Prediction of Miscibility of HTPB Curing System and Solvents by Molecular Dynamics Simulations

Liu Bo, Bu Xiaoyu, Wang Lin
Xi’an Institute of High Technology and Science, Xi’an 710025, P. R. China
liubopaper@163.com

Abstract. In order to study on HTPB curing system and solvent’s miscibility, molecular dynamic simulations were performed to analyze curing system’s miscibility with water, ethyl alcohol, methylbenzene, acetone and tetrahydrofuran from several aspects like solubility parameter, molecular configuration and density distribution. The results show that the computed results of the solubility parameter have high consistency with experimental values and the maximum relative error is less than 3%. The solubility parameter differences of acetone, tetrahydrofuran and curing system are relatively small with a homogeneous distribution and a relatively high miscibility. Methylbenzene’s miscibility is general while the ethyl alcohol’s and water’s miscibility are relatively poor.

1. Introduction
HTPB propellants’ curing system is mainly comprising of adhesives (hydroxyl-terminated polybutadiene, HTPB), curing agent (toluene diisocyanate, TDI), and crosslinking agent (tris-1-(2-methylaziridinyl) phosphinoxide, MAPO). These three components will have the cure reaction and conjugated reaction, and then form a three-dimensional reticular formation of curing system, which is the major skeleton of HTPB propellant, having an important effect on propellants properties. The curing system of propellant is unstable and easy to occur the oxidation reaction, conjugated reaction, chain scission and other chemical reaction, finally leading to an aging and invalid propellant.

In order to recover the high-energy components of aging propellant, suitable solvent must be selected to process the curing system. There are so many solvents with complicated properties; therefore, it is unrealistic to study simply by doing experiments. With the development of computational chemistry, molecular dynamics simulations have ever become a vital method to study the miscibility of blends [1-3]. The objectives of this study were to develop a computational model based on molecular dynamics method to predict the miscibility of curing system and solvent from three aspects, including solubility parameter, molecular configuration and density distribution, which will provide the important theoretical support for follow-up experiments and craft.

2. Model and Method

2.1. Model construction
In order to look for a suitable solvent of compatible curing system, according to the structural characteristics of HTPB curing system, five common solvents (water, ethyl alcohol, methylbenzene, acetone and tetrahydrofuran) were selected. The molecular models can be set up in accordance with the molecular structures of solvents. The results can be seen as Figure 1.
On the condition of 293K, 1.01×10⁵Pa, we firstly optimized the single molecular model and calculated the single point energy. Take the conformation with the lowest energy as the next initial one for simulation. Amorphous models of solvents were established according to different solvents’ molecular models and densities. For the purpose of assuring the accuracy and calculated quantity of the calculation, the “size effect” will be minimized and the atomic number of different solvent modules should be less than 1500. The amorphous model construction details of 5 solvents listed above can be observed in the Fig.1. Take H₂O as an example, its amorphous molecular model can be seen from the Fig.2. Models of other solvents will not be listed one by one.

Table 1 Model construction details of five solvents

| Solvents            | Formula | Numbers of molecular | Numbers of atoms | Density/(g·cm⁻³) |
|---------------------|---------|----------------------|------------------|-----------------|
| Water               | H₂O     | 400                  | 1200             | 1.00            |
| Methylbenzene       | C₇H₈    | 100                  | 1500             | 0.87            |
| Ethyl alcohol       | C₂H₆O   | 150                  | 1350             | 0.79            |
| Acetone             | C₃H₆O   | 150                  | 1500             | 0.79            |
| Tetrahydrofuran     | C₄H₈O   | 100                  | 1300             | 0.89            |

Figure 2. Simulated amorphous molecular model of water

2.2. Molecular Dynamics Simulation details

All the calculations were performed using the Materials Studio. In order to minimize unreasonable local structures inside the models, the molecular models were separately operated by annealing treatment. There are five circulations in total, firstly, improving the temperature from 300K to 600K, then to 300K. In every 60k, the molecular dynamics (MD) was operated in isothermal-isobaric (NPT) system, which will provide a reasonable balanced geometrical conformation for the next MD simulations to make the system reach equilibrium as fast as possible. Finally, the MD simulation was operated on NPT system at 350ps, 250ps for structural improvement and 100ps for result analyzing. Analyzing and calculating based on using MD to simulate tracks, and therefore many properties like solubility parameter and density distribution could be obtained.
Select the COMPASS force field in all simulation. The initial velocity of each molecule will be sampled according to Maxwell-Boltzmann random distribution of adopting the Velocity Verlet calculation. The electrostatic interaction and van der Waals force were separately measured with Ewald and Atom Based method. The Anderson thermostat and barostat were used to maintain the temperature and pressure, respectively.

3. Results and Discussion

3.1. Conclusion and Discussion

The judgment of MD system equilibrium mainly depends on temperature and energy, which means the fluctuation changes of temperature and energy are small and the deviation is less than 5%\[^{[4,5]}\]. Taking the HTPB curing system as an example, we will analyze the temperature and energy changes of 350ps-MD simulations at final 100ps. The changing situation of temperature and energy of MD at final 100ps is illustrated in Figure 3. The fluctuation changes of temperature and energy are both less than 5%, indicating the system has reached its equilibrium and can be used for functional analysis. Similarly, this method was performed to determine the solvents system.

![Figure 3. The temperature and energy as a function of MD simulation time](image)

3.2. Solubility Parameter

According to the principle of solubility parameter to determine the solvents’ miscibility\[^{[6]}\], when the solubility parameter of HTPB curing system is similar to the solvents’, the swelling process could be continue. The solubility parameter of HTPB curing system at 293K is 19.58 J\(^{1/2}\) cm\(^{-3/2}\) with molecular dynamics method. The results of the solvents’ solubility parameter could be seen as Table 2. The solvents’ \(\delta_{\text{MD}}\), solvents’ experiment \(\delta_{\text{Ref.}}\)\[^{[7]}\] as well as the difference \(|\Delta \delta_{\text{MD}}|\) of HTPB curing system’s and solvents’, were separately listed.

From Table 2, the 5 solvents’ calculated value remains higher agreement with experimental values and the maximum relative error are all less than 3%, indicating the reliability of solvents’ solubility parameter calculated by MD. There was great difference between different solvent’s and curing system’s solubility parameter \(|\Delta \delta_{\text{MD}}|\); among which acetone’s and tetrahydrofuran’s \(|\Delta \delta_{\text{MD}}|\) are relatively small (0.11 J\(^{1/2}\) cm\(^{-3/2}\) and 0.22 J\(^{1/2}\) cm\(^{-3/2}\) separately), indicating that acetone and tetrahydrofuran have higher miscibility with HTPB curing system; the value of water’s \(|\Delta \delta_{\text{MD}}|\) is maximum, which is 27.81 J\(^{1/2}\) cm\(^{-3/2}\), indicating that water has smaller miscibility with HTPB curing system.

| Solvents      | \(\delta_{\text{MD}}\) | \(\delta_{\text{Ref.}}\)\[^{[7]}\] | Relative error | \(|\Delta \delta_{\text{MD}}|\) = \(|\delta_{\text{MD}} - \delta_{\text{Ref.}}|\) |
|---------------|-----------------|-----------------|----------------|-----------------|
| Water         | 47.39           | 47.8            | 0.86%          | 27.81           |
| Methylbenzene | 17.87           | 18.3            | 2.35%          | 1.71            |
| Ethyl alcohol | 26.31           | 26.5            | 0.72%          | 6.73            |
3.3. Molecular Configuration
In order to have a further study on different solvents’ miscibility with HTPB curing system, five solvents and HTPB curing system were formed to the blend module. The molecular model parameters of 5 blends are shown as Fig.3. In order to make sure the accuracy and calculating amount, the molecular number of HTPB, TDI and MAPO in 5 blends remains the same, the number of atoms in the blends was about 4400 at total.

Table 3. Molecular models parameters of HTPB curing system and solvents

| Blends            | Number of HTPB | Number of TDI | Number of MAPO | Number of solvents | Number of atoms |
|-------------------|----------------|---------------|----------------|--------------------|-----------------|
| HTPB/acetone      | 5              | 5             | 2              | 90                 | 4424            |
| HTPB/tetrahydrofuran | 5             | 5             | 2              | 60                 | 4424            |
| HTPB/methylbenzene | 5             | 5             | 2              | 60                 | 4424            |
| HTPB/ethyl alcohol | 5             | 5             | 2              | 70                 | 4434            |
| HTPB/water        | 5             | 5             | 2              | 300                | 4424            |

The calculated molecular configuration of 5 blends could be seen as Figure 3. The red regions was in the presence of solvent molecules. After the MD -calculation, the molecular models of 5 blends become different: (1) there are more acetone molecules inside the HTPB curing system with a homogeneous distribution, indicating acetone’s high miscibility with HTPB curing system. Meanwhile, the distribution of tetrahydrofuran molecule is homogeneous, indicating tetrahydrofuran’s high miscibility with HTPB curing system. (2) Solvent molecules of water, ethyl alcohol and methylbenzene inside the blend model were obviously separated from the curing system, especially most of water molecules mainly distributed out of the curing system and there were no water molecule inside the curing system, indicating that water’s worst miscibility HTPB with curing system. As above explanation shown, the order of 5 solvents’ miscibility with curing system is Acetone > tetrahydrofuran > methylbenzene > ethyl alcohol > water, which was in accordance with conclusion of solubility parameter.
3.4. Density Distribution

Fig. 5 shows the density distribution of five blends. The differences between different blend’s density distribution were obviously find, leading to conclusions that: (1) among 5 solvents, density distribution of acetone and tetrahydrofuran was relatively homogeneous with lower density difference, indicating acetone’s and tetrahydrofuran’s good miscibility with HTPB curing system; (2) other solvents’ density distribution in the figure4 showed obvious density distribution with great density differences, indicating these three solvents were not mixed with curing system, which indicated their poor miscibility with curing system. These conclusions were in accordance with the structure of the solubility parameter and molecular configuration mentioned above, providing a further explanation for different solvent’s miscibility with curing system.

4. Conclusion

The molecular models of five solvents and HTPB curing system were established with molecular dynamics method, providing important theoretical supports for solvents’ miscibility with curing.
system by calculating the solubility parameter, molecular configuration and density distribution of curing system and solvents. The solubility parameter is a reference to determine solvent’s miscibility with curing system; after MD calculation on 5 solvents, the solubility parameter differences of acetone, tetrahydrofuran and curing system are small, with a homogeneous distribution and high miscibility. Methylbenzene’s miscibility remains general while the miscibility of ethyl alcohol and water is poor.

References
[1] Fu, X. L., Fan, X. Z., Ju, X. H., Qi, X. F., Li, J. Z., & Yu, H. J. 2015 RSC Advances 5 52844
[2] Gupta, J., Nunes, C., Vyas, S., & Jonnalagadda, S. 2011 The Journal of Physical Chemistry B 115 2014
[3] Zhao, Y., Zhang, X., Zhang, W., Xu, H., Xie, W., Du, J., & Liu, Y. 2016. The Journal of Physical Chemistry A 120 765
[4] Taylor, D. E., Strawhecker, K. E., Shanholtz, E. R., Sorescu, D. C., & Sausa, R. C. 2014 The Journal of Physical Chemistry A 118 5083
[5] Yang, H., Ze-Sheng, L., Qian, H. J., Yang, Y. B., Zhang, X. B., & Sun, C. C. 2004. Polymer, 45 453
[6] Belmares, M., Blanco, M., Goddard, W. A., Ross, R. B., Caldwell, G., Chou, S. H., & Thomas, C. 2004 Journal of computational chemistry 25 1814
[7] Burke, J. 1984. Solubility parameters: theory and application.