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PVB/sepiolite nanocomposites as reinforcement agents for paper

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Abstract: In order to improve the mechanical properties of paper, 1, 3 and 5 wt. % of sepiolite were dispersed in a poly(vinyl butyral) (PVB) matrix and coated onto the surface of schrenz (110 g m^{-2}). Deagglomerated sepiolite nanofibers in the PVB matrix on the paper surface were observed by scanning electron microscopy. The glass transition temperature of schrenz with PVB/sepiolite coatings was not changed with increasing content of sepiolite. Two different methods were used to evaluate the mechanical properties of the paper sample reinforced with PVB/sepiolite nanocomposites: tensile testing and nanoindentation. The values of breaking force and tensile energy absorption of the reinforced paper samples obtained by tensile testing were increased by up 10 %. The values of the reduced elastic modulus and hardness obtained by nanoindentation were increased by up to 78 %. The best improvement of the mechanical properties was shown by the paper sample coated with PVB/3 wt. % sepiolite nanocomposite.

Keywords: nanocomposites; sepiolite; mechanical properties; nanoindentation.

INTRODUCTION

The paper industry is a broad industry with increasing demands. These demands are caused primarily by the different applications of paper, its functionality, influence on the environment and cost. The cellulose, fillers and additives make paper a composite and have significant influences on the properties of the final product. Nanoparticles have already found application in papermaking processes to improve various properties of paper.[1–3]

Poly(vinyl butyral) (PVB) is the product of the condensation of poly(vinyl alcohol) (PVA) with *n*-butyraldehyde in an acid environment. It is a tough and transparent polymer with high impact energy absorption and excellent adhesive properties, which is mainly used in the auto industry for laminated safety glass

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for windshields.[4] In addition, PVB is used as a high-barrier layer to prevent moisture permeation in device sealing.[5]

Sepiolite ($Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4 \cdot 8H_2O$) is a natural, fibrous clay mineral having a large specific surface area and high porosity.[6] The unique fibrous structure of sepiolite is formed by blocks and interior channels along the fiber direction. Sepiolite has many known uses, *i.e.*, as an effective sorbent material.[7–10] a catalyst and catalyst support,[11] a membrane for ultrafiltration,[12] a filler in polymer composites,[13,14] *etc*.

Polymer/clay nanocomposite materials, in which a small amount of inorganic filler is added into the polymer matrix, have been intensively investigated because of their superior physical, mechanical, and electrical properties in comparison to conventional polymer composites. Sepiolite as a filler in nanocomposites has been intensively investigated in recent years.[15–25] For example, a nanocomposite based on sepiolite and gelatin showed a significant improvement in the mechanical properties, such as the Young modulus and compressive collapse strength.[15] Fukushima *et al.*[16] investigated poly(lactic acid) (PLA) and poly(ε--caprolactone) (PCL) composites with sepiolite prepared by melt blending and obtained thermo-mechanical improvements of the PLA and PCL matrices due to the good dispersion and high polymer/filler interaction. A new method of nanocomposite preparation was developed by Ma *et al.*[19] using supercritical CO_2--assisted mixing for polypropylene/sepiolite nanocomposites. An improvement in the yield stress was observed for the nanocomposites processed in this way compared to those processed by the traditional melt compounding due to the better dispersion of sepiolite in polymer. The main conclusion from all this research was that sepiolite significantly improved the mechanical properties of the nanocomposites. In addition, paper coated by starch modified with sepiolite nanoparticles, obtained in a previous investigation,[26] showed improved mechanical properties, including elongation at break, bursting strength and flat crush.

Tensile testing is a fundamental material test in which a sample is subjected to a controlled tension until failure. The results from the test are commonly used to select a material for an application and to predict how a material would react under other types of forces. The properties that are directly measured *via* a tensile test are ultimate tensile strength and maximum elongation. The load *versus* elongation curves could be converted into stress *versus* strain curves. The stress–strain curve relates the applied stress to the resulting strain and each material has its own unique stress–strain curve.

Nanoindentation is a relatively new technique that enables the determination of elastic modulus (E_r) and hardness (H) of a material on submicron scales.[27] For indentation, a probe is forced into the surface at a selected rate and to a selected maximum force. In scratch testing, the probe is dragged across the sample surface. The force, rate, length and angle of the scratch are controlled. Nanoindent-

ation is performed in conjunction with atomic force microscopy (AFM). The area for testing is located by AFM imaging, and indentations and scratching marks are imaged by AFM after testing. A three-sided, pyramid-shaped diamond probe tip is typically used to indent, scratch and image the sample. The depth of the indentation is measured from the AFM image to evaluate hardness. A force-displacement curve obtained during indentation also provides indications of the mechanical and physical properties of the material. This technique is useful for nanocomposites due to its sensitivity to the filler content, filler dispersion, as well as to the interfacial nanofiller–matrix adhesion. Information on heterogeneities of the composite material, which derive from the matrix morphology or uneven distribution of the filler, can be readily detected by means of nanoindentation.[28,29]

Sepiolite as a nanofiller in a PVB matrix has not been sufficiently investigated. Hassan *et al*.[31] synthesized electrospun PVB nanocomposite fibers reinforced with pure sepiolite and ultrasound functionalized sepiolite. The modification of the sepiolite with amino silanes led to better dispersion and deagglomeration of the sepiolite inside the nanocomposite fibers and to significant improvement of the thermo-mechanical properties.

In the present study, sepiolite was dispersed in a PVB matrix and coated onto paper type schrenz. The mechanical properties of the paper reinforced with sepiolite/PVB were investigated by tensile testing and nanoindentation. To the best of our knowledge, the system sepiolite/PVB for this purpose has not been previously reported in the literature. The main goal of these investigations was to determinate the influence of sepiolite nanoparticles in the PVB matrix on the mechanical properties of reinforced paper.

EXPERIMENTAL

The paper used in this study was type schrenz with a grammage of 110 g m^{-2} produced by FHB (Belgrade Paper Mill, Serbia). The natural sepiolite sample was obtained from the deposit Tolica Kosa (Serbia). Poly(vinyl butyral) powder (Mowital B60HH, Kuraray Specialties Europe) and absolute ethanol (Superlab, Belgrade, Serbia) were used. The characterization of sepiolite (XRD, FTIR, textural characteristics and particle size distribution) was given in a previous publication.[26] The size of the sepiolite particles was about 0.5 μm and the specific surface area was 330 m^2 g^{-1}.

A polymer solution was prepared by dissolving 10 wt. % poly(vinyl butyral) powder in absolute ethanol under vigorous stirring for 24 h. Subsequently, sepiolite was dispersed in the PVB solution under vigorous stirring at three concentrations: 1, 3 and 5 wt. %. Paper samples were coated by short immersion of sheets (15 cm×20 cm) in the prepared solutions. The immersion time of each paper sample was 30 s. Control sample was coated with pure PVB solution. Another control sample was schrenz without any coating. After coating, the samples were dried under ambient conditions (25 °C) for 24 h.

The surface morphology of the paper samples was studied by field emission scanning electron microscopy (FESEM, Tescan MIRA 3 XMU) at 10 kV. The samples were sputter-coated with Au/Pd alloy before analysis.

In order to determine the glass transition point, differential scanning calorimetry (DSC) measurements were conducted using a TA DSC Q10 instrument, calibrated with indium standards. The temperature range was from 30 to 80 °C at a heating rate of 10 °C min^{-1} under a dynamic nitrogen flow of 50 mL min^{-1}. The glass transition point was determined using the midpoint of the initial transition slopes.

The breaking force was determined using a Shimadzu AG–X plus Universal testing machine. All tests were performed at room temperature adjusted at crosshead speed of 10 mm min^{-1}. The dimensions of specimens were 100 mm×15 mm. All experiments were performed in triplicate.

The nanoindentation test was performed using a Hysitron TI 950 Triboindenter equipped with a Berkovich diamond tip with *in situ* scanning probe microscopy (SPM) imaging (Hysitron, MN). The hardness and reduced elastic modulus were calculated from the curves using the Oliver and Pharr method.[30] The indentation maximum load was set to be 0.5 mN for all samples. The loading and unloading times, as well as the hold time at the peak force, were set to 25 s each. The nanoindentation measurements were performed at nine positions on each sample. The mean values of the nine measurements were used for further analysis.

RESULTS AND DISCUSSION

Microstructure of reinforced paper

Due to its high specific area and nanoscale dimensions, sepiolite prefers agglomeration into micrometric stacks or bundles due to van der Waals interactions, ionic interactions and/or hydrogen bonds. For this reason, it is very important to ensure homogenous distribution of sepiolite in a polymer matrix. The micrographs of schrenz and schrenz reinforced with PVB are given at Figs. 1 and 2. From these micrographs, it is obviously that the PVB penetrated through the cellulose fiber and formed layer on the surface of the schrenz. Retention of a reinforcement agent on fiber intersections leads indirectly to an increase in the contact area of the fibers and of paper strength.

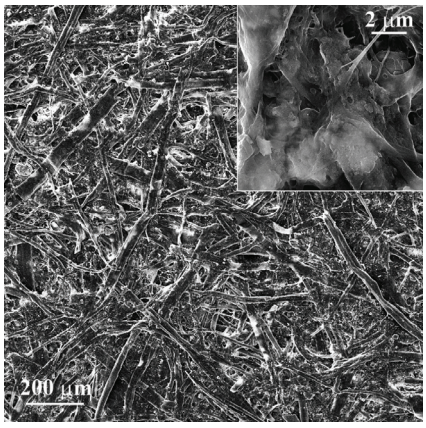

Fig. 1. Micrograph of schrenz.

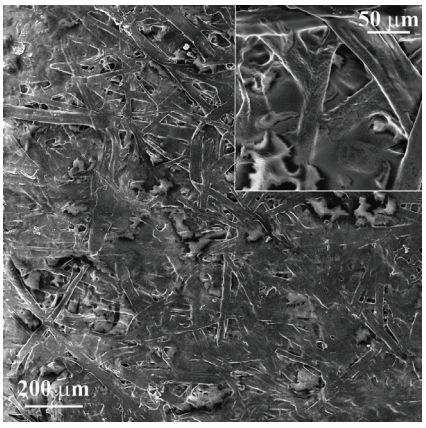

Fig. 2. Micrograph of schrenz reinforced with PVB.

The micrographs of schrenz reinforced with PVB with 1, 3 and 5 wt. % sepiolite are given in Figs. 3–5, respectively. Dispersed sepiolite bundles could be observed on the sample of schrenz with PVB/sep 1 wt. % (Fig. 3, inset). The samples of schrenz with PVB/sep 3 wt. % and PVB/sep 5 wt. % also contained sepiolite bundles but their distribution on the paper surface was not homogenous. The reason for the inhomogeneous distribution of sepiolite in these samples could be the preparation method of the PVB/sepiolite coatings. As was shown in a previous investigations,[26] ultrasonification could provide more energy and result in further separation and better dispersion of sepiolite in the PVB matrix.

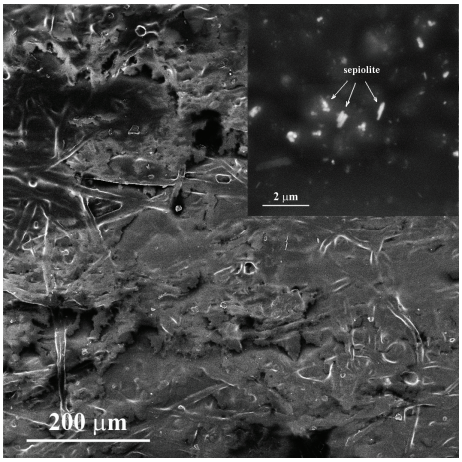

Fig. 3. Micrograph of schrenz reinforced with PVB/sep 1 wt.%.

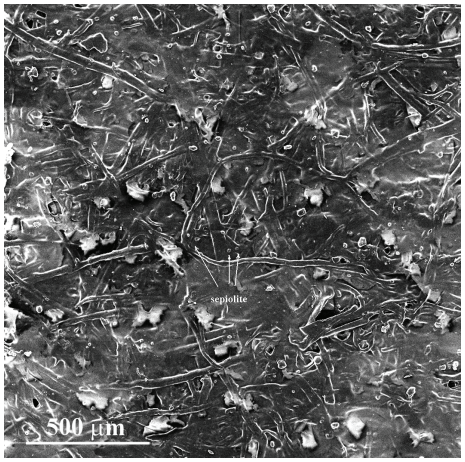

Fig. 4. Micrograph of schrenz reinforced with PVB/sep 3 wt.%.

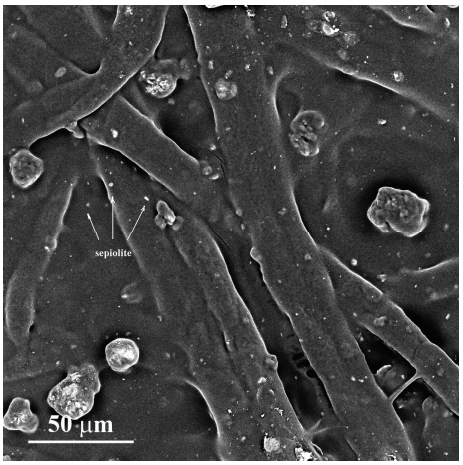

Fig. 5. Micrograph of schrenz reinforced with PVB/sep 5 wt. %.

DSC analysis of the reinforced paper

In order to investigate the influence of sepiolite on the glass transition temperature of the composite with poly(vinyl butyral), DSC analysis was performed. The DSC curve of pure PVB film and schrenz with PVB/sepiolite coatings are presented in Fig. 6. The glass transition of pure the PVB film was shifted towards lower temperatures, as compared with that of the pure PVB, without any solvent (t_g = 65 °C).[32] The reason for this decrease could be the presence of the residual solvent, which acted as plastifier and led to the reduction of the t_g value. The sample of schrenz with pure PVB showed an increase in the glass transition temperature to ~6 ≈ 1 °C. The t_g values of the samples did not change with increasing content of sepiolite in the PVB coating. These results could suggest that the presence of sepiolite in PVB coatings has no significant influence on the t_g values.

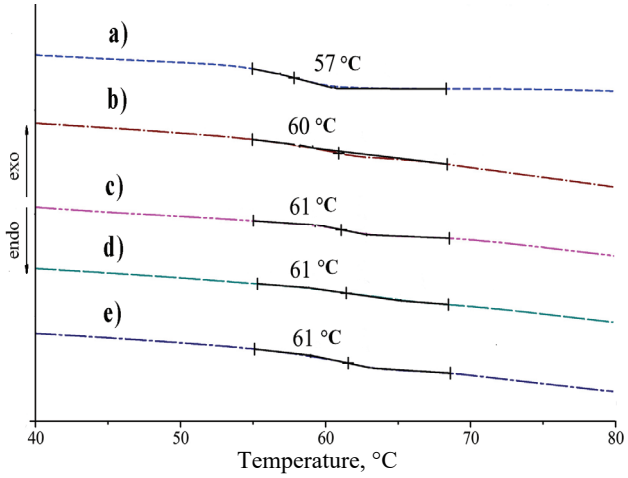

Fig. 6. DSC scans of pure PVB (a), schrenz/PVB (b), schrenz/PVBsep1 wt. % (c), schrenz/PVBsep3 wt. % (d) and schrenz/PVBsep5 wt. % (e).

Mechanical properties obtained by tensile testing

The stress–strain curves obtained in the tensile testing are presented in Fig. 7 and the values of the break forces and tensile energy absorption (*TEA*) derived from the curves are given in Table I. The value of the break force of sample coated with PVB compared to sample of pure schrenz increased by approximately 50 %. The addition of 1 and 3 wt. % sepiolite increased the break force of the paper sample by 4 and 9 %, respectively. Contrarily, the addition of 5 wt. % sepiolite to the PVB coating decreased the value of the break force of the paper. The reason for this decrease could be the inhomogeneous dispersion of the sepiolite in the PVB coating (Fig. 5). Krook *et al.*[33] investigated the properties of a montmorillonite–polyethylene extrusion-coated paperboard. Tensile measurements per-

formed on the isolated polymer–clay coating indicated that the films became stiffer and exhibited a lower fracture strain with increasing filler content. In the present investigations, increasing the sepiolite content in the PVB coating led to agglomeration of the sepiolite nanofibers, which resulted in the poorest mechanical properties.

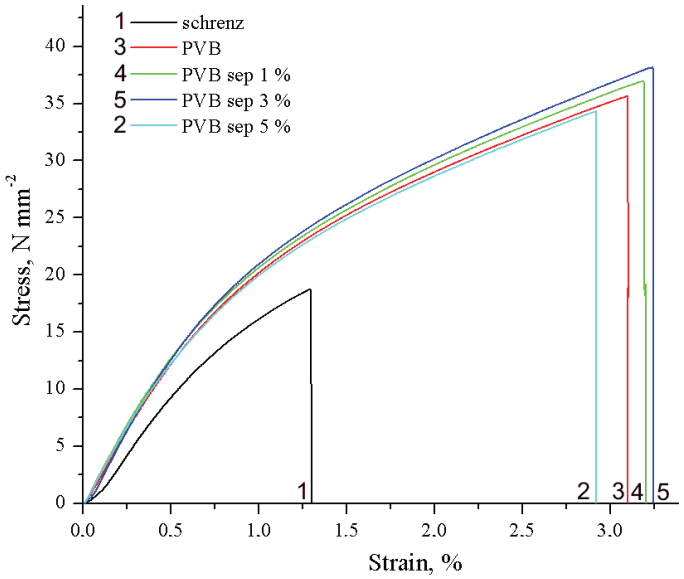

Fig. 7. The stress–strain curves of the paper samples.

Table I. The results of the tensile testing of the paper samples

Sample	Break force, N	*TEA* / J m^{-2}
Schrenz	60.37	9.28
PVB	108.74	48.15
1 wt. % sep	112.99	51.70
3 wt. % sep	118.25	53.65
5 wt. % sep	106.16	43.54

Tensile energy absorption (*TEA*) represents the work done when a specimen is stressed to rupture and is given by the integral of the tensile strength over the range of tensile strain from zero to the maximum strain. The *TEA* is expressed as the energy per unit area of the specimen (TAPPI T 494). The obtained results for *TEA* showed that the PVB coating on schrenz increased this value related to the pure schrenz by almost five times. The presence of 1 and 3 wt. % sepiolite in the PVB coating additionally increased the tensile energy absorption by up to 10 %. Similarly to the value of the break force for the sample coating with PVB/5 wt. % sep, the value of *TEA* for this sample also decreased.

Mechanical properties obtained by nanoindentation

The results of the nanoindentation test are presented in Table II and the experimental curve shows the dependence of depth in the loading–unloading cycle. Typical force–depth curves obtained in the nanoindentation tests of the paper samples are shown in Fig. 8a. The curves appear to be continuous without pop-in or pop-out during both the loading and the unloading phases. A plastic imprint of the indent for the schrenz reinforced with PVB/sep 3 wt. % with the scan trace near the indent is displayed in Fig. 8b. According to the results of the reduced elastic modulus and hardness, the reduced modulus for the schrenz coated with PVB increased by 150 % and the hardness by 75 % in comparison to that of the pure schrenz. The addition of 1 wt. % sepiolite to the PVB led to a slight increase in the reduced modulus and the hardness while the presence of 3 wt. % sepiolite in the PVB coating showed a modulus increase of 35 % and hardness increase of 78 %. The paper sample reinforced with PVB/sep 5 wt. % showed lowest values of modulus and hardness, almost the same as those for pure schrenz.

TABLE II. The results of the nanoindentation tests

Sample	Elastic modulus, GPa	Hardness, GPa
schrenz	1.80±0.42	0.16±0.07
PVB	4.53±2.48	0.28±0.22
1 wt. % sep	4.87±1.46	0.26±0.09
3 wt. % sep	6.11±0.84	0.50±0.11
5 wt.% sep	2.10±0.97	0.09±0.06

Charitidis *et al.*[34] also used nanoindentation for their investigation of the mechanical properties of nanocomposites based on PVB and multiwall carbon nanotubes. The composites that contained 1, 3 and 5 wt. % nanofiller showed improved mechanical properties compared to those for the pure PVB matrix, but the sample with 5 wt.% nanofiller showed rapid decrease in the values of the reduce modulus and hardness. The authors suggested that low concentrations of carbon nanotubes leads to good interfacial interactions and the stretching of the PVB chains. As the nanofiller concentration increased, there was larger agglomerates of particles that acted as mechanical defects and increased the stiffness of the resulting composite.

In order to evaluate the mechanical properties of the paper sample reinforced with the nanocomposites PVB/sepiolite, the data obtained by tensile testing and by nanoindentation were compared. The best improvement of mechanical properties, observed by both methods, was shown by the paper the sample coated with the PVB/3 wt. % sepiolite nanocomposite.

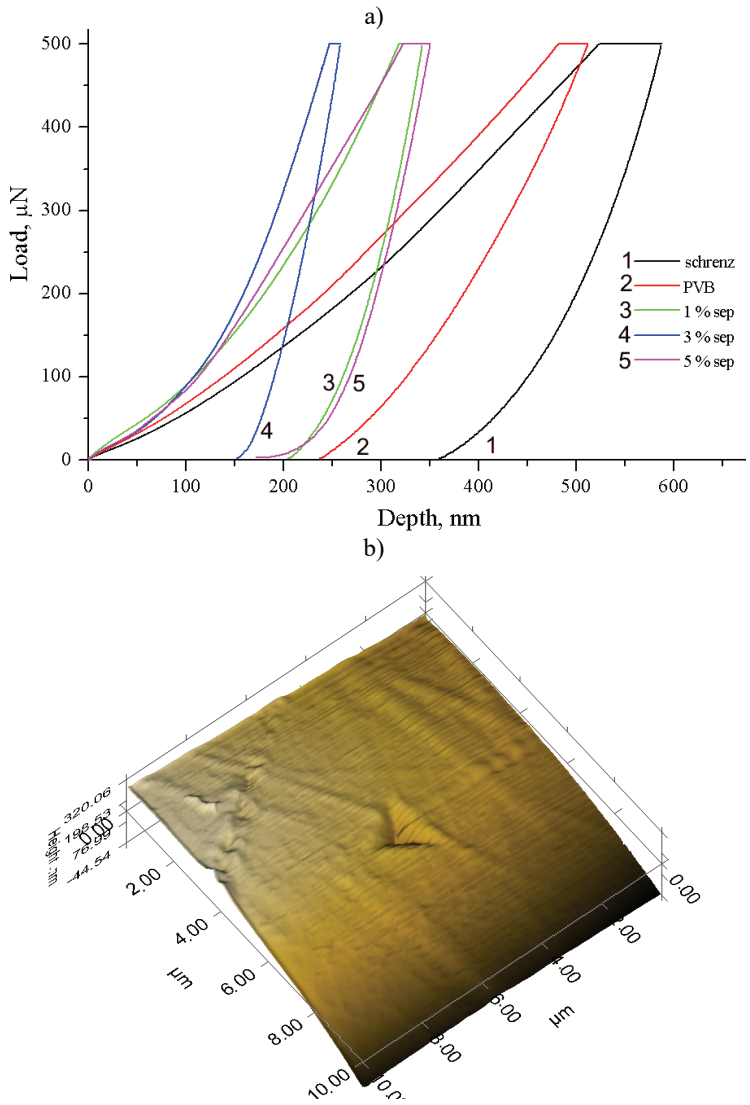

Fig. 8. Force–depth curves for different paper samples (a) and indent imprint of schrenz reinforced with PVB/sep 3 wt. % (b).

CONCLUSION

The mechanical properties of paper reinforced with sepiolite dispersed in PVB were studied in these investigations. Two sets of data, by tensile testing and nanoindentation, were obtained.

The presence of sepiolite in the PVB coating showed no significant influence on the t_g values of the polymer. The values of the break force and the tensile

energy absorption of the paper samples were increased by up to 10 %. The nano-indentation tests showed increases in the hardness and modulus. The paper sample reinforced with nanocomposite PVB/3 wt. % sepiolite exhibited the best improvements of the mechanical properties as measured by both methods.

The investigations performed in this study showed that coating with PVB/ /sepiolite improved the mechanical properties of the paper. The application of this system as a strengthening agent for paper could result in better quality of the final product.

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И З В О Д

PVB/СЕПИОЛИТ НАНОКОМПОЗИТИ ЗА ОЈАЧАВАЊЕ ПАПИРА

ИВОНА ЈАНКОВИЋ-ЧАСТВАН, СЛАВИЦА ЛАЗАРЕВИЋ, ДУШИЦА СТОЈАНОВИЋ, ПРЕДРАГ ЖИВКОВИЋ, РАДА ПЕТРОВИЋ и ЂОРЂЕ ЈАНАЋКОВИЋ

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У циљу побољшања механичких својстава папира, 1, 3 и 5 мас. % нановлакана сепиолита је дисперговано у поли(винил-бутиралу) (PVB) и наношено на schrenz површину (110 g m^{-2}). Скенирајућом електронском микроскопијом су уочена нановлакна сепиолита у PVB матрици на површини папира. Са порастом садржаја нановлакана сепиолита у PVB/сепиолит премазима, температуре остакљивања се нису значајно мењале. Коришћене су две различите методе за испитивање механичких својстава узорака папира ојачаних PVB/сепиолит нанокомпозитима: испитивање затезне чврстоће у огледима истезања и наноиндентација. Вредности силе кидања и рада који је потребан да би се папир трајно оштетио за ојачање узорака, добијене испитивањем кидалицом су повећане до 10 %. Вредности редукованог модула еластичности и тврдоће ојачаних узорака, добијене наноиндентацијом повећане су до 78 %. Узорци папира ојачани са PVB/3 мас. % сепиолита су показали највеће побољшање механичких својстава.

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REFERENCES

1. Z. Yan, Q. Liu, Y. Deng, A. Ragauskas, *J. Appl. Polym. Sci.* **97** (2005) 44
2. M. Sababi, J. Kettle, H. Rautkoski, P. M. Claesson, E. Thormann, *ACS Appl. Mater. Inter.* **4** (2012) 5534
3. Z. Hu, Y. Deng, *Powder Technol.* **140** (2004) 10
4. A. M. Torki, I. Živković, V. R. Radmilović, D. B. Stojanović, V. J. Radojević, P. S. Uskoković, R. R. Aleksić, *Int. J. Mod. Phys., B* **24** (2010) 805
5. J. Yin, H. Zhu, Y. Wang, Z. Wang, J. Gao, Y. Mai, Y. Ma, M. Wan, Y. Huang, *Appl. Surf. Sci.* **259** (2012) 758
6. K. Brauner, A. Preisinger, *Schweiz. Mineral. Petr. Mitt.* **6** (1956) 120
7. S. Lazarević, I. Janković-Častvan, D. Jovanović, S. Milonjić, Dj. Janaćković, R. Petrović, *Appl. Clay Sci.* **37** (2007) 47

8. V. Marjanović, S. Lazarević, I. Janković-Častvan, B. Potkonjak, Dj. Janaćković, R. Petrović, *Chem. Eng. J.* **166** (2011) 198
9. S. Lazarević, I. Janković-Častvan, Z. Radovanović, B. Potkonjak, Dj. Janaćković, R. Petrović, *J. Serb. Chem. Soc.* **76** (2011) 101
10. C. Maqueda, P. Partal, J. Villaverde, J. L. Perez-Rodriguez, *Appl. Clay Sci.* **46** (2009) 289
11. A. N. Okte, E. Sayinsoz, *Sep. Purif. Technol.* **62** (2008) 535
12. Q. K. Wang, T. Matsuura, C. Y. Feng, M. R. Weir, C. Detellier, E. Rutadinka, R. L. Van Mao, *J. Membrane Sci.* **184** (2001) 153
13. L. Gonzalez, A. Rodrıguez, A. Marcos-Fernandez, A. del Campo, *J. Appl. Polym. Sci*. **79** (2001) 714
14. C. H. Cho, M. S. Cho, J. H. Sung, H. J. Choi, M. S. Jhon, *J. Mater. Sci.* **39** (2004) 3151
15. M. Frydrych, C. Wan, R. Stengler, K. U. O'Kelly, B. Chen, *J. Mater. Chem.* **21** (2011) 9103
16. K. Fukushima, D. Tabuani, G. Camino, *Mat. Sci. Eng., C* **29** (2009) 1433
17. H. E. Miltner, N. Watzeels, A. Goffin, E. Duquesne, S. Benali, P. Dubois, H. Rahier, B. van Mele, *J. Mater. Chem.* **20** (2010) 9531
18. N. García, J. Guzmán, E. Benito, A. Esteban-Cubillo, E. Aguilar, J. Santarén, P. Tiemblo, *Langmuir* **27** (2011) 3952
19. J. Ma, E. Bilotti, T. Peijs, J. A. Darr, *Eur. Polym. J.* **43** (2007) 4931
20. K. Fukushima, A. Fina, F. Geobaldo, A. Venturello, G. Camino, *Express Polym. Lett.* **6** (2012) 914
21. A. Nohales, R. Muñoz-Espí, P. Félix, C. M. Gómez, *J. Appl. Polym. Sci.* **119** (2011) 539
22. E. Franchini, J. Galy, J. F. Gérard, *J. Colloid Interface Sci.* **329** (2009) 38
23. S. Xie, S. Zhang, F. Wang, M. Yang, R. Séguéla, J. M. Lefebvre, *Compos. Sci. Technol.* **67** (2007) 2334
24. A. L. Vicosa, A. C. O. Gomes, B. G. Soares, C. M. Paranhos, *Express Polym. Lett.* **3** (2009) 518
25. A. Choudhury, A. K. Bhowmick, C. Ong, *Polymer* **50** (2009) 201
26. I. Jankovic-Castvan, S. Lazarevic, D. Stojanovic, P. Zivkovic, R. Petrovic, Dj. Janaćković, *Starch* **67** (2015) 373
27. A. Schuh, *Mater. Today* **9** (2006) 32
28. L. Shen, I. Y. Phong, L. Chen, T. Liu, K. Zeng, *Polymer* **45** (2004) 3341
29. A. K. Dukta, D. Penumadu, B. Files, *J. Mater. Res.* **19** (2004) 158
30. W. C. Oliver, G. M. Pharr, *J. Mater. Res.* **7** (1992) 1564
31. S. Ahmed Ben Hassan, D. Stojanović, A. Kojović, I. Janković-Castvan, Dj. Janaćković, P. Uskoković, R. Aleksić, *Ceram. Int.* **40** (2014) 1139
32. http://www.kuraray.eu/fileadmin/Downloads/pvb/TDS_Mowital_EN_2015.pdf
33. M. Krook, M. Gällstedt, M. S. Hedenqvist, *Packag. Technol. Sci.* **18** (2004) 11
34. C. A. Charitidis, E. P Koumoulos, M. Giorcelli, S. Musso, P. Jagadale, A. Tagliaferro, *Polym. Compos.* **34** (2013) 1950.