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Preparation of Bio-polyurethane Using Castor Oil and Antibacterial Hybrid Films Thereof with Silver-doped Hydroxyapatite

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Abstract: The hybrid films of bio-polyurethane (Bio-PU) and silver-doped hydroxyapatite (HA-Ag) for breathable and antibacterial textile applications. The Bio-PU was synthesized using a mixture of castor oil based polyol with petroleum based poly(ethylene glycol). Silver doping to hydroxyapatite(HA) was carried out through ion exchange mechanism between calcium ion in HA and silver ion (Ag^+) in aqueous solution of $AgNO_3$. The concentration of Ag^+ was controlled to 100-300 ppm. The existence of silver in HA was proved using SEM-EDS while the silver doping amount was estimated by measuring residual concentration of Ag^+ after doping using ICP-OES. It was found that the hybrid films exhibited excellent antibacterial activity against bacteria of *S. aureu*s and *K. pneumonia* by showing 99.9 % reduction of bacteria.

Keywords: Biomass-based polyol, Castor oil, Bio-polyurethane, Hydroxyapatite, Silver doping, Antibacterial activity

Introduction

Interest in sustainable materials has begun to increase promoting the replacing of petroleum-derived materials with renewable ones in the production of polymers [1,2]. Accordingly, research has been carried out to apply bio-based materials obtained from renewable resources in more fields from a social and environmental viewpoint.

Polyurethane (PU) has been used extensively due to their excellent physical properties and high versatility in chemical structure [3]. PU is generally synthesized from an isocyanate as hard segment and polyol as soft segment. Poly(ethylene glycol) (PEG) and poly(propylene glycol) are the typical polyols basically derived from the petrochemical industry. PU based on vegetable raw materials is attracting worldwide attention [4-6]. As polyol consisting soft segment in PU, various kinds of vegetable oils, like castor, soybean, sunflower and rapeseed oils have been used [7-9]. Among them, castor oil is widely used as a starting material for many industrial products including PU because it is abundant, chemically stable, renewable natural resource, and biodegradable as well as suitable for the synthesis of PU due to inherent hydroxyl groups [10,11].

On the other hand, among diverse application of PU, hydrophilic PU thin films are widely used for the purpose of waterproof and breathable textiles. Moreover, interest in the environment and the value of LOHAS consuming have been increased progressively. Therefore, there is also growing interest in research to impart antibacterial properties to consumer products including textiles. There are many methods for imparting antibacterial properties to textile products. Recently, it has been preferred to combine inorganic nano-particles with low human body toxicity into polymers [12]. Silver (Ag) has been most extensively studied and used to prepare antibacterial materials [13,14] including textiles in the form of nano-silver or silver doped inorganic particles [15]. Among the inorganic particles, hydroxyapatite [HA; $Ca_{10}(PO_4)_6(OH)_2$] and their composites have attracted much attention as materials suitable for preparing materials as a sorbent to heavy metal ions such as Ag [15], Cd^{2+} and Pb^{2+} [16-19].

In this study, the hybrid of bio-polyurethane prepared by using castor oil based polyol and silver doped nano-particles were prepared and characterized properties including antibacterial activity for the application of waterproof and breathable films.

Experimental

Figure 1 shows a schematic diagram for the scope of the study.

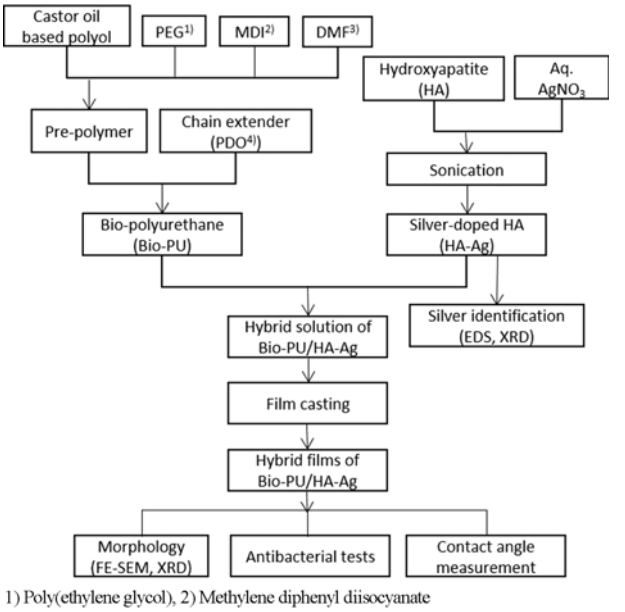

Figure 1. A schematic diagram for the scope of the study.

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Materials

The castor oil-based polyol (Bio-polyol) was purchased from Hokoku Co. (Japan). Table 1 shows the specification of the Bio-polyol. Poly(ethylene glycol)(PEG, M_w=2,000 g/mol), methylene diphenyl diisocyanate (MDI) and silver nitrate ($AgNO_3$) were supplied by Daejung Chemicals & Metals (Korea). Chain extender, 1,3-propanediol (PDO) were purchased from Taewon Syschem Co. (Korea). Hydroxyapatite was supplied by Samjo Co. (Korea).

Table 1 shows the specification of castor oil based polyol.

Table 1. Specification of castor oil based polyol

Properties	Value
Acid value (KOHmg/g)	0.2
Hydroxyl value (KOHmg/g)	55.5
Moisture (%)	0.01
Molecular weight (g/mol)	2,022

Table 2. Feed composition for the synthesis of bio-polyurethane

Polyol		Diisocyanate	Chain extender	Solid content (%)
Bio-polyol (wt%)	PEG (wt%)	MDI (wt%)	PDO (wt%)	
25	35	37	3	30

Table 3. Preparation conditions for the silver-doped hydroxyapatite (HA-Ag)

Sample code	HA amount (g)	$AgNO_3$ aq. solution			Time (hr)
		Ag^+ concentration (ppm)	Solution volume (m*l*)	Ag^+ amount (g)	
HA-Ag(100)	1.0	100	50	5.0×10^{-3}	12
HA-Ag(200)		200		1.0×10^{-2}	12
HA-Ag(300)		300		1.5×10^{-2}	12

Synthesis of Bio-PU Using Castor Oil Based Polyol

The condition of the Bio-PU synthesis is summarized in Table 2. The synthesis comprises two main steps; first, the bio-polyol was mixed with the PEG in dimethyl formamide (DMF), and second, the polyol mixture was reacted with MDI in a 4-neck flask with high speed stirring for 4 hours at 70 °C in nitrogen atmosphere to result in the pre-polymer with isocyanate end groups, followed by reaction with PDO as a chain extender in the presence of a catalyst to produce viscous Bio-PU solution. The solid content was adjusted to 30 wt%. The viscosity of the Bio-PU solution was measured using a spindle #64 of Brookfield viscometer.

Silver Doping of Hydroxyapatite

Silver doping of HA powder was carried out by dipping HA in aqueous solution of silver nitrate ($AgNO_3$) followed by sonication and shaking for 5-720 min at 30 °C. The conditions for the preparation of the silver-doped hydroxyapatite (HA-Ag) are summarized in Table 3. The initial concentration of Ag^+ was controlled in the range of 100-300 ppm. the crystal structure and morphology were analyzed using XRD (X-MAX/2000-PC, Rigaku), SEM (FE-SEM, JSM-6500F, JEOL) and TEM (JEM-2100, JEOL), respectively.

The silver doping amount in HA was measured using an Energy Dispersive Spectrometer (EDS) which is attached to SEM and an Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, 720-ES, Varian). The particle size distribution of HA and HA-Ag in DMF followed by sonication was analyzed using a Zeta Potential Analyzer (ELSZ, Otsuka Elec.).

Preparation of Bio-PU/HA-Ag Hybrid Films

Bio-PU/HA-Ag hybrid solution was prepared by mixing as-synthesized Bio-PU solution and HA-Ag dispersed in DMF by sonication for 5 min according to the composition, as summarized in Table 4. The Bio-PU content in the mixture was controlled to 20 wt% for the subsequent film

Table 4. Hybrid composition of bio-polyurethane (Bio-PU) and hydroxyapatite (HA) or silver-doped hydroxyapatite (HA-Ag)

Hybrid code	Bio-polyurethane		Hydroxyapatite		Ag^+ doping condition (ppm)
	parts	g	parts	g	
Bio-PU	100	30	-	-	-
Bio-PU/HA2.5			2.5	0.75	
Bio-PU/HA5.0			5.0	1.50	
Bio-PU/HA-Ag(100)2.5			2.5	0.75	100
Bio-PU/HA-Ag(100)5.0			5.0	1.50	100
Bio-PU/HA-Ag(200)2.5			2.5	0.75	200
Bio-PU/HA-Ag(200)5.0			5.0	1.50	200
Bio-PU/HA-Ag(300)1.0			1.0	0.30	300
Bio-PU/HA-Ag(300)2.5			2.5	0.75	300
Bio-PU/HA-Ag(300)5.0			5.0	1.50	300

casting using a knife-type film casting machine. The film thickness after dried at 120 °C for 3 min was controlled to *ca.* of 30 °C.

Tests of Antibacterial Activities

Antibacterial activities of Bio-PU/HA-Ag hybrid films were investigated by shaking flask assay method (KS J4206:2008) with *S. aureus* (ATCC 6538) as the model Gram-positive bacteria, and *K. pneumonia* (ATCC 4352) as the model Gram-negative bacteria. The antibacterial activities were evaluated by bacterial reduction rate using the following equation (1):

$$\text{Antibacterial activity (\%)} = (M_a - M_b)/M_b \times 100 \quad (1)$$

where M_a and M_b are the average concentration of bacteria to 10^6 colony (CFU) of the control and the real samples, respectively.

Measurement of Contact Angle

The contact angles of the hybrid films of Bio-PU and HA or HA-Ag were obtained by using a contact angle analyzer (Phoenix300, SEO). The contact angle was measured after 3 seconds of dropping for stabilization of the water droplet.

Results and Discussion

Synthesis of the Bio-polyurethane

Polyurethane is generally synthesized from an isocyanate reaction with polyol. PEG is preferred as polyol for consisting hydrophilic ether-type soft chain in polyurethane structure for the breathable application. The hydrophilic characteristics is essential requirement for the application of non-porous breathable films. Figure 2 represents the Bio-PU synthesis mechanism using castor oil based polyol through pre-polymer technique. As the castor oil based bio-polyol is hydrophobic, hydrophilic PEG was used together with the bio-polyol. The pre-polymer process for the Bio-PU synthesis mechanism comprises two main steps, as shown in the figure. First, mixture of the Bio-polyol and PEG was reacted with MDI (diisocyanate) in DMF with stirring for 4 hr at 70 °C under nitrogen atmosphere to achieve pre-polymer with isocyanate end groups. Second, the pre-polymer was reacted with PDO(chain extender) in the presence of a catalyst at high speed stirring for 30 minute at 70 °C to produce the viscous Bio-PU solution. The solid content was adjusted to 30 wt%. The viscosity of as-polymerized Bio-PU solution was *ca*. 50,000 cps measured using a spindle #64 of Brookfield viscometer.

Preparation and Characterization of the Silver Doped HA

It is known that absorption of heavy metal ions by HA occurs through mechanism of ion exchange and complex formation, as depicted in the equation (2) and Figure 3. It is known that the Ca^{2+} of HA can be substituted by monovalent ions as well as divalent and trivalent cations [20,21]. Therefore, the HA structure allows the substitution of Ca^{2+} ions with Ag^+ ions.

$$Ca_{10}(PO_4)_6(OH)_2 \xrightarrow{AgNO_3(aq)} Ca_{10-x}Ag_x(PO_4)_6(OH)_2 \quad (2)$$

Silver doping to HA was performed by dipping HA powder in aqueous silver nitrate at Ag^+ concentration of 100-300 ppm. Identification and quantitative analysis of silver in HA could be performed using EDS and ICP-OES. Figure 4 represents the change of the silver doping amount in HA according to the Ag^+ concentration of the doping solution. The EDS peak for elemental Ag (inset) is the evidence for the existence of Ag in HA. As the concentration of Ag^+ increased in the doping solution, the elemental

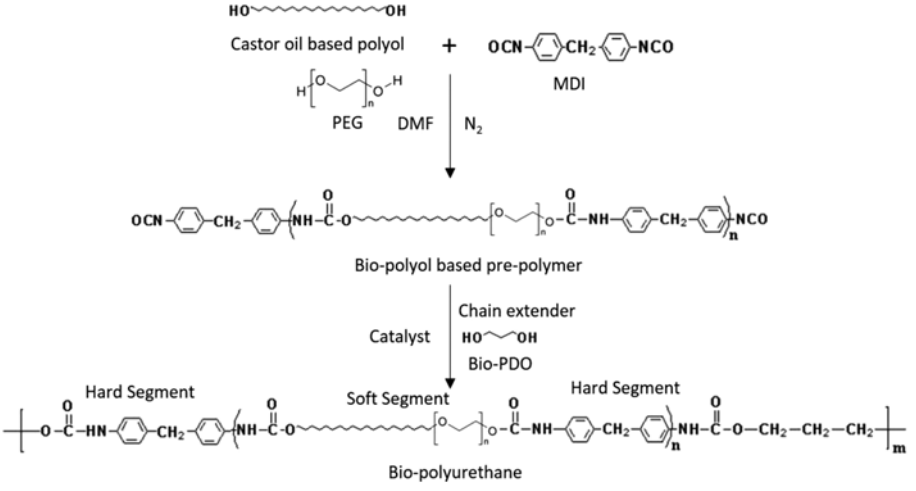

Figure 2. Schematic representation of the bio-polyurethane synthesis mechanism using castor oil based polyol through pre-polymer technique.

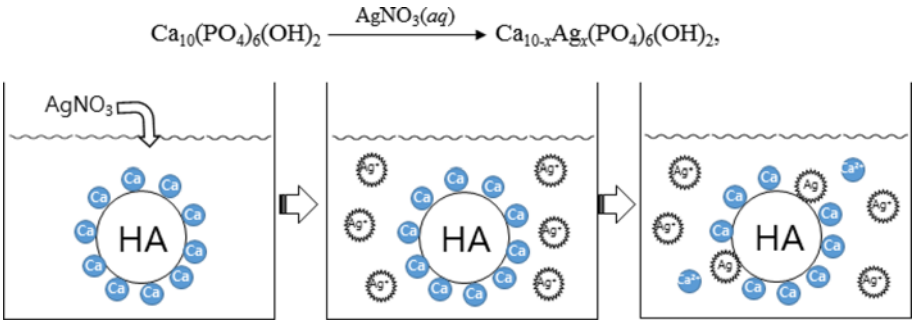

Figure 3. Schematic diagram showing silver doping mechanism of hydroxyapatite through ion-exchange reaction between calcium ion of hydroxyapatite and silver ion in aqueous silver nitrate.

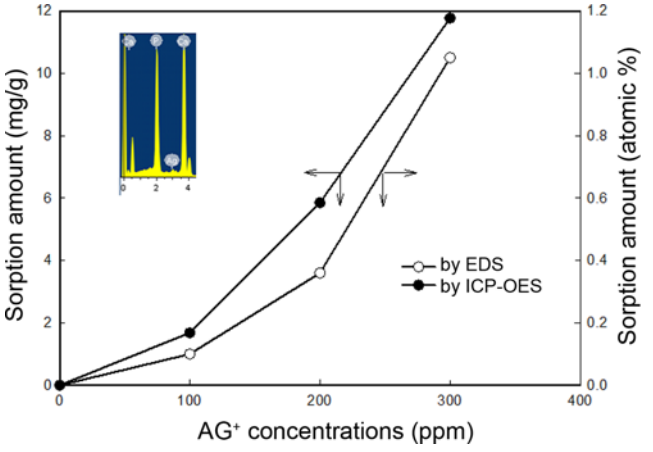

Figure 4. shows the silver amount doped in HA according to the silver ion concentration in the aqueous solution of silver nitrate for the doping. The inset shows EDS spectrum of HA-Ag(300) identifying silver element.

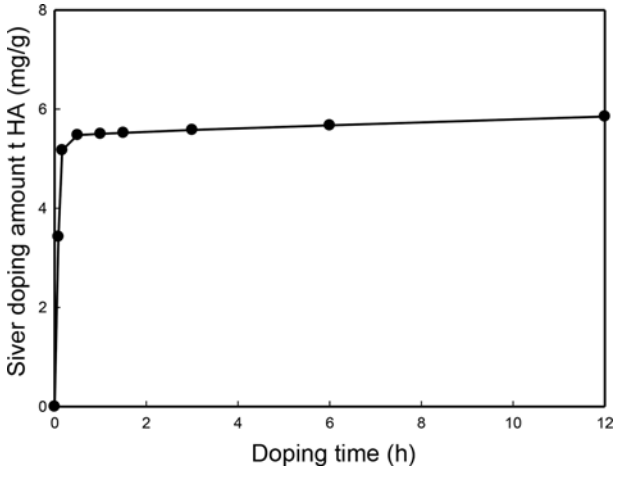

Figure 5. Silver doping amount to HA according to doping time at 200 ppm of Ag^+.

amount of Ag in HA increased. The maximum amount of silver in HA from the EDS spectrum was *ca.* 1.2 atomic% for the HA-Ag prepared at 300 ppm of silver ion

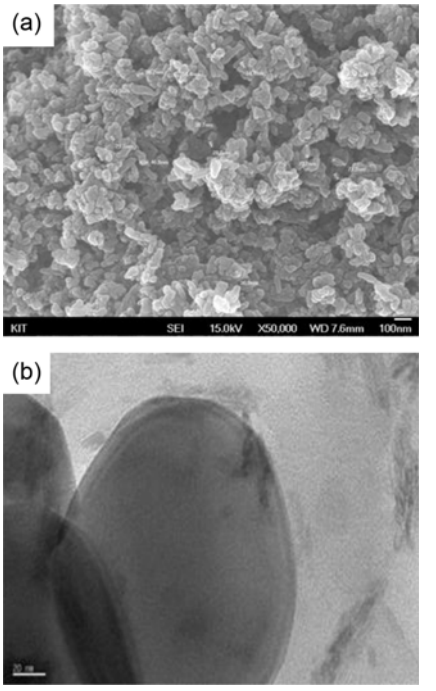

Figure 6. FE-SEM image of HA (a) and TEM image (×150,000) of HA-Ag(300) (b).

concentration. Thus, it can be concluded that silver was successfully doped to HA.

Moreover, the silver absorption amount by HA could be also determined by analyzing the residual concentration of Ag^+ in the solution after doping. As noted in the figure, the two results by EDS and ICP-OES show the same increasing trend. At the range of feeding concentration of silver ion in the doping solution, it was concluded that the actual doping amount in HA increases almost linearly according to the feeding amount.

Figure 5 represents the kinetic behavior of the silver doping in HA. It was found that most of doping was occurred in less than 15 min after dipping. After that up to 12 hours, there was little increase in doping amount.

Figure 6 shows FE-SEM(a) and TEM(b) images of HA-

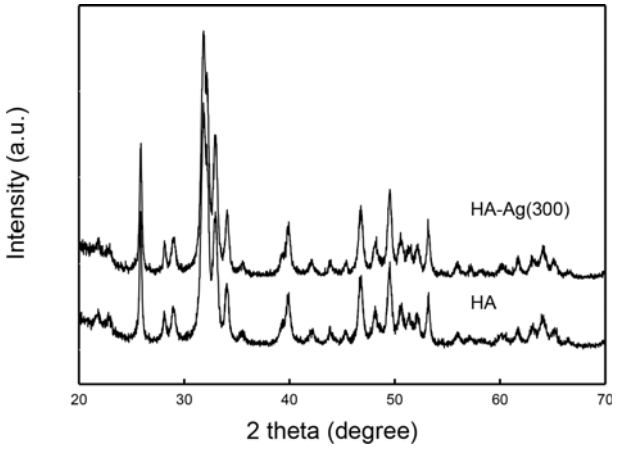

Figure 7. Comparative representation of XRD patterns of HA and HA-Ag(300).

Ag(300). It is notable that the individual HA particle has an elliptical shape with approximately 20-100 °C in length. It was hard to detect, however, a significant trace of silver nano-particles in HA by electron microscopy implying that silver was introduced to HA at atomic level. Similarly, there was no detectable difference after doping as shown in Figure 7 due to negligible amount of silver doping to HA.

Preparation and Characterization of Bio-PU/HA-Ag Hybrid Films

The hybridization of HA or HA-Ag particles with Bio-PU was carried out by mixing the particles in Bio-PU solution in DMF followed by sonication. As HA and HA-Ag particles are agglomerated, they were treated with sonication in DMF before mixing with Bio-PU solution to separate into individual particles or at least the smaller agglomerates. Figure 8 represents the particle size distribution of HA and HA-Ag in DMF after sonication for 10 min. It is seen that the average particle sizes of HA and HA-Ag were 100-200 nm. Thus, it can be presumed that the particles were well separated to individual size by sonication treatment even though some increase of size after silver doping.

Figure 9 shows the FE-SEM images of pristine Bio-PU(a) and its composite containing 5 wt% of HA-Ag(300) (b). The specimens for FE-SEM were cryo-fractured in liquid nitrogen to make natural cross-section. The HA-Ag were found to be well dispersed in Bio-PU matrix.

As the main purpose of the Bio-PU is breathable non-porous type film for textiles, hydrophilic properties of the film surface is a key requirement. Surface energy data were calculated from the contact angle values obtained using distilled water and diiodomethane using the following equations (3) and (4) which is derived from Owens-Wendt model [22].

$$\gamma_{L1}(1+\cos\theta_1) = 2(\gamma_S^d \gamma_{L1}^d)^{1/2} + 2(\gamma_S^p \gamma_{L1}^p)^{1/2} \quad (3)$$

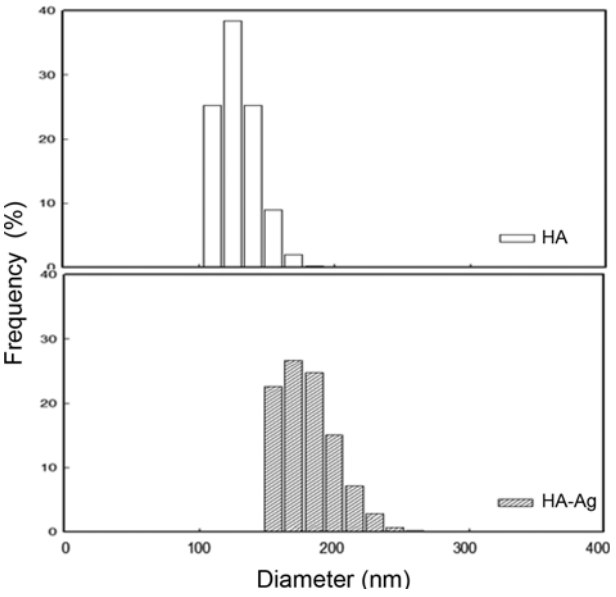

Figure 8. Particle-size distribution of HA and HA-Ag(300) after sonication in DMF for 10 min.

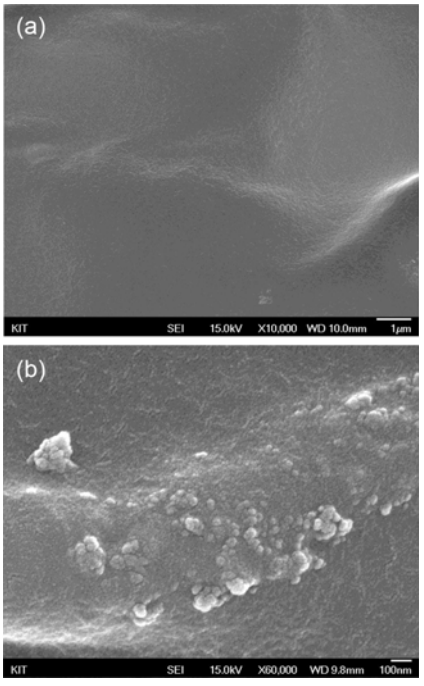

Figure 9. FE-SEM cryo-fractured images of pristine Bio-PU (a) and its composite containing 5 wt% of HA-Ag(300) (b).

$$\gamma_{L2}(1+\cos\theta_2) = 2(\gamma_S^d \gamma_{L2}^d)^{1/2} + 2(\gamma_S^p \gamma_{L2}^p)^{1/2} \quad (4)$$

where γ_S is the surface free energy of Bio-PU/HA for Bio-PU/HA-Ag hybrid films, γ_L is the surface free energy of the measured liquid and θ is the contact angle. The superscripts d and p refer dispersion and polar components in the surface

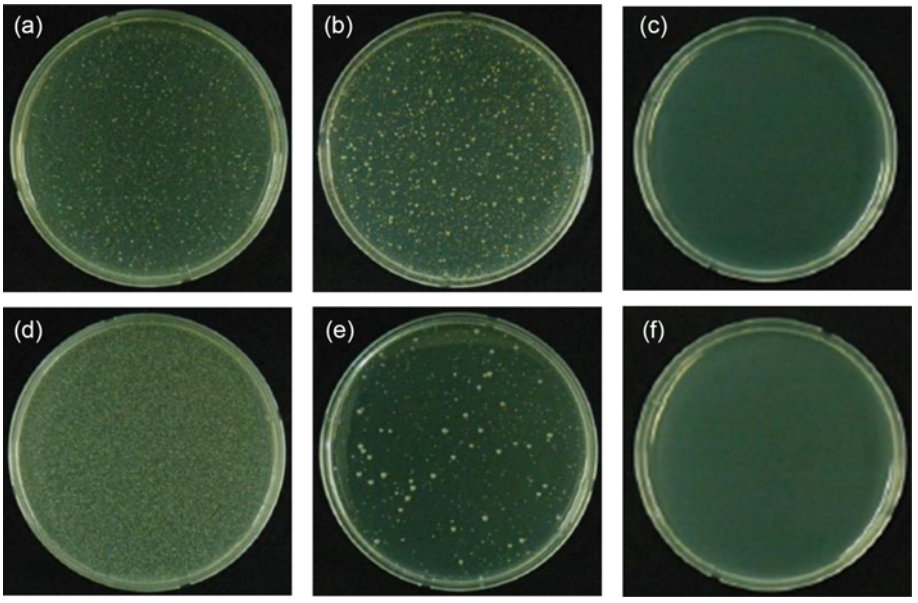

Figure 10. Antibacterial test plates of *S. aureus* (a-c) and *K. pneumonia* (d-f): Bio-PU (a, d), Bio-PU/HA-5.0 (b, e), Bio-PU/HA-Ag(300)-5.0 (c, f).

Table 5. Contact angles of polar water and dispersive diiondomethane, and the components of surface energy for the Bio-PU and its hybrid films with HA or HA-Ag

Hybrid film code	Contact angle, θ (°)		Surface energy, γ (mJ/m^2)		
	Water	Diiodomethane	Polar component (γ_s^p)	Dispersion component (γ_s^d)	Total (γ_s)
Distilled water			51.0	21.8	72.8
Diiodomethane			0.4	50.4	50.8
Bio-PU	75.62	27.94	42.65	4.38	47.03
Bio-PU/HA2.5	81.68	22.60	45.29	2.06	47.39
Bio-PU/HA5.0	81.81	22.41	45.37	2.01	47.39
Bio-PU/HA-Ag(100)2.5	81.68	22.63	45.28	2.06	47.47
Bio-PU/HA-Ag(100)5.0	81.72	22.46	45.34	2.04	47.38
Bio-PU/HA-Ag(200)2.5	81.57	22.52	45.30	2.08	47.42
Bio-PU/HA-Ag(200)5.0	81.70	22.54	45.31	2.05	47.36
Bio-PU/HA-Ag(300)1.0	81.02	22.54	45.24	2.24	47.47
Bio-PU/HA-Ag(300)2.5	80.73	22.65	45.17	2.32	47.49
Bio-PU/HA-Ag(300)5.0	80.74	22.52	45.21	2.31	47.61

energy, respectively. The subscripts 1 and 2 denote water and diiodomethane, respectively. Thus, the dispersion and polar components of the Bio-PU films could be obtained by solving the simultaneous equations with the measured contact angles and the known component values, γ_L^p and γ_L^d values of two liquids, as noted in Table 5. Table 5 is the summary of the contact angles and the surface energy for the neat Bio-PU and the hybrid films. The contact angle of Bio-PU increased from 75.6° to 81.8° for water while it decreased from 27.9° to 22.4° for diiodomethane when HA was added to Bio-PU by 5 wt%. The hybrids of Bio-PU and HA-Ag exhibited similar results as hybrid of HA. Accordingly, polar component of Bio-PU increased and dispersion component decreased with apatite addition. From the analysis of surface energy, it was concluded that hydrophilic properties of Bio-PU improved by addition of the inorganic HA and HA-Ag.

Antibacterial Activities of Bio-PU/HA-Ag Hybrid Films

The mechanism of the antibacterial effect of Ag doped nanoparticles is not yet clearly elucidated. A possibility is

Table 6. Antibacterial activity of Bio-PU, Bio-PU/HA and Bio-PU/HA-Ag hybrid films against *S. aureus* and *K. pneumonia* according to HA-Ag contents

Sample code	Reduction of bacteria (%)	
	S. aureus	*K. pneumonia*
Bio-PU	17.4	41.4
Bio-PU/HA-5.0	78.3	82.4
Bio-PU/HA-Ag(100)-2.5	99.9	99.6
Bio-PU/HA-Ag(100)-5.0	99.9	99.9
Bio-PU/HA-Ag(300)-1.0	99.9	97.3
Bio-PU/HA-Ag(300)-2.5	99.9	99.5
Bio-PU/HA-Ag(300)-5.0	99.9	99.9

the gradual release of Ag^+ ions from Ag-nanoparticles, followed by their disruption on ATP production and DNA replication [22]. The antibacterial activity of Bio-PU, Bio-PU/HA and Bio-PU/HA-Ag hybrid films against *S. aureus* and *K. pneumonia* according to silver doping amount and filler content is summarized in Table 6. As shown in Table 6, the numbers of the two bacteria were significantly reduced by HA-Ag in the hybrids. Regarding to the hybrid with HA-Ag(300), 1.0 wt% was enough to exhibit 99.9 % reduction rate against *S. aureus* while 5.0 wt% was required against *K. pneumonia*. Figure 10 is photographs showing the results after antibacterial test of Bio-PU and the hybrid films in *S. aureus* and *K. pneumonia* bacterial solutions, respectively. They show clear antibacterial activity of the hybrid films with silver doped HA.

Conclusion

Biomass based polyurethane was successfully synthesized by using castor oil as a polyol for the soft segment in polyurethane. The Bio-polyol solution in DMF had enough molecular weight for film casting. HA could be doped with silver by simple dipping method in a aqueous $AgNO_3$ solution. The maximum amount of silver doped in HA was evaluated to approximately 12 mg per gram of HA by ICP-OES measurement. No silver particle, however, was detected by TEM because silver was doped to HA through a ion-exchange mechanism. Silver doping was found to occur in less than 15 min after dipping. The average size of HA-Ag after sonication in DMF was measure to a range of 150-200 nm by a Zeta-potential analyzer. The hybrid films of Bio-PU and the inorganic fillers (HA or HA-Ag) were found to become more hydrophilic with increasing of the filler amount in Bio-PU, which is essential for the breathable thin films of PU. The hybrid films containing 2.5 wt% of HA-Ag prepared from the aqueous solution of 300 ppm silver ion demonstrated excellent antibacterial activities against *S. aureus* and *K. pneumonia* by showing 99.9 % reduction of bacteria.

Acknowledgement

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References

1. Y. Xia and R. C. Larock, *Green Chem*., **12**, 1893 (2010).
2. C. K. Williams and M. A. Hillmyer, *Polym. Rev.*, **48**, 1 (2008).
3. M. A. Alaa, K. Yusoh, and S. F. Hasany, *J. Mech. Eng. Sci.,* **8**, 1507 (2015).
4. I. Javni, Z. S. Petrovic, A. Guo, and R. Fuller, *J. Appl. Polym. Sci.*, **77**, 1723 (2000).
5. I. Javni, W. Zhang, and Z. S. Petrovi, *J. Appl. Polym. Sci*., **88**, 2912 (2003).
6. J. John, M. Bhattacharya, and R. B. Turner, *J. Appl. Polym. Sci*., **86**, 3097 (2002).
7. K. C. Pradhan and P. Nayak, *Adv. Appl. Sci. Res.*, **3**, 3045 (2012).
8. L. T. Yang, C. S. Zhao, C. L. Dai, L. Y. Fu, and S. Q. Lin, *J. Polym. Environ*., **20**, 230 (2012).
9. C. W. Shan, M. I. Ghazali, and M. I. Idris, *J. Auto. Mech. Eng*., **7**, 1031 (2013).
10. O. Saravari and S. Praditvatanakit, *Prog. Org. Coat*., **76**, 698 (2013).
11. D. Vashist and M. Ahmad, *Int. J. Auto. Mech. Eng*., **10**, 2155 (2014).
12. H. C. Cha and Y. H. Kim, *Text. Sci. Eng.*, **45**, 214 (2008).
13. M. Rai, A. Yadav, and A. Gade, *Biotechnol. Adv*., **27**, 76 (2009).
14. S. H. Jeong, S. Y. Yeo, and S. C. Yi, *J. Mater. Sci.*, **40**, 5407 (2005).
15. D. H. Lee and B. G. Min, *Fiber. Polym*., **15**, 1921 (2014).
16. X. Wang and B. G. Min, *J. Sol-Gel Sci. Technol.*, **43**, 99 (2007).
17. X. Wang and B. G. Min, *J. Sol-Gel Sci. Technol.*, **45**, 17 (2008).
18. X. Wang, J. H. Kim, and B. G. Min, *Fiber. Polym*., **9**, 263 (2008).
19. X. Wang and B. G. Min, *Rev. Roum. Chim*., **55**, 443 (2010).
20. S. T. Ramesh, N. Rameshbabu, R. Gandhimathi, P. V. Nidheesh, and M. Srikanth Kumar, *Appl. Water Sci*., **2**, 187 (2012).
21. Z. Evisa, B. Yilmazb, M. Ustac, and A. L. Aktugc, *Ceram. Int.*, **39**, 2359 (2013).
22. D. K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.*, **13**, 1741 (1969).
23. A. Panacek, L. Kvitek, R. Prucek, M. Kolar, R. Vecerova, N. Pizurova, V. K. Sharma, T. Nevecna, and R. Zboril, *J. Phys. Chem. B*, **100**, 16248 (2006).