

Preparation of Silanized-Chitosan via Solution-Casting Method: Study on the Mechanical, Water Adsorption and Swelling Area Properties

O A Saputra¹, W A Lestari¹, M Nauqinida¹, W E Prasetyo¹, D S Handayani¹

¹Chemistry Department, Faculty of Mathematic and Natural Sciences, Sebelas Maret University Surakarta, Indonesia.

E-mail: oziadisaputra@student.uns.ac.id

Abstract. Silanizing of chitosan has been prepared using the solution-casting method. The silanizing agent is 3-glycidiloxypropyl trimethoxysilane (GPTMS). The compounding of chitosan/GPTMS was conducted for 1 hour at 80°C by varying GPTMS compound (5-20 wt %) and the final product is referred as Cs/GPTMS. The mechanical properties, including tensile strength, elongation and young modulus were tested according to ASTM D882-02. The addition of 15 % of GPTMS was able to improve the tensile strength value up to 55.66%. However, the elongation decreased to 64.89 %. Moreover, the water adsorption and swelling area properties were studied in this research to evaluate the material ability. Both of water adsorption and swelling area properties decreased by the presence of GPTMS in chitosan. The Cs/GPTMS materials to be promising candidate materials for plastic engineering due to their properties meet the requirement.

1. Introduction

Today, plastic technology has interestingly attention worldwide. Most important fields, including packaging, automotive, aerospace, house hold appliance, electronic device, and others are based on plastics [1-3]. Plastic as composites become strong hold in daily life in many application due their properties such as light weight, good mechanical properties, transparency, and low cost [4-6]. Polypropylene, polyethylene, polyvinyl chloride, and others based plastics are obtained from petroleum resources, becomes limited due to their availability in the nature decrease. Moreover, petroleum based plastics are non-biodegradable and most of them end up overburdening on landfill. This can lead to be a pollution and non-environmental friendly [7-8]. Environmental and sustainable issue challenged research and technology to replaced petroleum based plastic with the biodegradable material, like bioplastic. Lately, the shift toward sustainable production systems has focused attention on bioplastics. Bioplastics are types of plastics that are made from plant sources and/or can be decomposed by microbial activity. It has more environmental friendly properties and their using same as conventional plastics [8].

Production and export of shrimp in Indonesia continues to increase and cause of increasing of waste shrimp shells. Waste of shrimp heads are reaching 35-50% from the total weight of the shrimp

¹ Chemistry Department, Faculty of Mathematic and Natural Sciences, Sebelas Maret University Surakarta, Indonesia.



and have chitin content of 60-70%. Chitin can be processed into chitosan with a yield of 15-20%. Chitosan has biodegradable, renewable and non-toxic properties [9-10]. Thus, chitosan can be one of the promising alternative candidates for bioplastic fabrication due their environmentally friendly and biodegradation properties. In recent years, significant attention has been given to a new class of bioplastic materials represented by chitosan bioplastic as the promising alternative to conventional plastics due to their superior properties. However the main drawback of chitosan films with their combined properties has been restricted due to their inherent water sensitivity and relatively low stiffness and strength, especially in moist environments [11]. Numerous studies have focused on improving the physical properties of biopolymer based films by decreasing the hydrophilicity and improving the mechanical properties. Modification of chitosan to improve the mechanical properties has been carried out by several researchers, such as the addition of filler compound [12], fiber reinforcement [13], crosslinked [14] and other. Beside its poor mechanical properties, chitosan also has a high water uptake. In several applications, such as bio-plastic packaging, this water absorption capability must be reduce without eliminating the biodegradation properties. Consequently, chitosan modification is necessary in order to improve the adhesion between fibre and matrix which yield composites with poor properties. Moreover, for the mechanical properties improvement and decrease the water adsorption as bioplastics which compare to virgin chitosan [26-29].

Silane coupling agent, 3-glycidiloxypropyl trimethoxysilane (GPTMS) have methoxysilane group that able to form a siloxane network [15]. The presences of this network are able to act as cross-linking in the polymer chain and improve the mechanical properties. Saputra et. al. [16] has been reported that the addition of hybrid filler GPTMS against polypropylene/empty fruit bunch fiber (PP/EFB) bio-composites was able to increase the tensile strength and Young's modulus but decrease the elongation while providing the degradable properties of the plastic. It also investigated that the presence of GPTMS can reduce the water uptake of PP/EFB bio-composites. So in this study will be investigated the effect of GPTMS on mechanical properties and water absorption of chitosan membrane as an environmentally friendly bioplastics and behave like conventional plastic.

2. Experimental

3. 1. Materials

Materials which used for the study includes chitosan (Cs) was supplied from PT BIOTECH SURINDO, Indonesia with medical grade, Acetic acid (CH_3COOH) and sodium hydroxide (NaOH) were analytical purity grade and purchase from Merck. 3-glycidiloxypropyl trimethoxysilane (GPTMS) was obtained from Sigma Aldrich. Acetic acid used in this study was prepared in 1.5% of concentration. Sodium hydroxide also prepared in 1 M of concentration.

3. 2. Fabrication of Bio-Plastic Chitosan/GPTMS

About 2 gr of chitosan was dissolved in 1.5% acetic acid (100 mL) using three neck bottom flask. The solution process was performed in room temperature about 1 hour. The addition of acetic acid was slowly until gel-solution formed. Then, temperature was raised to 70 °C under stirring condition. Amount of GPTMS (0, 5, 10, 15 and 20 %wt) was added and the mixture was stirred for 1 hour. The mixture then poured in stainless steel template and dried at 50 °C for 24 hours. The bio-plastic Cs/GPTMS washed with 1 M NaOH for acetic acid removal, then washed again several times with distilled water. The bio-plastic dried at room temperature for one to two days. The product was characterized using FTIR, also for raw material (chitosan).

2.3. Mechanical and Swelling Test of Cs/GPTMS Bio-plastic

Mechanical properties of bio-plastic were tested with according to ASTM D882-02 standard method. The mechanical properties which measured in this study are tensile strength (MPa), elongation (%) and Young's Modulus (MPa). The applying cross head speed is 10 mm/min and the thickness of the sample is 4 mm.

Samples with initial weight (W_o) such as chitosan, Cs/GPTMS (0-20%) immersed in a container of water with a variety of immersion time 0, 24, 48 and 72 hours. Sample weight after soaking was recorded as the final weight (W_i), then determined the percentage of water absorption capacity (%WA) by equation 1.

$$\%WA = \frac{(W_i - W_o)}{W_o} \times 100\% \dots\dots\dots(1)$$

3. Result and Discussion

3.1. Chemical Interaction of Cs/GPTMS Bio-plastic

Manufacturing of Cs/GPTMS bio-plastic has been successfully performed via casting solution method. Chemically, chitosan and GPTMS were able to perform chemical interactions. Since, both chitosan and GPTMS had an active group as their active site for chemically reaction. While, chitosan has hydroxyl and amine group. In other hand, GPTMS has unstable oxirene ring as it active group [15]. The chemical interaction possibility between chitosan and GPTMS was showed in Fig 1, where the opening bond of the oxirene group cause the lone pair electrons of the hydroxy group in chitosan was possible to attract with the carbon atom partial positive of oxirene group. Another possibility may also occur, where the amine group of chitosan can undergo chemically interactions with GPTMS, due nitrogen atom in the amine group has a lone-pair electrons that can be donated to a carbon atom partial positive in the GPTMS compound.

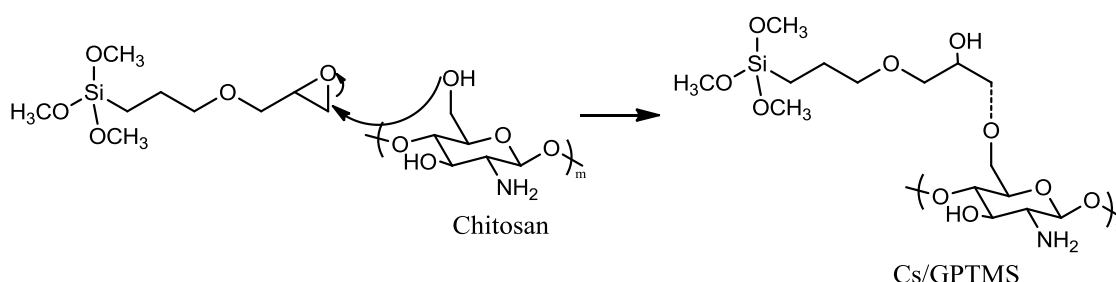


Figure 1. Possible chemical interaction between Chitosan and GPTMS

To proving the existence of chemical interaction between chitosan and GPTMS can be analyzed using FTIR spectroscopy. Fig 2 shows a shift of the $-NH_2$ typical peak from 3080 cm^{-1} and 2886 cm^{-1} to 3395 cm^{-1} and 3141 cm^{-1} , as well as the loss of absorption at 3581 cm^{-1} which is the characteristic band of hydroxy group (OH), was indicate that chitosan was chemically interaction with the other compound, in this case referred as GPTMS. This chemical interaction formed the ether linkage, which is evidenced by the appearance of absorption at 1020 cm^{-1} which characteristic of the ether absorption peak. In addition, a strong absorption at 1087 cm^{-1} which is the typical peak of the Si-O-Si group also shifted to 1050 cm^{-1} in the FTIR spectrum of Cs/GPTMS. Even more interesting is the disappearance of the medium absorption at 910 cm^{-1} which is the characteristic absorption oxirene group, thus strengthening the allegations of chemical interactions between hydroxyl groups of chitosan and oxirene group on GPTMS. Therefore, the loss of the hydroxyl absorption of chitosan and oxirene on GPTMS proved that both these groups interact chemically in accordance with the illustration in Fig 1.

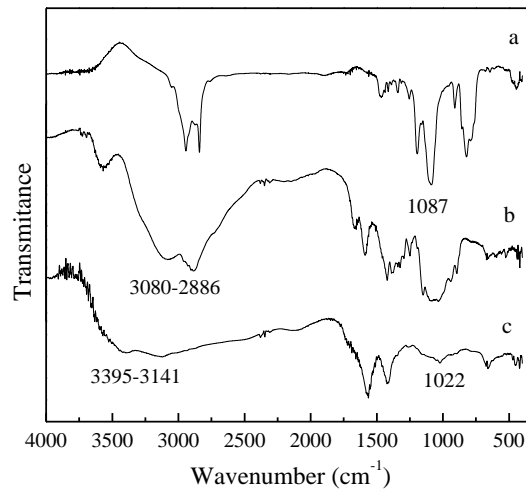


Figure 2. FTIR spectrum of (a) GPTMS, (b) chitosan and (c) Cs/GPTMS

3.2. Mechanical Properties of Cs/GPTMS Bio-plastic

The mechanical properties such as tensile strength (TS) of the Cs/GPTMS bio-plastics can be seen in Fig. 3. Chitosan as the polymer matrix has a tensile strength of 24.5 MPa. The addition of the GPTMS with the lowest (5%) and highest (20%) concentration was turned out to have an impact on the decreasing of tensile strength which compare to virgin chitosan by 14.48% and 6.79%, respectively. It was possible due at low concentrations, distribution of GPTMS was uneven, thus impact on the decreasing TS value. Whereas at high concentrations (20%), the GPTMS was gathering at a certain point and caused this point become brittle. So, in the tensile strength testing, the C4 formula has lower tensile strength than chitosan, which is caused by the ease of sample to fracture. However, the C2 (GPTMS 10%) and C3 (GPTMS 15%) formulas was led to the increase of the TS value, which is 9.95% and 55.66%, respectively. The increasing of the TS value was possible by homogenous distribution of the GPTMS on chitosan matrices. In addition, GPTMS also can formed a crosslink network, thereby increase the mechanical strength of the Cs/GPTMS bio-plastic [14,15]. The significantly increasing of the TS value was obtained in the C3 formula (GPTMS 15%). This allows, the addition of GPTMS can form a good siloxane network, so it has a high tensile strength due to strong chemical interaction between the matrix of chitosan by the presence of a cross-link network of the silane groups [16]. Fig. 4 showed the possibility of siloxane network which acts as crosslinker in the Cs/GPTMS bio-plastics.

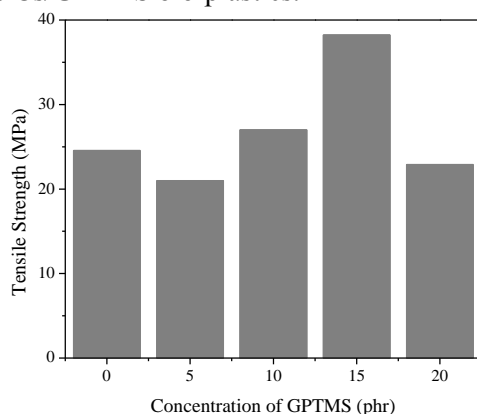


Figure 3. Tensile strength of composites

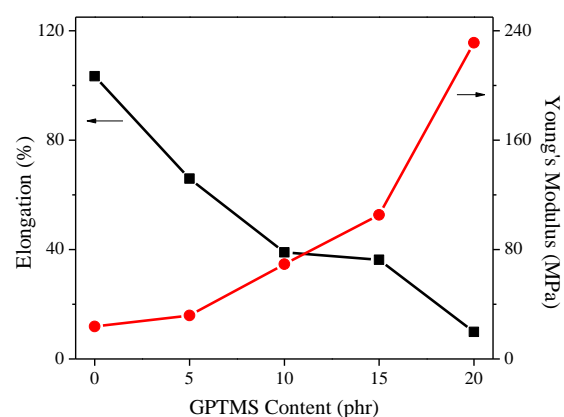


Figure 4. Elongation and YM of composites.

The existence of the siloxane network as a crosslinker turned out to have an impact on the stiffness of the Cs/GPTMS bio-plastics. It can be seen in Fig. 4., that the increasing of GPTMS content in the chitosan matrix reduced significantly of chitosan elongation. Decreasing of elongation or elasticity properties of this material prove that GPTMS able to act as a crosslinker agent causing decreased elasticity of the chitosan due to the decreasing of polymer chain flexibility. The addition of 20% GPTMS was cause to lowering of the elongation percentage by 90.42%. This is because, not only to forming crosslinking, the uneven distribution of GPTMS at high concentration may also conducted at a certain point that can decrease the elasticity of the chitosan.

Stiffness of the Cs/GPTMS bio-plastics increased with increasing of GPTMS content. Addition of the excess amount GPTMS was given the brittle nature of the chitosan matrix, wherein the Young's modulus value of the C4 formula (GPTMS 20%) increased by 873.32% or 231.2 MPa. While the GPTMS 15% (C3) composition was increase to 343.28% or 105.3 Mpa. The increasing of YM value on C3 is not as significant in the C4, it is possible at C3 flexibility of the polymer chain of the chitosan was greater than C4, where the presence of the silane as crosslinker group at C3 is less than the C4 so that the level of rigor on C4 higher than C3.

3. 3. Water Absorption Properties

It is very significant to study in detail the water absorption behavior in order to measure not only the consequences that the water absorbed may have, but also how this water uptake can be minimized in some way. The water absorption testing was intended to determine of bio-degradation properties of the Cs/GPTMS bio-plastics which seen from their ability to absorb water. Water absorption testing on this research was carried out for 4 days, where every 24 hours, the weight after immersion was recorded. The weight increasing of the bio-plastics after soaking is demonstrate of easiness to degrade due high surface polarity. The water adsorption of various bioplastics is described in Fig. 5. Chitosan (C0) has high water adsorption percentage which is 88.9% after saturated condition. This is due to chitosan is hydrophilic polymer, thus the water is easy to adsorbed. However, after modification with 15% GPTMS, the water adsorption decreased to 555.0% at immersing time 4 days (Water adsorption C3= 13.57%). The addition of GPTMS which high concentration was able to decreased the water adsorption. This is due to, the presence of siloxane network in chitosan surface can act as water barrier due their hydrophobic properties.

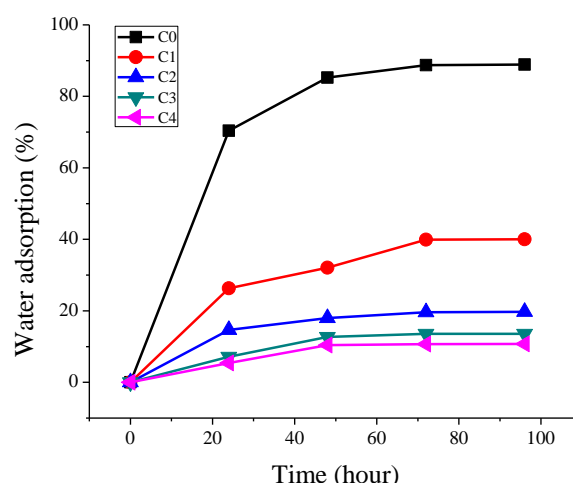


Figure 5. Water adsorption of various bioplastic at different contact time

Chitosan has degradable properties (indicated by the ability of water absorption), non-toxic and environmentally friendly [17,18]. Chitosan also classified as a biocompatible material [19]. Therefore,

after water adsorption testing, chitosan without the addition of GPTMS has very high water absorption ability. However, the higher addition of the GPTMS content was able to reduce water absorption ability of chitosan, but not to eliminate the water absorption ability of the material. Although the percentage of water absorption of bio-plastics chitosan filled with GPTMS was decreased, but the Cs/GPTMS still be categorized as bio-degradable material due to have water absorption ability though not significant as chitosan. The low water absorption capabilities of Cs/GPTMS bio-plastics due to the presence of crosslinked between the chitosan, causing the material more dense and the water was difficult to get in on to chitosan matrix.

4. Conclusion

The addition of the GPTMS on chitosan matrices was successfully achieved due both active groups of the raw materials can perform chemically interactions as evidenced by losing of typical absorbance band of the each functional group in Chitosan and GPTMS. The addition of GPTMS has affected on the mechanical properties of the chitosan, while GPTMS with 15% content was significantly improve the tensile strength value, by 55.66% compared to the virgin chitosan. Moreover, the addition of GPTMS also increased the rigidity of the virgin chitosan by the presence of siloxane network as cross-linker. The existence of this cross-linker also decreased the water absorption properties or bio-degradation ability. Nonetheless, Cs/GPTMS bio-plastics still categorized as bio-degradable material because it still has the water absorption ability but not significant like virgin chitosan.

Acknowledgement

Authors would like to acknowledge to Indonesian Directorat General of Higher Education for financial support from Program Kreatifitas Mahasiswa (PKM) 2015.

References

- [1] Jeyanthi S, Rani J J 2012 *Int. J. Physc. Sci.* **7** 5765
- [2] Hufenbach W, Bohm R, Thieme M, Winkler A, Mader E, Rausch J, Schade M 2011 *Mater. Des.* **32** 1468
- [3] Tall S, Albertsson A C, Karlsson S 2001 *Polym. Adv. Technol* **12** 279
- [4] Garces J M, Moll D J, Bicerano J, Fibiger R, Mcleod D G 2000 *Adv. Mater* **12** 1835
- [5] Friedrich K, Almajid A A 2013 *Appl. Compos. Mater* **20** 107
- [6] Xiao K Q, Zhang L C, Zarudi I 2007 *Compos. Sci. Technol* **67** 177
- [7] Suharty N S, Ismail H, Dihadjo K, Nizam M, Firdaus M 2014 *Adv. Mater. Res* **950** 18
- [8] Storz H, Vorlop K D 2013 *App. Agric. Forestr. Res* **63** 321
- [9] Pal P, Banat F 2014 *J. Nat. Gas Sci Eng* **18** 227
- [10] Chao A C, 2008 *J. Membrane Sci* **311** 306
- [11] Prashanth K V, Harish K L, Shamalab T R, Tharanathan R N 2005 *Int. Biodeter. Biodegr* **56** 115
- [12] Spinks G M, Shin S R, Wallace G G, Whitten P G, Sun I Kim S I, Kim S 2006 *J Sensor. Actuat. B-Chem* **115** 678
- [13] Albanna M Z, Bou-Akl T H, Walters III H L, Matthew H W T 2012 *J. Mech. Behav. Biomed* **5** 171
- [14] Lopez C R, Bodmeier R 1997 *J. Control. Release* **44** 215
- [15] Ren L, Tsuru K, Hayakawa S, Osaka A 2002 *Biomater* **23** 4765
- [16] Saputra O A, Prasetyo W E, Pramono E, Handayani D S, Kurnia, Pujiasih S, Arifagama I 2015 *Prosiding Seminar Nasional Kimia* 181
- [17] Kim J H, Jegal J, Lee K H J 2003 *Membrane Sci* **213** 273
- [18] Kumar M N V R, Muzzarelli R A A, Muzzarelli C, Sashiwa H, Domb A 2004 *J. Chem. Rev.* **104** 6017
- [19] Jameela S R, Jayakrishnan A 1995 *Biomater* **16** 769