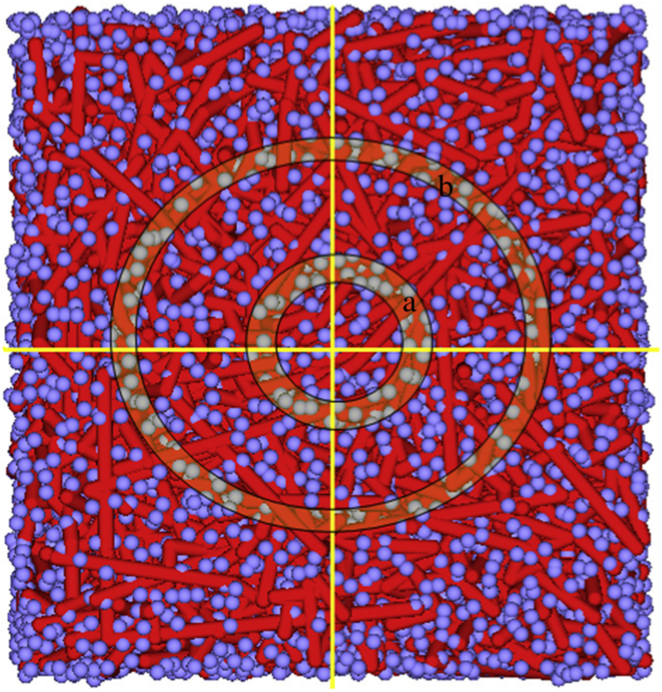

Fig. 1. Plane schematic representation of two spherical shells for particle accounting.

3. Results and discussion

3.1. Understanding of phase separation in mesoscale

In the process of phase separation in NEPE propellants, the binder chains should congregate first from plasticizer solution. Then some binder chains or chain segments would form crystal or just aggregate together while most plasticizer comes into being the liquid phase. According to the theory of macromolecular solution, the system of polymer binder and small molecular plasticizer in NEPE propellants can be taken as one kind of macromolecular solution [3,26]. At certain conditions, the mixed binder and plasticizer can coexist stably. When a condition, for example the temperature, changed, the phase separation between mixed binder and plasticizer may happen. In real NEPE propellants, the polymer binder was crosslinked into three-dimensional network. The macroscopic phase separation will not take place spontaneously. The phase separation, which can be of occurrence and has influence on propellants performance, is mesoscale. Therefore the rule and influence facts of the phase separation should have the mesoscale character. The mesoscale study methods, which contented mesoscale characterization, should be more suitable than others. That is why the present study chose DPD.

When temperature is decreased, according to the equation

$$\Delta G = \Delta H - T\Delta S \le 0 \tag{1}$$

the second part $T\Delta S$ will reduce because the ΔS between mixed state and phase separation state is stable or changes little, then ΔG will increase if ΔH changes a little or keep constant also. The change of ΔG from ≤ 0 to ≥ 0 is the thermodynamic reason of phase separation. Whereas, on the basis of dynamic theory, the motion of molecule will become slow with the temperature decreasing. In a velocity scope, the moving chains or chain segments that moved close would congregate. However, if the temperature is very low, the chains move very slowly. Then the phase separation will be hard to take place. Therefore the last phase morphology is the competition result of thermodynamic and dynamic factors. In a mixed system of DPD simulation, if the interaction changes from attraction to repulsion, going with the elongation of time, the mixed repulsing materials will aggregate and then the phase separation will take place finally. In the NEPE propellant, the chemical structure of binder and plasticizer is not changed, therefore the interaction between them is constant. However, for the binder chains, at a certain condition such as at low temperature, their ability of crystallization will buildup. In the view of DPD simulation, the interaction among binder chains will change from repulsion to attraction, therefore they will get together. The following studies focused on the dynamic process of phase separation and assumed that the interaction just changed from repulsion to attraction.

3.2. Simulation reproduction of phase separation

In the initial state of simulation system, the red particles, which connected into chains by five Fraenkel spring bonds, were mixed uniformly with the free blue particles. This state corresponds to the NEPE propellant in which the phase separation between binder and plasticizer has not take place. Subsequently, the temperature of the system decreased suddenly from high to low, to a point the phase separation will take place easily. In the corresponding simulation system, the interaction among binder chains changed from attraction to repulsion. Then the simulation process starts.

The result is shown in Fig. 2 . As shown in this figure, the number of blue particles in spherical shell *a* is decreased from the beginning to about 6000 steps. (For interpretation of the references to colour in this text, the reader is referred to the web version of this article.) After a short decrease, the number in shell *b* increased till about 6000 steps. In the later stage, both the numbers in shell *a* and *b* changed little. That is to say, the phase separation took place from the beginning and reached an equilibrium soon. The reproduction of phase separation verified that the present simulation system and conditions can realize the real process of phase separation between binder and plasticizer in NEPE propellant.

3.3. Influence of temperature on phase separation

The system simulated the state before phase separation taking place in the propellants between polymer binder and small molecular plasticizer. First we let the temperature and interaction parameter between red and blue particles *wa* keep stable. After the system runs 30 000 steps, the number of blue particles in two spherical shells *a* and *b* kept steady and almost no change was observed as shown in Fig. 3. Each datum point in this figure and the following ones was an average of 1000 step-measurements. Each set of data is an average from 20 repeated calculations since the dynamic process includes random factor. The information of Fig. 3 was that the phase separation did not take place and the simulation system was stable. Then we let *wa* keep unchanged while the temperature keep decreasing with steps, as shown in Fig. 4. After the system run 30 000 steps, the number of blue particles in two spherical shells kept stable also. The changing trend of blue particles' number in two spherical shells was almost the same as those in Fig. 3. This result suggests that only temperature drop cannot lead to the generation of the phase separation in present system.

Next step, the temperature was set to keep constant while the interaction parameter increased with steps as shown in Fig. 5(a). When $wa < 12.5$, the red and blue particles were allure. The smaller of the *wa*, the stronger of the attraction; when $wa > 12.5$, the red and blue particles were repulsive. The bigger of the *wa*, the stronger of the repulsion. When the steps were 12 500, $wa = 12.5$. The interaction between blue and red particles was equal to those between themselves. Fig. 5(b) showed that before 12 500 steps, the number of blue particles in two spherical shells had almost no change, which means that the blue particles were distributed uniformly and the phase separation did not occur. After the system

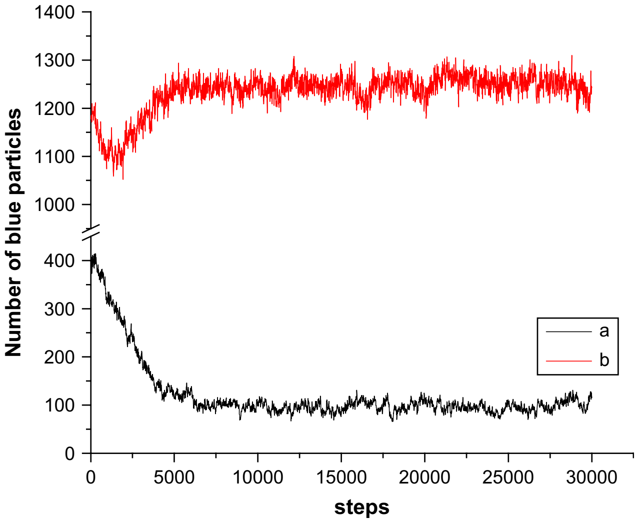

Fig. 2. Changes of blue particles' number in two spherical shells when parameter of interaction changed.

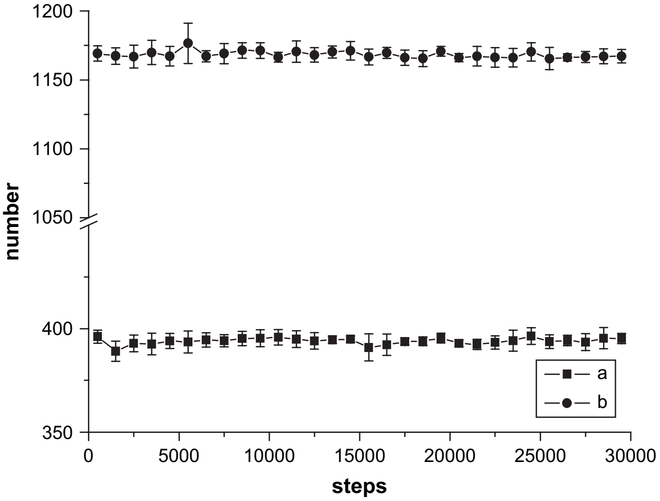

Fig. 3. Changes of blue particles' number in two spherical shells when temperature and parameter of interaction *wa* keep stable.

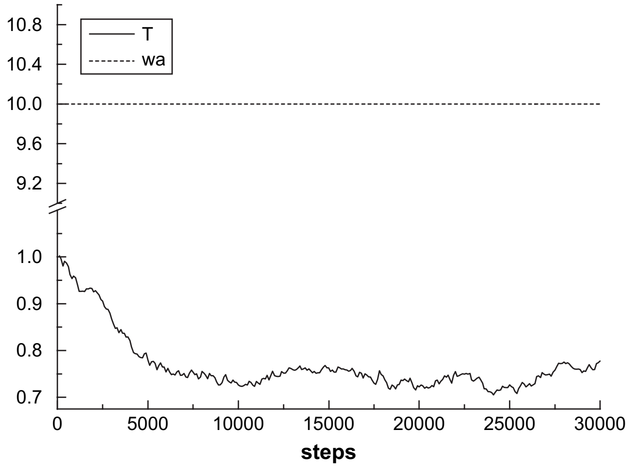

Fig. 4. Temperature decreases while parameter of interaction *wa* keeps stable.

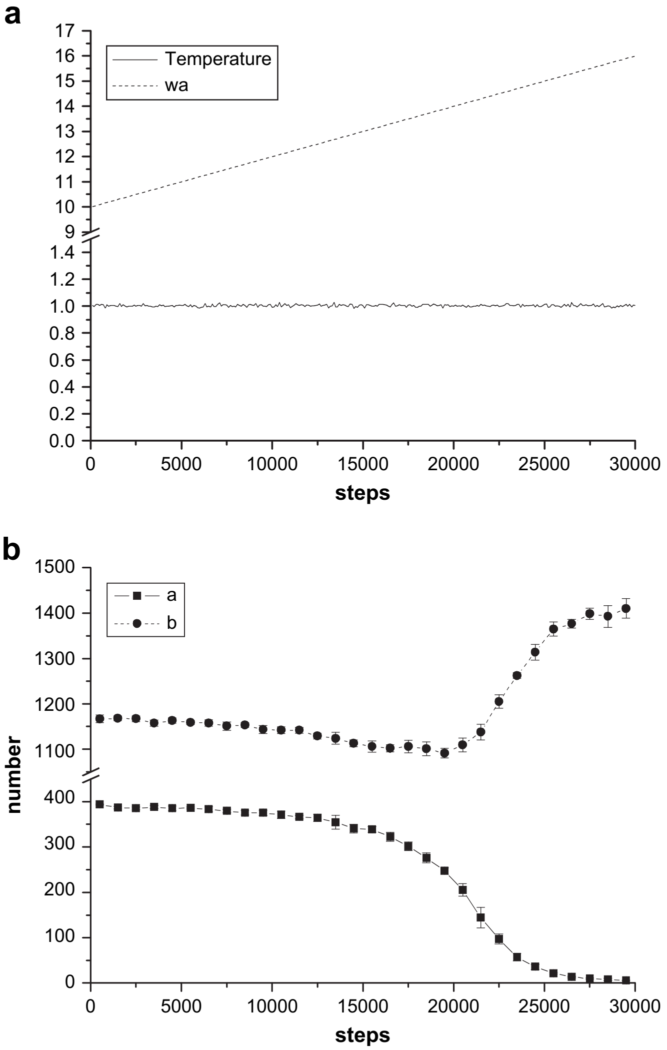

Fig. 5. Temperature keeps stable while parameter of interaction keeps increasing: (a) change of temperature and interaction parameter (b) changes of blue particles' number in two spherical shells.

run 12 500 steps, in company with the increasing of *wa*, the repulsion between red and blue particles become strong and strong. From attraction to repulsion, the distance between blue and red particles will increase step by step, which cause the two kinds of particles move in reverse direction. Since the red particles were connected into chains and entangled each other, they would aggregate to the system center while the free blue particles will spread out to the outer part of the system. Therefore in the inner spherical shell *a*, the number of red particles became greater and greater while the number of blue one became lesser and lesser; in the outer part of the system, the trend was inverse. Because the spherical shell *b* was not located near the boundary of the simulation system but at middle part ($5 \le r_b \le 6$), as shown in Fig. 1, therefore the number of blue particles in spherical shell *b*, as shown in Fig. 5(b), decreased a little first with the interaction changing from attraction to repulsion until the separation reached a certain degree. Then the change of blue particles' number in two spherical shells became sharp, which means the phase separation took place. Lastly the curves became mild again, this means the phase separation reached equilibrium.

When the system temperature decreased in terms of 1, 2, 3, three trends are shown in Fig. 6(a) while the *wa* increased with steps as shown in Fig. 5(a), the number of blue particles in the two

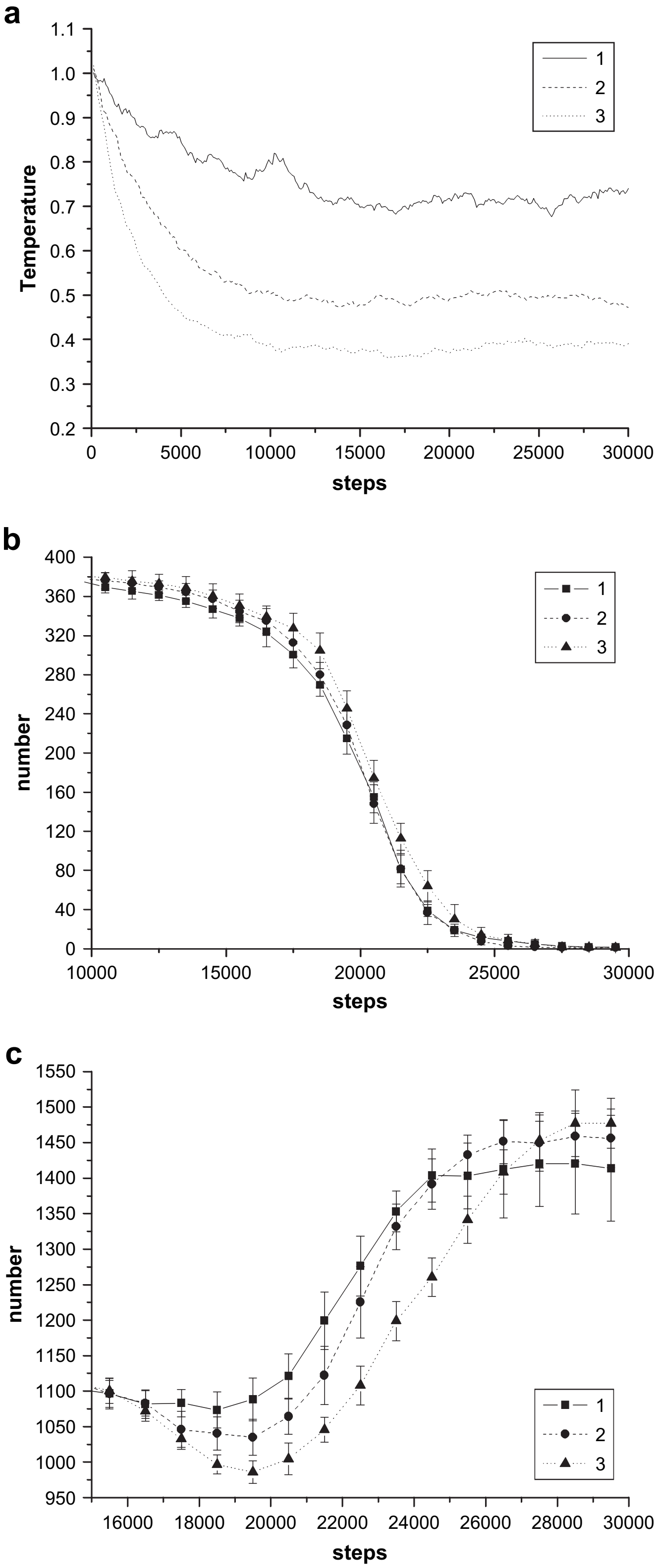

Fig. 6. Influence of temperature on the process of phase separation: (a) three kinds of decreasing of temperature, (b) changes of blue particles' number in spherical shell *a*, (c) changes of blue particles' number in spherical shell *b*.

spherical shells changed differently, as shown in (b) and (c). Fig. 6(b) is the changes of blue particles' number in spherical shell *a* while (c) is those of spherical shell *b* when temperature falling in three ways. It was apparent, as shown in the two figures, that when

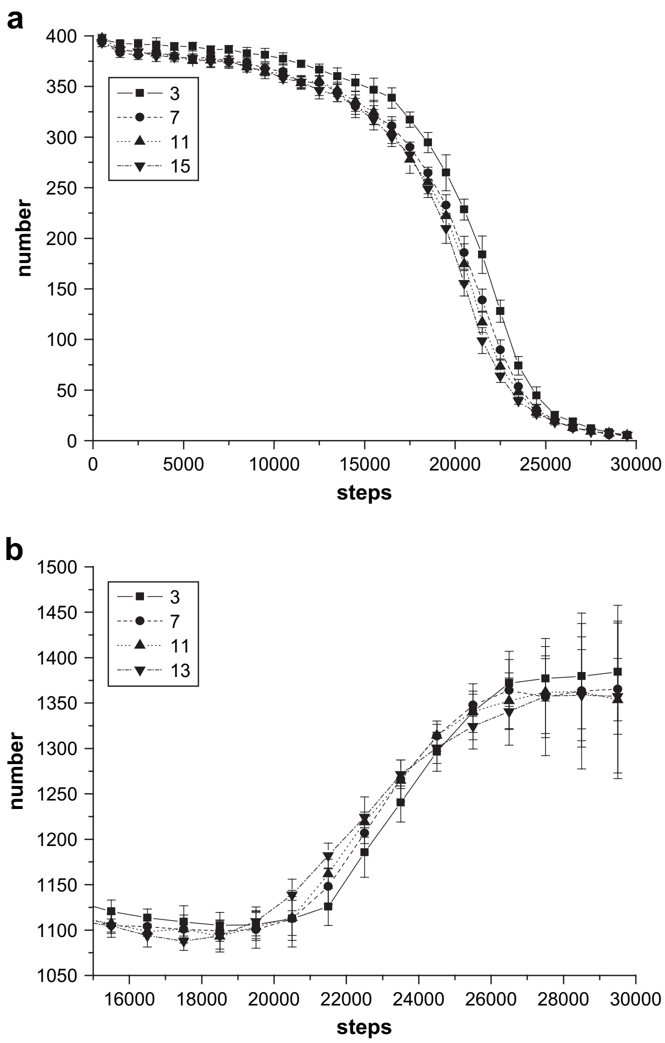

Fig. 7. Influence of chain length on process of phase separation: (a) changes of blue particles' number in spherical shells *a* (b) change of blue particles' number in spherical shells *b*.

temperature was high, the change of the curve or the starting point of phase separation was earlier than those at low temperature. The reason was that accompanied by the falling down of system temperature, the motion of particles becomes slow, which is just like the phenomena of viscosity increasing. In this case the particles need more strong impulse to move. Therefore only when the repulsive interaction becomes very strong, the phase separation can take place. However, at the last period, as shown in the two figures especially in (c), the three trend curves changed inversely. The results need more experiments to test. The cause possibly was that when temperature fell down the system entropy was decreased, which means the phase separation was complete or the binder and plasticizer phases are more pure. Therefore there were more blue particles in spherical shell *b* than that at high temperature.

3.4. *Influence of chain length on phase separation*

The theory of polymer solution says that when temperature keeps stable, the long polymer chains will separate out earlier than the short ones with the decreasing of solution solubility, [26]. To different batches of NEPE propellants, the degree of polymerization of the binder may be different. To examine the influence of degree of polymerization on phase separation, this article studied simulation systems in which the chain length was different. All the different systems have the same condition, that is, the temperature keeps constant and wa increases as shown in Fig. 5(a). The curves in (a) and (b) of Fig. 7 represented the phase separation processes, in which the chains content 3, 7, 11 and 15 spring bonds, respectively. Fig. 7(a) showed the changes of blue particles' number in spherical shell *a* while (b) showed that in spherical shell *b*. The two figures showed that in company with the increasing of chains length, the initial point of phase separation or the milestone of the curve from mild to sharp becomes earlier and earlier. This phenomenon is in agreement with the rule of molecular weight dependability on phase separation in polymer solution. However, at the last period, similar to those in Fig. 6(c), as shown in Fig. 7(b), the four trend curves changed inversely. More blue particles in spherical shell *b* area if the system contained more short chains. The reason may be that, the short chains are easy to form crystal than long chains and the crystals formed by long chains are not very pure as those formed by short chains. Therefore the phase separation to long chains system was less complete or the degree of phase separation was smaller than those consisting of short chains.

4. Conclusions

We presented a new phase separation behavior of macromolecular binder and small molecular plasticizer from mesoscale interaction. Using DPD mesoscale simulation method and a new two spherical shells method to characterize phase separation quantitatively, we simulated the phase separation process of polymer binder and small molecular plasticizer in NEPE propellants. The influences of temperature and chains length on the process of phase separation were investigated in details. The dynamic simulation results showed that the temperature impacted the motion of particles. While the interaction between binder and plasticizer was an important factor of affecting the phase separation behavior. Along with the temperature fall, the phase separation took place later and later whereas the extent of phase separation was increased. In a range, the longer of the polymer chains in simulation system, the earlier of the phase separation occurs between polymer and small molecule. However, with increasing the length of polymer chains, the degree of phase separation decreased.

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