

## OPTIMIZATION OF THE SELF HEALING PROCESS IN LOW SURFACE ENERGY COATINGS USING MESOSCOPIC SIMULATIONS.

Kateryna S. Lyakhova<sup>1</sup>, Bart J. Markvoort<sup>2</sup>, Catarina A. Esteves<sup>3</sup>, Bert de With<sup>4</sup>

<sup>1</sup>Eindhoven University of Technology, Department of Chemical Engineering and Chemistry  
Den Dolech 2, 5612 AZ Eindhoven, the Netherlands  
Email: [k.lyakhova@tue.nl](mailto:k.lyakhova@tue.nl)

<sup>2</sup>Eindhoven University of Technology, Department of Biomedical Engineering  
Den Dolech 2, 5612 AZ Eindhoven, the Netherlands  
Email: [a.j.markvoort@tue.nl](mailto:a.j.markvoort@tue.nl)

<sup>3</sup>Eindhoven University of Technology, Department of Chemical Engineering and Chemistry  
Den Dolech 2, 5612 AZ Eindhoven, the Netherlands  
Email: [a.c.c.esteves@tue.nl](mailto:a.c.c.esteves@tue.nl)

<sup>4</sup>Eindhoven University of Technology, Department of Chemical Engineering and Chemistry  
Den Dolech 2, 5612 AZ Eindhoven, the Netherlands  
Email: [g.d.with@tue.nl](mailto:g.d.with@tue.nl)

**Keywords:** Self-healing, Polymer, Simulation, Low-Surface-Energy Coating

### ABSTRACT

Low-surface-energy coatings are currently used in many industrial applications due to their exceptional properties such as self-cleaning or anti-fouling behavior. Such functionalities are often related to surface chemistry. Performance of such coatings and long-term durability are strongly related to the ability of low-surface energy groups to recover at the top surface.

Previously within our group there was proposed a new mechanism of the recovery of surface functionalities [1, 2] which involves rearrangement and reorientation of the dangling chains (containing low-surface-energy groups) located in the bulk material. Still detailed understanding of the self-healing process was missing and self-healing was not optimized. That is why a combined simulation/experimental approach was applied to study the low surface energy coatings. Simulation techniques were involved for optimization of the self healing process.

We use a coarse grained simulation method (dissipative particle dynamics) to gain more information about dynamics of self-healing process. In dissipative particle dynamics (DPD) the system of beads interacting with each other via pairwise additive forces, comprising of conservative force  $F^C$ , dissipative force,  $F^D$ , and random force  $F^R$  (see equation 1) are confined in the simulation box .

$$F_i = \sum_{j \neq i} (F_{ij}^C + F_{ij}^D + F_{ij}^R) \quad (1)$$

Conservative force is a soft repulsive force. The combination of random and dissipative forces acts as a thermostat in DPD. Random force 'heats' the system while dissipative force damps out increase in temperature. Coarse grained model allows reaching larger length scales and longer time scales<sup>1</sup>. Further the equations of motion are discretized and solved numerically.

First using DPD we model the process of crosslinking of polymer network (a polycaprolactone network). The three-armed polymer with varying length is crosslinked using a three-functional crosslinker. All the parameters are brought to correspondence with experimental system. The influence of different parameters on the surface segregation of low-surface-energy groups was considered (such as crosslink density, network mobility, interaction strength, polymer precursor length).

In the next stage dangling chains carrying the low-surface energy (fluorinated) groups were introduced to the system. The segregation of the fluorinated dangling chains at the polymer/air interface was modeled. We have varied different parameters in order to make the surface segregation of fluorine in combination with bulk concentration optimal. The formation of depletion zone was observed in the layer next to the interface. The size of depletion zone was studied as function of polymer precursor length and dangling (fluorine-containing) chains. We have also studied the influence of different dynamical factors to the fluorine profile.

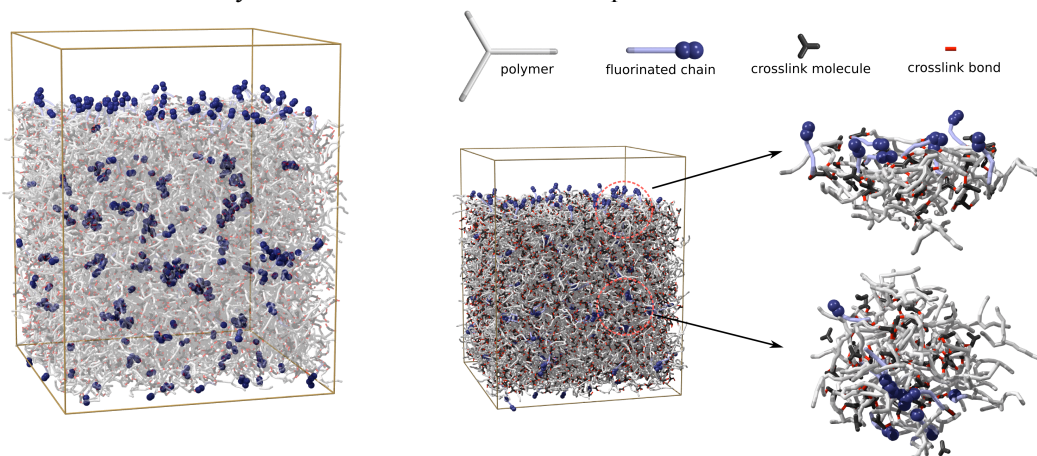


Figure 1. Surface and bulk segregation of fluorinated groups at the coating/air interface

Finally, the self replenishing of fluorinated chains after damage of polymer films was studied. First we model a piece of bulk material. After equilibration and crosslinking we cut part of the film. After damage we observe recovery of fluorine concentration at the air/polymer interface. Many dynamic factors were studied (such as delay of crosslinking, speed of crosslinking). Using mesoscopic simulations we were able to create and to control the segregation of the low surface energy groups at the polymer-air interface. After damage fluorine profile recovers at the polymer-'air' surface. We found a very good correspondence between simulations and experiment.

## REFERENCES

- [1] T. Dikic, S.J.F. Erich, M. Ming, H.P. Huinink, P. C. Thüne, R.A.T.M. van Benthem and G. de With, Fluorine depth profiling by high-resolution 1D magnetic resonance imaging, *Polymer* **48**, 2007, pp. 4063-4067.
- [2] T. Dikic, W. Ming, P.C. Thüne, R. van Benthem, G. de With, Well-defined polycaprolactone precursors for low surface-energy polyurethane films, *J. Pol. Sci. A*, **46**, 2008, pp. 218-227.
- [3] R.D. Groot and P.B. Warren, Dissipative particle dynamics: Bridging the gap between atomistic and mesoscopic simulation *J. Chem. Phys.* **107**, 1997, pp. 4423-4435.