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APPROXIMATION OF MATERIAL BEHAVIOUR OF PLLA POLYMER IN HAp/PLLA BIOCOMPOSITE MATERIAL USING NANOINDENTATION AND FINITE ELEMENT METHOD

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ABSTRACT

In this work, a combination of nanoindentation experiment and finite element modeling is proposed in order to obtain approximate material behavior of PLLA polymer in hydroxyapatite (HAp)/poly-L-lactide (PLLA) composite. Knowing these properties is important since the processing conditions used in hot pressing of composites with thermoplastic matrix strongly influence final mechanical properties of material in the solid state. A bi-linear material behavior is adopted for the polymer phase of the HAp/PLLA composite. Material behavior model, stress-strain curve, is determined by modulus of elasticity, yield stress and work-hardening rate. This combined method is proposed to determine material behavior before (modulus of elasticity) and after yield point (work hardening rate) of polymer phase after the hot-pressing of the composite.

Key words: Nanoindentation, Finite element model, Biocomposites

INTRODUCTION

Composites with bioactive ceramic such as hydroxyapatite (HAp) and a bioresorbable polymer such as poly-L-lactide (PLLA) are widely used for prosthetic applications aimed to replace damaged hard tissues. Using neat polymer properties as inputs in various predictive models could result in poor agreement with experimental results [1-5]. Mechanical experiments performed on the neat polymer usually derive material property inputs for such models. Implicit in the use of these measured properties is that the materials mechanically behave the same in the composite as they do individually. While it is unlikely that properties of the ceramic particles_would change, there is a distinct possibility that polymer properties could chemically change as a result of the consolidation and/or cure processes. Knowing accurate material behavior of the hydroxyapatite (HAp)/poly-L-lactide (PLLA) composite is important from mechanical point of view especially when used as load carrying elements. As opposed to ceramic phase, the processing conditions used in hot pressing of composites with thermoplastic matrix strongly influence final mechanical properties of material in the solid state. There is a need for precise measurements of these properties.

Fifty years ago, and using very simple concepts, Tabor [6,7] showed that the indentation hardness of metals is directly related to the uniaxial yield stress. Nano-indentation is recently applied method for precise characterization of biomedical materials such as ultra-high-molecular-weight polyethylene, sintered bioceramic powders and functionally graded bioactive composites [8,9].

As suggested by previous work, loading and unloading curves obtained from conical or pyramidal indentation tests cannot uniquely determine the stress–strain relationship of a given indented material. In recent years, efforts have been made to establish a general method for the evaluation of the plastic mechanical properties of different materials (mostly metals) using data obtained from conical or pyramidal indentation tests. Methods such as a reverse and forward analysis algorithms in which the post yield behaviour and yield stress are determined using the indentation curve are still not perfect and have limitations. One of the principal developments in this investigation area is related to the application of the finite element (FE) method.

Almost all studies dealing with problems in FE modeling of nanoindentation experiment assume generally two types of post-yield material behavior:

(i) power law strain hardening - $\sigma = R\varepsilon^n$ or,

(ii) linear work hardening - $\sigma = \eta\varepsilon$,

where R represents strengthening coefficient, n-strain hardening exponent and η-work-hardening rate. In cases when material behavior is well known, as is for most of metals, for modeling purposes it is reasonable to a adopt power law strain hardening for post yield behavior. Conversely, when this behavior is uncertain, as presented here, it is acceptable to adopt approximated bilinear material behavior for PLLA matrix.

The objective of this work is to show that an acceptable approximation of the material behavior of PLLA can be deduced from results obtained by nanoindentation test performed with a sharp indenter and FE simulations. This combined method is proposed to determine material behavior before (modulus of elasticity) and after yield point (work hardening rate) of polymer phase after the hot-pressing of the composite.

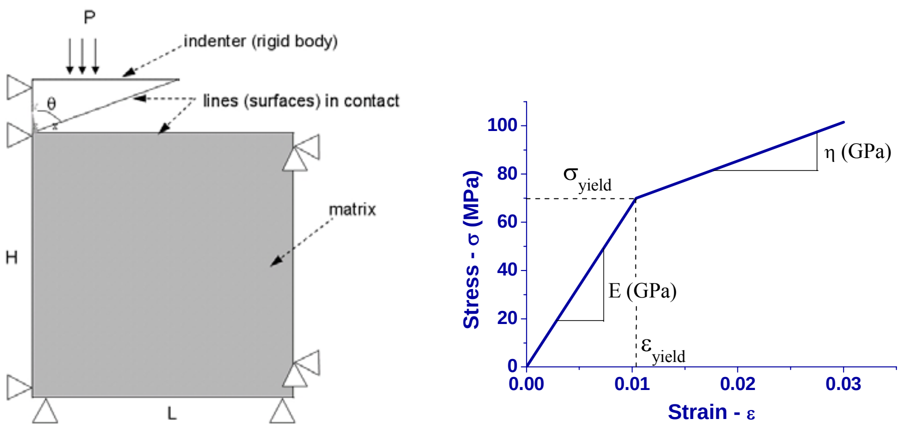
EXPERIMENTAL DETAILS

Calcium hydroxyapatite (HAp)/poly-L-lactide (PLLA) composite with the mass ratio 80:20 was selected as the test material for the present study. Calcined HAp granules with 200-500 µm in size were used. Commercial PLLA (Fluka, Germany) with molecular weight of 100,000 g/mol was used as a polymer matrix. The composite powder was compacted in rectangular mould by hot pressing at temperature of 165ºC and pressure of 5 tons for 7 min.

Nanoindentation experiments were carried out using a Triboscope Nanomechanical Testing System (Hysitron, Minneapolis, MN) equipped with a Berkovich indenter and *in situ* imaging mode. The frequently used method proposed by Oliver and Pharr [10], involves the extrapolation of a tangent to the top of the unloading curve to determine the depth (a combination of elastic and plastic displacement) over which the indenter is in contact with the specimen at the maximum load, P_{max}. The slope of the unloading curve also provides a measure of the contact stiffness, which can be used with the contact area to determine the elastic modulus. The modulus obtained, sometimes referred to as the reduced modulus, E_r, which is related with material properties of indented specimen and indenter. If stiffness of indenter is much greater than stiffness of specimen, as is here, this relationship is given by: $E_r = E/(1 - \nu^2)$, where E is Young's modulus and ν is the Poisson's ratio of indented specimen. The composite processing details and testing procedure are described in brief in Uskokovic et al. [11].

MODELING PROCEDURE

FE model of nanoindentation process is based on a similar model used by Dao et al. [12]. A schematic of the present 2D model and its boundary conditions are shown in Fig.1(a). The model was created and solved using the ANSYS 5.7 FE package using six-noded plane structural solid elements (an option of 8-noded solid structural elements) and contact line elements associated with contact lines. Since the considered model of nanoindentation is a contact problem, analyses were performed in the framework of large deformation theory with geometrical and material nonlinearity. In the case of this axisymmetric model, the indenter rigid surface is conical, which is not the same as the Berkovich indenter used in the experiments. However, previous work has shown that a conical half apex angle, θ, of 70.3º produces the same contact depth and area as a Berkovich indenter, [12], allowing a 3D model to be treated as a 2D one. A finer mesh is used in the contact region, resulting in at least ten elements in contact with the rigid line at maximum displacement. No discernable differences in the results have been shown by simulation when varying the friction coefficient [13]. Therefore, it is acceptable to assume the contact between the conical indenter with a half apex angle, of 70.3º and the specimen as frictionless [14].



a) *b)*

Fig. 1 Schematic of FE model with applied boundary conditions (a), and a schematic representation of the stress–strain constitutive law used for FE model (b).

All materials are modeled as isotropic, elastic–plastic solids using the classical plasticity model with Von Mises criterion. ANSYS allows the use of a bilinear material behavior, where the initial slope is the Young's modulus E, and σ_{yield} and η represent, respectively, the initial yield stress (defined at zero plastic strain) and the work-hardening rate for plastic deformation. The constitutive behavior of the material used for the FE modeling is shown schematically in Fig. 1(b). This material property can be defined as: $\sigma = E\,\varepsilon$ for the strain $\varepsilon < \varepsilon_{yield}$; and $\sigma = \sigma_{yield} + \eta(\varepsilon - \varepsilon_{yield})$ for $\varepsilon \geq \varepsilon_{yield}$.

The diamond indenter was modeled as a rigid body. A parametric study of 52 simulations was conducted. The chosen cases represent the range of mechanical behavior: E, varied from 6.4 to 6.8 GPa, σ_{yield} adopted to be 70 MPa [15,16], and η varied from 1.1 to 1.6 GPa. The Poisson's ratio was held constant at 0.45.

Previous studies [13,17], showed that specimen dimensions of H=L=20μm were found to be large enough to approximate the behavior of a semi-infinite half-space, which is the case when the L and H values approach infinity. As reported, required size of plain polymer area, needed for precise indentation test, should be in diameter at least 50 times maximal penetration depth of indenter (L / h_{max} ≥ 25). This condition is relatively easy to fulfil in horizontal plane, by observing surface of indented area, while at the vertical direction it is impossible to know whether there is a hard ceramic phase beneath the indented surface causing false matrix indentation response. Therefore it is important to know how vicinity of invisible ceramic phase located under indenter, beneath the surface, influence matrix response in nanoindentation experiment. Simulation was first done for the model with H=L=20μm. Calculated indenter force at maximum indentation depth from this simulation was denoted as P_{un}. Consequently, H dimension was decreased gradually to the value of 2 μm with the boundary condition in which, all nodes positioned on $y = -H$ have constrained displacement in x and y directions. During the variation of the H dimension, the value for L was held constant at 20μm.

RESULTS AND DISCUSSION

Figure 2 shows required relative indenter force, P/P_{un}, for reaching predetermined maximal penetration depth of h_{max}= 350 nm, as a function of H/h_{max} for previously adopted matrix material properties. In the case of real elastic matrix material property, by decreasing dimension H, normalized indenter force for reaching maximal penetration depth increases apparently. This is expected having in mind that lower H simulating vicinity of hard ceramic phase assumed in the model. These simulations demonstrate, in one hand, that it was reasonable to adopt model dimensions, H=L=20μm resulting in L/h_{max}= H/h_{max}=60.4 and, at the other, that even hard ceramic phase is positioned close to indented surface, it would not significantly influence matrix response.

Further, it is also interesting to analyze shape of load-displacement curve for different values of H decreasing from 20 to 2 μm (Fig. 3). It is obvious that only for small values of h, shape of load-depth curve remain almost the same at the beginning part of loading curve. Major differences become noticeable at higher values of penetration depths.

As mentioned, three parameters define shape of load-depth curve: modulus of elasticity (E), initial yield stress (σ_{yield}) and work-hardening rate (η). This experimental curve can be considered to be a micro-mechanical fingerprint of the sample's response. But, Pelltier [18] and Cheng and Cheng [19], showed that the same loading and unloading curves can be constructed from different stress–strain relationships. Consequently, the inverse problem seems not to be unique. This phenomenon, independent of the used stress–strain curve function (linear [18] or power-law [19–21] work hardening) is essentially caused by the geometric self-similarity of conical or pyramidal indenters. Pelletier [22] have demonstrated that the same loading and unloading *P–h* curve may be matched by using two different uniaxial stress–strain relationships assuming (i) an elastic fully-plastic solid and (ii) an elastic–plastic with linear strain-hardening solid. In other words, Pelletier showed that a given experimental *P–h* curve may be matched by several load–displacement curves obtained with FE model using various bilinear constitutive laws by varying values of σ_{yield} and η. This phenomenon is quite true, but if values of E and σ_{yield} are previously determined for given load-depth curve then there is unique value of η for indented material as presented in folowing section. Problem exists when values for σ_{yield} and η are unknown.

As mentioned before, efforts have been made to establish a general method for the evaluation of the elastic-plastic mechanical properties of different materials using data obtained from conical or pyramidal indentation tests. These efforts, more or less successful, suffer from one problem: they were done mostly on metals. On question why on metals, the only answer is verification. It is relatively easy to verify obtained stress-strain curves by simple uniaxial tension test. Almost all of proposed methods, if applicable, are dealing with materials with relatively small hardening coefficients, small values of elastic recovery (up to 15%) and moderate to high values of modulus of elasticity ,e.g. [22,23]. As it is known, polymers such as PLLA is expected to have opposite from previously mentioned. Consequently, it is a great challenge to determine the constitutive equation for PLLA material bearing in mind that verification with uniaxial tension test is almost impossible due to reasons already discussed.

Almost all studies dealing with nanoindentation experiments showed that the loading curve may be described mathematically using a power law $P=Kh^n$, where n is a constant for given material and for a specific indenter tip geometry [24]. For homogeneous materials, with a mechanical constitutive law which is assumed to be elastic fully-plastic, Loubet et al. [25] deduced that n was equal to 2 (Kick's law) and showed that the constant K depended on the elastic properties (elastic modulus, Poisson's ratio), the yield stress and the semi-angle of the equivalent conical indenter. Another way to describe the relation between the applied load and the indentation depth during the loading phase is the use of a polynomial function [24]. Experimental measurements on metals, [22], have proved that a second-order polynomial law ($P=Ah^2+Bh$) is sufficient and gives a good approximation for a large range of indentation depths.

As a result of previous discussion, it is very important to describe properly the loading curve. In fact, the loading curve may be described using a Kick's law, $P=Kh^2$, or the polynomial law, $P=Ah^2+Bh$. There are two important things: (i) indented sample is a homogeneous material and (ii) some conclusions derived from loading part of *P-h* indentation curves for other tested materials could be applicable on indented specimen. Hence it is important to analyze possibility of describing the shape of loading curve of indented specimen using a power law or the polynomial law.

FE analysis performed in this work confirmed that, for a bilinear material behavior, the loading part of simulated *P-h* indentation curve may be described using the polynomial law, $P=Ah^2+Bh$, where values for coefficient B are almost negligible. This means that the Kick's law, $P=Kh^2$ is sufficient for describing the shape of loading curve. This observation is in agreement with results obtained for polymers [14].

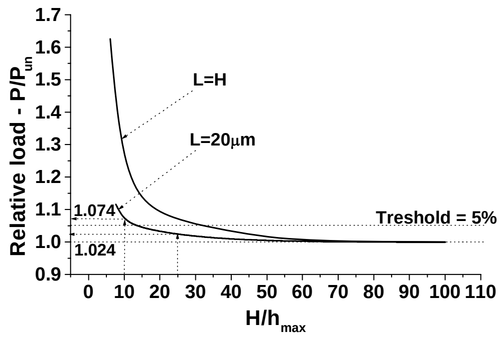


Fig. 2. Relative indenter force, P/P_{un}, for reaching predetermined maximal penetration depth of h_{max}= 350 nm, as a function of H/h_{max}.

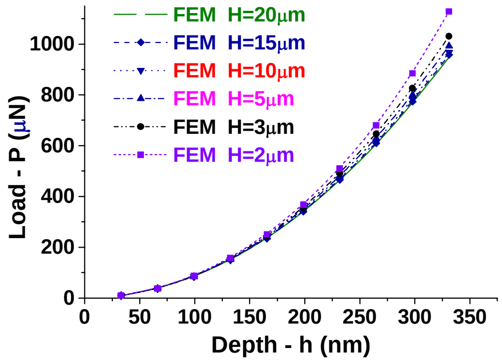


Fig. 3. Load-depth curves for numerical model with constant value of L=20μm and different values of H

By analyzing loading parts of P-h curves, a selection of valid result is made following the rule that only the results that comply with Kick's law are suitable. Hence, remaining curves and their indentation output (modulus of elasticity-*E*) are now suitable as an input for FE modeling of nanoindentation process performed on material with bilinear material behavior in order to obtain value for work hardening rate. This results in approximate material behavior of PLLA polymer in hydroxyapatite (HAp)/poly-L-lactide (PLLA) composite.

Example of proposed procedure is given through Figures 4, 5 and 6 where selected experimental *P-h* curves are presented. Characteristic values for selected indents (8,12 and 14) obtained from a set of experimental results in terms of *P-h* curves are presented in Table1. All selected indents were probed remote from HAp ($L/h_{max} \geq 25$) in order to avoid noticeable influence of HAp on the elastic response of the matrix.

Table1. Characteristic experimental values for selected indents (8,12 and14).

Indent No.	Modulus of elasticity - *E*	Maximal indenter depth - h_{max}	Maximal inden ter load - P_{max}	Distance from closest ceramic phase-*L*	L/h_{max}
8	6,749 GPa	331 nm	945 μN	12μm	36,25
12	6,479 GPa	345 nm	937 μN	18μm	52,17
14	6,455 GPa	350 nm	940 μN	24μm	68.57

Young's modulus of PLLA, in FE simulations of selected nanoindentations, is taken to be as presented in Table 1. As discussed before, work hardening rates for PLLA matrix must be assumed for each selected indent model until a perfect match between FE and experimental results at the maximal indentation load and depth.

Loading curves of Indents no. 8 and 12, as presented in Figures 4 and 5, do not follow Kick's law as well as it was impossible to simulate presented curves by FE model using inputs presented in Table 1. Therefore results obtained from these curves presented in Figures 4 and 5 should be neglected. It should be noted that *P-h* curve of indent 12 is much closer to Kick's law and numerical simulation than *P-h* curve of indent 8. Also, it is obvious that load values of FE results, for indents number 8 and 12, are lower than experimental ones resulting in higher work hardening rates for reaching predetermined values for P and h_{max} in FE simulations as shown in Figures 4 and 5.

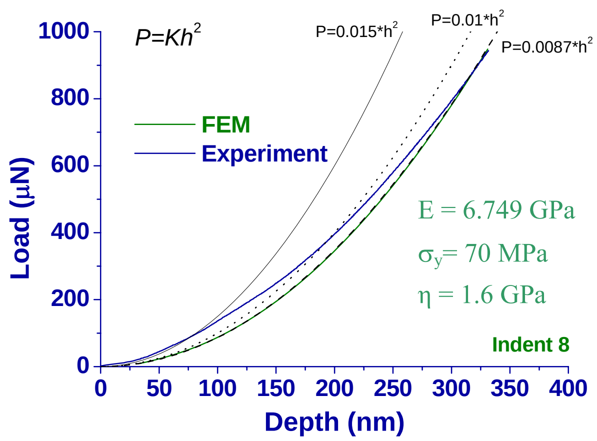


Fig. 4. Load-depth curve for indent number 8.

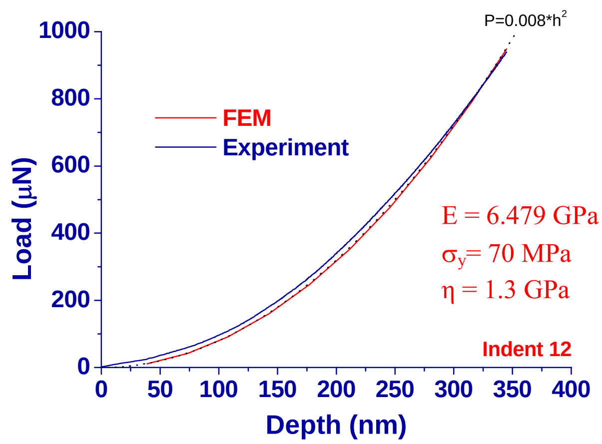


Fig. 5. Load-depth curve for indent number 12.

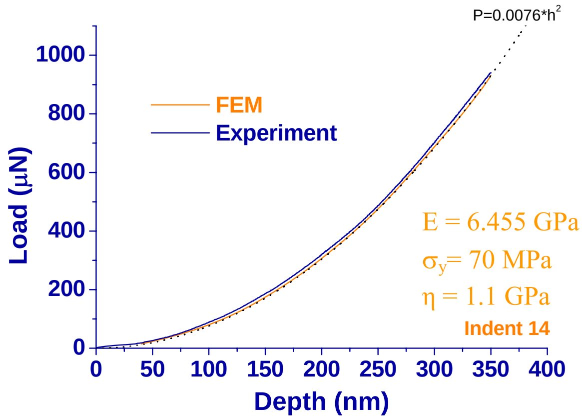


Fig. 6. Load-depth curve for indent number 14

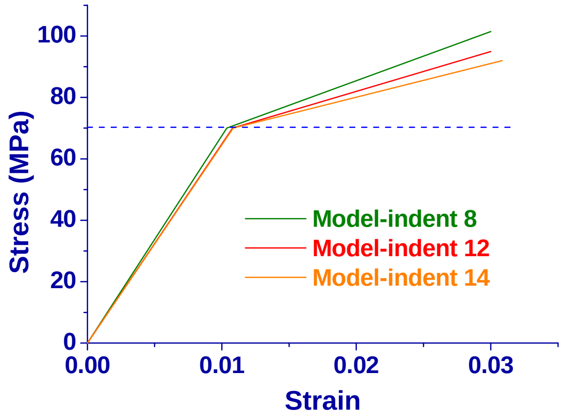
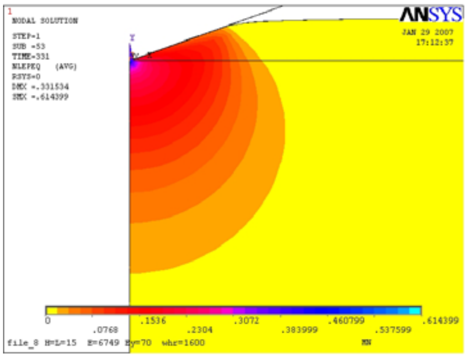
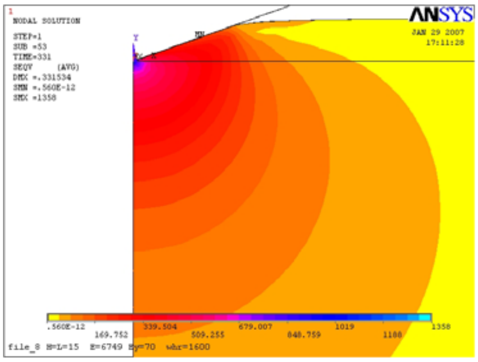


Fig. 7. Approximated material behavior for selected indents (8,12 and 14).

On the other hand, loading curve of indent 14 almost perfectly follows Kick's law in form P=0.0076h^2, Figure 6. FE simulation of indent number 14 showed that almost a perfect match exist between experimental and simulated load-depth curve in whole range of indentation depths for following values of bilinear material behavior: E=6.455GPa, σ_{yield}=70 MPa and E_T=1.1GPa, as presented at Figure 6. After reconsideration of selected and simulated indents, it is obvious that the indent number 14 should be chosen as the representative one. Figure 7 shows approximated bilinear material behavior for selected indents (8,12 and14). This is resulting in precise value of elastic modulus of indented material and possible value of work hardening rate of assumed bilinear material behavior. Obtained value for elastic modulus of indented material is in accordance with value obtained by Shikinami and Okuno [26], E=6.5GPa.

Figure 8 shows the equivalent plastic strain and von Mises equivalent stress within the PLLA matrix near the tip of the conical indenter, indicating stress and strain field directly beneath the indenter. It should be noticed that the volume that is affected by indenter penetration is relatively small causing possibility of precise measurement on matrix surface. These results demonstrate the power of nanoindentation as an experimental method in determination of material properties in particulate biocomposites.





(a) *(b)*

Fig. 8 Contour plots of (a) plastic strain and (b) von Mises equivalent stress (in MPa).

CONCLUSIONS

Determining the true stress–strain curve of a polymer material such as PLLA by using hardness measurement is a complex problem and can only give an approximation of the rheology of the indented solid. In order to determine parameters defining the PLLA matrix stress-strain behavior in cured composite through a combination of nanoindentation experimental and FE modeling methods, a comprehensive parametric study of 52 numerical simulations was conducted. Applied FE simulations of nanoindentation process (load-displacement curves) were performed in order to verify the measured modulus of elasticity and determine the work-hardening rate of the PLLA matrix in the HAp reinforced biocomposite material. This method also selects precise values of the modulus of elasticity by eliminating "false" results. Also, it is shown that the vinicity of invisible hard ceramic phase located under indenter, beneath the surface, would not significantly influence matrix response in nanoindentation experiment for applied indenter loads, up to 1mN, coresponding to indentation depths up to 400 nm.

It is clearly shown that it may be possible to determine the approximate material behavior of the matrix in cured composite through a combination of nanoindentation and FE modeling methods. The proposed method is applicable not only to polymer matrix composites, but also to other composite materials with similar morphology, such as metal matrix composites, particle reinforced biomaterials as well as substrate coatings and thin films.

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REFERENCES

[1] C.C.P.M. Verheyen, J.R. de Wijn, C.A. van Blitterswijk and K. de Groot: J. Biomed. Mater. Res. Vol 26 (1992), p. 1277.

[2] W. Suchanek and M. Yoshimura: J. Mater. Res. Vol 13 (1998), p. 94.

[3] N. Ignjatovic, S. Tomic, M. Dakic, M. Miljkovic, M. Plavsic and D. Uskokovic: Biomaterials Vol 20 (1999), p. 809.

[4] T. Furukawa, Y. Matsusue, T. Yasunaga, Y. Nakagawa, Y. Okada, Y. Shikinami, M. Okuno and T. Nakamura: J. Biomed. Mater. Res. Vol 50, (2000), p. 410.

[5] I. Balac, P.S. Uskokovic, R. Aleksic and D. Uskokovic: J. Biomed. Mater. Res. Vol 63 (2002), p. 793.

[6] D. Tabor In: P.J. Blau, B.R. Lawn, editors. Microhardness indentation techniques in materials science and engineering. ASTM STP 889. Philadelphia, PA: ASTM; 1986. p. 129.

[7] D. Tabor: Philos. Mag. A Vol 74 (1996), p. 1207.

[8] R. Roop Kumar and M. Wang: Mater. Lett. Vol 55 (2002), p. 133.

[9] K. Park, S. Mishra, G. Lewis, J. Losby, Z. Fan and J.B. Park: Biomaterials Vol 25 (2004), p. 2427.

[10] W.C. Oliver and G.M. Pharr: J. Mater. Res. Vol 7 (1992), p. 1564.

[11] P.S. Uskokovic, C.Y. Tang, C.P. Tsui, N. Ignjatovic and D.P. Uskokovic: J. Eur. Ceram. Soc. Vol 27 (2007), p. 1559.

[12] M. Dao, N. Chollacoop, K.J. Van Vliet, T.A. Venkatesh and S. Suresh: Acta. Mater. Vol 49 (2001), p. 3899.

[13] J.L. Bucaille, S. Stauss, E. Felder and J. Michler: Acta Mater. Vol 51 (2003), p. 1663.

[14] J.R. Gregory and S.M. Spearing: Compos. Sci. Technol. Vol 65 (2005), p. 595.

[15] N.A. Weir, F.J. Buchanan, J.F. Orr, D.F. Farrar and A. Boyd: Biomaterials Vol 25 (2004), p. 3939.

[16] G. Perego, G.D. Cella and C. Bastioli: J. Appl. Polym. Sci. Vol 59 (1996), p. 37.

[17] I. Balać, C.Y. Tang, C.P. Tsui, D.Z. Chen, P.S. Uskoković, N. Ignjatović and D.P. Uskoković: Mater. Sci. Forum Vol 518 (2006), p. 501.

[18] H. Pelletier, J. Krier, A. Cornet and P. Mille: Thin Solid Films Vol 379 (2000), p. 147.

[19] Y-T Cheng and C-M. Cheng: Int. J. Solids Struct. Vol 36 (1999), p. 1231.

[20] S.V. Hainsworth, H.W. Chandler and T.F. Page: J. Mater. Res. Vol 11 (1996), p. 1987.

[21] M. Dao, N. Chollacoop, K.J. van Vliet, T.A. Venkatesh and S. Suresh: Acta Mater. Vol 49 (2001), p. 3899.

[22] H. Pelletier: Tribol. Int. Vol 39 (2006), p. 593.

[23] J.M. Antunes, J.V. Fernandes, L.F. Menezes and B.M. Chaparro: Acta Mater. Vol 55 (2007), p. 69.

[24] F. Frohlich, P. Grau and W. Grellmann: Phys. Stat. Sol. A Vol 42 (1977), p. 79.

[25] J.L. Loubet, J.M. Georges and G. Meille (In: P.J. Blau, B.R. Lawn, editors), Microindentation Tech. Mater. Sci. Engng. ASTM STP 889 (1986), p. 72.

[26] Y. Shikinami and M. Okuno: Biomaterials Vol 20 (1999), p. 859.