

# SIMULATION OF MICROINDENTATION PROCESS FOR NANOCOMPOSITES BASED ON POLYPROPYLENE

## СИМУЛАЦИЯ НА МИКРОИНДЕНТАЦИОННИЯ ПРОЦЕС ЗА ПОЛИПРОПИЛЕНОВИ НАНОКОМПОЗИТИ

Assoc. Prof. Dr. Zamfirova G.<sup>1</sup>, Ass. Prof. Dr. Cherneva S.<sup>2</sup>, Ass. Prof. Gaydarov V.<sup>1</sup>

<sup>1</sup>Todor Kableshkov University of Transport, 158 Geo Milev str., Sofia, Bulgaria

<sup>2</sup>Institute of Mechanics, Bulgarian Academy of Sciences, Acad. G. Bonchev str., bl. 4, Sofia-1113, Bulgaria,

**Abstract:** The process of microindentation of nanocomposites based on polypropylene was simulated numerically by means of finite-element method (FEM). As a result numerical load-displacement curves were obtained for a certain set of material parameters. The trial-error approach is applied to find most appropriate set which gives the best fit with the experimental load-displacement curves. At the end results, which were obtained through numerical simulations gave good coincidence with the experiment. Moreover the distributions of equivalent Von Mises stress in investigated materials during the process of microindentation, as well as the distribution of the equivalent plastic strain after unloading are determined.

KEYWORDS: MICROINDENTATION, DSI TEST, FEM, POLYPROPYLENE NANOCOMPOSITES

### 1. Introduction

Indentation experiment becomes very rapidly a popular technique to determine the mechanical properties such as elastic modulus and hardness. This technique, also known as depth-sensing indentation (DSI), or instrumented indentation testing (IIT) is widely used to investigate the material behavior of micro- and nanoscale level. There are many advantages using this approach for mechanical investigation - it is non-destructive, easy, simple, fast, requires very small volumes of materials, measurements allow to establish structural non-homogeneity and imperfections.

Many times when measurements are carried out on such a small scale the object investigated show different properties from those of bulk materials [1]. This fact is very important when study thin materials, multilayer samples or pieces where standard mechanical measurements are inapplicable. Recently, numerical studies seems to be applied parallelly with the experimental research on microscales. Numerical methods can determine some properties or parameters that usually are difficult to obtain from experiments. They can also provide suggestions and give a guide for experiments. The aim of present paper is to compare the result obtained by final element analysis (FEA) and those experimentally measured by indentation approach for isotactic polypropylene and its composites filled with multiwall carbon nanotubes (MWCNTs).

### 2. Experiments

This test is based on the measurement of load-displacement curves at constant loading speed. The loading part of the indentation cycle may consist of an initial elastic contact, followed by a plastic flow, or yield, within the specimen at higher loads. For viscoelastic materials the relationship between load and depth of penetration is not linearly dependent, i.e. for a given load the resulting depth of penetration may depend on the rate of load application as well as on the magnitude of the load itself. The measurements were performed on a Dynamic Ultra Micro Hardness Tester DUH-211S from Shimadzu Japan according to standard (ISO 14577-1). The test conditions were: regime - load-unload; the indenter - Vickers pyramid; loading speed - 2.66 mN/s; maximum force P - 100 mN. All measurements were performed at room temperature. The dynamic hardness DH, Martens hardness HMs and indentation hardness  $H_{it}$  were directly measured by the tester according to the above mentioned standard (fig. 1).

### 3. Materials

The samples studied were prepared by mixing isotactic polypropylene "Buplen" 6231 (Lukoil Neftochim) and commercial masterbatch of 20 wt. % MWCNTs in polypropylene (Hyperion Catalysis Int.). Typical outside diameter range of the tube is was from 10 to 15 nm, the lengths between 1 and 10  $\mu\text{m}$ . The masterbatch was diluted to different carbon nanotube concentrations in the range of 0.05 to 1 wt. % with virgin iPP at melt temperature

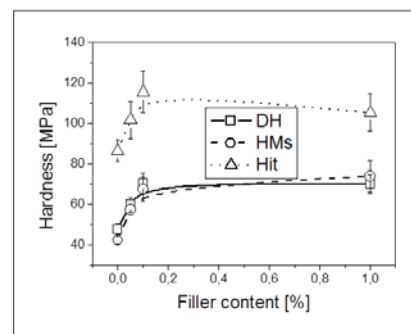


Fig. 1 Dynamic hardness DH, Martens hardness HMs and indentation hardness  $H_{it}$  vs. filler content in the composites

of 200 °C. The composites were extruded and further calendered as sheets of about of 1.5 mm thickness. We did not study the sample with MWCNTs content higher than 1% because we had established by previous microhardness experiments that the mechanical properties of such samples worsen. It is due to the strong intermolecular interactions between the nanotubes leading to significant agglomeration.

### 4. Finite-element modeling of microindentation process

#### 4.1. Boundary value problem

The boundary value problem is defined under the following assumptions: a) the indentation process is quasistatic; b) the deformable axisymmetric specimen is composed by an isotropic linear elastic-plastic with linear hardening material; c) normally indenter's material is very hard (usually this is a material with elastic modulus  $\approx 10^3$  GPa). For that reason it is accepted, that the indenter can be modeled as a rigid body; d) the friction forces in the contact area are neglected; e) no stress-strain prehistory is taken into account.

The equation of motion of the deformable body is:

$$(1) \quad \sigma_{ij,j} = 0,$$

where  $\sigma_{ij}$  is the Cauchy stress tensor. Because of the axial symmetry the boundary condition on  $G_1$  is (see fig. 2):

$$(2) \quad u_{y|G_1} = 0$$

The deformable body is imposed on a rigid base and this gives the following boundary condition on the surface  $G_5$ :

$$(3) \quad u_{x|G_5} = 0$$

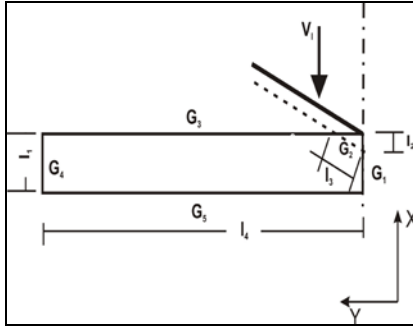


Fig. 2 Scheme of the boundary value problem

The indenter I is penetrated from the side of contact surface  $G_2$  with a prescribed velocity  $v_1$ . The length of the contact zone  $l_2$  during the deformation process changes. On the contact zone the velocity is given as:

$$(4) \quad v_{G_2} = v_I$$

#### 4.2. Material model

The material model used in present work is elastic-plastic with linear hardening. The model involves the following material parameters: Young modulus, Poisson ratio, yield strength, strength coefficient.

The strain tensor  $\varepsilon_{ij}$  is used to describe the deformation in a material point belonging to the investigated material:

$$(5) \quad \varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i}),$$

where  $\{u_1, u_2, u_3\}$  is the displacement vector of the material point at position  $\{x_1, x_2, x_3\}$  in the reference configuration. The material model applied to the investigated polymer materials is described below.

The total strain tensor  $\varepsilon_{ij}$  is a sum of the elastic strain tensor  $\varepsilon_{ij}^e$  and the plastic strain tensor  $\varepsilon_{ij}^p$ :

$$(6) \quad \varepsilon_{ij} = \varepsilon_{ij}^e + \varepsilon_{ij}^p$$

The elastic strain tensor is related to the stress tensor through the Hooke's law:

$$(7) \quad \varepsilon_{ij}^e = \frac{1+\nu}{E} \delta_{ij} + \frac{1-2\nu}{3E} \sigma_{kl} \delta_{kl} \delta_{ij},$$

where  $E$  is the Young modulus and  $\nu$  is the Poisson ratio of the particular material.

Following the von Mises yield criterion yielding occurs in a point when the next validates:

$$(8) \quad F(\sigma_{ij}, \varepsilon^p) = \frac{3}{2} s_{ij} s_{ij} - \sigma_p^2(\varepsilon^p) = 0,$$

where  $s_{ij}$  is deviator of the stresses and  $\varepsilon^p$  is the equivalent plastic strain. The flow stress  $\sigma_p$  of the material depends on the accumulated plastic strain and the value of the initial yield stress  $\sigma_p^{0.2}$ . If the initial yield stress is exceeded the material starts to show plastic yielding. It is assumed that the material is isotropic with linear hardening behavior. In this case the evolution of  $\sigma_p$  during plastic deformation is given by:

$$(9) \quad \sigma_p(\varepsilon^p) = \sigma_p^{0.2} + K \varepsilon^p,$$

where  $K$  is the strength coefficient.

The accumulated equivalent plastic strain is given by:

$$(10) \quad \varepsilon^p = \int_0^t \sqrt{\frac{2}{3} \dot{\varepsilon}_{ij}^p \dot{\varepsilon}_{ij}^p} dt$$

According to the associated plastic flow rule the plastic strain rate is given by

$$(11) \quad \dot{\varepsilon}_{ij}^p = \dot{\lambda} \frac{\partial F}{\partial \sigma_{ij}},$$

where  $\dot{\lambda}$  is the plastic multiplier.

#### 4.3. Indentation test procedure modeling

The process of indenter penetration and separation from the specimen is simulated as a contact problem. It is evident from the experiment that the deformation caused by the indenter is located in a small area around the indenter. For that reason a boundary value problem is defined in a cylindrical domain around the indenter's tip with sufficiently large radius compared to the size of the indenter. The radius is chosen in such way that the deformation due to the penetration vanishes at the lateral and the bottom of the considered cylindrical domain. The friction forces on the contact surface are neglected. The experiment that has to be numerically simulated is a microindentation, where the indenter is a tetrahedral Vickers' pyramid with tip angle  $136^\circ$ . Because of geometrical symmetry the considered domain can be reduced and only one fourth of the whole domain is used for posing and solving the boundary value problem. Often the problem is simplified by substituting the geometry of the Vickers' pyramid with the circular cone with an angle of  $70,3^\circ$  between the axis and the generatrix. Such an approach has been applied for example in [2–4]. In this case the problem can be considered as an axisymmetric one. The geometry of the 2D model is shown in fig. 2.

#### 4.4. Numerical simulations

The above described process of microindentation is modeled numerically. The finite element model have been developed using the finite-element code MSC.MARC [5]. The boundary value problem is based on the model described in Sections 4.1, 4.2 and 4.3. The geometry of the domain is given on fig. 2:  $l_1 = 0.5$  mm,  $l_4 = 2$  mm.

The relation between  $l_3$  and  $l_4$  is  $\frac{l_3}{l_4} = \frac{1}{20}$ . In this way the influence

of boundary conditions on the numerical solution is avoided [6].

As the initial values for the material properties of investigated materials, we took the material characteristics of polypropylenes from the literature [7, 8]. They are given in second column of Table 1. For the modeling process of microindentation, 4 series of finite element simulations with 3600 four-nodes isoparametric finite elements with full integration have been performed (fig. 3). The experimental and calculated load-displacement curves were then compared. In this way we performed a trial-error procedure in order to obtain the material parameter set that gives the best fit to the experimental data. They are shown on third column of Table 1.

Table 1. Initial values for numerical simulations (taken from literature) and material parameter set, which gives the best fit with experimental results

| Material<br>0% CNTs | Initial values |      |      |       | Best fit   |      |      |       |
|---------------------|----------------|------|------|-------|------------|------|------|-------|
|                     | $\sigma_p$     | K    | E    | $\nu$ | $\sigma_p$ | K    | E    | $\nu$ |
| Units               | MPa            | -    | MPa  | -     | MPa        | -    | MPa  | -     |
| PP+0%               | 20             | 1.6  | 963  | 0.35  | 54         | 1.6  | 750  | 0.35  |
| PP+0.05%            | 25             | 1.44 | 1333 | 0.35  | 60         | 1.44 | 1000 | 0.35  |
| PP+0.1%             | 25             | 1.48 | 1579 | 0.35  | 64         | 1.48 | 1100 | 0.35  |
| PP+1%               | 25             | 1.38 | 1930 | 0.35  | 50         | 1.38 | 1200 | 0.35  |

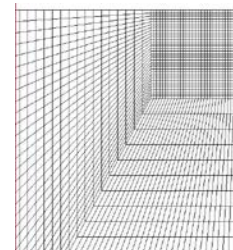


Fig. 3 Enlargement part from FE mesh for the 2D model around the indenter

## 5. Results

Comparison between experimental and numerical load- displacements curves is given on figures 4 ÷ 7. The distribution of equivalent Von Mises stress in investigated materials during the modeled process of microindentation, as well as the distribution of the equivalent plastic strain after unloading are shown on figures 8 ÷ 15.

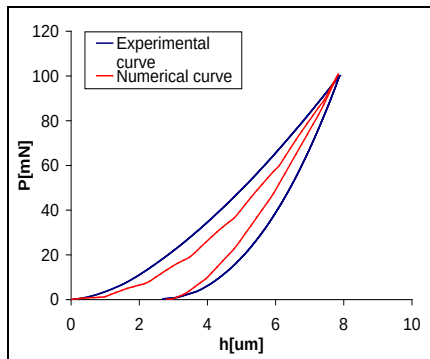


Fig. 4 Comparison between experimental and numerical load-displacement curves for PP+0%CNTs

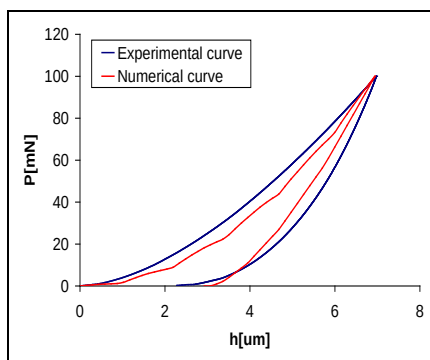


Fig. 5 Comparison between experimental and numerical load-displacement curves for PP+0.05%CNTs

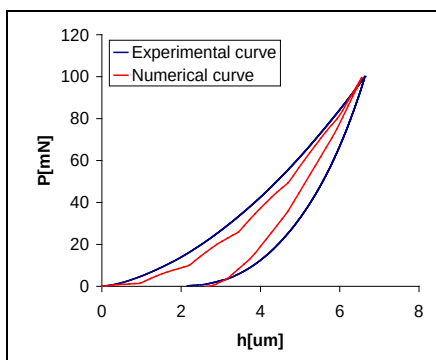


Fig. 6 Comparison between experimental and numerical load-displacement curves for PP+0.1%CNTs

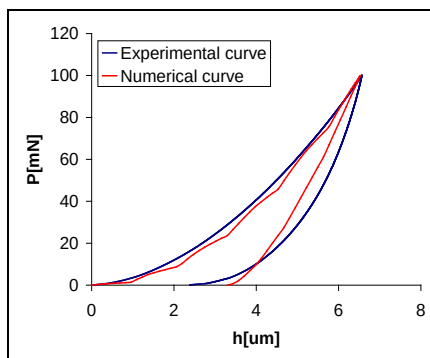


Fig. 7 Comparison between experimental and numerical load-displacement curves for PP+1%CNTs

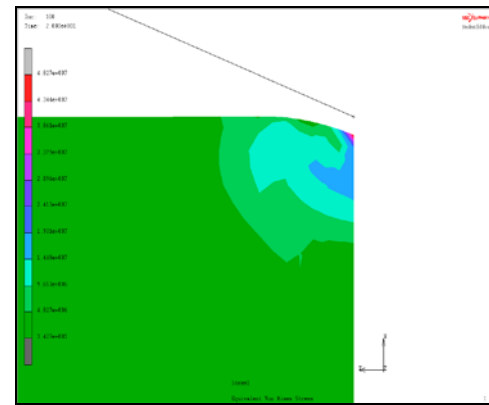


Fig. 8 Distribution of equivalent Von Mises stress in PP+0%CNTs

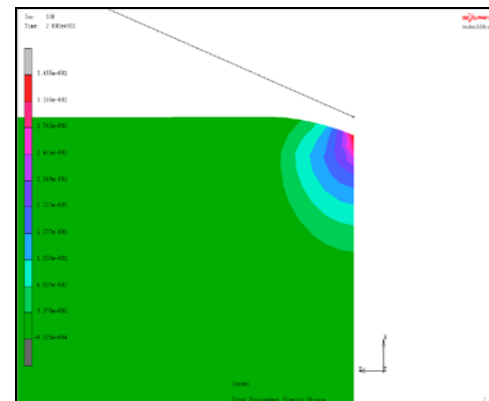


Fig. 9 Distribution of the equivalent plastic strain in PP+0%CNTs

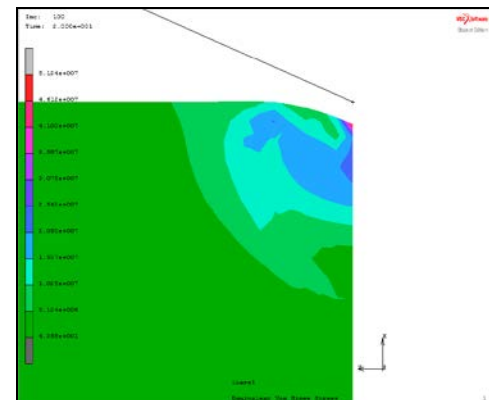


Fig. 10 Distribution of equivalent Von Mises stress in PP+0.05%CNTs

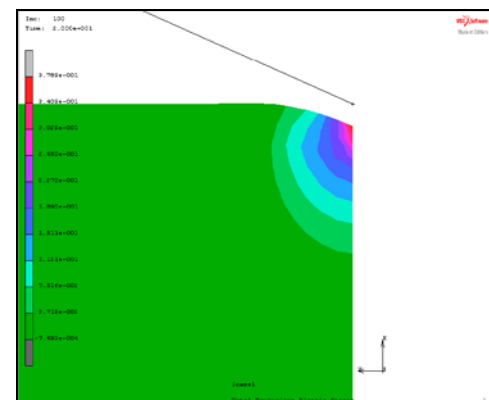


Fig. 11 Distribution of the equivalent plastic strain in PP+0.05%CNTs

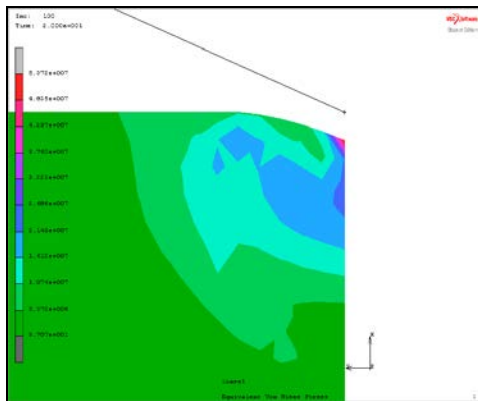


Fig. 12 Distribution of equivalent Von Mises stress in PP+0.1%CNTs

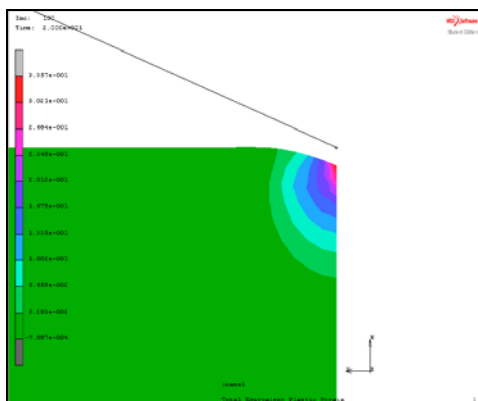


Fig. 13 Distribution of the equivalent plastic strain in PP+0.1%CNTs

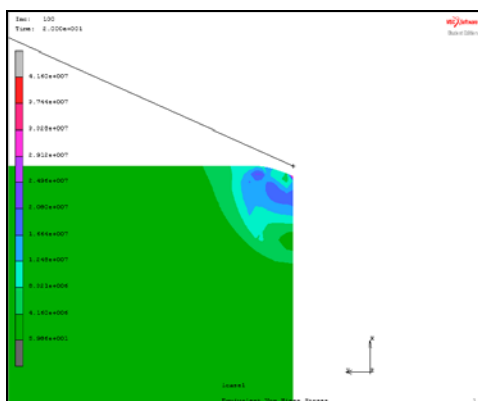


Fig. 14 Distribution of equivalent Von Mises stress in PP+1%CNTs

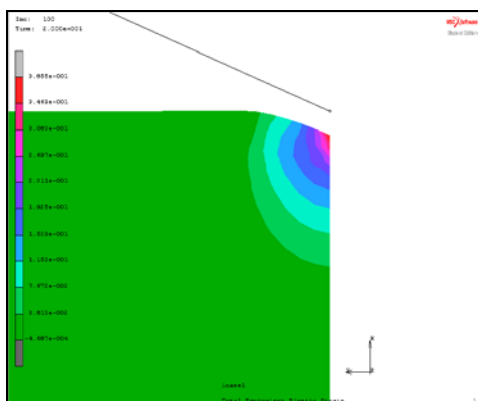


Fig. 15 Distribution of the equivalent plastic strain in PP+1%CNTs

## 6. Conclusions

In present work we have investigated mechanical properties of nanocomposites based on polypropylene with different carbon nanotube concentrations in the range of 0.05 to 1 wt. %. Four series of numerical simulations was achieved by means of the finite element method and the results were compared with experimental results from microindentation measurements. In this way, a trial and error procedure was performed in order to obtain the material parameter set that gives the best fit to the experimental data. The constitutive model used in the finite element model is based on the Von Mises yield criterion in combination with a linear hardening law. From microindentation experiment we obtained that with increasing carbon nanotube concentrations in investigated polypropylene samples from 0 to 0.1%, their indentation hardness increase too, but after 0.1% becomes constant. We obtained by means of numerical simulations that with increasing carbon nanotube concentrations in investigated polypropylene samples from 0 to 0.1%, their yield strength increase too, but after 0.1% decrease and their Young's modulus increase with increasing carbon nanotube concentrations from 0 to 1%. Numerical simulations by means of finite-element method, which we realized, gave us additional information about mechanical properties of investigated materials, which is impossible to obtain by means of microindentation experiment only. Moreover this hybrid experimental-numerical approach save money and time for preparing of test samples and realizing additional experiments (for example tensile tests) in order to obtain yield strength, Poisson ratio and the strength coefficient of investigated materials.

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## References

- [1] Stauss, S., P. Schwaller, J.-L. Bucaille, R. Rabea, L. Rohra, J. Michler, E. Blankb, Determining the Stress-Strain Behavior of Small Devices by Nanoindentation in Combination With Inverse Method - Microelectron Eng., 67–68, 2003, pp. 818–825.
- [2] Hay, J. C., A. Bolshakov, G.M. Pharr, A critical examination of the fundamental relations used in the analysis of nanoindentation data - J. Mater. Res. 14, 1999, pp. 2296–2305.
- [3] Pharr, G.M., A. Bolshakov, Understanding nanoindentation unloading curves - J. Mater. Res. 17 (10), 2002, pp. 2660–2671.
- [4] Bolshakov, A., G.M. Pharr, Inaccuracies in sneddon's solution for elastic indentation by a rigid cone and their implications for nanoindentation data analysis, in: Proceedings of the Conference "Spring Meeting of the Materials Research Society" CONF-960401-16, Materials Research Society, San Francisco, USA, May 1996.
- [5] MSC. Software Corp., USA, MSC.MARC User's Guide, 2003.
- [6] Cherneva, S., R. Iankov, Investigation on the influence of the boundary conditions by simulation with finite element method of microindentation process, in: Proceedings of the Thirty Sixth Spring Conference of the Union of Bulgarian Mathematicians, St. Konstantin & Elena Resort, Varna, Bulgaria, 2007, pp. 197–202.
- [7] Zhou, Y., P. K. Mallick, Effects of Temperature and Strain Rate on the Tensile Behavior of Unfilled and Talc-Filled Polypropylene. Part I: Experiments - Polymer Eng. and Sci., 42, (12), 2002, pp.2449-2460.
- [8] Hesheng Xia, Qi Wang, Kanshe Li, Guo-Hua Hu, Preparation of polypropylene/carbon nanotube composite powder with a solid-state mechanochemical pulverization process - J. of App. Polym.Sci., 93, Issue 1, 2004, pp. 378–386.