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# MODELING OF SELF–HEALING MATERIALS AND FITTING PARAMETERS PROCEDURE

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**Abstract:** The surface defects of the material are difficult to detect and difficult to repair. A big challenge in materials science is to design „smart" synthetic systems that can re-establish the continuity and integrity of the damaged area. Recent research of the nanocontainers with the process of self-healing materials promises a good avenue for new smart nanocoating interfaces. We use continuum modeling approach to investigate coating substrates that contain nanoscale defects with healing agents. Here we use Finite Element Method (FEM) with different diffusivity and fluxes. The fitting procedure from simulations is performed to determine diffusion coefficient and the diameter of nanocontainers to match experimental results. We also show the risk map from the calculations of the creepage and coverage.

**Keywords:** self-healing material process, finite element methods (FEM), nanocoating, fitting.

## 1. INTRODUCTION

Corrosion degradation of materials and structures is one of important issues that lead to depreciation of investment goods. Two main approaches, an active and a passive one, are currently used for corrosion protection. The passive corrosion protection is achieved by deposition of a barrier layer preventing contact of the material with the corrosive environment [1, 2].

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" or "inhibition" are a relatively new terms in material science and means a self-recovery of initial properties of the material after destructive actions of external environment. It is an urgent demand for industrial applications to initiate development of an active healing mechanism for polymer coatings and adhesives [3−6].

In this study we presented FEM modeling approach. We begin by describing the details of the nanocontainers healing concept by FEM methodology. We then discuss the effects of fitting parameters such as diffusion coefficient and diameter of nanocontainers. These findings provide guidelines for formulating nanocomposite coatings that effectively heal the surfaces through the self-assembly inhibitors into the defects.

## 2. METHODS

### 2.1 Nanocontainers healing concept

The initial process of nanocontainer breaking starts at a random position where a crack occurred. Inside the nanocontainers are healing agents – inhibitors. We assume that nanocontainers are fixed in the coating layer (pretreatment or primer layer) as presented in Fig. 1.

Nanocontainers release the „self – healing" agent particles which are filling the space inside a crack in order to bond it and to protect the crack from further propagation. We modeled a process of self-healing using continuum model in which we have convective-diffusion process for inhibitors binding to the substrate surface.

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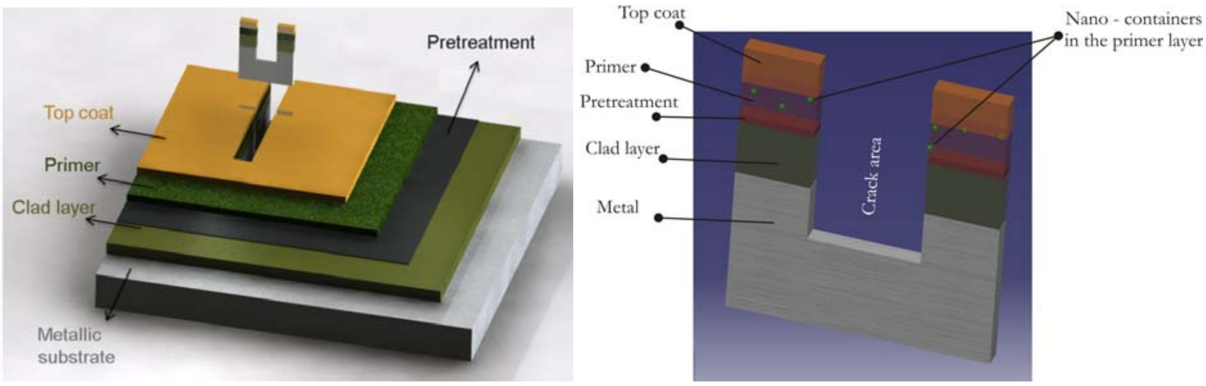


*Figure 1. Model with nanocontainers in primer layer*

## 2.2 FEM model

The mass transport process for inhibition system of coating is governed by convection – diffusion equation,

$$\frac{\partial c}{\partial t}+v_x\frac{\partial c}{\partial x}+v_y\frac{\partial c}{\partial y}+v_z\frac{\partial c}{\partial z}=D\left(\frac{\partial^2 c}{\partial x^2}+\frac{\partial^2 c}{\partial y^2}+\frac{\partial^2 c}{\partial z^2}\right)+q^{wall} \quad (1)$$

where $c$ denotes the concentration of inhibitors; $v_x, v_y$ and $v_z$ are the velocity components in the coordinate system $x,y,z$; and $D$ is the diffusion coefficient, assumed to be constant, of the transported material; and $q^{wall}$ is flux of the binding process for inhibitors which adhere on the substrate surface. A similar concept is used for calculation of the volume of inhibitors which are possible to diffuse on the scratch surface. Diffusivity coefficient and wall binding flux are the fitting parameters in FEM model. The drawback of continuum approach is that particle-particle interaction cannot be modeled while the benefit is a possibility of modeling a large substrate area.

## 2.3 Fitting parameters

The goal is to determine diffusion coefficient and diameter of nanocontainers so that computer simulations match experiments. We used a simplex optimization method developed by John Nelder and Roger Mead [7] to reach the best fit. This is a nonlinear procedure which involves only function evaluations (no derivatives). The best fit minimizes the sum of squared residuals, a residual being the difference between an experimental value of the creepage distance and the creepage distance provided by a simulation. We have four different experimental creepages defined with 1200 points all together, thus we have 1200 residuals. The sum of squared residuals is calculated as:

$$SE=\sum_{i=1}^{1200}\left(p_i-t_i\right)^2 \quad (2)$$

where $p_i$ is the creepage distance for $i$-th point calculated by simulation and $t_i$ is target (experimental) creepage distance for $i$-th point. We achieved minimum error (SE=3082) with diffusion coefficient value 0.32 [$m^2$/s] and diameter of nanocontainers 0.092 [nm].

# 3. RESULTS

## 3.1 FEM results

The continuum model consists of mesh size of 50,000 finite elements where inhibitors are randomly prescribed as the influx boundary conditions. The coverage of the inhibitors on the substrate surface is presented in Fig. 2. The scratch dimension is 0.1x100 mm, the primer layer is 4000 nm, nanocontainer diameter is 400 nm. The percentage of inhibitor inside nanocontainers is 20% and the percentage of nanocontainers in the primer or pre-treatment layers is 10%. The convection velocity is assumed to be zero due to dominant diffusion process. The binding flux was prescribed to be unit which depends on the mechanical property of scratch, with no water inclusion on the surface.

Distribution of inhibitors on the scratch surface for time = 6h is presented in Fig. 2. The inhibitors fluxes are randomly distributed along the plate, which cause higher coverage near these plate sides.

## 3.2 Fitting results

We developed an online application where a user can change input parameters and get different creepage results. The interface of that software application is shown in Fig. 3.

Results from the fitting parameters calculations are shown in Figure 4. It can be observed that the experimental results (blue color) and results obtained by simulations (red color) are very similar. The reason for error deviation is a big error that occurs at the points where the experiment has very large creepage distance (for example, third experiment at the height around 15 mm creepage distance is about 10 mm), but from the histogram we can see that most of the points for both, computer simulation and experiment, have creepage distance around 2 mm.

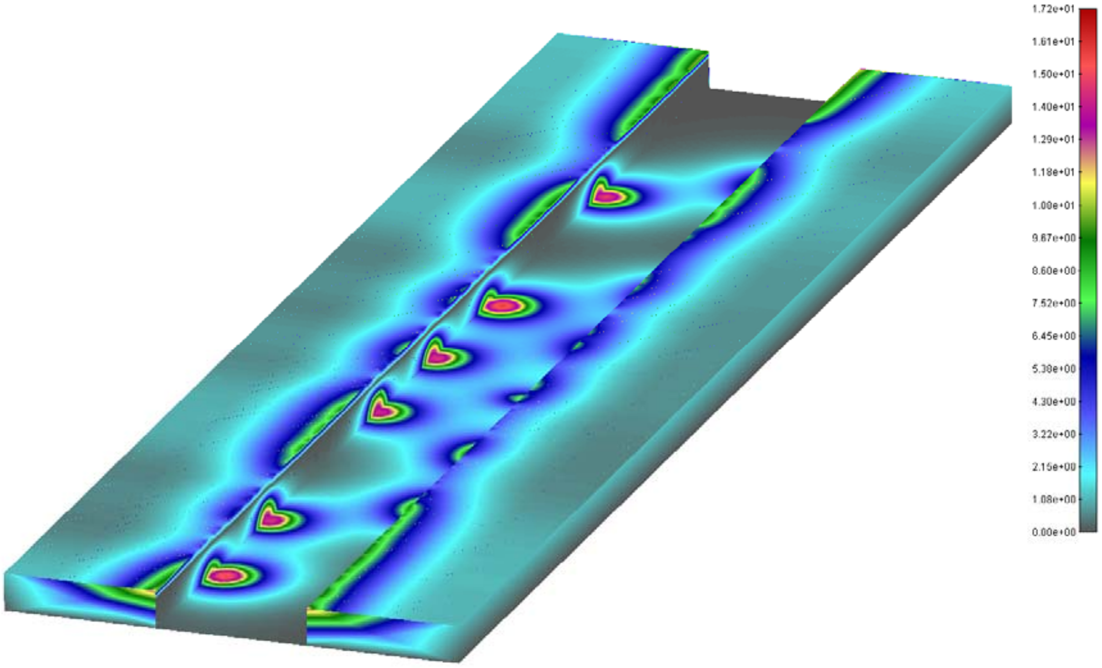

*Figure 2. Coverage of the inhibitors on the substrate surface. The width of the scratch is 0.1mm and the length is 100mm.*

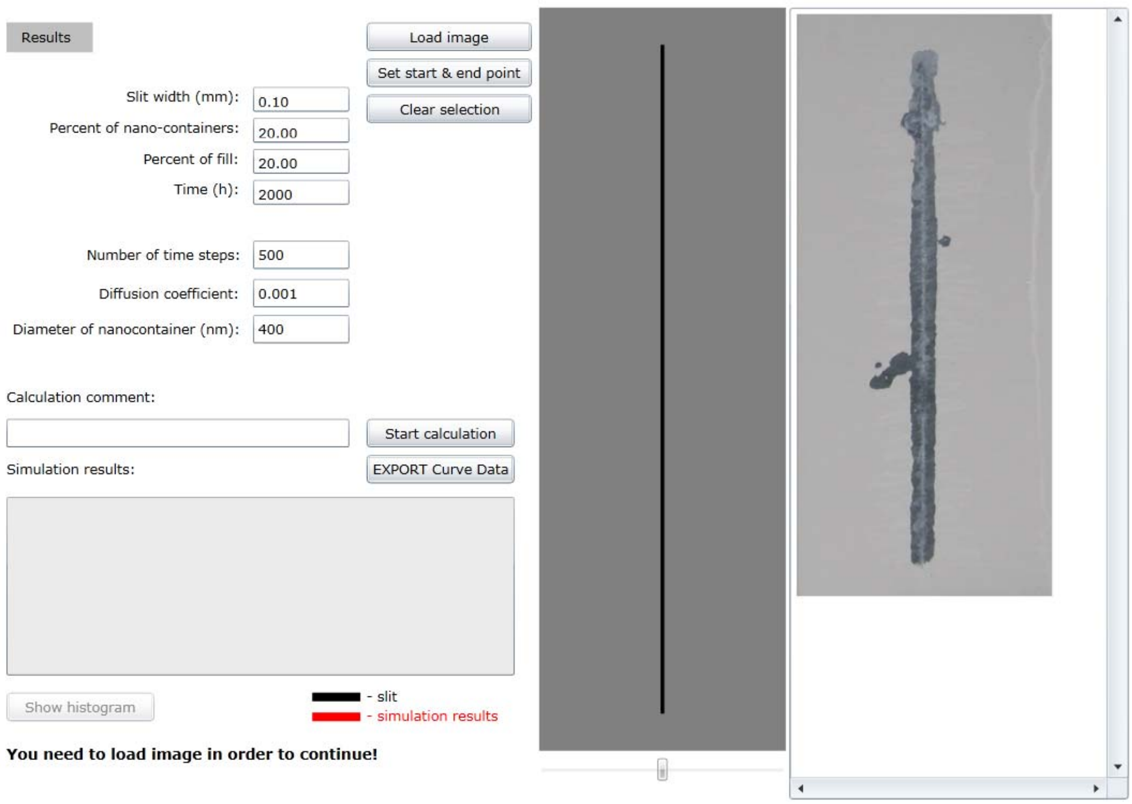


*Figure 3. Online application interface.*

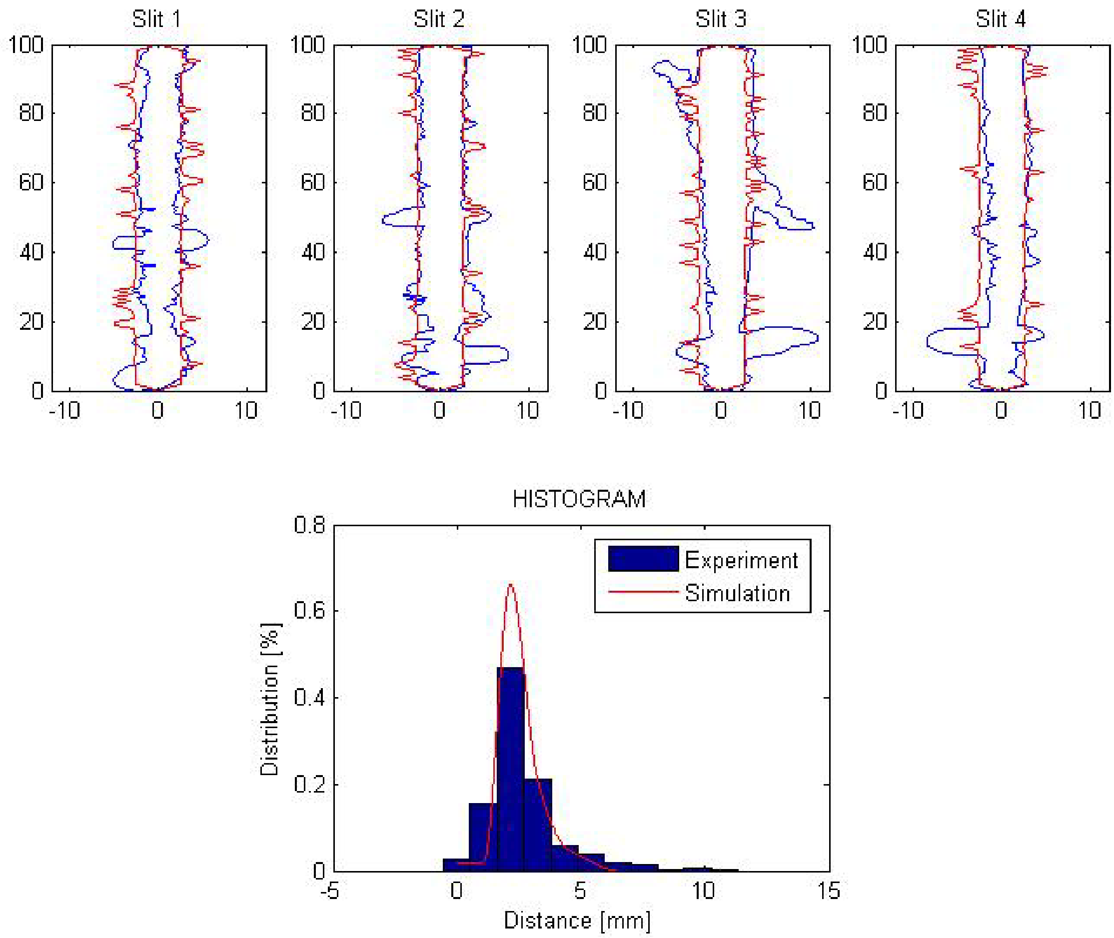


*Figure 4. Comparison of the experimental and computer simulation results*

The results for risk – map calculations are shown in Fig. 5. and Fig. 6.

The average and maximum creepages and average coverage after 300h for different slit width (slit width is in the range of 0.1-1.1mm) is shown in Fig. 5. The obtained results are in good agreement with experimental results. Maximum creepage on the side of the scratch is 0.94mm, and the average creepage is 0.88mm. It can be seen that as slit width increases and total percentage of inhibitors decreases creepage increases, and vice versa. The coverage of the bottom of the scratch is increased if the slit width is smaller and if the number of total percentage of inhibitors is increased.

The corrosion is progressing during the time. So, the results for 2000h show greater creepage (worse protection) on side and better coverage of the bottom (because inhibitors are spilled on the bottom surface during time) which is expected. The results can be seen in Figure 6. The maximum creepage on the side of the scratch is 2.29mm, and the average creepage is 2.16mm.

## 4. CONCLUSIONS

In this study we used FE computer modeling methods to provide guidelines for designing self-healing systems. Also we used data mining technology to fit parameters of interest and to find the best diffusion coefficient and diameter of nano-container for the given model size. With this technology we can optimize the number of nanocontainers and inhibitors during experiments and real protection procedures in the industry.

## ACKNOWLEDGEMENT

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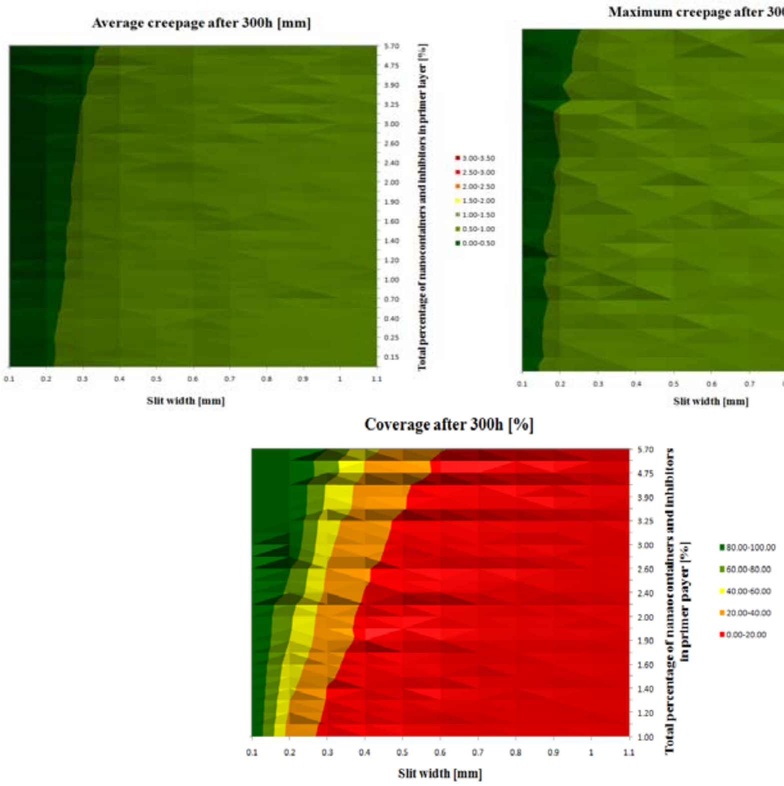


*Figure 5. Average creepage, maximum creepage and average coverage after 300 hours*

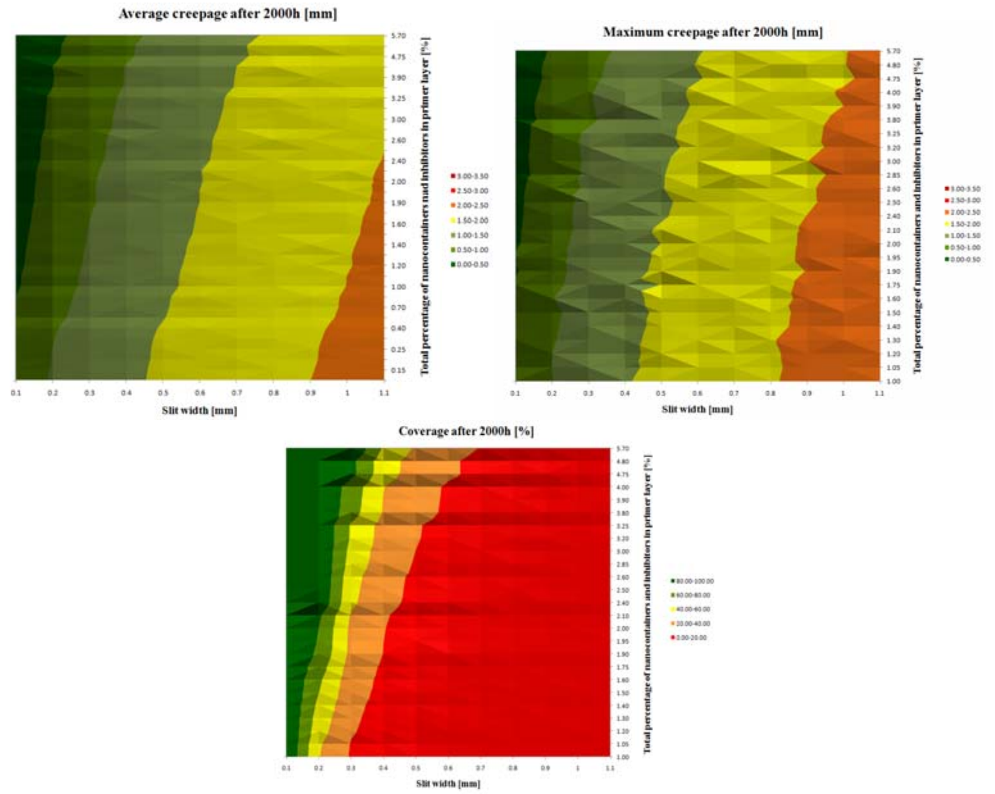


*Figure 6. Average and maximum creepages and average coverage after 2000 hours.*

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## МОДЕЛИРАЊЕ САМОВЕЗУЈУЋИХ МАТЕРИЈАЛА И ПОСТУПАК ФИТОВАЊА ПАРАМЕТАРА

**Сажетак:** Површинске дефекте у материјалу је тешко открити и санирати. Велики изазов у науци о материјалима је дизајн „паметних“ синтетичких система који могу да поново изграде континуитет и интегритет оштећене области. Недавна истраживања наноконтејнера са процесом самовезивања материјала обећавају нови пут за нове паметне нанопокривајуће заштите. Користимо континуално моделирање за истраживање покривања површина са самовезујућим материјалима које садрже оштећења на нивоу наноскале. Користимо метод коначних елемената са различитим дифузионим коефицијентима и флуксевима. Поступак фитовања користећи симулације примењена је да би се одредили коефицијенти дифузије и пречник наноконтејнера у односу на експерименталне резултате. Од прорачуном добијених резултата урађена је мапа ризика која показује ризик од прогресије корозије и прекривеност слита.

**Кључне речи:** Самовезивни процеси у материјалу, метод коначних елемената, нанопокривање, фитовање.