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Computer simulation of an synthetic ultraviolet absorbent in the interface of DMB and DMF

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Abstract This work studies the aggregation of an synthetic ultraviolet absorbent, named 2-hydroxy-4-perfluoroheptanoate-benzophenone (HPFHBP), in the interface between two solvents which can not completely dissolve each other. The aggregation is studied by computer simulations based on a dynamic density functional method and mean-field interactions, which are implemented in the MesoDyn module and Blend module of Material Studios. The simulation results show that the synthetic ultraviolet absorbent diffuse to the interface phase and the concentration in the interface phase is greater than it in the solvents phase.

Introduction

Coating is very popular and important to improve surface properties of the substrate, such as appearance, adhesion, wetability, corrosion resistance, wear resistance and scratch resistance [1]. The organic coatings used in atmosphere, normally contain some photo-sensitive components which are responsible for the adsorption of ultraviolet and the gradual disability of coating, such as discoloration, embrittlement, degradation and crack.

To mitigate the damage of ultraviolet on organic coatings, it is the most common solution to add ultraviolet adsorbents (UVA) or hindered amine light stabilizers (HALS) [2-4]. The added UVA in organic coatings can greatly mitigate the damage of ultraviolet by rapid transformation of energy the adsorbed ultraviolet into vibration-rotation energy of molecules through intramolecular hydrogen bond and then releases as heat [5]. However, serious aging like yellowing can also be observed in the systems based on aromatic polyurethane because in the thin surface layer of coating, UVA or HALS is little and its protection of aromatic polyurethane from ultraviolet of solar is absent so the early yellowing of coatings resulted by ultraviolet is very marked. What's more, the radicals resulted from the aging of aromatic polyurethane will react with UVA or HALS to degrade its structure and reduce its concentration in surface layer [6]. Consequently, the aging of aromatic polyurethane coating is accelerated. The early yellowing of coating can be slowed if the UVA or HALS could be enriched in surface layer of coating even the additive amount of UVA or HALS is decreased.

Bin Xiang [7] et al. developed a serials new perfluoroalkyl ultraviolet adsorbents named 2-hydroxy-4-perfluoroheptanoate-benzophenone(HPFHBP), based on 2,4-Dihydroxybenzophenone. In order to study the working mechanism of HPFHBP in some solvents, in this work, we carry out computational simulations of its behaviors of phase separation and interfacial adsorption in the mixture of dimethylbenzene (DMB) and N,N-dimethylformamide (DMF). The computer simulations were finished in mesodyn method[8,9] based on density functional theory which had been used to study the evolution of micelles such as Fraaije[10,11], Lam[12,13], and Xu[14,15] et al.

Computational simulations

In the MesoDyn method, the molecules are defined on a coarse-grained level as “Gaussian chains of beads”. Each bead is of a certain component type representing covalently bonded groups of atoms such as those given by one or a few monomers of a polymer chain. Chemically specific information about the molecular ensemble enters into Mesodyn via material parameters such as the self-diffusion coefficients of the bead components, the Flory-Huggins interaction parameters, the bead sizes and the molecular architecture (chain length, branching, etc.). For the Gaussian chain representing the repeat units, every solvent molecule is regarded as a bead because of the small size of the solvent molecules of DMB or DMF. The beads of DMB and DMF are marked as A and B, respectively. As illustrated in Figure 1, the beads of HPFHBP are marked as C for the perfluoroalkyl chains and D for the remains.

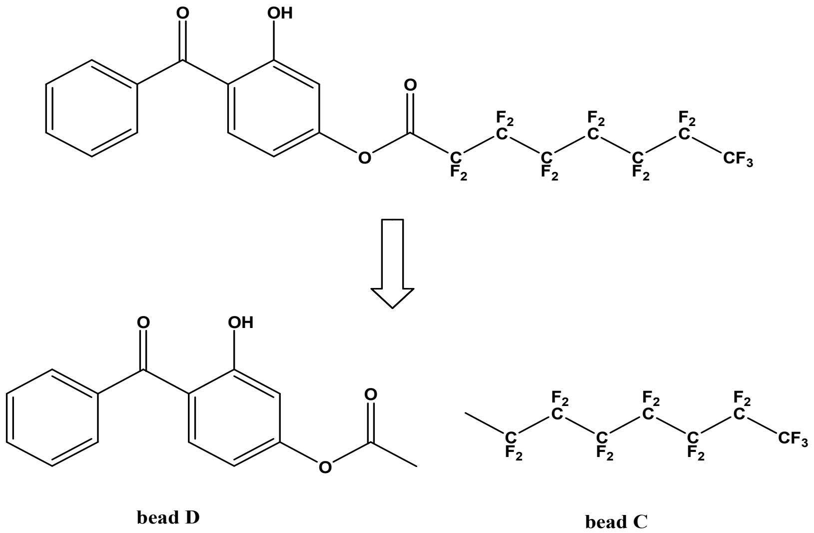

Figure 1 Bead C and D of 2-hydroxy-4-perfluoroheptanoate-benzophenone. (C for the perfluoroalkyl chains and D for the remains)

The interaction energy of such beads is calculated by the equation of $E_i = x RT/1000$, in which x is the interaction parameter and obtained by the calculation finished in Blend module of Materials Studio (MS) using optimized structures of each beads. The simulations using Blend module gives variant interaction parameter x and then we use average values of the Blend simulations to calculate interaction energy E_i. The interaction energies of such beads are exhibited in Table 1.

Table 1 Interaction energies of beads A, B, C and D (kJ/mol)

	Bead A	Bead B	Bead C	Bead D
Bead A	0	10.9589	3.8626	13.8665
Bead B	10.9589	0	6.1116	11.1114
Bead C	3.8626	6.1116	0	28.3859
Bead D	13.8665	11.1114	28.3859	0

Significant phase separation can be observed in the mixture of DMB and DMF. In the simulations using Mesodyn module of MS, DMB and DMF are treated as two incompatible solvents. The amount of HPFHBP is much lower than that of DMB or DMF so that, in the Mesodyn simulations, the volume ratio of DMB to DMF and HPFHBP is 46:46:8. The other factors of the simulations are default values of the Mesodyn Module. The simulations are paused while the step 5, 55, 155, 355, 755, 1555, 3155 and 4955 of the calculation is finished to obtain the density profiles of each bead on XY section.

Results and discussion

In the following Figures 2 to 5, the colors of bead A, B, C and D are red, green, blue and pink, respectively. In each figure, the first snapshot from left demonstrates the contributions of bead A and bead B in the mixture while the second snapshot from left shows the contributions of bead A, bead B and bead C. The third snapshot from left gives the contributions of bead A, bead B and bead D in the mixture.

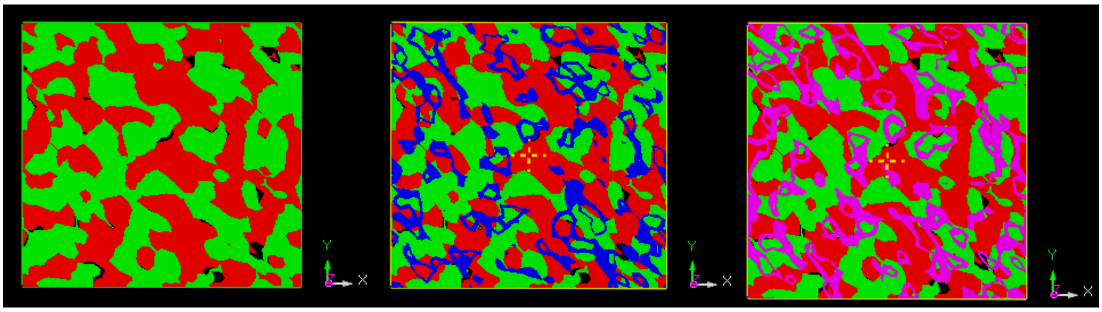

Figure 2 Snapshot of the density profiles of beads on XY section while the step 5 of calculation is finished

In figure 2 we can see that the distributions of beads A, B, C and D are uniform in the mixture. No phase separation can be observed in the mixture at the incipient stage of mixing. As shown in Figure 3, same beads start to gather together. Beads C and D start to migrate to the interface of beads A and B, reflecting that phase separation begins and part of HPFHBP migrates to the interface of DMB and DMF.

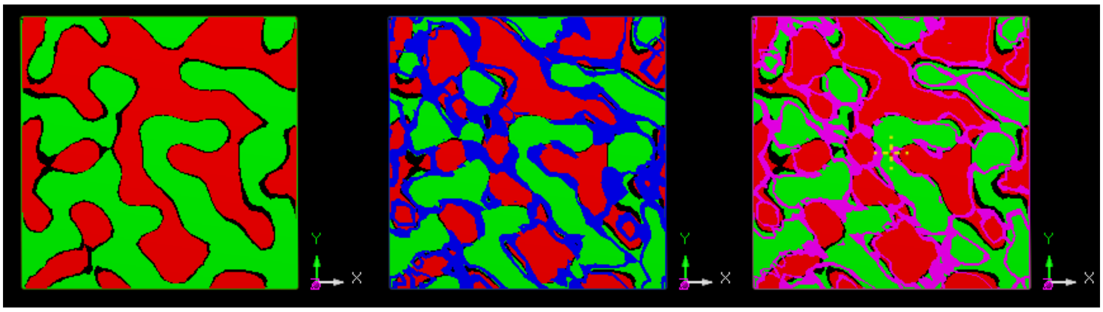

Figure 3 Snapshot of the density profiles of beads on XY section while the step 55 of calculation is finished

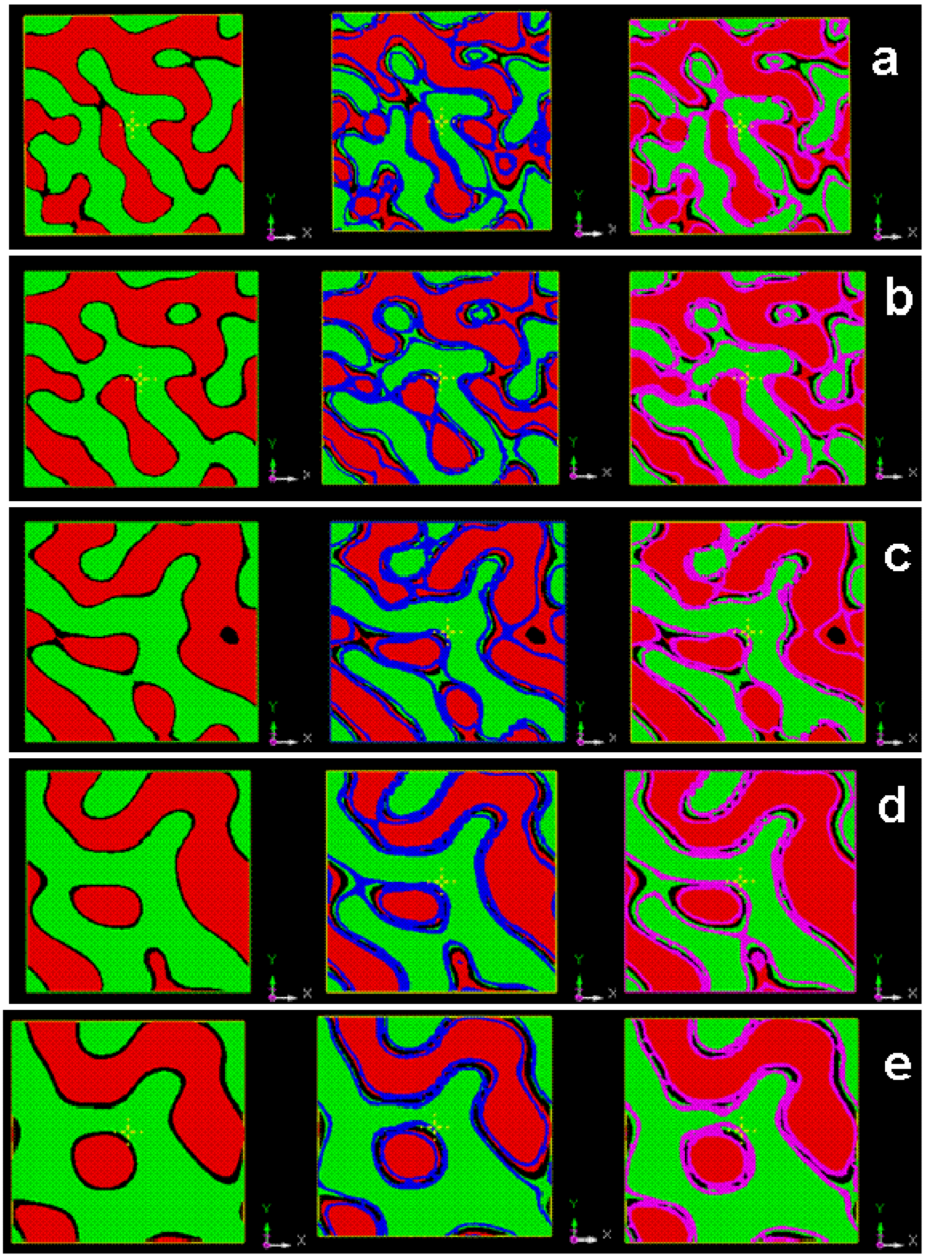

Figure 4 Snapshots of the density profiles of beads on XY section while the step a) 155; b) 355; c) 755; d) 1055; e) 3155 of calculation is finished

In figures 4, we can see that same beads gather together to arise big parts of each beads, demonstrating significant phase separation. Most bead A gathers together and migrates to the top right of each snapshot while most bead B migrates to the bottom left of each snapshot. Most beads C and beads D are found at the interface of beads A and B with a uniform distribution alone the interface. The mixture exhibits significant characteristics of phase separation and interface adsorption. In the mixture of DMB, DMF and HPFHBP, the phases of DMB and DMF are separated because of their incompatibility. Consequently, a certain part of HPFHBP migrates to the interface of DMB and DMF.

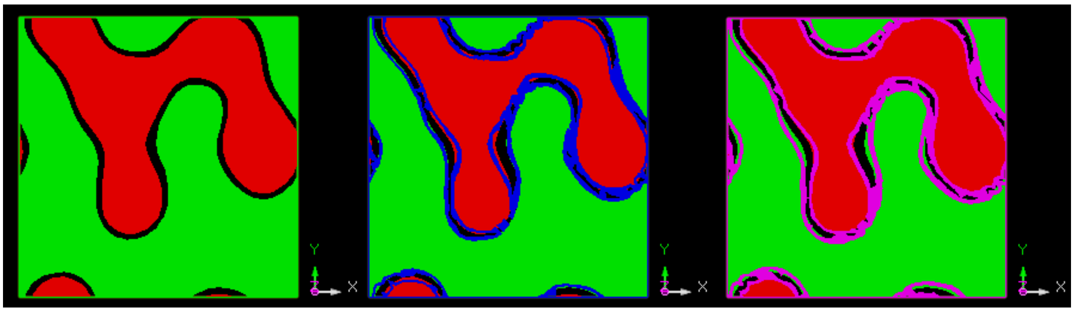

Figure 5 Snapshot of the density profiles of beads on XY section while the step 4955 of calculation is finished

In Figure 5, we can see that the mixture has totally separate into two conjugate phases. DMB is solvent in one phase with DMF and HPFHBP as solutes. In another phase, DMF is solvent with DMB and HPFHBP as solutes. It can be seen in Figure 5 that a certain part of HPFHBP is adsorbed on the interface of the DMB and DMF phases while some other HPFHBP is found in either DMB phase or DMF phase. The Gibbs free energy of the mixture decrease with the decreasing surface tension of the interface because the gathering of HPFHBP in the interface. The compatibility of two solvents is reflected by the interaction energy of corresponding beads. Normally, the mixture is incompatible if the interaction energy of corresponding beads is positive. In Table 1, we can see that the interaction energies between each pair of beads A, B, C and D are all positive, reflecting that such beads are incompatible. However, small amount of HPFHBP can dissolve in the phase of DMB or DMF because of the effect of entropy increase in the process of dissolution.

In Figure 5, it can be found that blue beads are mostly located on the edge of the aggregate of red beads. This can be explained by the lower interaction energy (3.8626 kJ/mol) between beads C and A than that (6.1116kJ/mol) between beads C and B. The interaction energy (**13.8665** kJ/mol) between beads D and A is higher than that (**11.1114** kJ/mol) between beads D and B. Consequently, pink beads are mostly located on the edge of the aggregate of green beads. As a result of the interaction of beads C and D, which construct the molecules of HPFHBP, a certain part of HPFHBP is located on the interface of DMB and DMF. The interface adsorption of HPFHBP on the interface of DMB and DMF is valuable for the further development of such new UVA. The UVA, which can be well adsorbed on the interface of different solvents, should reasonably works well.

Conclusion

In this work, the aggregation of a synthetic ultraviolet absorbent-HPFHBP, in the interface between DMB and DMF, has been studied by Mesodyn simulations. It is found that surfactant can be absorbed in the interface of two incompatible solvents. The mesodyn simulations demonstrate that

HPFHBP is adsorbed in the interface of DMB and DMF phases while DMB phase separates from DMF phase. This reflects that HPFHBP behaves in such incompatible solvents system like a surfactant, which diffuses to the interface of two phases.

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