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DPD Simulation of Self-Healing Process of Nanocoating

N. Filipovic[*1,2,3], D. Petrovic[2], A. Jovanovic[4], S. Jovanovic[4], D. Balos[4], M. Kojic[2,3,5]

[1] University of Kragujevac, Faculty of Mechanical Engineering
fica@kg.ac.yu
[2] Research and Development Center for Bioengineering 'BIOIRC', Kragujevac, Serbia
deyan.petrovic@gmail.com
[3] Harvard School of Public Health, Boston, USA
nfilipov@hsph.harvard.edu; mkojic@hsph.harvard.edu
[4] Steinbeis Advanced Risk Technologies GmbH, Stuttgart, Germany
jovanovic@risk-technologies.com
[5] Department of Biomedical Engineering, University of Texas Medical Center at Houston, USA
**Corresponding author*

Abstract

Biological systems have the ability to heal wounds and this analogy could also be applicable in materials damage. The surface defects of the material are difficult to detect and difficult to repair. Recent research of the nanocontainers with process of self-healing materials promises a good avenue for new smart nanocoating interfaces. We use Dissipative Particle Dynamics (DPD) computer simulation method to investigate coating substrates that contain nanoscale defects with nanocontainers filled with healing agents.

The numerical simulation uses the three usual DPD forces: repulsive, dissipative and random forces, as well as additional forces for process of polymerization inside random positioned cracks in the nanocoating layer. The initial results show the process of breaking of nanocontainers and realization of healing agents with initial polymerization of the outside particles. The future application of DPD simulation coupled with risk assessment technology could help faster development of new active multi-level protective systems for future vehicle materials.

Keywords: Nanocoating, self-healing process, healing agents, nanocontainers, DPD simulation

1. Introduction

Small size defects can appear on a material surface. Such defects have a substantial effect on the mechanical properties of material. To protect this material failure the coating systems are employed on a wide range of engineering structures, from cars to aircrafts, from chemical factories to household equipment. The "self-healing" is a relatively new term in material science which means a self-recovery of initial properties of the material after destructive actions of the external environment. It is an urgent demand for industrial applications to initiate the development of an active healing mechanism for the polymer coatings and adhesives.

The autonomic healing concept is firstly published in White et al. (2001) where a microencapsulated healing agent is embedded in a structural composite matrix containing a catalyst capable of polymerizing the healing agent, as schematically shown in Fig. 1.

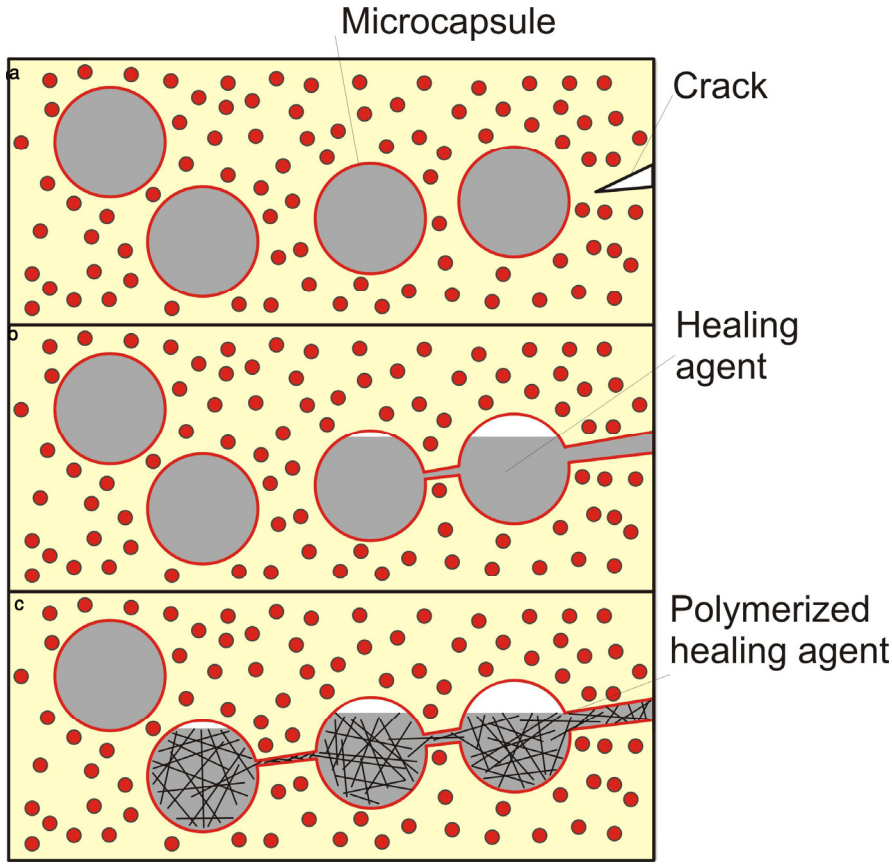


Fig. 1. A nanocoating self-healing scheme. A healing agent is inside micorcapsuled nanocontainers while surrounding composite matrix contains a catalyst for polymerizing the healing agent. (a) Cracks form in the matrix wherever damage occurs; (b) The crack ruptures the microcapsules, releasing the healing agent into the crack plane through capillary action; (c) The healing agent contacts the catalyst, triggering polymerization that bonds the crack faces closed (According to White et al 2001).

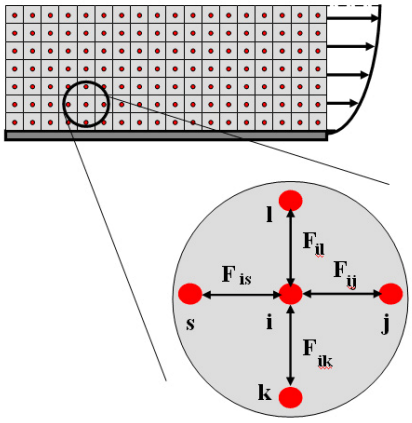
2. DPD model

The coating layer with nanoscopic noach can be modeled using molecular dynamics (Tyagi et al. 2004). Another approach to this problem is a mesoscoping modeling using the DPD method (Hoogerbrugge and Koelman, 1992, Jovanovic and Filipovic, 2006). Motion of each DPD particle (further called 'particle') is described by the following Newton law equation:

$$m_i \dot{\mathbf{v}}_i = \sum_j (\mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R) + \mathbf{F}_i^{ext} \tag{1}$$

where m_i is the mass of particle "i"; $\dot{\mathbf{v}}_i$ is the particle acceleration as the time derivative of velocity; $\mathbf{F}_{ij}^C$, $\mathbf{F}_{ij}^D$, and $\mathbf{F}_{ij}^R$ are the conservative (repulsive), dissipative and random (Brownian) interaction forces, that particle "j" exerts on particle "i", respectively, provided that particle "j" is within the radius of influence r_c of particle "i"; and $\mathbf{F}_i^{ext}$ is the external force exerted on particle "i", which usually represents gradient of pressure or gravity force as a driving force for the fluid domain (Boryczko et al. 2003). The total interaction force $\mathbf{F}_{ij}$ (Fig. 2) between the two particles is

$$\mathbf{F}_{ij} = \mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R \tag{2}$$



$$\mathbf{F_{ij}} = \mathbf{F_{ij}^{Conservative}} + \mathbf{F_{ij}^{Disipative}} + \mathbf{F_{ij}^{Random}}$$

Fig. 2. Interaction forces in the DPD method.

The component forces can be expressed as (Groot and Warren 1997)

$$\begin{aligned} \mathbf{F}_{ij}^C &= a_{ij}(1-r_{ij}/r_c)\mathbf{r}_{ij}^0 \\ \mathbf{F}_{ij}^D &= -\gamma w_D(\mathbf{v}_{ij}\cdot\mathbf{e}_{ij})\mathbf{r}_{ij}^0 \\ \mathbf{F}_{ij}^R &= \sigma w_R \xi_{ij}\mathbf{r}_{ij}^0 \end{aligned} \tag{3}$$

In equation (3), a_{ij} is the maximum repulsion force per unit mass, r_{ij} is the distance between particles i and j, $\mathbf{r}_{ij}^0 = \mathbf{r}_{ij}/r_{ij}$ is the unit vector pointing in direction from j to i, γ stands for the friction coefficient, and σ is the amplitude of the random force. Also, w_D and w_R are the weight functions for dissipative and random forces, dependent on the distance r from the particle i; and ξ_{ij} is a random number with zero mean and unit variance. The interaction force is equal to zero outside the domain of influence, r_c, hence $F_{ij} = 0$ for $r_{ij} > r_c$.

Further, in order that a DPD fluid system possess a Gibbs–Boltzmann equilibrium state, the following relation between the amplitudes of the weight functions of dissipative and random forces, w_D and w_R, must hold:

$$w_D = w_R^2 \tag{4}$$

Also the amplitude of the random force σ is related to the absolute temperature T,

$$\sigma = \left(2k_B T\gamma\right)^{1/2} \tag{5}$$

where k_B is the Boltzmann constant. The weight functions can be expressed in a form (Groot and Warren 1997) given as

$$w_D = (1 - r_{ij}/r_c)^2, \quad w_R = 1 - r_{ij}/r_c \tag{6}$$

The particles used in this study represent both self-healing agents and surrounding coating material with different material characteristics. This was done by taking into account different repulsion force coefficient a_{ij}. The additional interaction forces between two particles inside self-healing agents are added similarly as it was done in a model of thrombosis in Filipovic et al. (2008a,b). These attractive forces are expressed as

$$F_a = k_{sf}(1 - L_{sf}/L_{sf}^{max}) \tag{7}$$

where L_{sf} is the distance of the self-healing particle from the wall or another self healing particle, k_{sf} is effective spring constant and L_{sf}^{max} is the maximum length of self-healing particle attractive domain.

A schematics of the concept of the self-healing agent realizing is shown in Fig. 3. It is first modeled the initial process of nanocontainer breaking at the random position where a crack position is assumed. The nanocontainer membrane is approximated by one layer of particles (red particles in Fig. 3) which is broken by some random process seeded with the clock time for each simulation. We consider that nanocontainers are fixed in coating layer so the membrane particles are fixed in the DPD space domain. A specific algorithm for treating the boundary condition for these nanocontainer particles is implemented. The surrounding material is modeled by simple DPD particles (yellow particles) which can start to interact with self-healing (green particles) agent in order to make a process of polymerization. This simple model does not represent a total self-healing process, it is rather an initial model for the self-healing agent realizing and moving of this material around the nanocontainer.

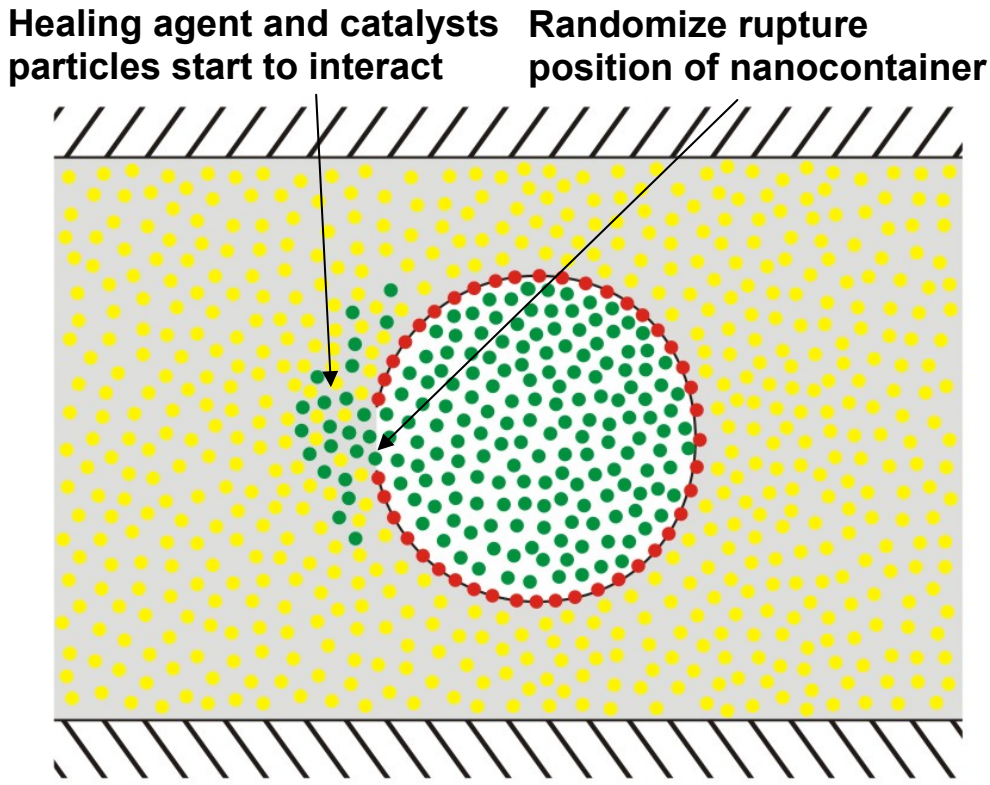


Fig. 3. Realizing of self-healing agent. After nanocontainer membrane (red particles) is broken due to the crack action at a random position, the catalysts particles (yellow particles) start to interact with the self-healing (green particles) material in order to generate the polymerization process.

Another model could capture a more realistic scenario where a crack occurs at a random position and there is more then one nanocontainer in the space (Fig. 4). In this model the particles from self-healing agent are filling the space inside a crack in order to bond it and to protect it from further propagation. We modeled a process of polymerization introduced by an additional spring force which connects particles between themselves and also those attached to the walls of the crack - by using equation (7). Other free particles are moved into the domain without this spring force until a specific probability function is activated for the bonding to the wall.

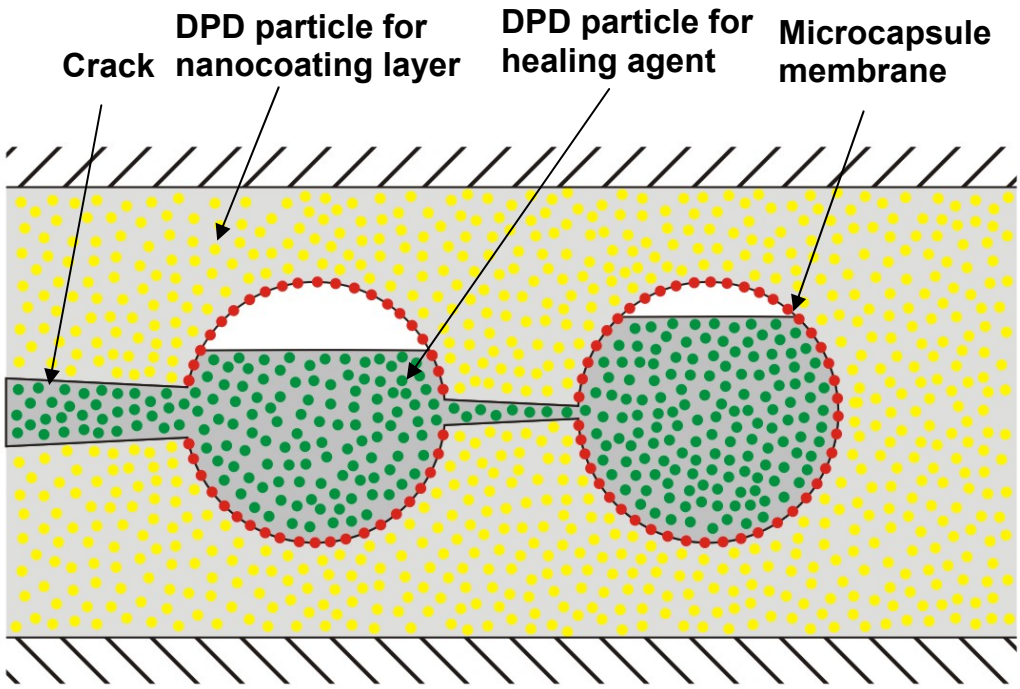


Fig. 4. Self-healing concept for simple example of one crack and two nanocontainers

3. Results and discussion

A software for the initial DPD simulation was developed. Menu dialog interface for input parameters with their description is shown in Fig. 5. The external force is assumed to act on all particles. User can specify a DPD domain by defining a number of particles in X and Y directions. The basic material DPD constants : viscosity friction and repulsive force coefficient, are also prescribed. An additional repulsive force coefficient is given for particles inside the nanocontainer in order to keep them close after breaking of nanocontainer and realize into surrounding structural matrix which contains simple DPD particles. A random process of breaking membrane from nanocontainer is implemented.

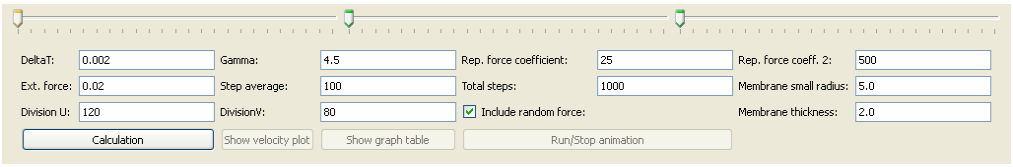


Fig. 5. Menu of the input parameters interface for a 2D DPD simulation of the nanocontainer breaking and self-healing agent realizing. **DeltaT** is the time step for DPD simulation; **Ext. force** is the external force which acts in X direction on all particles to produce motion; **Division U** is the total number of particles in X direction at initial time; **Division V** is the total number of particles in Y direction at initial time; **Gamma** is the viscosity friction coefficient used in DPD equations; **Step average** is the total number of steps for writing results for animation; **Total steps** is the total number of time steps for the entire simulation; **Rep. force. coefficient** is the repulsive force coefficient used for repulsive force for all particles around the nanocontainer; **Rep. force. coeff. 2** is the repulsive force coefficient used for the repulsive force for particles inside the nanocontainer; **Membrane small radius** is radius of the nanocontainer; **Membrane thickness** is thickness of the nanocontainer membrane; **Include random force** checking button is used for including/excluding random force in a DPD calculation; **Calculation** button starts the program execution; **Run/Stop animation** button is used for start/stop animation which obtained from the DPD calculated results.

One of the screenshot for a self-healing particle realizing is shown in Fig. 6. The self-healing material is shown by the yellow particles, while the red particles are considered to be fixed in the space domain. The surrounding particles are denoted by the gray color.

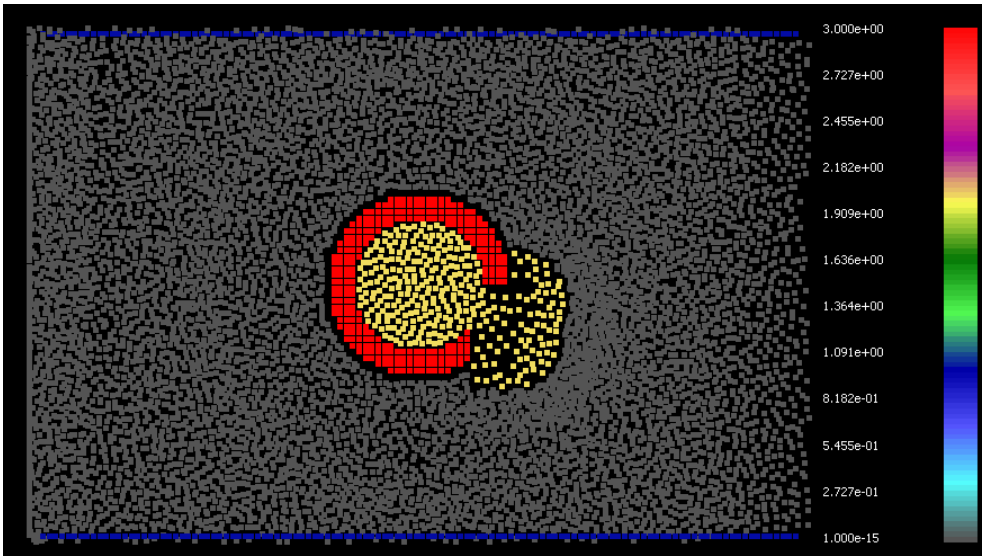


Fig. 6. Screen shot of the DPD particle self-healing realizing into the surrounding material. Yellow particles represent the self-healing material, red particles are considered to be fixed in space domain, while their breaking is randomized with clock time seeded function. Surrounding particles are shown in gray.

A real scenario of realizing self-healing agents is to assume particle motion only inside the crack domain. We modeled a 2D rectangle crack domain having the length of 16 *mm* and depth of 0.1 *mm*. Total number of DPD particles was 16 000 (1600x10). The attractive force on both walls (bottom and upper) was specified by equation (7), with effective spring constant $k_{sf} = 1$ *N*/*m*. The total number of time steps for simulation was 300 000. The resulting volume fraction distribution over the axial length of crack, averaged over 40 000 last time steps, is shown in Fig 7. As expected, a uniform volume fraction occurred on the surface wall.

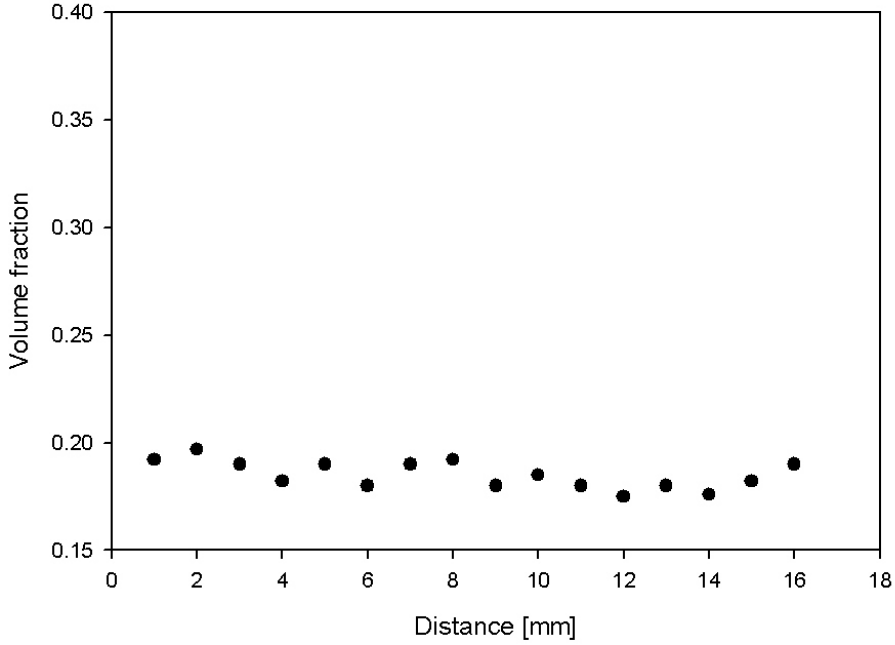


Fig. 7. Volume fraction along the crack of length 16 *mm* and depth 0.1*mm*, obtained by a simple 2D analysis. The data are averaged over 40 000 last time steps. Total time steps for DPD calculation was 300 000.

4. Conclusions

An initial DPD simulation for nanocontainer breaking and self-healing agent realizing was developed. The random position of nanocontainer as well as random breaking part of nanocontainer membrane were modeled by a clock time seeded function. Only the realizing of the self-healing agent into surrounding material and crack space is considered. A user friendly software was developed for the ease of the DPD model generation. Initial results showed the agent particles moved into surrounding structure matrix and volume fraction distribution inside a small rectangle crack domain. Future work will include generation of multiple nanocontainers with assumed "density" in given regions. Also modeling of agent "spill" into the crack, including the capillarity effect and different branched cracks, will be considered. We will also analyze a coupling of this modeling and a risk assessment technology, which could help faster development of new active multi-level protective systems for future industrial materials.

Acknowledgments

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