Pre-treatment of glass substrates and post treatment of the surface of single and multiple Chitosan film by heated as wettability

E Rahmawati* and S Agustina
Department of Physics Education STKIP Bima Yogyakarta Indonesia
*Email: rahmawatieka89@gmail.com

Abstract. In this approach, chitosan thin films have been prepared using single and multiple dip coating method. The glass substrates was heated 100 0C as a pre-treatment and the fabricated thin film were post heated in various temperature: 100 0C, 210 0C, 220 0C and the effect of pre and post heat treatment on their wetting, structural and morphological properties has been investigated. Scanning electron microscopy (SEM and contact angle measurement have been applied for the characterization and study of thin film surfaces. The results of SEM exhibit the aggregation and formation of chitosan films on the surface of substrate changed through applying heat pre-treatment substrates and increasing of heat post temperature to the chitosan surface. Wettability studies showed that the contact angle of prepared thin films was influenced by various parameters such as heat pre-treatment on glass substrates, variation of heat post-treatment and surface morphology.

1. Introduction
Physical and chemical properties of the polymer will influence the functionality, performance, and ultimately the applicability of a polymer itself [1-3]. One of the important and interesting features of many polymers is their surface properties. There are a large number of studies have been focused on the characterization and modification of the surface properties [4-7]. Polymer surface modification can be achieved using physical and chemical methods, in which existing functional groups are altered and new physical properties are produced. The purpose of surface treatment is mainly to improve certain mechanical and performance-related properties. Some unique properties are mainly use in industrial, medical and biological application based polymers are hardness, bacterial repellence, biocompatibility, appropriate wettability, surface conductivity. With the development of coating preparation technology, a substrate surface pre-treatment, e.g. sand blasting, grinding and polishing or honing, is required for improving the performance of the coatings [8-9]. Different pre-treatment processing results in different substrates surface roughness, and its evaluation is very important for many fundamental problems such as friction, adhesion property, contact deformation, heat and electric current conduction, tightness of contact joints and positional accuracy[10]. Pre and post treatment of the thin films can be done to get the new surface properties of thin film. There are many scientific works on molecularly smooth surface [11-13], but just a little of them work on wettability and spreading phenomena of real engineering surfaces [14]. Different friction properties can be achieved by controlling surface roughness. Reduction in friction and wear usually observed for smooth but not polished surfaces [15]. Wettability is usually quantified in terms of observed contact angles, so from a practical point of view, a simple methodology is needed to account for the heterogeneous rough surface influence on wetting and contact angle measurements, which indicates the degree of wetting when a solid and liquid interact. Large contact angles (< 90°) correspond to low wettability. Small contact angles (< 90°) correspond to high wettability. Surface with a water contact angle approaching zero is classified as super hydrophilic (super high
wettability) and a surface with a contact angle >150 is usually categorized as super hydrophobic (super low wettability). Wetting phenomenon of composite materials had been investigated by Cassie and Baxter [16], where the rough surfaces is able to capture water by trapping process in the roughness properties. Pre-treatment glass substrate by Ar/O\textsubscript{2} ion beams for the as-sputtered rough zinc oxide thin films has been done [17]. Applying Ar and O\textsubscript{2} ion obtained the changing of morphology and resulted rougher surface than untreated one. While [18] irradiate the polystyrene thin film by ultra violet to enhanced the hydrophobicity of film effect to bio-immobilization. The different roughness surface of thin films polymers can be done by choosing the different solvent of polymers itself. Setyawan et al [19] using chloroform, toluene, xylene, THF as the solvent of polystyrene to get the difference surface of thin films coated on QCM.

In this paper we focus on the treatment of glass substrate to obtain the altered wettability of chitosan thin film by doing heat pre-treatment of the substrates and post heat treatment to chitosan filmsingle and multipledipcoating. Chitosan is inert, hydrophilic, biocompatible and biodegradable, it has attracted scientific and industrial interest in widely differing fields.

2. Experimental Section

2.1 Sample preparation
Glass substrate rectangular block was used as substrates, fixed size was 10 mm ×10 mm×4.76mm. All the substrates were cleaned for 10 minutes in methanol 97% and it be aerated then. To make chitosan thin film, we used whitish ivory chitosan with degree 84% of deacetylation which obtained from shrimp shells, it was acquired from chemistry laboratory of STKIP (Bima, Indonesia).

Coating was performed by using a single and multiple dip coating. Glass substrates was immersed in chitosan solution for 10 minutes and it be drawn vertically with a constant velocity. For multiples chitosan thin films, glass substrates was obtained by immersing and drying for each 10 minutes for three times repeating coating alternately.

Wettability alteration is done by doing heated pre-treatment of the glass substrate and heated post-treatment of the chitosan films for un-heated pre-treatment substrates. Glass substrate was heated with 100 °C for an hour before coating chitosan and it be heated with 100 °C after coating. For heat post-treatment of un-heated substrates, chitosan films on glass substrates were heated on 100 °C, 210 °C, 220°C for an hour.

2.2 Characterization of morphology
The morphology of the surfaces was characterized by scanning electron microscopy (SEM) standard on JJSM-6510LA.

2.3 Water contact angle measurement
The contact angle of chitosan thin films: heat pre-treatment and post-treatment were measured by using the sessile drop technique to measure the water contact angle (WCA) between drop water and chitosan film. Water droplets from a micropipette were placed on the surface of chitosan films. The drop water was captured by canon Eos 1200D with 18.0 MP 5184 x 3456 resolution and the image was analysed by CorelDraw X4.

3. Discussion
The coated chitosan film in two different single and multiple dip coating method were obtained. Applying heat pre-treatment substrate and heat post treatment chitosan films produced different morphology and wettability of films.
Figure 1 shows that heat pre-treatment on glass substrate obtained the groovy and rough films for both single and multiple dip coating. And it will be more groovy and rougher for multiple coating for heat pre-treatment glass substrate. Glass particle agglomerate become a secondary particle for heat pre-treatment to glass substrate. Then all of the particle established a larger cluster in micro scale at the bottom but it still in nano scale at the top of surface. So, when chitosan was coated on the heat pre-treatment glass substrate, it will attend the groovy and rougher of surface.

Heat post treatment was one of the ways to do the surface modification get different wettability of surface. From figure 2, the SEM images indicated that the surface morphology was not significantly sensitive to the temperature post heat treatment for single dip coating films. Chitosan thin film was transparent and smooth. On the other hand, the surface morphology of the multiple dip coating film was sensitive to heat post treatment. The surface was transparent but little wavy at certain position. It indicates the increment of temperature heat post-treatment can change the distribution of grains on the surface of chitosan films. Chitosan thin film was heated at temperature 210 °C different in 7 with its glass transition temperature (Tg) 203°C based on the careful DSC and DMA measurements [20]. It effected the movement of polymer chain of chitosan easily. Temperature influenced the mobility of polymer’s chain as the increasing of kinetic energy; that is, the energy of objects in motion. It is actually an effect of random motion of molecules, whether they are polymer molecules or small molecules. So that, lumps that initially accumulate would move to find the best place and the surface become smoother. By increasing the heating temperature, the chitosan thin film surface become smoother all ways. Actually, to get information about chitosan grain can be obtained by AFM (Atomic Force Microscopy).
Single dip coating

a   b   c

Multiple dip coating

d   e   f

Figure 2. SEM images of chitosan thin films by post heat treatment: a) single dip coating film at temperature 100°C b) single dip coating film at temperature 210°C c) single dip coating film at temperature 220°C d) multiple dip coating film at temperature 100°C e) multiple dip coating film at temperature 210°C f) multiple dip coating film at temperature 220°C.

The surface roughness will effect to wettability. Tailoring the roughness and chemical composition of the surface can be used to enhance the related hydrophilicity and hydrophobicity. In particular, nano and microtextures have been used to produce hydrophobic coating on different surfaces.
Figure 3. Image water drop on chitosan thin films between heat un pre-treatment and heat pre-treatment substrate.

Table 1. Contact angle between heat un pre-treatment and heat pre-treatment substrate.

|                     | Heat un pre-treatment substrate | Heat pre-treatment substrate |
|---------------------|---------------------------------|------------------------------|
| Single coating      | 64                              | 67                           |
| Multi coating       | 84                              | 89                           |

It was explained before that glass substrate heat pre-treatment develop the rougher surface compare to heat un pretreatment. From the table 1, it can be seen that heat pre-treatment substrate obtained the higher water contact angle than untreated substrate, and it will be higher for multiple thin film. Values of measured apparent contact angle can be strongly affected by the roughness of the measured surface. When water drop onto the rough surface, the air would be trapped in the middle of roughness. Based on Cassie- Baxter, getting smaller interact surface area of particles with water, it will cause the larger contact angle. Chemically, wettability was influenced by polar molecule at surface, so that there will be an attraction between surface molecules and polar H₂O.

The contact angle value versus temperature has also been illustrated in Figure 4 and table 2 below. As can be seen, for both thicknesses, the contact angle gradually decreases with increasing in post heat temperature.
Figure 4. Image water drop on chitosan thin films was effected by temperature post heat treatment of un pre-treatment substrate: a) single layer film at temperature 100 °C b) single layer film at temperature 210 °C c) single layer film at temperature 220 °C d) multiple film at temperature 100 °C e) multiple film at temperature 210 °C f) multiple film at temperature 220 °C.

Table 2. Temperature post heat treatment of un pre-treatment substrate effect to contact angle of chitosan thin film.

| Temperature (°C) | Single coating | Multi coating |
|-----------------|----------------|--------------|
| 100 °C          | 64             | 84           |
| 210 °C          | 54             | 76           |
| 220 °C          | 38             | 60           |

It can be conclude that pre-treatment for substrates and post treatment of the surface obtained the hydrophilic surface cause the watercontact angle less than 90°. Despite these chitosan can be modified and be used in wettability technology, pure chitosan films also show some disadvantages such as poor mechanical properties, high brittleness and high water sensitivity, thereby limiting their extensive applications [21-22]. Pure chitosan film displays high moisture absorption because of its hydrophilic character, thereby resulting in films with relatively poor mechanical properties at high humidity [23]. The water low resistance of chitosan thin film can be seen below. It was obtained after 20 minutes water droplet on surface.
4. Conclusion
Heat pre-treatment and post treatment of glass substrates and chitosan film result the altered wettability of chitosan thin film. Heat treatment influences the roughness of film for both single and multiple chitosan film. Glass substrate which undergo the heat treatment obtained the rougher surface and it has low wettability than other untreated surface. While the various heat post treatment surface has good wettability cause the hydrophilic properties with smoother surface. But unfortunately, the pure chitosan film has low water resistance. So it need to be modified with other material and using the other method to result the high quality thin film.

References
[1] Morent R, DeGeyter N, Desmet T, Dubruel P and Leys C 2011 Plasma Process. Polym. 8 171–190
[2] De Geyter N and Morent R 2012 Engineering and Technology 225–246
[3] Borges A, Benetoli L, Licínio M, Zoldan V, Santos-Silva M, Assreuy J, Pasa A, Debacher N and Soldi V 2013 Mater. Sci. Eng. 33 1315–24
[4] Zhao J H, Sheadel DA and Xue W 2012 Physical 187 43–49
[5] Yoshida S, Hagiwara K, Hasebea T and Hotta A 2013 Surf. Coat. Tech. 233 99–107
[6] Woo SK, Min H, Lee J-O and Song YH 2014 Appl. Surf. Sci. 295 198–202
[7] Kolskáa Z, Rezníčková A and Nagyová M 2014 Polym. Degrad. Stab. 101 1–9
[8] Svaň F, Rudolphi A K and Wallén E 2003 Wear 254 1092-98
[9] Harlin P, Bexell U and Olsson M 2009 Surf. Coat. Tech. 203 1748-55
[10] Gadelmaawla E S2002 J. Mater. Process. Technol. 123 133-45
[11] Narayan Prabhu K, Fernades P and Kumar G 2009 Mater. Des. 30(2) 297-305
[12] Hay KM, Dragila MI and Liburdy J 2008 J. Colloid Interface Sci. 325 472-7
[13] Extrand CW and Kumagai Y1997 J. Colloid Interface Sci. 191 378–83
[14] Kubiak KJ, Mathia TG and Wilson MCT 2009 Proc. of 14th Congrèse International De Métrologie Paris
[15] Kubiak KJ and Mathia T G 2009 Wear 267 315-21
[16] Cassie ABD and Baxter S1944 Trans. Faraday Soc. 40 546
[17] Wendi Zhang, Eerke Bunte, Martina Luysberg, Philipp Spiekermann, Florian Ruske and Jürgen Hüpkes 2011 Surf. Coat. Tech. 205 S223-S228
[18] Setyawan P, Sakti, LayliAmaliya, Nike F. Khusnah and Masruroh 2017 Jurnal Teknologi 79(3) 61-67
[19] Setyawan PS, Rahmawati E and Robiandi F 2016 Conf. Proc. Of ICTAP American institute of Physic doi: 10.1063/1.4943712
[20] Sakurai K, Maegawa T and Takahashi T 2000 Polymer 41 7051–56
[21] Thakhiew W, Devahastin S and Soponronnarit S 2013 J. Food Eng. 119 140–149
[22] Liu M, Zhou Y, Zhang Y, Yu C and Cao S 2013 Food Hydrocoll. 33 186–91
[23] Cervera M F, Karjalainen M, Airaksinen S, Rantanen J, Krogars K, Heinamaki J, Colarte A I and Yliruusi, J. 2004 Eur. J. Pharm. Biopharm 58 69–76

Figure 5. chitosan low water resistance after 20 minutes water droplet.
Acknowledgements

The authors thank for the financial support from Directorate General of Higher Education (DIKTI), Ministry of National Education Indonesia.