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MODELING OF SELF-HEALING PROCESS IN NEW NANOCOATING OF SURFACES BY MATERIAL WITH CONTAINERS FILLED WITH HEALING AGENTS

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Abstract: During exploitation of structures, surface cracks may develop, thus it is being investigated a new technology which uses nanocoating by material with nanocontainers that have healing agents for material polymerization. Experiments for this new nanocoating process are too expensive and their control has not yet been thoroughly investigated; hence, computer modeling can play important role.

In this paper, the process of nanocoating is simulated by Dissipative Particle Dynamics (DPD) method. Besides the standard repulsive, dissipative and random forces, used in the DPD method, here it is introduced the additional polymerization force between two particles within nanocontainer. The initial results demonstrate motion of the healing agent particles into surrounding structural matrix and volume fraction distribution inside a small rectangle crack domain.

Keywords: self-healing material process, dissipative particle dynamics (DPD), nanocoating.

1. INTRODUCTION

The process of coating is necessary to extend lifetime and utility of manufactured components. Due to growing trend in production of nanoscale devices, there is a particular need to create materials for healing the nanoscale defects that arise in these devices. Whether localized in such miniature devices or more macroscopic components, nanoscale notches and scratches can have a substantially deleterious effect on the mechanical properties of the entire system.

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. There is an urgent demand for industrial applications to initiate the development of an active healing mechanism for the polymer coatings and adhesives.

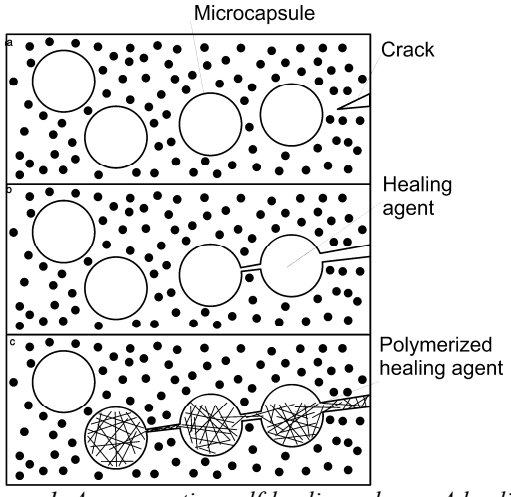

Figure 1. A nanocoating self-healing scheme. A healing agent is inside micorcapsuled nanocontainers while surrounding composite matrix contains a catalyst for polymerizing the healing agent. (a) Cracks form in the matrix wherever damage occurs; (b) The crack ruptures the microcapsules, releasing the 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 [1])

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The autonomic healing concept is firstly published in [1] 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.

2. DPD MODEL

The molecular dynamics is one of the approaches for the modeling of the coating layer with nanoscopic noach [2]. Another approach is a mesoscoping modeling using the DPD method [3], [4]. If we consider the motion of DPD particles, each of that motion 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 [5]. The total interaction force $\mathbf{F}_{ij}$ (Fig. 2) between the two particles is

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

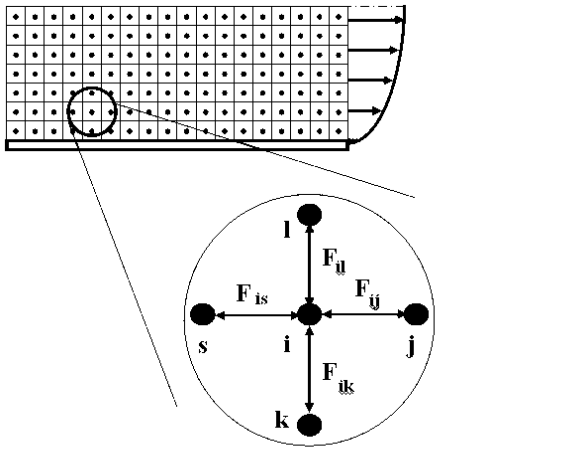

Figure 2. Interaction forces in the DPD method

The component forces can be expressed as [6]:

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

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 [6] given as

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

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 [7,8]. These attractive forces are expressed as

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

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.

The schematics of the concept of the self-healing agent realizing is shown in Fig. 3. The initial process of nanocontainer breaking is modeled first 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 crack occurs at a random position and there is more then one nanocontainer in the space. 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.

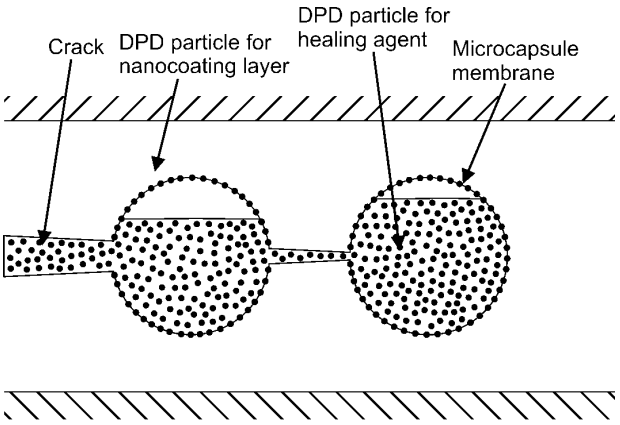

Figure 3. Self-healing concept for simple example of one crack and two nanocontainers

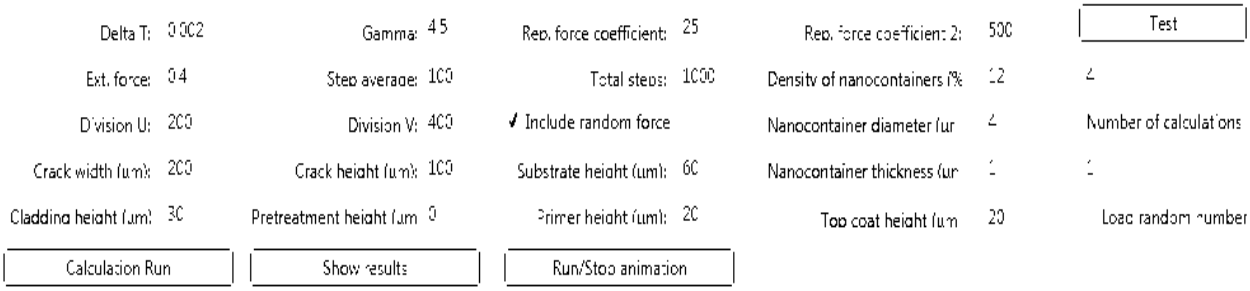

Figure 4. Menu of the input parameters interface for a 2D DPD simulation of the nanocontainer breaking and self-healing agent realizing. DeltaT is the time step for DPD simulation; Ext. force is the external force which acts on all particles to produce motion; Division U is the total number of particles 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; Nanocontainer diameter is diameter of the nanocontainer; Nanocontainer thickness is thickness of the nanocontainer membrane; Crack width, crack height, cladding height, pretreatment height, substrate height, primer height, top coat height are dimensions of different layers in example like on figure 5; Include random force check 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.

3. RESULTS AND DISCUSSION

The software for the initial DPD simulation was developed. Menu dialog interface for input parameters with their description is shown in Fig. 4. 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 position of nanocontainers inside of nanocoating layer is implemented.

One of the screenshots of a self-healing particle realizing is shown in Fig. 4. The self-healing material is shown by the yellow particles, while the red particles (membranes of nanoconainers) are considered to be fixed in the space domain. The surrounding particles are denoted by the blue color.

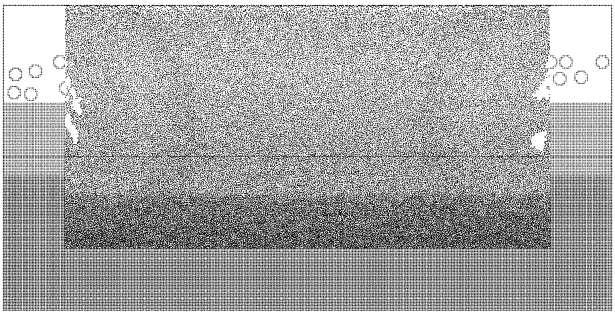

Figure 5. Screen shot of the DPD particle self-healing realizing into the surrounding material. Yellow particles represent the self-healing material, red particles are considered to be fixed in space domain, while their breaking is made by crack. Surrounding crack particles are shown in blue

4. CONCLUSIONS

We developed an initial DPD simulation for nanocontainer breaking and self-healing agent realizing. The random positions of nanocontainer as well as random breaking part of nanocontainer membrane were modeled by a clock time seeded function. User friendly software was developed to facilitate 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 the given regions. We will consider modeling of agent "spill" into the crack, including the capillarity effect and different branched cracks. We will also analyze biomaterial crack analysis coupling with a risk assessment technology, which could help a faster development of new active multi-level protective systems for biomaterials.

ACKNOWLEDGMENTS

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МОДЕЛИРАЊЕ САМОВЕЗУЈУЋЕГ НОВОГ ПРОЦЕСА НАНОПОКРИВАЊА ПОВРШИНА МАТЕРИЈАЛОМ СА КОНТЕЈНЕРИМА ИСПУЊЕНИМ ВЕЗИВНИМ САДРЖАЈЕМ

Сажетак: У току коришћења конструкција појављују се површинске пукотине тако да се истражује нова технологија која користи нанопокривање материјалом са наноконтејнерима у којима су садржани везивни агенти за полимеризацију материјала. Експерименти за овај нови процес нанопокривања су веома скупи, а њихова контрола још увек није детаљно испитана; због тога компјутерско моделирање може имати значајну улогу.

У овом раду је процес полимеризације коришћењем наноконтејнера симулиран методом „дискретна честична синамика". Осим стандарних одбојних, вискозних и случајних сила које се користе у овој методи, уведена је и додатна сила полимеризације између две честице у наноконтејнеру. Почетни резултати показују кретање честица везивних агената у окружујућу матричну структуру као и фракциону запреминску дистрибуцију унутар мањих правоугаоних домена пукотина.

Кључне речи: самовезивни процеси у материјалу, дискретна честична динамика, нанопокривање.