Characteristic of nanoparticle-chitosan system: solution and thin film study

M Nasir* and R I Sugatri

Research Unit for Clean Technology, Indonesian Institute of Sciences (LIPI) Komplek LIPI Bandung, Jalan Sangkuriang, Gedung 50, Bandung 40135, Indonesia

*Email: mnasir71@yahoo.com

Abstract. Nanoparticle (NP)-chitosan system is very important composite nanomaterial related to their unique properties and applications. In this work, chitosan was composited by two types of nanoparticle i.e. silver nanoparticles (Ag (NP)) and activated nanocarbon (ANC), respectively. The presence of nanoparticle in chitosan system gave effect to viscosity of solution and hydrophilicity of thin film. In Ag (NP)-chitosan system, the addition of 10, 15 and 25% (v/v) Ag (NP) suspension increased their viscosity. Different result was obtained for ANC-chitosan system, where addition of 0.1, 0.5 and 1.5% (w/v) of ANC decreased viscosity of solution. This property affected distribution of the nanoparticles in chitosan thin film and its hydrophilicity. The chitosan thin film nano-composite had higher hydrophilicity than pure chitosan. Infrared spectrum analysis showed that nanoparticles which were composited in chitosan system gave shifting in O-H stretching vibration, C=O stretching vibration (amide I) and N-H bending and C-N stretching (amide II).

1. Introduction

Chitosan (β (1→4) links 2- amino-2-deoxy-D-glucopyranose) is the most important derivate of chitin which is soluble in acidic aqueous media and is used in many applications such as food, cosmetic, biomedical and pharmaceutical applications [1]. Chitosan has antibacterial activities and it has been proven excellent building blocks to produce films with controlled molecular architecture, allowing for synergy between distinct materials [2]. Linear structure of this polysaccharide renders their film tough, flexible and transparent [3]. Chitosan thin film is used as one of the food packaging material in biopolymer [4] and antibacterial [5]. To improve pure chitosan film properties, it can be modified by adding distinct materials such as nanoparticle or other polymers.

The composite of chitosan with other substance such as CuO, Cu nanoparticle, Ag nanoparticle, nanocarbon, carbon nanotubes, graphene oxide, montmorillonite, ZnO and TiO2[5–16] will give effect to its function and characteristics. The addition of metal particles such as silver or copper into polymer produced novel antimicrobial materials [17]. It was reported by Tamayo et al [18] that copper-polymer nanocomposite showed excellent antimicrobial properties. The addition of CuO in chitosan system enhanced tensile strength and stiffness [6]. Furthermore, CuO-chitosan thin film can be used as a photocatalyst to degrade organic contaminants [7] and enhanced the antibacterial activities [10]. Raghavendra et al [5] combined two different materials such as chitosan and Ag nanoparticles. The antibacterial properties of Ag-chitosan nanocomposite films more effective inhibited gram-positive and gram-negative microorganisms than pure chitosan. Montmorillonite-CuO composite was successfully used to modify of the chitosan film. The composite film showed intense antibacterial activity and
improved mechanical properties more than 50% compared with pure chitosan [19]. In nanocarbon system, modified carbon nanoparticle into chitosan film can be used for application in sensing, electrocatalysis, or adsorption [13]. In these cases, chitosan was used in many applications due to abundant chelating groups including primary and secondary hydroxyl groups as well as highly reactive amino group.

In this work, we combined nanoparticle i.e. silver nanoparticle (Ag (NP)) and activated nanocarbon (ANC) into chitosan solution, respectively, to produce nanoparticle-chitosan thin film. The presence of other materials in chitosan film gave effect to their characteristics such as contact angle, the porous of the film and roughness [4,5,20].

The characteristic of nanoparticle-chitosan thin films composite was observed including the viscosity of solution composite, fluorescence microscope of thin film to observe distribution of nanoparticle in chitosan system, IR spectrum, the surface morphology by Scanning Electron Microscopy (SEM) and water contact angle.

2. Experimental

2.1. Materials
Chitosan medical grade (94.50% deacetylated) was obtained by PT. Biotech Surindo. Tri-sodium citrate dehydrate and silver nitrate were purchased from Merck. Carbon granule, potassium hydroxide and acetic acid glacial were purchased from PT. Brataco.

2.2. Synthesis of silver nanoparticle (Ag (NP))
An amount of 1mM silver nitrate and 1% (w/v) tri-sodium citrate with ratio 10:1 (v/v) were dissolved in distilled water, respectively then mixed. The mixture was heated in a modified microwave oven (Panasonic, 900W) which was connected with refluxing system in low condition for 5 min.

2.3. Activation of nanocarbon
Carbon granule was grinded, sieved and then milled by a High Energy Milling E3D (HEM-E3D) for 25 h to obtain nanocarbon. Nanocarbon was activated by using 20% (w/v) potassium hydroxide which had been dissolved in distilled water with ratio nanocarbon:KOH solution 1:4 (w/v). The mixture was stirred for 24 h at room temperature, neutralized with distilled water, then oven-dried.

2.4. Synthesis of nanoparticle-chitosan system
2.4.1. Ag (NP)-chitosan solution. Ag (NP)-chitosan solution was made from Ag (NP) suspension in chitosan system of 5, 15, and 255% (v/v). The 2.5 g of chitosan (2.5% w/v) was dissolved in 75, 85 and 95 mL acetic acid (2% v/v), respectively. The mixture was stirred for 12 h at room temperature. The Ag (NP) suspension was added into chitosan solution 5 mL, 15 mL and 25 mL, respectively, then stirred for 1 h at room temperature.

2.4.2. ANC-chitosan solution. ANC-chitosan solution was made from ANC in chitosan system of 0.1, 0.5 and 1.5% (w/v). The 2.5 g of chitosan (2.5% w/v) was dissolved in 100 mL acetic acid (2% v/v) followed by stirring for 12 h at room temperature. The ANC of 0.1, 0.5 and 1.5 g were added into 100 mL of chitosan solution, respectively, stirred for 1 h then sonicated for 1 h.

2.4.3. Preparation of thin film. All bubbles in the nanoparticle-chitosan were eliminated before casting onto mold which was made up of flat glass and coated by aluminium foil. The solutions were poured into mold and allowed to dry at 50-60°C for 12 h.

2.5. Characterization
The viscosity of nanoparticle-chitosan solution was determined by Brookfiled Viscometer DV-I Prime. The thin film composite was characterized by fluorescence microscope Meiji Techno America Japan to
observe distribution of nanoparticle in chitosan system. Fourier Transform Infrared Spectroscopy (FTIR) Shimadzu IR Prestige 21 was used to analyse the interaction of nanoparticle and chitosan. Surface morphology was analyzed by Scanning Electron Microscopy (SEM) SEMSU3500. Calculating water contact angle used the equation: \[ \frac{\theta}{2} = \tan^{-1}\left(\frac{h}{d}\right) \] with \( \theta \) = contact angle, \( d \) = diameter, \( h \) = height. Pure chitosan thin film was characterized for comparison.

3. Results and discussion
Chitosan membrane is the ability of beta-(1,4)-linked D glucosamine with certain degree deacetylation to re-form supramolecular structures via hydrogen bonding after evaporation of the solvent [20]. Chitosan thin films composite were developed by blending nanoparticle and chitosan with varied concentration.

3.1. Viscosity analysis
Silver nanoparticles (Ag (NP)) were synthesized by microwave method. The method can produce Ag which has smaller particles and high stability with faster reaction [21–26]. In the nanoparticle-chitosan system, nanoparticles were added into chitosan solution to disperse nanoparticles in chitosan matrix. The addition of difference of nanoparticles into chitosan solution gave a different effect on viscosity.

![Figure 1. Correlation between concentration of nanoparticle-chitosan solution and viscosity.](image)

In Figure 1, it showed that the addition of Ag (NP) suspension in10%, 15%, and 25%-chitosan solution enhanced viscosity value to 148.60, 154.85, and 198.55 cP for Ag (NP), respectively compared with pure chitosan solution of 136.90 cP. This was caused by the well dissolution of mixture consisted of acidic chitosan solution (pH < 6.5) and acidic Ag (NP) suspension (pH 5.23 to 6.25) [27]. Alfrey et al [28] explained that the polymer in a favorable solvent will exhibit a high intrinsic viscosity. The long chain molecule of the polymer will be surrounded by a solvated hull which tends to prevent polymer-polymer contacts. Uncurled configurations are favored, and the mean value of any property represents a more extended shape than the unbiased mean. Since an extended of uncurled configuration is associated with a high intrinsic viscosity.
Figure 2. Fluorescence microscope image of nanoparticle-chitosan thin film composite (100x).
Figure 3. SEM image of pure chitosan and nanoparticle-chitosan composite thin films.
Different case occurred in ANC-chitosan solution of which the viscosity of solution composite depends on the concentration of ANC. Volume fraction, heterogeneous, and homogeneous mixtures affected on viscosity [29]. A particle with sizes with greater volume fractions has low viscosity value and viscosity of the heterogeneous mixture is greater than the homogeneous mixture [30]. When ANC was added into chitosan solution, it disperses in the chitosan solution. Nevertheless, ANC-chitosan solution formed a heterogeneous mixture. It shows in Figure 2 some aggregates of ANC in chitosan solution and it did not distribute well. Boylu et al [30] reported that high volume fractions in the system provided more void space which caused lower viscosity and greater fluidity. Carbon with low volume fractions exhibits a rather compacted structure, and thus the fluid that forms a suspension with the carbon cannot easily enter the intergranular void spaces in carbon. Even if the fluid enters those void spaces it cannot move or flow freely within the occupied sites. In ANC-chitosan solution, increasing activity of polymer-polymer contacts with lower fraction volume of ANC resulted in greater resistance. This caused increasing its viscosity of 117.40, 124.30, 165.05 cP for 1.5, 0.5, and 0.1% (w/v) ANC in chitosan solution.

3.2. Nanoparticle-chitosan thin film composite
Fluorescence microscope of chitosan and nanoparticle-chitosan thin films is shown in Figure 2. Nanoparticle dispersed in chitosan matrix.

Different from ANC-chitosan film, increasing concentration of nanoparticle in Ag (NP)-chitosan thin film tends to disperse in chitosan matrix well. The morphology of nanoparticle-chitosan thin film composite is shown in Figure 3. SEM image clearly shows the coarse surface of pure chitosan thin film with the presence deposit of chitosan. On the other hand, the surface of Ag (NP)-chitosan thin film composite seems smooth also with aggregates and deposited on the surface.

Figure 3c shows morphology of Ag(NP)-chitosan thin film composite. The composite morphology has flowers-like shape. In this case, the polymer acts as capping agent on the surfaces of Ag (NP) to form flowers-like [31,32]. It was suggested that the morphology of ANC-chitosan thin film composite depends on the addition of ANC into chitosan matrix. The increase of ANC caused the rough surface and tends to form aggregate.

3.3. Infrared spectrum analysis
The chemical compositions of chitosan and the nanoparticle-chitosan composite thin films were examined by FTIR spectroscopy. The spectrum of pure chitosan thin film at 3381.21 cm⁻¹ showed the vibration of O-H, at 2933.73 and 2893.22 cm⁻¹ for bending of C-H, at 1629.85 cm⁻¹ stretching vibration of C=O (amide I), at 1546.91 cm⁻¹ as bending vibration of N-H and stretching of C-N (amide II), at 1409.96 cm⁻¹ bending CH₂ in CH₂OH, 1153.43 and 1091.71 vibration of C-O-C.

In Ag (NP)-chitosan thin film composite, 3381.21 cm⁻¹ peak of O-H stretching vibration of pure chitosan was shifted to 3360.00 cm⁻¹ and it became broader. The peak at 1629.85 cm⁻¹ due to C=O stretching vibration (amide I) was shifted to 1624.06 cm⁻¹ and the 1546.91 cm⁻¹ peak of N-H bending and C-N stretching (amide II) was shifted to 1554.63 cm⁻¹. The reaction involved the Ag (NP) was bound by amino and hydroxyl group of chitosan chain [33]. The presence of ANC in ANC-chitosan thin film composite caused the lower intensity if compared with pure chitosan thin film. In addition, the shifting to 3385.07, 1620.21, and 1523.76 cm⁻¹ showed O-H stretching, C=O stretching (amide I), and N-H bending and C-N stretching vibration (amide II), respectively.

Nanoparticles existence in chitosan system caused shifting in O-H stretching vibration at 3300-4000 cm⁻¹, C=O stretching vibration (amide I), and N-H bending and C-N stretching (amide II), indicated the interaction between nanoparticle with chitosan [34,35].
Figure 4. IR spectrum of nanoparticle-chitosan thin film composite.

Figure 5. IR Spectrum of Ag (NP)-chitosan with concentration of Ag (NP) (a) 10%, (b) 15%, (c) 25%.
The concentration of nanoparticles which was added into chitosan solution also gave an effect toward its IR spectrum. Figure 5 shows that increasing concentration of Ag (NP) caused shifting to lower wave number. The O-H stretching vibration of pure chitosan was 3381.21 cm\(^{-1}\) shifted to 3373.50, 3375.43, and 3360.00 cm\(^{-1}\) for addition of Ag (NP) 10%, 15%, and 25%, respectively. Increasing the concentration of nanoparticle also changed the band of O-H stretching vibration. The O-H vibration spectrum becomes wider. The N-H bending and C-N stretching (amide II) vibration band peak of composite also shifted to 1548.84, 1535.34, and 1554.63 cm\(^{-1}\) for Ag (NP) 10%, 15%, and 25%, respectively. The vibration band peak of pure chitosan thin film is 1546.91 cm\(^{-1}\). It can be assumed that there was an interaction between the nanoparticle with O-H and N-H in chitosan.

3.4. Contact angle analysis
The hydrophilicity of nanoparticle-chitosan thin film composite was observed by measuring the contact angle of water droplet on the surface of the thin film. Every type of nanoparticles in chitosan matrix gave a different effect on water contact angle.

![Figure 6. Correlation between concentration of nanoparticle-chitosan thin film and water contact angle.](image)

| Concentration of nanoparticle-chitosan thin film | Water contact angle (°) |
|-----------------------------------------------|--------------------------|
| Chitosan                                      | 70                       |
| Ag (NP) 10%-chitosan                          | 66                       |
| ANC 0.1%-chitosan                             | 68                       |
| Ag (NP) 15%-chitosan                          | 69                       |
| ANC 0.5%-chitosan                             | 70                       |
| Ag (NP) 25%-chitosan                          | 71                       |
| ANC 1.5%-chitosan                             | 72                       |
Pure chitosan thin film is a hydrophilic membrane with a contact angle of water of 73.89°. The addition of nanoparticle in chitosan matrix decreased contact angle of water droplet. In Ag (NP)-chitosan thin film composite, increasing concentration of Ag (NP) in chitosan matrix tended to increase the hydrophilicity. Mohdy et al [36] also reported that adding Ag (NP) in polymer increased the hydrophilicity of membrane composite. The water contact angle of Ag (NP) 10, 15, and 25% (v/v) was 71.34, 63.80, and 67.58°, respectively. Nevertheless, inconsistent decrease of contact angle in respective concentration was caused by the imperfect of Ag (NP) distribution in chitosan matrix. The affinity between Ag (NP) and water might be possible to the high hydrophilicity.

On the other hand, as for ANC-chitosan thin film composite, the addition of ANC in chitosan matrix caused the hydrophilicity. The water contact angle of ANC 0.1, 0.5, and 1.5% (w/v) in chitosan matrix was 66.64, 64.33, 68.94°, respectively. Increasing concentration of ANC affected the surface roughness. ANC 1.5%-chitosan shows higher roughness than ANC 0.1%-chitosan thin film composite. The higher surface roughness composite will give higher water contact angle. However, ANC was not distributed well in chitosan matrix (see Figure2), due to high hydrophilicity of ANC 0.5%-chitosan if compared with ANC 0.1%-chitosan. Depends on the concentration and type of nanoparticle, the addition of nanoparticle in chitosan system increased its hydrophilicity.

4. Conclusion
Nanoparticle-chitosan thin film composite was synthesized successfully by mixing nanoparticle and chitosan solution. The concentration and type of nanoparticle affected the viscosity and hydrophilicity. In Ag (NP)-chitosan system, increasing concentration of Ag (NP) in chitosan matrix decreased the viscosity of solution composite and enhanced the hydrophilicity. In ANC-chitosan system composite, increasing concentration of nanoparticles decreased the viscosity of the solution. In addition, the presence of ANC tended to form aggregation on thin film composite and caused roughness as well decreased the hydrophilicity.

Acknowledgments
The authors gratefully acknowledge to Ministry of Research, Technology and Higher Education of the Republic of Indonesia which has funded this research.

References
[1] Rinaudo M 2006 Prog. Polym. Sci. 31 603-32
[2] Pavinnato F J, Caseli L and Oliveira O N 2010 Biomacromol 11 1897-908
[3] Vieira M G A, da Silva M A, dos Santos L O and Beppu M M 2011 Eur. Polym. J. 47 254-63
[4] Sivaselvi K and Ghosh P 2017 Mater. Today: Proc. 4 442-51
[5] Raghavendra G M, Jung J, Kim G and Seo J 2016 Int. J. Biol. Macromol. 84 281-8
[6] Zubair M, Najeeb F, Mohamed M, Saeed A, Ramis M K, Abdul Mujeeb M S and Sarojini B K 2014 Amer. J. Polym. Sci. 4 40-5
[7] Kumar P S, Selvakumar M, Babu S G, Jaganathan S K, Karuthapandian S and Chattadhyay S 2015 RSC Adv. 5 57493-501
[8] Nayak V, Jyothi M S, Balakrishna R G, Padaki M and Ismail A F 2015 Chem. Open 4 278-87
[9] Al-Naamani L, Dobretsov S and Dutta J 2016 Innovative Food Sci. Emerging Technol. 38 231-7
[10] Widiarti N, Sae J K and Wahyuni S. 2017 IOP Conf. Ser.: Mater. Sci. Eng. 172 012036
[11] Shim I-W, Noh W-T, Kwon J, Cho J Y, Kim K-S and Kang D H 2002 Bull. Korean Chem. Soc. 23 563-6
[12] Cioffi N, Torsi L, Ditaranto N, Tantillo G, Ghibelli L, Sabbatini L, Bleve-Zacheo T, D’Alessio M, Zambonin P G and Traversa E 2005 Chem. Mater. 17 5255-62
[13] Rassaei L, Silanpaa M and Marken F 2008 Electrochim. Acta 53 5732-38
[14] Ganesh S, Arockiadoss and Ramaprabhu S 2010 AIP Conf. Proc. 1276 158-62
[15] Qiu J D, Xie H Y and Liang R P 2008 Microchem. Acta 162 57-64
[16] Wang S-F, Shen L, Zhang W-D and Tong Y-J 2005 Biomacromol. 6 3067-72
[17] Palza H, Quijada R and Delgado K 2015 *J. Bioact. Compat. Polym.* **30** 366–80
[18] Tamayo L, Azócar M, Kogan M, Riveros A and Páez M 2016 *Mater. Sci. Eng. C* **69** 1391-409
[19] Nouri A, Yaraki M T, Ghorbanpour M, Agarwal S and Gupta V K 2018 *Int. J. Biol. Macromol.* **109** 1219-31
[20] Clasen C, Wilhelms T and Kulicke W M 2006 *Biomacromol.* **7** 3210-22
[21] Hong Z, Cao Y and Deng J 2002 *Mater. Lett.* **52** 34-8
[22] Volanti D P, Keyson D, Cavalcante L S, Simões, Joya M R, Longo E, Varela J A, Pizani P S and Souza A G 2008 *J. Alloys Compounds* **459** 537-42
[23] El-Trass A, ElShamy H, El-Mehasseb I and El-Kemary M 2012 *Appl. Surface Sci.* **258** 2997-3001
[24] Guo L, Tong F, Liu H, Yang H and Li J 2012 *Mater. Lett.* **71** 32-5
[25] Rejith S G and Krishnan C 2013 *Mater. Lett.* **106** 87-9
[26] Tran T H and Nguyen V T 2014 *Int. Scholar. Res. Notices* **2014** 856592
[27] Mori Y, Tagawa T, Fujita M, Kuno T, Suzuki S, Matsui T and Ishihara M 2011 *J. Nanopart. Res.* **13** 2799-806
[28] Alfrey T, Bartovics A and Mark H. 1942 *J. Am. Chem. Soc.* **64** 1557–60
[29] Elbishari H, Satterthwaite J and Silikas N 2011 *Int. J. Mol. Sci.* **12** 5330-8
[30] Boylu F, Dincer H and Atesok G 2004 *Fuel Proc. Technol.* **85** 241-50
[31] Ali P and Rouollah S 2011 *Mater. Res. Bull.* **46** 1860-5
[32] Ning Z, Dongsheng L and Deren Y 2014 *Nanoscale Res. Lett.* **9** 302
[33] Mori Y, Ono T, Miyahira Y, Nguyen V Q, Matsui T and Ishihara M 2013 *Nanoscale Res. Lett.* **8** 93
[34] Rahnama A and Gharagozlu M 2012 *Opt. Quant. Electron.* **44** 313-22
[35] Ahmad M B, Lim J J, Shameli K, Ibrahim N A and Tay M Y 2011 *Molecules* **16** 7237-48
[36] Mohdy A, Abou-Okeil A, El-Sabagh S and El-Sawy S M 2015 *Int. Scholar. Sci. Res. Innov.* **9** 1149-54