MODELLING OF SELF-HEALING SURFACE STRUCTURED COATINGS

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ABSTRACT

For many current engineering applications the performance of materials depends strongly on the surface properties of the top layer. In many cases a hydrophobic/superphydrophobic top surface is desired (for example for easy-to-clean/self-cleaning applications). The durability of coatings will be substantially extended if the layer which provides the hydrophobic/superhydrophobic property will have ability to self-heal.

Previously, hydrophobic coatings with a self-healing surface were reported by our group. These coatings can recover a sufficiently high concentration of the low-surface-energy groups at the air/polymer interface. The bulk material serves as reservoir of the low-surface energy component (fluorinated polymer dangling chains). A mechanism of self-replenishing involves the reorientation of the dangling chains which carry the fluorinated group. Silica particles where incorporated into the polymer system in order to introduce the surface roughness leading eventually to higher contact angles of the polymer coating. Our goal is to create a model of the a self-healing superhydrophobic coating.

In this work we use the mesoscopic modelling technique (dissipative particle dynamics) in order to study several aspects of these polymer/particle coating: 1) the segregation of the low surface energy groups at the top surface of the coating.; 2) the self-healing response of the system and 3) the dynamics and distribution of crosslinks in the polymer system in presence of relatively large silica particles. For these studies we considered the distribution of the low surface energy groups in a confined geometry at the interfaces available. The minimal thickness of the polymer layer which provides self-healing ability was also calculated.

All the relevant parameters (crosslinking conditions, polymer precursor and dangling chain length and distance between particles) were changed systematically. The simulations give a valuable insight into the details of microstructures and dynamics and guide experiments towards the choice of the system with the maximal self-healing efficiency.

1. INTRODUCTION

The surface properties of polymeric materials are generally determined by the chemical groups present at their surface. The preferential location of the low surface energy chemical groups at the surface is crucial for the low-adhesion properties

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which are of high interest for various engineering fields. Controlling the surface segregation of such chemical groups, would allow maintaining the materials properties at high performance level all through its service lifetime. Previously the self-healing mechanism for the low-surface energy coatings was proposed and well studied within our group [1,2]. Introducing the surface roughness allows transition from hydrophobic to super hydrophobic surfaces. We use a combined experimental/simulation approach to study surface structured low-surface energy coatings.

2. METHOD

Modelling of self-healing low-surface energy surface structured coatings was performed using the coarse grained simulation method. Dissipative Particle Dynamics (DPD). This method is a coarse grained of-lattice simulation technique which involves movement of coarse grained particles (beads) in the box with discrete timestep. Beads represent fluid regions as well as parts of molecules. Beads interact with simplified repulsive pair-potential. This method was chosen in order to reach the time-scales and length-scales of interest. The traditionally used DPD simulation method was modified in order to allow the formation of chemical crosslinks. The presence of silica particles was modelled by introducing to the simulation system a wall which consists of immobile beads. Also the spherical particles consisting of large amount of beads (~32000) where introduced to the simulation box. The system was parameterized using relevant experimental data. In previous work we have obtained a very good agreement between experiment and simulation results and can rely on the simulation parameters.

The molecular model of the system is shown in Figure 1. The caprolactone (CL) unit was chosen as a minimal volume corresponding to the single bead. The crosslinking was realized by making beads CL-H and CR reactive. During crosslinking process the permanent bonds between these two beads can form. The beads which model Silica particle also can interact with crossliker and can form a permanent bond (mimicking the presence of OH groups at the particle surface).
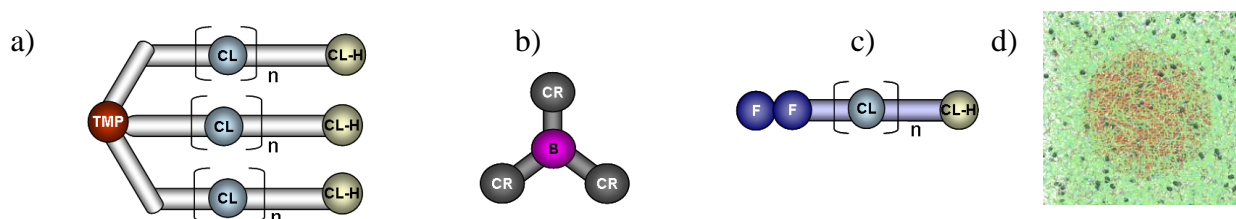

Figure 1: Coarse grained model used in DPD simulations. a) Model of polymer precursor (TMP-PCL$_{3n}$); b) model of crosslinker (tri-isocyanate), c) – model of fluorinated dangling chain (F$_{17}$C$_8$-PCL$_n$), d) model of silica particle incorporated in polymer coating.

3. RESULTS AND DISCUSSION

As the Silica particles used in experiment are ~700 nm in diameter (in contrast to a typical length scale of polymer ~1 nm) in our simulation we present a particle surface as a flat substrate consisting of immobile particles. A free polymer surface is

modelled by placing a layer of 'void' beads on a top of polymer coating. In this way the two interfaces are created : a polymer/particle and a polymer/air interface. The concentration of fluorine per layer in z-coordinate was calculated and summarized in fluorine profiles. First polymer coating was equilibrated and crosslinked (see Figure 2a). Then the damage of polymer layer was modelled by replacing the part of simulation box by 'void' component. Depth of damage was varied (see Figure2 b,c) The segregation of the low-surface energy groups at the newly formed interface was studied. The profiles are shown in Figure 2d. We found that there exists a critical polymer thickness at which bulk of polymer coating does not contain sufficient
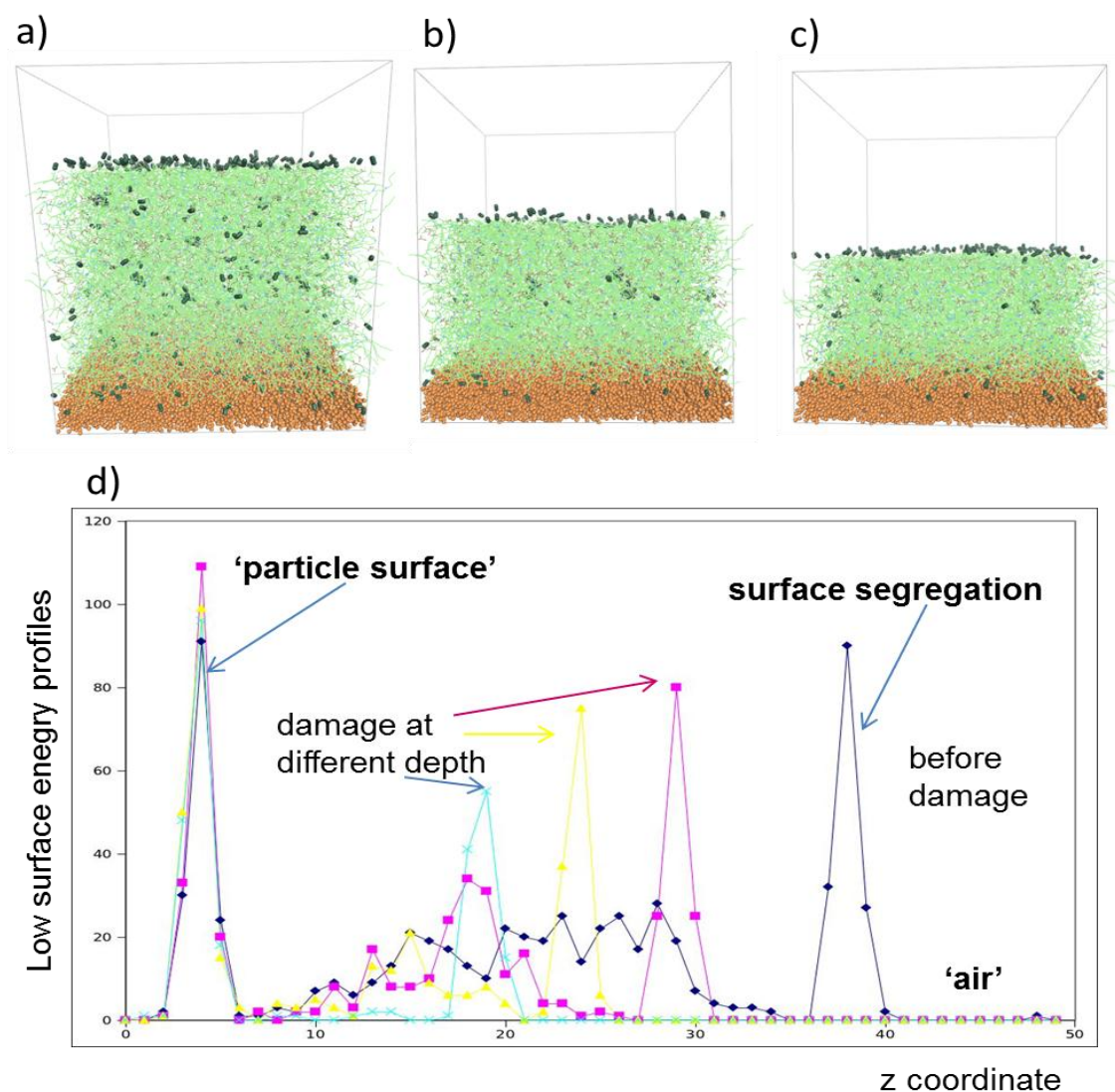

Figure 2. a) Simulation of the surface supported polymer film with one free surface before damage. The fluorinated beads are shown in dark green and are increased for visualisation purposes; b) and c) simulation of surface supported film after damage(different depth of cuts); d) profile of the low surface energy groups as function of z coordinates before and after damage.

concentration of the low surface energy groups and self-healing is not realized. In our previous study on self-healing coatings we have shown that the depletion layer is formed just below the interface layer enriched by the low-surface energy groups. We found that the depth of the depletion layer is not dependent of dangling chain length.

In the supported polymer film fluorinated groups are segregated at the two interfaces: polymer-air and polymer-particle interface and the region of the low fluorine concentration is doubled. We found that at thickness of polymer film ~10 nm no self-healing observed. This imposes a restriction on the concentration of particles in composite system.

Further the self-healing behavior of the system was studied starting from the bulk material. The bulk material is modeled as a polymer film sandwiched between the two particle surfaces. Similar to the previous approach first the model system was crosslinked and equilibrated. After this pretreatment the part of simulation box was replaced by 'void' component creating a new polymer/air interface.
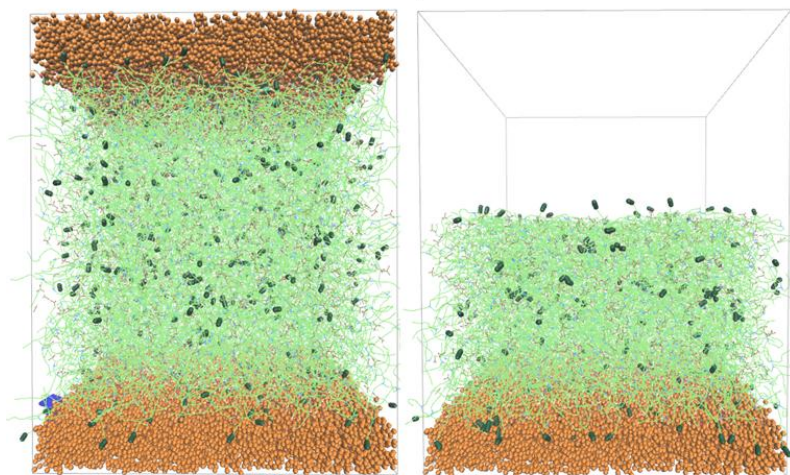

Figure 3. Simulation of the sandwiched polymer film before (left) and after (right) damage. Fluorinated beads are shown in dark green and are increased for visualisation purposes. The 'void' component is not shown.

4. CONCLUSIONS

Self healing ability of the polymer system contating dangling chains was studied. The segregation of the low-surface energy groups in the presence of Silica particles was modelled. We found that there exists a critical polymer layer at which the surface properties of the system are not healed.

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