Chemistry: Bulgarian Journal of Science Education *Volume 26 Number 4, 2017* *Природните науки в образованието*

Experiments
Експерименти в природните науки

COMPARISON STUDY OF DIFFERENT INORGANIC SILICA BASED REINFORCEMENT KAOLIN AND 3-GLYCYDILOXYPROPYLTRIMETHOXYSILANE ON MECHANICAL, WATER UPTAKE AND SWELLING AREA PROPERTIES OF CHITOSAN COMPOSITES

Ozi A. Saputra, Windy A. Lestari, Dheo A. Saputra,
Kartika S. Rini, Edi Pramono
Sebelas Maret University – Indonesia

Abstract. The blending of chitosan with different types of silica-based reinforcement materials, kaolin clay and (3-glycidyloxypropyl) trimethoxysilane via solution casting method had been carried out. This study was focused on the mechanical, water uptake and swelling area comparison between chitosan/kaolin (referred as Cs/Kao) and chitosan/(3-glycidyloxypropyl) trimethoxysilane (Cs/GPTMS) composites. Fourier transform infra-red (FTIR) characterization was also conducted in this study for functional group analysis. Mechanical properties, such as tensile strength, elongation percentage and young's modulus, were performed according to ASTM D882-02 standard method. Based on the mechanical test, it can be concluded that different types of silica-based reinforcement materials resulted different mechanical properties. The GPTMS filled chitosan had higher tensile strength value than Cs/Kao at 15% filler loading but lower in another concentrations. Moreover, water uptake and swelling area value of Cs/GPTMS was lower than Cs/Kao at 15% filler content.

Keywords: chitosan; composites; kaolin; GPTMS; silica-based reinforced materials

Introduction

Chitosan is derived from chitin obtained from deacetylation process (Chen et al., 2007). Chitosan is the second abundant polymer after cellulose having biodegradable, biocompatible and non-toxic properties (Shirosaki et al., 2009; Zha et al., 2008). It is useful material for various purposes such as treatment of wastewater, ion-exchanger, functional matrix and surfactants (Liu et al., 2004; Zha et al., 2008). Lately, chitosan has been attracting much attention due to it has not only good cationic exchange capacity and proton conductivity, but also good performance in affinity sorption for purification (Chao, 2008). However, chitosan has poor physical or mechanical properties and high swelling degree in an aqueous system. This drawbacks are not favorable in some application such as in purification or proton exchange membrane (Jiang et al., 2006). Therefore, modification of chitosan to obtain good mechanical and low swelling properties is very necessary conducted.

Modification of chitosan to create better properties was reported by previous researchers. It was mentioned that many new materials combined with chitosan, such as organic polymer (i.e., gelatin (Huang et al., 2005), chitosan-gelatin scaffolds have gained much attention in various tissue engineering applications. However, the underlying cell-matrix interactions remain unclear in addition to the scaffold degradation and mechanical characteristics. In this study, we evaluated (ipolyvinyl alcohol (Jia et al., 2007), poly(lactic acid) (Ravi Kumar et al, 2004) and inorganic materials (i.e. carbon nanotubes (Wang et al., 2005), glass/ceramic particles (Caridade et al., 2013; Habraken et al., 2007; Lee et al., 2009; Luz & Mano, 2012) and layered silicates (Wang et al., 2007), formed good properties of chitosan composites with according to their appropriation. Mechanical properties is one of the important properties in some applications. Furthermore, water uptake and swelling area properties also become substantial properties in membrane purification, separation, and many others. Therefore, some researchers developed chitosan-based materials having excellent mechanical properties and low swelling value. The inorganic chemical compound containing silica such as TEOS (tetraethyl orthosilicate) was able to act as reinforcement in the chitosan matrix to produce good mechanical properties as well as low swelling value (Pandis et al., 2014). Another research also reported that another silica compound obtained from nature, such as halloysite nanotubes (HNTs), enhanced mechanical properties of chitosan (De Silva et al., 2013). The silica-based reinforcement materials are promising modifier to improve the chitosan performance. However, the investigation on differences of silica-based reinforcement on chitosan composites properties like mechanical and swelling is not yet studied. Thus, in this research compared the silica-based reinforced materials between inorganic chemicals compound and natural materials. It used two kinds of silica sources type, inorganic chemical compound (GPTMS) and natural material (kaolin). This study was focused on the comparison on the mechanical and water uptake ability of two kind composites kaolin or GPTMS reinforced chitosan.

Experimental

Materials

Chitosan was obtained from Biotech Surindo Corp. Indonesia. Chemicals such as acetic acid and sodium hydroxide were available from Merck. 3-glycidyloxypropyl trimethoxysilane (GPTMS) was purchased from Sigma-Aldrich. Kaolin (referred as Kao) was purchased from Brataco Corp. Indonesia.

Blending of chitosan/kaolin (Cs/Kao) and chitosan/GPTMS (Cs/GPTMS)

Both Cs/Kao and Cs/GPTMS were prepared using solution casting method. About 2 g of chitosan were dissolved in acetic acid (1.5%, 80 mL) in room temperature. Then, amounts of Kao or GPTMS (Table 1) was added in chitosan solution and mixed at 80 ^{O}C about 1 hour. The mixing solution was casted in template at 50 ^{O}C for 24 hours. Both Cs/Kao and Cs/GPTMS composites were washed with sodium hydroxide (1 M) to remove the acetic acid and washed again with distilled water several times. The composites were dried at room temperature for one or two days.

Table 1. Cs/Kao and Cs/GPTMS composites formulation

Formulation	Chitosan (phr)	Filler Content (phr)	
		Kaolin	GPTMS
A0	100	-	-
A1	100	5	-
A2	100	10	-
A3	100	15	-
B1	100	-	5
B2	100	-	10
B3	100	-	15

Characterization of Cs/Kao and Cs/GPTMS composites

`Functional group analysis was conducted using FTIR (Fourier Transform Infra-Red) spectroscopy. FTIR test was recorded using IRPrestige-21 SHIMADZHU with 45 times number of scans. The sample was prepared in pellet form by mixing it with KBr powder. In this study, Morphology of optimum Cs/Kao composite was studied by SEM (Scanning Electron Microscopy) JEOL/EO JSM-6510.

Mechanical test was conducted according to ASTM D882-02 standard method using UTM (Universal Testing Machine) Ray-Run M500-50CT. The applied cross-head speed was 10 mm.min^{-1}. The measured mechanical properties were tensile strength (TS), elongation (E), and Young's Modulus (YM) using Eqs. (1-3), respectively.

$$\mathrm{TS\ (MPa)} = \frac{\mathrm{F}}{\mathrm{A}} \tag{1}$$

$$\mathrm{E\ (\%)} = \frac{(\mathrm{L} - \mathrm{Lo})}{\mathrm{Lo}} \times 100\% \tag{2}$$

$$\mathrm{YM\ (MPa)} = \frac{\mathrm{TS}}{\mathrm{Strain}} \tag{3}$$

where, F is a force at break (N); A is an area of specimen test (m^2); Lo and L are specimen length before and after the mechanical test (m); and the strain was measured with Eq. (4).

$$\text{Strain} = \frac{(\text{L} - \text{Lo})}{\text{Lo}} \tag{4}$$

Water uptake testing was carried out by immersing the samples (Cs/Kao and Cs/GPTMS) with initial weight (Wo) in water for 1 hour. Afterward, the sample was weighted and recorded as the final weight (Wi). Then, the percentage of water uptake was determined by Eq. (5). Swelling Area properties was conducted with same procedure as water uptake testing, where area before (Ao) and after (Ai) immersion were recorded to determine swelling area using Eq. (6).

$$\text{Water uptake (\%)} = \frac{(\text{Wi} - \text{Wo})}{\text{Wo}} \times 100\% \tag{5}$$

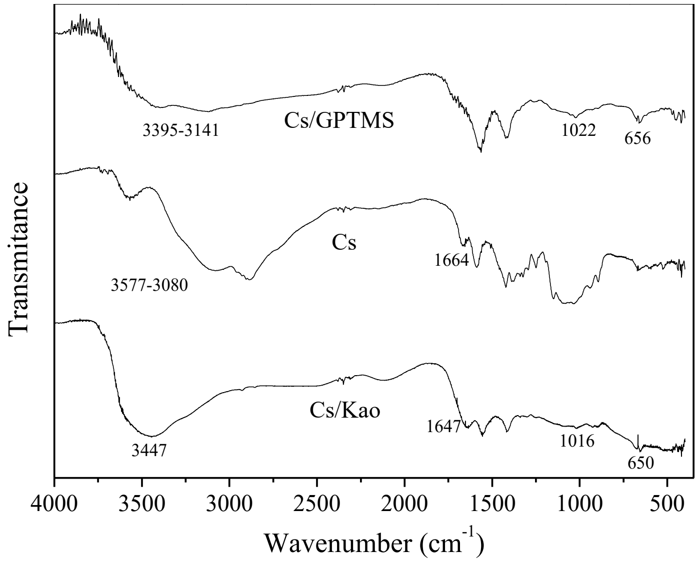
$$\text{Swelling Area (\%)} = \frac{(\text{Ai} - \text{Ao})}{\text{Ao}} \times 100\% \tag{6}$$

Results and discussion

Synthesis of the composites

Preparation of Cs/Kao and Cs/GPTMS composites were performed via solution casting method. After blending process, the mixing solution was poured in stainless steel template and dried for 24 hours at 50 ^{O}C. The functional group analysis of final product was characterized by FTIR spectroscopy. Fig. 1 shows IR spectrum of chitosan, Cs/GPTMS and Cs/Kao. Chitosan has specific absorbance band at around 3577 cm^{-1} and 3080 cm^{-1} corresponding to NH_2 stretching vibration. The N-H bending vibration of chitosan was appeared in 1664 cm^{-1} (Chao, 2002). A characteristic strong and broadband at 3080 cm^{-1} overlapped with the -NH_2 stretching vibration corresponded to hydroxyl (O-H) group stretching vibration (Chen et al., 2007).

An investigation using FTIR technique evidenced that Cs/GPTMS has successfully synthesized. A disappearance of absorbance peak at 1664 cm^{-1} in Cs/GPTMS IR spectrum indicated that amine group formed covalent bonding with GPTMS (Burmistrov et al., 2014; Liu et al., 2004). The opening ring of GPTMS oxirane group can be achieved by attributing of acid (H^+), Fig. 2. The amine group of chitosan acting as good nucleophilic formed a covalent bond with carbocation of oxirane ring.



Figire 1. FTIR spectrum of Cs, Cs/GPTMS and Cs/Kao

Fig. 3 illustrates a hydrogen bonding interaction between chitosan and kaolin. Kaolin has two layers consisted of Si-O tetrahedral and Al-OH octahedral. Chitosan-kaolin interaction could be intercalated or exfoliated (Cole, 2008). The IR spectrum of chitosan and Cs/Kao was not significantly different. In the Cs/Kao IR spectrum has an absorbance peak at 1647 cm^{-1} corresponding to N-H group bending vibration. However, the N-H stretching vibration was not found due to it overlapped with the hydroxyl group of both chitosan and kaolin.

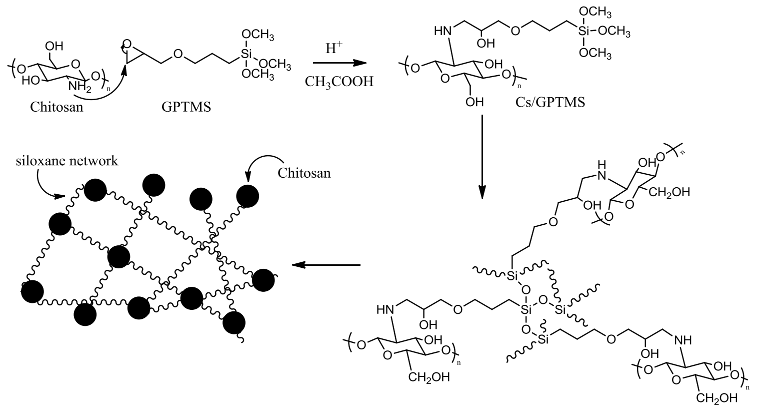


Figure 2. Illustration of chemical interaction between chitosan and GPTMS

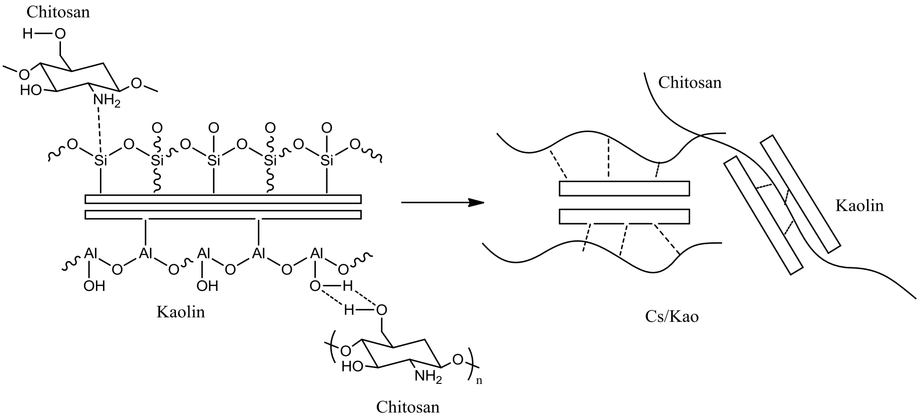
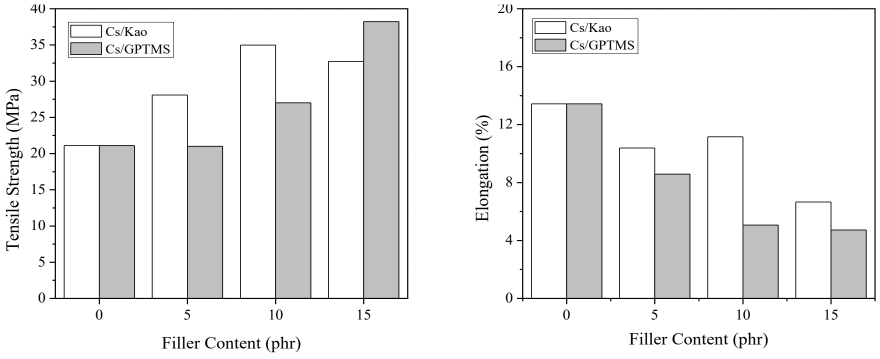


Figure 3. Illustration of chitosan-kaolin interaction

Mechanical properties

Mechanical properties such as tensile strength, elongation and young's modulus were evaluated to determine mechanically of materials ability to use in various applications. Tensile strength comparison between Cs/GPTMS and Cs/Kao composites can be seen in Fig. 4a. An increasing of filler content on the Cs/GPTMS composites improved the tensile strength. On the other hand, it decreased elongation percentage. The presence of GPTMS compound in chitosan matrix act as crosslinking agent (Gonçalves et al., 2005; Liu et al., 2004)hydrolysis, porosity, crosslinking, impregnation of diclofenac sodium (DS. Furthermore, by increasing the crosslink compound affected in the improving of tensile strength. For example, the tensile strength of composites containing 5%, 10% and 15% GPTMS were 21.1 Mpa, 27.1 Mpa and 38.2 Mpa, respectively. Since the polymer chain of chitosan was composed with GPTMS cross-link agent, thus it turned the composites to be more rigid and robust (Gonçalves et al., 2005; Sadaq et al., 2013). hydrolysis, porosity, crosslinking, impregnation of diclofenac sodium (DS However, due to the presence of cross-link agent, the strain of Cs/GPTMS materials decreased. It can be seen in Fig. 4b that the higher of GPTMS content led to decrease of elongation percentage, while elongation of B1 composites was 8.58% and decrease to 5.07% and 4.72% by addition of 10% and 15% GPTMS, respectively.

Tensile strength of Cs/Kao in the addition of 15% kaolin decreased to 6.7% compared to composites containing 10% of kaolin. It was due to low adhesion interaction between chitosan and kaolin caused by an aggregation of kaolin in chitosan matrix as evidenced by SEM image in Fig. 5. The aggregate of kaolin facilitated a breaking process while tensile test. This aggregation was also caused the increasing of brittleness of Cs/Kao composites. It can be seen that in Fig. 2, the elongation percentage of Cs/Kao with 15% filler content was 6.6%, decreasing from 11.2% at 10% of kaolin content.



a b

Figure 4. (a) Tensile strength and (b) elongation comparison of Cs/GPTMS and Cs/Kao

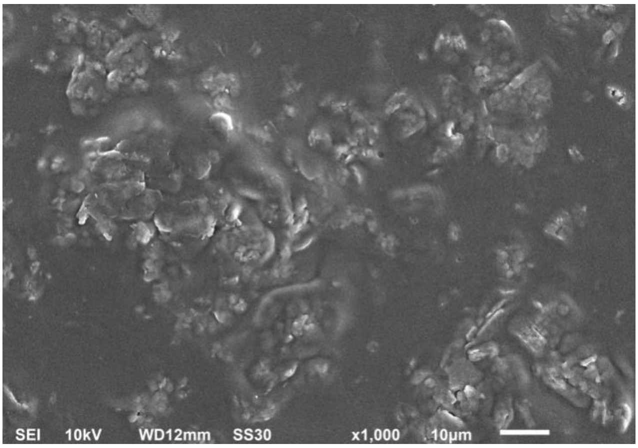


Figure 5. SEM image of Cs/Kao composites surface

Young's modulus reflected the brittleness properties of materials (Su et al., 2014). The higher of young's modulus value indicated of high brittleness. The Young's modulus of both Cs/GPTMS and Cs/Kao are presented in Fig. 6. In this study, with the addition of GPTMS in chitosan matrix was able to increase young's modulus value than kaolin filler. It was mean that GPTMS led chitosan to become brittle. It was caused by GPTMS act as crosslink agent making the composites more rigid or less elastic (Gonçalves et al., 2005; Liu et al., 2004; Rinaudo, 2006)scanning, and transmission electronic microphotograghy. Energy dispersive X-ray Si-mapping analysis demonstrated the homogeneous dispersion of silica in chitosan polymer domains. The formed chitosan-silica hybrid materials exhibited improved thermal stability and low degree of swelling in water. The hydrophilicity of chitosan membranes was maintained after the crosslinking reaction. This approach provided a convenient way to prepare crosslinked chitosan and chitosan-silica hybrid materials and the materials were potentially applied in biomaterials and separation membranes. ?? 2004 Published by Elsevier Ltd.”, “author” : [{ “dropping-particle” : “”, “family” : “Liu”, “given” : “Ying Ling”, “non-dropping-particle” : “”, “parse-names” : false, “suffix” : “” }, { “dropping-particle” : “”, “family” : “Su”, “given” : “Yu Huei”, “non-dropping-particle” : “”, “parse-names” : false, “suffix” : “” }, { “dropping-particle” : “”, “family” : “Lai”, “given” : “Juin Yih”, “non-dropping-particle” : “”, “parse-names” : false, “suffix” : “” }], “container-title” : “Polymer”, “id” : “ITEM-1”, “issue” : “20”, “issued” : { “date-parts” : [[“2004”]] }, “page” : “6831-6837”, “title” : “In situ crosslinking of chitosan and formation of chitosan-silica hybrid membranes with using ??-glycidoxypropyltrimethoxysilane as a crosslinking agent”, “type” : “article-journal”, “volume” : “45” }, “uris” : [“http://www.mendeley.com/documents/?uuid=6685e8c0-5e1f-4e4e-bfb5-1ac6c5a2eca3”] }, { “id” : “ITEM-2”, “itemData” : { “DOI” : “10.1080/02652040110065422”, “ISBN” : “0265204011”, “ISSN” : “0265-2048”, “PMID” : “11837972”, “abstract” : “In this work chitosan microspheres were prepared by the simple coacervation method and crosslinked using epichlorhydrin or glutaraldehyde for the controlled release of diclofenac sodium. The effects of the crosslinking agents on chitosan microspheres over a 12-hour period were assessed with regard to swelling, hydrolysis, porosity, crosslinking, impregnation of diclofenac sodium (DS. Unlike the Cs/GPTMS, brittleness of Cs/Kao was influenced by aggregation effect. While, at the high aggregate form, the rigid composite was resulted. However, a good distribution of kaolin caused good adhesion interaction between kaolin and chitosan and generated good mechanical properties as well as strain value of the composite (Ma & Eggleton, 1999).

Table 2. Mechanical properties value increasing of Cs/Kao compare to Cs/GPTMS

Filler content (phr)	Increasing (%)*		
	Tensile strength	Elongation	Young’s Modulus
5	33.7	21.2	10.4
10	29.5	120.2	-41.2
15	-14.4	41.2	-39.4

Table 2 reveals an increasing of the mechanical value of Cs/Kao compare to Cs/GPTMS. It was investigated that kaolin reinforced chitosan at 15% loading filler content has low tensile strength value than Cs/GPTMS. However, the tensile strength value of Cs/Kao at 5 and 10% loading content were higher than Cs/GPTMS, up to 33.7% and 29.5%, respectively. Although GPTMS act as crosslink agent, kaolin reinforced chitosan has good mechanical properties. The good chemical interaction between chitosan and kaolin made good adhesion between them affecting in mechanical properties. In this investigation, it has been found that kaolin reinforced chitosan has good elasticity compare to Cs/GPTMS composites. It was caused by silica of GPTMS forming siloxane network. This siloxane group will form cross-link network between the chitosan matrixes as seen in Fig. 2. Meanwhile, in kaolin, silica is in the form of a tetrahedral SiO_4 group which join together to make a silicate layer (Valášková et al., 2007).previously expanded by intercalation with 20??wt.% and 40??wt.% urea (U This silicate not formed a cross-linked network but it intercalated and exfoliated (Xie et al., 2011; Zhang et al., 2007). Thus, it slightly decreased on chitosan elasticity compared to Cs/GPTMS composites.

Water uptake and swelling area properties

Water uptake properties are the ability of material to absorb water. This ability is also referred as biodegradability properties. Water uptake of both Cs/Kao and Cs/GPTMS are displayed in Fig. 7a. Water uptake trends of Cs/Kao composites showed that the filler addition was analog with enhancement of water uptake percentage. When high content of filler is loaded, the water uptake value increased because of both chitosan and kaolin are a hydrophilic material indicated by the presence of polar hydroxyl group (Milošev et al., 2015). The presences of hydroxyl group act as water binding in Cs/Kao composites. The higher of kaolin content enhanced the number of hydroxyl group in Cs/Kao composites. Consequently, an increasing of water uptake was achieved. However, in Cs/GPTMS composites, the higher of GPTMS content decreased the water uptake value. This occurred due to silane group of GPTMS formed siloxane network (Liu et al., 2004). The presence of this network caused Cs/GPTMS difficult to absorb water.

Swelling area properties have same trends as water uptake ability, where the higher of kaolin content improved the swelling area value as shown in Fig. 7b. In the other hand, a decreasing of swelling area was achieved when introducing of GPTMS in chitosan matrix.

Comparison data of Cs/Kao and Cs/GPTMS water uptake and swelling area values were presented in Table 3. Water uptake value of Cs/Kao containing 5, 10, and 15% of kaolin were 88.89%, 105.88%, and 252.17%, respectively. The water uptake values of Cs/Kao composites were 0.5, 1.2, and 7.6 times higher than Cs/GPTMS composites at 5, 10 and 15% of loading content, respectively. The same thing occurred in Cs/Kao swelling area values, where they were 1.4, 3.9 and

7.2 times higher than Cs/GPTMS composites at same filler content. This evidenced that kaolin enhanced both water uptake and swelling area properties. However, the presence of GPTMS reduced both water uptake and swelling area value of chitosan matrix.

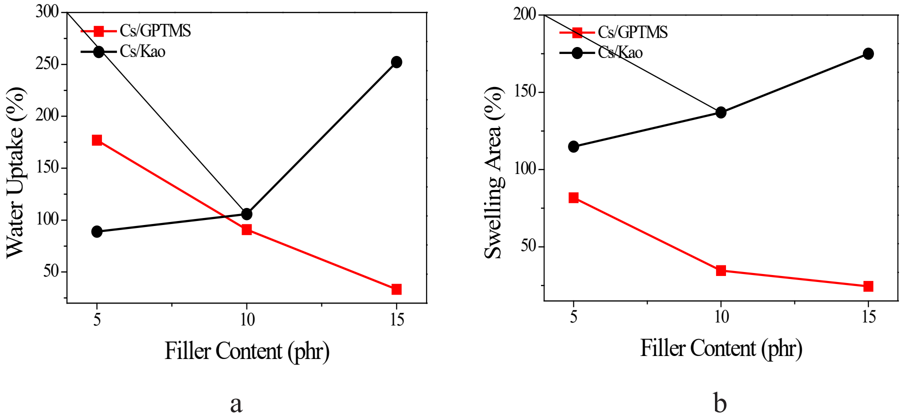


Figure 7. (a) Water uptake and (b) Swelling area properties of Cs/Kao and Cs/GPTMS composites

Table 3. Water uptake and swelling area comparison of Cs/Kao and Cs/GPTMS composites

Filler content (phr)	Water uptake (%)		Comparison (Kao:GPTMS)	Swelling area (%)		Comparison (Kao:GPTMS)
	Cs/Kao	Cs/GPTMS		Cs/Kao	Cs/GPTMS	
5	88.89	176.92	0.5	114.88	81.82	1.4
10	105.88	90.91	1.2	136.92	34.61	3.9
15	252.17	33.33	7.6	175	24.44	7.2

Conclusion

The mechanical, water uptake and swelling degree properties between Cs/Kao and Cs/GPTMS composites were significantly different. The increasing of GPTMS loading content improved the tensile strength but it reduced the elasticity. The tensile strength of Cs/Kao composite depends on the good distribution of kaolin in chitosan, while the tensile strength value decreased when chitosan was loaded 15% of kaolin. However, the tensile strength of Cs/Kao at 5 and 10% were higher than Cs/GPTMS at same loading content. The increasing of filler content was also enhanced both water uptake and swelling area values of Cs/Kao, but it was neither Cs/GPTMS. Based on the data, it was concluded that different kind of silica-based reinforcing materials had a different effect on mechanical properties as well as for water uptake and swelling area properties.

Acknowledgments: Author(s) would like to acknowledge to Indonesian Directorate General of Higher Education for financial support through Program Kreatifitas Mahasiswa (PKM) 2015.

REFERENCES

Burmistrov, I.N., Shatrova, N.V., Mostovoy, A.S., Mazov, I.N., Kuznetsov, D.V., Panova, L.G., Gorokhovsky, A.V. & Yudin, A.G. (2014). Mechanical properties of (surface-modified potassium polytitanate small additives)/epoxy composite materials. *Polymer Eng. & Sci.*, *54*, 2866 – 2871.

Caridade, S G., Merino, E.G., Alves, N.M., Bermudez, V. de Z., Boccaccini, A R. & Mano, J.F. (2013). Chitosan membranes containing micro or nano-size bioactive glass particles: evolution of biomineralization followed by in situ dynamic mechanical analysis. *J. Mech. Behavior Biomed. Mater., 20*, 173 – 183.

Chao, A.-C. (2008). Preparation of porous chitosan/GPTMS hybrid membrane and its application in affinity sorption for tyrosinase purification with *Agaricus bisporus*. *J. Membrane Sci., 311*, 306 – 318.

Chen, J.H., Liu, Q.L., Zhang, X.H. & Zhang, Q.G. (2007). Pervaporation and characterization of chitosan membranes cross-linked by 3-aminopropyltriethoxysilane. *J. Membrane Sci., 292,* 125 – 132.

Cole, K.C. (2008). Use of infrared spectroscopy to characterize clay intercalation and exfoliation in polymer nanocomposites. *Macromolecules*, *41*, 834 – 843.

De Silva, R.T., Pasbakhsh, P., Goh, K.L., Chai, S.-P. & Ismail, H. (2013). Physico-chemical characterisation of chitosan/halloysite composite membranes. *Polymer Testing*, *32*, 265 – 271.

Gonçalves, V., Laranjeira, M. & Fávera, V. (2005). Effect of crosslinking agents on chitosan microspheres in controlled release of diclofenac sodium. *Polímeros: Ciência E Tecnologia*, *15*, 6 – 12.

Habraken, W.J.E.M., Wolke, J.G.C. & Jansen, J.A. (2007). Ceramic composites as matrices and scaffolds for drug delivery in tissue engineering. *Adv. Drug Delivery Rev., 59*, 234 – 248.

Huang, Y., Onyeri, S., Siewe, M., Moshfeghian, A. & Madihally, S.V. (2005). In vitro characterization of chitosan-gelatin scaffolds for tissue engineering. *Biomaterials*, *26*, 7616 – 7627.

Jia, Y.-T., Gong, J., Gu, X.-H., Kim, H.-Y., Dong, J. & Shen, X.-Y. (2007). Fabrication and characterization of poly (vinyl alcohol)/chitosan blend nanofibers produced by electrospinning method. *Carbohydrate Polymers*, *67*, 403 – 409.

Jiang, Z., Yu, Y. & Wu, H. (2006). Preparation of CS/GPTMS hybrid molecularly imprinted membrane for efficient chiral resolution of phenylalanine isomers. *J. Membrane Sci., 280*, 876 – 882.

Lee, E.-J., Shin, D.-S., Kim, H.-E., Kim, H.-W., Koh, Y.-H. & Jang, J.-H. (2009). Membrane of hybrid chitosan-silica xerogel for guided bone regeneration. *Biomaterials*, *30*, 743 – 750.

Liu, Y.-L., Su, Y.-H. & Lai, J.-Y. (2004). In situ crosslinking of chitosan and formation of chitosan-silica hybrid membranes with using γ-glycidoxypropyltrimethoxysilane as a crosslinking agent. *Polymer*, *45*, 6831 – 6837.

Luz, G.M. & Mano, J.F. (2012). Chitosan/bioactive glass nanoparticles composites for biomedical applications. *Biomedical Materials*, *7*, art. no. 54104.

Ma, C. & Eggleton, R.A. (1999). Surface lsayer types of kaolinite : a high-resolution transmission electrom mictoscope study. *Clays & Clay Minerals*, *47*, 181 – 191.

Milošev, I., Kapun, B., Rodič, P. & Iskra, J. (2015). Hybrid sol–gel coating agents based on zirconium(IV) propoxide and epoxysilane. *J. Sol-Gel Sci. & Tech., 74*, 447 – 459.

Pandis, C., Madeira, S., Matos, J., Kyritsis, A., Mano, J.F. & Ribelles, J.L.G. (2014). Chitosan-silica hybrid porous membranes. *Materials Sci. & Engineering C*, *42*, 553 – 561.

Ravi Kumar, M.N.V, Bakowsky, U. & Lehr, C.M. (2004). Preparation and characterization of cationic PLGA nanospheres as DNA carriers. *Biomaterials*, *25*, 1771 – 1777.

Rinaudo, M. (2006). Chitin and chitosan: properties and applications. *Progr. Polymer Sci., 31*, 603 – 632.

Sadaq, S.I., Seetharamaiah, N., Pamar, J.D. & Mehar, A. (2013). Characterization and mechanical behavior of composite material using FEA. *Int. J. Eng. Res., 2*, 125 – 131.

Shirosaki, Y., Tsuru, K., Hayakawa, S., Osaka, A., Lopes, M.A., Santos, J.D., Costa, M.A. & Fernandes, M.H. (2009). Physical, chemical and in vitro biological profile of chitosan hybrid membrane as a function of organosiloxane concentration. *Acta Biomaterialia*, *5*, 346 – 355.

Su, Y.-C., Wang, C.-Y. & Don, T.-M. (2014). Mechanical properties and fracture behavior of dual-curable epoxyacrylate composites filled with different functionalized silica particles. *Polymers & Polymer Composites*, *22*, 31 – 39.

Valášková, M., Rieder, M., Matějka, V., Čapková, P. & Slíva, A. (2007). Exfoliation/delamination of kaolinite by low-temperature washing of kaolinite-urea intercalates. *Appl. Clay Scie.*, *35*, 108 – 118.

Wang, S.-F., Shen, L., Zhang, W.-D. & Tong, Y.-J. (2005). Preparation and mechanical properties of chitosan/carbon nanotubes composites. *Biomacromolecules*, *6*, 3067 – 3072.

Wang, X., Du, Y., Luo, J., Lin, B. & Kennedy, J.F. (2007). Chitosan/organic rectorite nanocomposite films: structure, characteristic and drug delivery behaviour. *Carbohydrate Polymers*, *69*, 41 – 49.

Xie, H., Jia, Z., Huang, J. & Zhang, C. (2011). Study on the preparation of superabsorbent composite of chitosan-g-poly (acrylic acid)/kaolin by in-situ polymerization. *Int. J. Chem.*, *3*(3), 69 – 74.

Zha, F., Li, S., Chang, Y. & Yan, J. (2008). Preparation and adsorption kinetics of porous γ-glycidoxypropyltrimethoxysilane crosslinked chitosan-β-cyclodextrin membranes. *J. Membrane Sci. 321*, 316 – 323.

Zhang, B., Li, Y., Pan, X., Jia, X. & Wang, X. (2007). Intercalation of acrylic acid and sodium acrylate into kaolinite and their in situ polymerization. *J. Phys. & Chem. Solids*, *68*, 135 – 142.

✉ **Edi Pramono**
Chemistry Department
Faculty of Mathematics and Natural Science
Sebelas Maret University
36A, Jl. Ir. Sutami
Surakarta, Indonesia
E-mail: edi.pramono.uns@gmail.com