Available online at www.sciencedirect.com
ScienceDirect
Polymer 48 (2007) 887–893
polymer
www.elsevier.com/locate/polymer

A molecular simulation study of a series of cyclohexanone formaldehyde resins: Properties and applications in plastic printing[☆]

Hua Ren, Qiuyu Zhang*, Xiaowei Chen, Wen Zhao, Junping Zhang,
Hepeng Zhang, Rui Zeng, Shu Xu

Department of Applied Chemistry, School of Science, Northwestern Polytechnical University, No 127 Youyi Road, Xi'an 710072, China

Received 11 August 2006; received in revised form 12 December 2006; accepted 12 December 2006
Available online 8 January 2007

Abstract

The solubility of a series of cyclohexanone formaldehyde resins (including cyclohexanone formaldehyde resin (CFR), acetylated CFR and complete oxime of CFR) in a variety of solvents (tetrachloromethane, alcohol, toluene and ethyl ether) were studied by means of Monte Carlo approach; the free energies of mixing were estimated, which indicated results being consistent with the experimental fact. Independent cohesive energy densities (CEDs) of CFRs were computed by molecular dynamics (MD) simulation, from which we obtained the solubility parameters of CFR, acetylated CFR and complete oxime of CFR as follows, 19.45(0.22), 17.30(0.11) and 21.41(0.27) $\mathrm{MPa}^{1/2}$. Compatibility of CFRs with a dimer acid-based polyamide (D1007E [Xiaodong Fan, Yulin Deng, John Waterhouse, Peter Pfromm. J Appl Polym Sci 1998;68:305–14.]) was estimated from the CEDs; the calculation results indicated that these three CFRs were compatible with D1007E. In addition, the interactions between coating layers (pure D1007E, D1007E with CFR, D1007E with acetylated CFR and D1007E with complete oxime of CFR, molar ratio 3:1) and a polystyrene substrate layer were investigated, in an effort to identify the effect of CFRs in plastic printing application. All the results of this work confirmed that molecular simulation techniques can be used as a tool for investigating the properties and applications of CFRs.

Keywords: Cyclohexanone formaldehyde; Modification; Monte Carlo

1. Introduction

The CFR has low molecular weight and shows unique compatibility with a great number of polymers. It is soluble in most organic solvents such as aromatic hydrocarbons, ketones, esters, alcohols, etc. Because of its good compatibility, it is usually used as a coating additive. A lot of work on modifying the CFR has been done [2–5] in order to widen its application fields, however, the effects of these modifications on the application in some specific fields, such as plastic printing, etc., have not been extensively studied. The properties, such as solubility in solvents and compatibility with some polymers will influence the application of modified CFRs. Here we focus on the application of plastic printing; hence we studied the compatibility of CFRs and D1007E (D1007E is a dimer acid polyamide, typically used as a toner resin for printers and copiers [1]), the interaction between D1007E layers with CFRs and a polystyrene plastic layer, in an effort to identify the effects of modifications on CFRs in the field.

Traditionally, "trial-and-error" experiments should be carried out to identify the effects of such modifications, but they usually cost a lot of time and money. A more innovative approach, which can investigate the properties of polymers is the molecular simulation technique. In the past decade, molecular modeling has been successfully employed to help solve critical industrial problems. In the case of polymer science, many physicochemical properties have been accurately computed using modeling technologies. Many different algorithms can be employed to compute those properties, such as Monte Carlo sampling, dynamics simulations, etc.

[☆] Grant sponsor: National Nature Science Foundation of China, 20374039.

[*] Corresponding author. Tel./fax: +86 29 88495304x801.
E-mail address: qyzhang@nwpu.edu.cn (Q. Zhang).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.12.016

In this study, we combined the Monte Carlo sampling and dynamics molecular simulation to investigate the properties of CFRs. Comparisons between simulation results and experimental results were made. In addition, some possible results were also estimated. Special attention should be paid so that the polycyclic structures of CFRs posed more difficulties in the dynamics simulation steps compared with chain molecules, in order to give such molecular systems a relatively quick equilibration, a high–low pressure dynamics simulation procedure was applied.

2. Methods and calculations

The simplest and best known theory of the thermodynamics of mixing and phase separation in binary systems is the Flory–Huggins model [6]. The general expression for the free energy of mixing of a binary system is:

$$\frac{\Delta G_{\mathrm{mix}}}{RT} = \frac{\phi_{\mathrm{b}}}{n_{\mathrm{b}}}\ln \phi_{\mathrm{b}} + \frac{\phi_{\mathrm{s}}}{n_{\mathrm{s}}}\ln \phi_{\mathrm{s}} + \phi_{\mathrm{b}}\phi_{\mathrm{s}}\chi \tag{1}$$

Where ΔG_{mix} is the molar free energy of mixing, ϕ_{i} is the volume fraction of component i (i = b or s), n_{i} is the degree of polymerization of component i (i = b or s), χ is the interaction parameter, T is the absolute temperature, and R is the gas constant.

The first two terms represent the combinatorial entropy. This contribution is always negative, hence favoring a mixed state over the pure components. The last term is the free energy due to interaction. If the interaction parameter, χ, is negative then this term favors a mixed state.

$$\chi = \frac{E_{\mathrm{mix}}}{RT} \tag{2}$$

Where E_{mix} is the mixing energy, that is, the difference in free energy due to interaction between the mixed and the pure states. From Eqs. (1) and (2), it can be clearly seen that if either ΔG_{mix} or E_{mix} is obtained, the solubility and miscibility of the CFRs will be easily estimated.

In this study, blends module of Materials Studio software package [7] was used to estimate molar free energies of mixing between CFRs and a variety of solvents, including tetrachloromethane, alcohol, toluene and ethyl ether. Discover and amorphous cell of Materials Studio software were used to perform dynamics simulations to investigate the cohesive energy densities, from which the compatibility between CFRs and D1007E was estimated by calculating the mixing energy E_{mix}. At last, the interaction energies between coating layers (pure D1007E, D1007E with CFR, D1007E with acetylated CFR and D1007E with complete oxime of CFR, molar ratio 3:1) with a polystyrene substrate layer were calculated.

For all these simulations, COMPASS forcefield was used, which is an ab initio-based forcefield to have been parameterized using extensive data for molecules in the condensed phase [8]. Consequently, COMPASS is able to make accurate predictions of structural, conformational, vibrational, cohesive and thermophysical properties for a broad range of compounds both in isolation and in condensed phases.

2.1. Determination of solubility through free energy of mixing

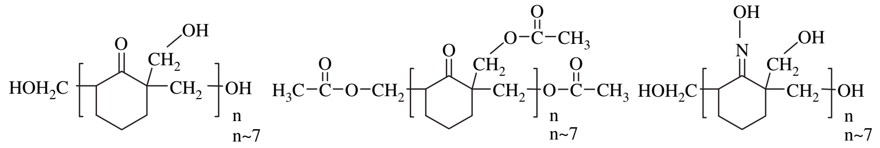
Blends module of Materials Studio combines a modified Flory–Huggins model and molecular simulation techniques to calculate the compatibility of binary mixtures. Two important extensions to the Flory–Huggins model are employed:

- Blends incorporates an explicit temperature dependence on the interaction parameter. This is accomplished by generating a large number of pair configurations and calculating the binding energies, followed by temperature averaging the results using the Boltzmann factor and calculating the temperature-dependent interaction parameter.
- Blends is an off-lattice calculation, meaning that molecules are not arranged in a regular lattice as in the original Flory–Huggins theory. The coordination number Z_{ij} (Z_{ij}, is the number of molecules of component j that can be packed around a single molecule of component i within the excluded-volume constraints) is explicitly calculated for each of the possible molecular pairs using molecular simulations.

These two extensions to the classical Flory–Huggins theory of mixing are documented in publications by Blanco [9] and Fan et al [10].

The steps of the calculation procedure were as follows:

(I) Optimized the geometries of the repeat units (only one repeat representing a polymer molecule by using “head and tail atoms non-contact” method) of CFRs (Structure I), as well as the solvent molecules.
(II) Generated a huge number of configurations (typically 100,000) of the two molecules (CFR repeat units–solvent), calculated the interaction energy, E_{ij}, of each pair.
(III) Repeated the (II) procedure many times and then a probability distribution $P(E_{\mathrm{ij}})$ is constructed taking



a) CFR a) Acetylated CFR a) Complete oxime of CFR

Structure I.

temperature effects into account by weighting the distribution effects function with Boltzmann factor $e^{-E_{ij}/RT}$. The average energy is given by:

$$\langle E_{ij}(T)\rangle = \frac{\int dE_{ij} E_{ij} P(E_{ij}) e^{-\frac{E_{ij}}{RT}}}{\int dE_{ij} P(E_{ij}) e^{-\frac{E_{ij}}{RT}}} \quad (3)$$

(IV) Generated a huge number of clusters (one molecule of component i and Z_{ij} molecules of component j together is called a cluster) to determine how many solvent molecules could be packed around the polymer molecule. Following the method of Blanco [9,10], the coordination number Z_{ij} could be calculated. Then the mixing energy could be obtained by:

$$E_{mix} = \frac{Z_{bs}\langle E_{bs}(T)\rangle + Z_{sb}\langle E_{sb}(T)\rangle - Z_{bb}\langle E_{bb}(T)\rangle - Z_{ss}\langle E_{ss}(T)\rangle}{2} \quad (4)$$

Finally, according to Eqs. (1) and (2), the free energy of mixing of the binary system (CFR–solvent, modified CFR–solvent) could be determined.

2.2. Determination of the solubility parameters and mixing energy E_{mix} with D1007E

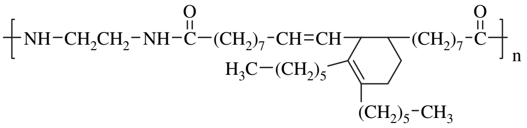
In order to calculate the mixing energy, E_{mix}, cohesive energy densities (CEDs) of CFRs with and without D1007E should firstly be calculated by constructing a series of 3D amorphous cells using amorphous cell module, and equilibrating them with Discover module. From CEDs, solubility parameters (δ) of CFRs and their binary mixture with D1007E were also easily obtained:

$$\delta = \sqrt{\mathrm{CED}} \quad (5)$$

The basic steps for generating and equilibrating the 3D periodic amorphous cells containing CFR molecules with and without D1007E oligomers were as follows:

(I) Built the CFR, modified CFR molecules (see Structure I, $n = 7$, isotactic, head-to-tail) and D1007E oligomers (see Structure II, $n = 1$), then optimize the geometries of these molecules using COMPASS forcefield through 5000-step energy minimization on each.

(II) Constructed periodic amorphous cells, each cell, respectively, contained (i) three CFR chains, (ii) three acetylated CFR chains, (iii) three complete oxime of CFR chains, (iv) four D1007E oligomers, (v) three D1007E oligomers with one CFR chains, (vi) three D1007E oligomers with one acetylated CFR chains, (vii) three D1007E oligomers with one complete oxime of CFR chains. All these cells were given an initially low target density of 0.5 g/cm^3, at a temperature of 298 K. A representative structure is shown in Fig. 1a.


D1007E

Structure II.

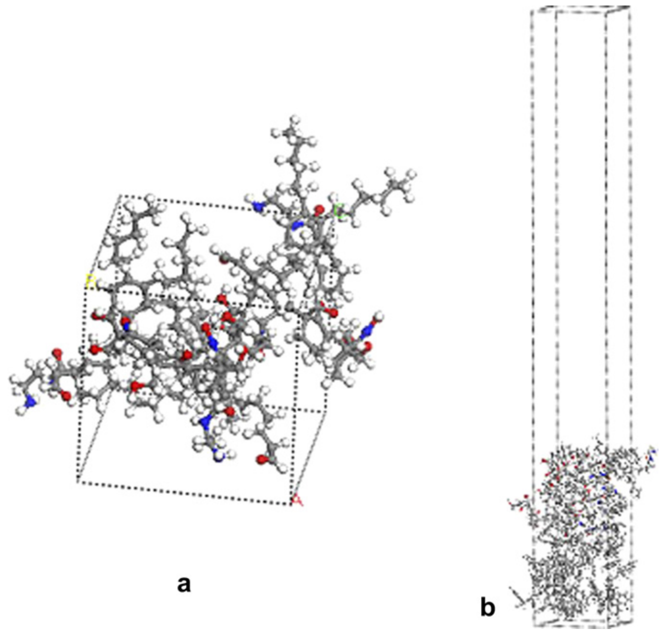


Fig. 1. A representative structure of 3D amorphous cells (a) and two-layer super cells (b).

(III) Employed a high pressure NPT dynamics using the velocity scaling thermostat and Berendsen [11] barostat, $P = 1$ GPa, for at least 100 ps. Then a low pressure NPT dynamics with $P = 0.0001$ GPa (1 atm) were applied for 1500 ps using the same thermostat and barostat until the density converged. This high–low pressure dynamics gave the system a relative quick equilibration.

(IV) Finally, performed a 100 ps NVT dynamics using Andersen thermostat for each production run.

The CEDs and solubility parameters were obtained by analyzing the trajectory files produced from steps (IV), then the energy of mixing which was related to the cohesive energy density of the blend and to that of the pure components could be calculated as follows [12]:

$$\Delta E_{mix} = \varphi_A \left(\frac{E_{coh}}{V}\right)_A + \varphi_B \left(\frac{E_{coh}}{V}\right)_B - \left(\frac{E_{coh}}{V}\right)_{mix} \quad (6)$$

2.3. Interactions with the polystyrene layer

A procedure similar to that in Ref. [13] was applied on two-layer super cells to calculate the interaction energies between the D1007E coating layers with and without CFR molecules and a polystyrene substrate layer. The following aspects of the simulation set up should be noted:

- As the super cells were relatively large (20.86 Å × 20.86 Å × 166.96 Å), containing about 2000 atoms, a group-based cutoff was used to speed up the simulation.
- 2D amorphous cells were built at the target densities from 2.2 steps for constructing two-layer super cells.
- The super cells with periodic boundary conditions were treated as a 3D periodic system for the dynamics simulations. The same polystyrene 2D layer (20.86 Å × 20.86 Å × 23.19 Å) was used for all the 2D layers of the D1007E with and without CFR molecules. Above the coating layer, a vacuum layer of 12 nm was added to avoid the effects of periodic boundary conditions. A representative structure is shown in Fig. 1b.
- Simulations on the two-layer super cells were performed in the NVT ensemble at 298 K, with a tail correction applied outside the cutoff of 9.5 Å using velocity scale thermostat for 200 ps, this was used to give the system an enough equilibration. Then for every 1 ps the energy of interaction between polystyrene substrate and the coating layers was evaluated using an 18 Å cutoff without tail correction and Andersen thermostat was used. A total of 300 energy evaluations were performed for each super cell (300 ps total production time). All the interaction energies were evaluated by using a proper BTCL script (imbedded in the Discover simulation module of Materials Studio is a scripting engine that governs the execution of all Discover jobs and provides very precise control of simulation jobs. The language used to drive this engine is called BTCL. With BTCL, scripts can be written to perform the most trivial of tasks that implement a new simulation algorithm, here we wrote a proper BTCL script to equilibrate the two-layer super cells and to collect interaction energies automatically).

3. Results and discussion

3.1. Solubility: free energy of mixing from Monte Carlo Sampling

By analyzing the results from blends, the molar free energies of mixing as a function of molar fraction were obtained. A negative value of molar free energy indicates that CFRs are soluble in the corresponding solvent.

The molar free energies at 300 K of CFR, acetylated CFR and complete oxime of CFR in toluene, ethyl ether, alcohol and tetrachloromethane vs. molar fractions are shown in Fig. 2. It can be clearly seen from Fig. 2a that CFR and acetylated CFR are soluble in toluene while complete oxime of CFR is not, which is in very good agreement with the experimental facts [4]. It is known that these three CFRs can be dissolved in alcohol, what Fig. 2c shows agrees well with this fact, in addition, it also indicates that acetylation of CFR will decrease its solubility in alcohol, this can be understood in terms of higher polarity of CFR than that of acetylated CFR.

The result shown in Fig. 2b suggests that these three CFRs will not be well soluble in ethyl ether, which agrees with the experiment although the trends for CFR and acetylated CFR are not as clear as that of oxime CFR. When the pairs of CFRs–CCl_4 were simulated, we found that acetylation would increase the solubility of CFR in CCl_4 (Fig. 2d), but using COMPASS forcefields, it still could not give a result well consistent with the experimental facts [4] (acetylated CFR is soluble in CCl_4), so we used Dreiding forcefield for validation. The result obtained by using Dreiding forcefield shown in Fig. 2d indicates a better result being consistent with experiment.

Special attention should be paid to the differences between these two forcefields; unlike class II forcefields, such as COMPASS, PCFF, etc., Dreiding belongs to class I forcefields. General force constants and geometry parameters for the Dreiding forcefield are based on simple hybridization rules rather than on specific combinations of atoms. The Dreiding forcefield is a purely diagonal forcefield with harmonic valence terms and a cosine-Fourier expansion torsion term. The umbrella functional form is used for inversions, which is defined according to the Wilson out-of-plane definition. The van der Waal's interactions are described by the Lennard-Jones potential. Electrostatic interactions are described by atomic monopoles and a screened (distance-dependent) Coulombic term. Hydrogen bonding is described by an explicit Lennard-Jones 12-10 potential [14]. The Dreiding forcefield models carbon, nitrogen, oxygen, and hydrogen most accurately.

For the CFRs–solvents binary system we studied, it is a cluster containing a polymer repeat unit and several small solvent molecules, Dreiding forcefield might give more accurate results for some of these cluster systems, so it is a good choice for validation; while COMPASS will give much better results for condensed materials.

However, we did not use Dreiding for all the blends simulation for two reasons: first, on average, Dreiding cannot give results as good as COMPASS and it cannot cover the periodic table as widely as COMPASS does; second, Dreiding forcefield cannot be applied to the next MD simulations, for the consistency of Monte Carlo and MD simulations, the same COMPASS forcefield was used.

3.2. Densities, CEDs, solubility parameters and compatibility from MD

Before production run, the system should firstly be fully equilibrated. Fig. 3 shows the densities of CFRs and the mixtures with D1007E during the NPT ($P = 0.0001$ GPa) equilibration steps. It can be seen that systems have been sufficiently equilibrated. The densities (with standard deviations in brackets) are contained in Table 1. For CFR, the calculated density is 1.1118(0.0182) g/cm^3, which is quite closed to the experimental value (1.1 g/cm^3) [15]. We have carried out systematic simulations with different time scales including 300, 500, 1000, and 1500 ps. With 1500 ps of equilibration time, we found that the system had been fully equilibrated and the differences of solubility parameters from 1000 to 1500 ps were within 3%, and the differences of densities were within 1.5%, which indicated that 1500 ps of equilibration time was enough. We also found that molecules with

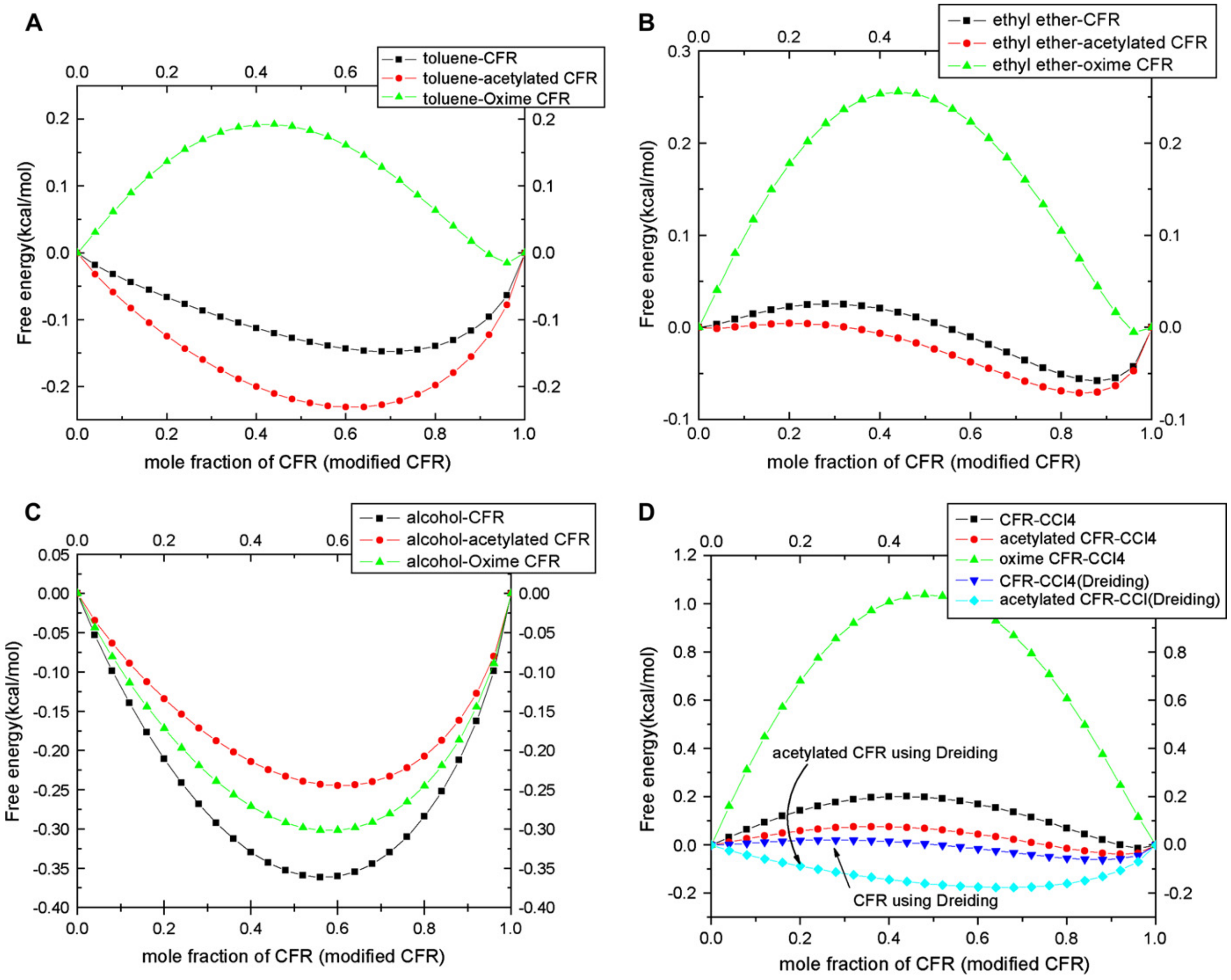


Fig. 2. Molar free energies of CFRs (modified CFRs) in four solvents vs. molar fractions.

high polar structures would take much longer time to be equilibrated, for example, for low polar molecules, acetylated CFR and D1007E, 300 ps was enough to be equilibrated, while for CFR and oxime CFR molecules, more than 1000 ps would be needed for fully equilibration.

Moreover, we have carried out systematic size checks and found that the dimension of amorphous cells applied in our work is proper enough to give reliable results. Because there are no reported works available, comparison of free energies between calculated values and reported ones has not been made.

Hildebrand solubility parameters from Bicerano connectivity indices method have been used as a comparison in some reported work [13], we presented the calculated solubility parameters in Table 1 (column 4), as well as the estimated values using Bicerano connectivity indices method (SYNTHIS module of Materials Studio software package [16]) are also listed in Table 1 (column 6). All the calculated solubility parameters of CFR and modified CFRs are lower than that obtained by Bicerano connectivity indices method. From a great number of simulations, we found that this was likely to be a systemic difference between these two methods.

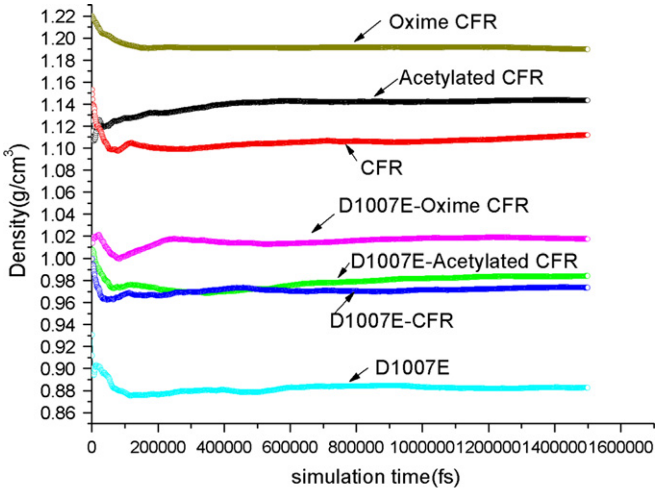


Fig. 3. Densities of 3D amorphous cells vs simulation time.

Table 1
Properties of polyamide D1007E, CFRs, modified CFRs and the binary system (molar ratio 3:1)

Molecule	Density (g/cm^3) Sim	Cohesive energy density (J/cm^3) (Sim)	Solubility parameter ($MPa^{1/2}$) (Sim)	Density (g/cm^3) (Synthia)	Solubility parameter ($MPa^{1/2}$) (Synthia (van Krevelen))	Molar volume (cm^3/mol) (Synthia)
Polyamide D1007E	0.8825(0.0192)	285.69(5.63)	16.90(0.17)	0.952	20.20	614.37
CFR	1.1118(0.0182)	378.33(8.72)	19.45(0.22)	1.1836	25.30	118.43
Acetylated CFR	1.1433(0.0164)	299.17(3.97)	17.30(0.11)	1.194	18.89	152.60
Oxime CFR	1.1897(0.0094)	458.67(11.46)	21.41(0.27)	1.232	24.43	125.94
Polyamide & CFR	0.9736(0.0167)	335.96(6.47)	18.33(0.18)	–	–	–
Polyamide and acetylated CFR	0.9840(0.0180)	322.59(6.32)	17.96(0.18)	–	–	–
Polyamide and Oxime CFR	1.0173(0.0155)	354.92(8.04)	18.84(0.21)	–	–	–

For more hydrogen bonds formed in oxime of CFR, its solubility parameter should be higher than that of CFR, the calculated values (CFR, 19.45(0.22) $MPa^{1/2}$; oxime CFR, 21.41(0.27) $MPa^{1/2}$) are consistent with this expectation, while values (CFR 25.30 $MPa^{1/2}$; oxime CFR, 24.43 $MPa^{1/2}$) from Bicerano connectivity indices method are not; hence, the simulated results are likely to be more reasonable. Moreover, solubility parameter could also be evaluated from Monte Carlo approach in step 2.1 using Eq. (7):

$$\chi(T) = \beta + \frac{V_1}{RT}(\delta_1 - \delta_2)^2 \tag{7}$$

Here we took CFR–toluene binary system, the calculated Flory–Huggins parameter $\chi = 0.718$ from step 2.1, $V_1 = 106\ cm^3/mol$ [17], was molar volume of toluene, $\beta = 0.34$, a value reported by Blanks and Prausnitz [18]. For $T = 298$ K and using $\delta_1 = 17.4\ MPa^{1/2}$, a reported value of solubility parameter for toluene [19], we obtained the solubility parameter for CFR $\delta_2 = 20.36\ MPa^{1/2}$, which was close to that calculated by MD method in this section, 19.45(0.22) $MPa^{1/2}$. The consistency of these two methods confirms that the solubility parameter of CFR is close to 20 $MPa^{1/2}$.

The molar blend ratio of CFRs with D1007E was 1:3 (mass ratio 1:1.2–1.7), in order to calculate the volume fraction ϕ_i, the molar volumes (see Table 1, column 7) of CFRs and D1007E estimated using SYNTHIS were used, the volume fraction can be estimated as follows:

$$\phi_A = \frac{V_{A\_mol} \times DP_A}{V_{A\_mol} \times DP_A + V_{B\_mol} \times DP_B}; \quad \phi_B = 1 - \phi_A \tag{8}$$

Where V_{A_mol} is the molar volume of component A (D1007E), V_{B_mol} is the molar volume of component B (CFRs); DP_A is the degree of polymerization of component A ($DP_A = 1$ for D1007E oligomers) and DP_B is the degree of polymerization of component B ($DP_B = 7$ for CFRs). From Eq. (5), the energy of mixing can be calculated. According to Eqs. (1) and (2), it can be concluded that a negative value of mixing energy indicates a favorable mixing. The mixing energy of CFR, acetylated CFR and complete oxime of CFR with D1007E is as follows: acetylated CFR–D1007E, −31.95 kJ/mol; CFR–D1007E, −21.53 kJ/mol; complete oxime of CFR–D1007E, −13.26 kJ/mol. From these results, it can be concluded that all the CFRs are compatible with D1007E at molar ratio 3:1; moreover, acetylation of CFR is likely to improve its compatibility with D1007E (decreased the mixing energy from −21.53 to −31.95 kJ/mol).

From the mixing energies, we can also conclude that the order of compatibility with D1007E is: acetylated CFR (−31.95 kJ/mol), CFR (−21.53 kJ/mol) and complete oxime of CFR (−13.26 kJ/mol), which is consistent with expectations from solubility parameters.

3.3. Interactions between two layers

The physical and chemical behaviors of molecules at surfaces play an important role in many technological applications. In an effort to identify how the CFR and modified CFRs affect the property of polyamide coating, we investigated the interactions between layers (pure D1007E, D1007E with CFR, D1007E with acetylated CFR and D1007E with complete oxime of CFR, molar ratio 3:1) and a same polystyrene substrate layer (here we chose an amorphous polystyrene substrate layer as a model of polystyrene substrate).

Bearing in mind that it was impossible to take all facts (such as solvents, pigment, fillers, etc.) into consideration in a molecular simulation study, the results were not expected to exactly agree with all experimental facts.

The interaction energies were plotted as a function of production time in Fig. 4. Average values were as follows (with

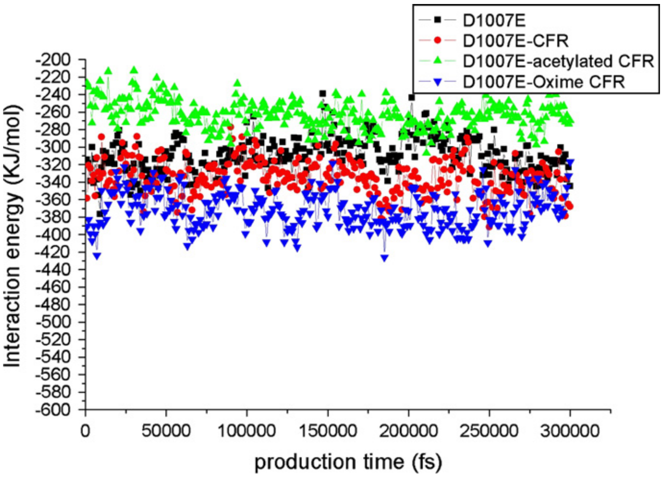


Fig. 4. Interaction energies vs production time (fs).

standard deviation in brackets): pure D1007E-polystyrene, −309.23(20.48) kJ/mol; D1007E with CFR−polystyrene, −334.58(19.93) kJ/mol; D1007E with acetylated CFR−polystyrene, −262.79(16.05) kJ/mol; D1007E with complete oxime of CFR−polystyrene, −371.47(20.57) kJ/mol.

The results' trend indicated that a more polar structure would give a favorable interaction. The layer of D1007E with oxime CFR gave the most favorable interaction (−371.47(20.57) kJ/mol), while the layer of D1007E with acetylated CFR had the poorest interaction with polystyrene substrate (−262.79(16.05) kJ/mol), these results indicated that the effect of rather polar structure played a dominative role, and the more polar the molecule structure was, the more favorable the interaction would be.

Compared with pure D1007E layer, the layer with oxime of CFR gave a more favorable interaction (increase about 20.13%) which indicated that the addition of oxime CFR could promote the adhesive properties of D1007E.

4. Conclusions

Simulations on CFR and modified CFRs suggest that acetylation improves the solubility of CFR in some solvents, especially in nonpolar solvents such as tetrachloromethane, toluene and ethyl ether; while oximation decreases the solubility of CFR. The solubility parameter of acetylated CFR is 17.30 (0.11) MPa$^{1/2}$) lower than that of CFR (19.45(0.22) MPa$^{1/2}$) and complete oxime of CFR is 21.41(0.27) MPa$^{1/2}$. All these simulated solubility parameters are systemically lower than that obtained by Bicerano connectivity indices method. These three CFRs are compatible with a dimer acid-based polyamide (D1007E), and acetylation of CFR is likely to improve its compatibility with this polyamide. High polar molecules will take much longer time to be fully equilibrated than that of low polar molecules. When oxime of CFR is added to D1007E, it will improve the adhesive property of this polyamide.

Acknowledgements

We express our thanks to Center for High Performance Computing of Northwestern Polytechnical University for partial support of this research.

References

[1] Fan Xiaodong, Deng Yulin, Waterhouse John, Pfromm Peter. J Appl Polym Sci 1998;68:305–14.
[2] Kizilcan Nilgün, Akar Ahmet. J Appl Polym Sci 1996;60(3):465–76.
[3] Kizilcan Nilgün, Akar Ahmet. J Appl Polym Sci 2005;98(1):97–101.
[4] Akar Ahmet, Öztürk Turan. Angew Makromol Chem 1988;156:49–58.
[5] Kizilcan Nilgün, Galioğlu Oya, Akar Ahmet. J Appl Polym Sci 1993;50:577–84.
[6] Flory PJ. Principles of polymer chemistry. Ithaca: Cornell University Press; 1953.
[7] Accelrys Inc. San Diego; 2004.
[8] Sun H. J Phys Chem B 1998;102:7338.
[9] Blanco M. J Comput Chem 1991;12:237.
[10] Fan CF, Olafson BD, Blanco M, Hsu SL. Macromolecules 1992;25:3667.
[11] Berendsen HJC, Postma JPM, van Gunsteren WF, DiNola A, Haak JR. J Chem Phys 1984;81:3684–90.
[12] Case FH, Honeycutt JD. Trends Polym Sci 1994;2(8):259–66.
[13] Eichinger BE, Rigby D, Stein J. Polymer 2002;43:599–607.
[14] Mayo SL, Olafson BD, Goddard WA. J Phys Chem 1990;94:8897–909.
[15] Shuying Chen. Fine Specialty Chem 2001;4:23–4.
[16] Bicerano J. Prediction of polymer properties. 3rd revised and expanded. New York: Marcel Dekker Inc.; 2002.
[17] Vicente Luis, Soto César, Pacheco-Sánchez Horacio, Hernández-Trujillo Jesús, Martinez-Magadán José Manuel. Fluid Phase Equilib 2006;239:100–6.
[18] Blanks RF, Prausnitz JM. Ind Eng Chem Fundam 1964;3:1.
[19] Barton AFM. CRC handbook of solubility parameters and other cohesion parameters. 2nd ed. Boca Raton: CRC Press; 1991.