MATEC Web of Conferences **4**, 05006 (2013)
DOI: 10.1051/matecconf/20130405006

Fabrication of the durable low refractive index thin film with chitin-nanofiber by LBL method

C.Tanaka and S.Shiratori
School of integrated Design Engineering, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama-shi, 223-8522, Japan
shiratori@appi.keio.ac.jp

Abstract. Durable low refractive index thin films with anti-reflection properties were successfully fabricated using chitin nanofibers (CHINF) obtained from crab shell. The low refractive index film was achieved by forming porous thin films; the porosity was produced by increasing the number of airspaces inside the membrane. The layer-by-layer (LBL) method was used to achieve the effective stacking of the CHINF. The influence of surface structure and refractive index under changes in the solution pH was investigated using scanning electron microscopy and ellipsometry. Transmittance of the fabricated film is 4.1 % higher than that of a glass substrate and refractive index film of that is 1.29. The films had abrasion resistance and antifogging properties because of the high mechanical strength and hydrophilicity of chitin. We believe this LBL film using CHINF is a promising candidate material to overcome the durability problems associated with optical thin films.

1 Introduction

A Chitin nanofibers (CHINF) have attracted much attention because of their high mechanical strength and biocompatibility. Crabs are crustaceans with an exoskeleton that forms like twisted plywood and has high tensile strength and bendability.[1,2] The shells of crustaceans are expected to be particularly useful for materials applications, because they are made from mineral salts, protein, and chitin; it is known that mineral salts can be removed using HCl, and proteins can be removed using NaOH.[1] However, if only these procedures are used, the surfaces of CHINF do not have any electrostatic charge. The CHINF surface is transformed from chitin to chitosan by deacetylation, which results in a positive charge on the CHINF, due to the presence of amine groups. The transparency of the solution changes depending on the deacetylation time.[3]

Antireflection (AR) films can effectively enhance the transparency in applications such as solar cells and display devices.[4-6] Single-layer AR coatings should meet the following two requirements: First, $d = \lambda/4n_f$, where d is the thickness of the film, λ is the wavelength of the incident light, and n_f is the refractive index of the film. Second, $n_f = (n_a n_s)^{1/2}$, where n_a is the refractive index of air, and n_s is the refractive index of the substrate. To meet these criteria, the refractive index of film should be 1.23, because that of glass substrates is almost 1.52. However, such a material does not exist. To fabricate a low refractive index film, therefore, porosity was introduced into a thin film. The porous thin film was obtained by increasing the number of airspaces inside the membrane. Additionally, antifogging coatings have self-cleaning properties due to their hydrophilic nature, thus eliminating light scattering from water droplets.[7-9]

In this work, we first removed the mineral salt and protein from the crab shell, making it possible to extract only chitin. Then, by depositing the deacetylated CHINF and Poly (acrylic acid) (PAA) using the layer-by-layer (LBL) method, the lower refractive index layer was fabricated. Because the LBL method has highly controlled performance and stability, due to the adsorption of electrostatic interactions under eco-friendly conditions in an all wet-process, a highly functional thin film with a nanometer scale thickness was successfully fabricated using the CHINF biomacromolecules.[10,11]

In previous studies, porous films were created using SiO_2 nanoparticles.[12-14]; however, these films did not show durability. Porous films have also been fabricated using hydrochloric acid treatment and the LBL method, and in this case the films refractive index was 1.18.[15] However, the transmittance was not investigated. Antifogging films that were fabricated for the lenses in safety goggles have been reported.[16] In that study, the refractive index was 1.54, and the thin films were durable. However, the transmittance of the fabricated films was very similar to that of glass substrates.

Our low refractive index films with CHINF showed abrasion resistance and antifogging properties, because chitin has high mechanical strength[2] and high hydrophilicity.[15,17]

CHINF with a diameter of approximately 10-20 nm have been extracted from crab shells.[1,18-21] In this study, a high optical transparency sheet was fabricated using the composite material of CHINF and the resin. In this transparent sheet, the coefficient of thermal expansion (CTE) was reduced by the presence of the CHINF. It was confirmed that the optical transmittance was stable over a large range of temperatures, despite large changes in the refractive index of the resin.[18,22-24]

Using the lower refractive index layer made from refined CHINF from a crab, we successfully fabricated a durable AR film. The fact that this functional thin film could be fabricated in a wet process to combine AR effects with high durability was one of the major advantages of using CHINF. These results suggested that crab shells, which are typically waste materials, have the potential to be used effectively in thin functional films made from natural biomacromolecule resources.

2 Materials and Methods

2.1 Materials

Poly (acrylic acid) (PAA, Mw=5,000, 1mg/ml) obtained from Wako and Crab shells were obtained from Kawai Hiryo, Poly (allylamine hydrochloride) (PAH, Mw = 58,000, 10 mM) was obtained from Sigma Aldrich (Japan), and colloidal silica nanoparticles (SiO_2, 0.03 wt%) were obtained from Nissan Chemical Industries (Japan), Ltd..

All polyelectrolyte dipping solutions were made using ultra-pure water (Aquarius GS-500.CPW, Advantec), and the pH was adjusted using NaOH and HCl.[25-27] The glass substrates were cleaned in a KOH solution (1:120:60 wt% KOH/H_2O/IPA) for 2 min, and this was followed by thorough rinsing with water.

2.2 Refinement of CHINF

The CHINF were fabricated using the following method: Dried crab shell powder was used for this study. The crab shells were purified to prepare the CHINF according to the methods described in the literature.[1,28] First, the crab shell powder was treated using 2 M HCl solution, for 2 days and at room temperature, to remove the mineral salts. After rinsing with an abundance of distilled water, the treated chitin powder was refluxed in a 2 M NaOH solution for two days, to remove the protein. Next, the pigment in the sample was removed using 1.7 wt% $NaClO_2$ in the buffer solution; this treatment was applied for 6 h at 80 °C. After the sample was rinsed thoroughly with distilled water, the sample was suspended in 33 wt% NaOH containing 0.03 g $NaBH_4$, as described in a previous study.[3] The CHINF solution was diluted to a concentration of 0.025 wt%.

2.3 Fabrication of the low refractive index film

The low refractive index layer was fabricated using a refined CHINF solution and PAA, using the LBL method. The glass substrate was alternately immersed (for 1 min) in the cationic CHINF solution and the anionic PAA solution, and was rinsed with water for 3 min and dried in blowing air after the deposition of each layer. Hereafter, the multilayer films are presented as (cationic solution and the pH of the cationic solution/anionic solution and the pH of the anionic solution)$_N$. N is number of layer.

2.4 Durability testing

Abrasion tests were carried out using an abrasion machine in cloth-on-plate contact configuration with a 100 g/cm^2 load. A piece of cotton was moved across the sample at 500 mm/min over a distance of 30 mm, for100 cycles. Antifogging tests were performed by cooling the half-coated glass substrate in a refrigerator at −22 °C for 30 min and then returning the substrate to a room-temperature environment.

2.5 Characterization

Transmission electron microscope (TEM) image measurement was conducted using TEM image.(Philips TEM120) Film thickness and refractive index were determined by ellipsometry measurements.(FiveLab MARY-102) Optical characterization of multilayer films was carried out using an ultraviolet−visible (UV−vis) spectrophotometer. (Shimadzu UV mini-1240) Surface images were captured by field-emission scanning electron microscopy (FE-SEM; Hitachi S-4700) and atomic force microscopy (AFM; Nanoscope IIIa, Digital Instruments). Zeta-potential measurements were conducted using Zeta-potential analyzer.(Otsuka Electronics ELS-8000)

3 Results and discussion

3.1 Fabricated CHINF solution

Figure 1 (a) shows TEM images of refined CHINF and figure 1 (b) shows AFM images of cast film of CHINF. CHINF were fully independent one by one and dispersed by deacetylation.; chitosan have amine group. It is known chitosan of pH 6.5 was not protonated[29,30], therefore zeta-potential of CHINF close in on 0 with increasing pH. (Figure 2) The pKa of chitosan is 6.5 and the protonated chitosan decrease with increasing pH.

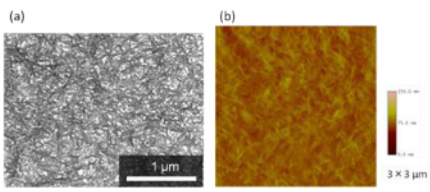


Fig. 1. (a) TEM image of CHINF and (b) AFM image of cast film of CHINF.

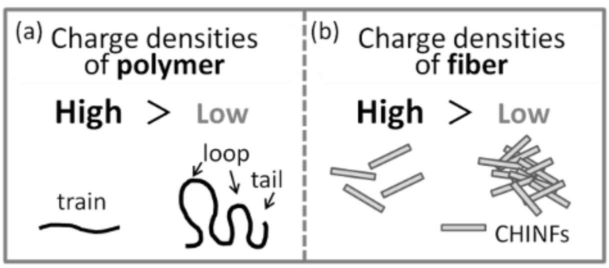
3.2 The influence of pH change

Figure 3 shows SEM images of various LBL films produced as the solution pH was changed for the CHINF and PAA. As shown in Figure 3, the surface structure changed drastically with changing solution pH. For polymer adsorption, there are three possible configurations. Only train configurations are present at high charge densities, while the occurrence of loop and tail configurations will increase at low charge densities.[31,32] (Scheme 1(a)) On the other hand, it is ease to aggregate between fibers at high charge densities, while fibers disperse individually at low charge densities.(Scheme 1(b))

The thin films for CHINF of the pH 5-6 have unhomogeneous and aggrigation of CHINF at low charge densities.(Scheme 1(b), Rigion I (Figure 3)) The refractive index of (CHINF 3.3/PAA 3.3) and (CHINF 5.0-6.0/PAA 3.3) were 1.29 and 1.40, respectively.(Table 1) Compared with the surface of the (CHINF 3.3/PAA 3.3) film, the surface of the (CHINF 5.0/PAA 3.3) film was more inhomogeneous, due to the aggregation between CHINF at high charge densities.(Scheme 1(a) and Figure 4) The transmittance of the (CHINF 5.0/PAA 3.3) film was low, due to the aggregation (Figure 4 (c)); therefore, the (CHINF 5.0/PAA 3.3) film did not have any AR properties, and the aggregation could be observed visually.

Additionally, the thin flms for PAA of the pH 5-6 flatten by burying porosity and refractive index of that increase about 1.45. Figure 5 shows AFM images and section analysis of (CHINF 3.3/PAA 3.3) and (CHINF 3.3/PAA 5.0). Additionally, the thin films made using PAA solution with pH 5-6 were flattened by train configurations at high charge densities.(Scheme 1(a), Region II(Figure 3)) (CHINF 3.3/PAA 5.0) film is flatten by train configurations of PAA, while (CHINF 3.3/PAA 3.3) film is porous by loop and tail configurations of PAA and dispersed CHINF.

On the other hand, (CHINF 3.3/PAA 3.3) film was porous by disperced fibers at high chage densities and polymer of tail and loop configurations at low charge densities. The refractive index and thickness of (CHINF 3.3/PAA 3.3) film is 1.29 and 64.89 nm.



Scheme. 1. Schematic illustrations of structures for (a) polymer and (b) fibers chain with different charge densities.

3.3 Durability evaluation

Figure 6 (a) and (b) shows the transmittance of before and after abrasion test for 100 cycles. Transmittance and surface structure were kept in spite of abrasion test. (Figure 6) It was demonstrated that one of the merits of the CHINF is high mechanical strength. As experimental comparison, the $(PAH/SiO_2)_3$ film was fabricated by LbL method. Figure 7 shows a surface image of the $(PAH/SiO_2)_3$ film before and after the abrasion tests for 10 cycles. The $(PAH/SiO_2)_3$ film was not durable by separation of film, because the contact area between the particles was smaller than that in the CHINF films. The surface structure of (CHINF 3.3/PAA 3.3) film was maintained by tangling of the CHINF.(Figure 6(c),(d))

Additionally, (CHINF/PAA) film have antifogging for hydrophilicity. The water contact angle at the (CHINF 3.3/PAA 3.3) film's surface was 15°. After cooled in refrigerator, the uncoated fogs immediately when moved in room temperature. On the other hand, the coated keeps high transparency. (Figure 8)

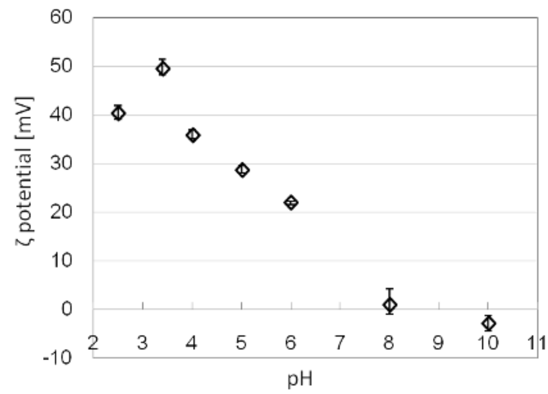


Fig.2. Zeta-potential of CHINF solution

Table. 1. The refractive index of the pH chang Refractive index with changing pH. The vertical column on the far left shows the pH values for PAA, and the horizontal row at the top shows the pH values for the CHINF solutions.

PAA↓ \ Chitin nanofibers →	2.5	3.3	4.0	5.0	6.0
2.5	1.33	1.41	1.32	1.38	1.41
3.3	1.37	1.29	1.34	1.42	1.42
4.0	1.33	1.36	1.31	1.37	1.45
5.0	1.47	1.45	1.32	1.31	1.41
6.0	1.40	1.45	1.41	1.43	1.38

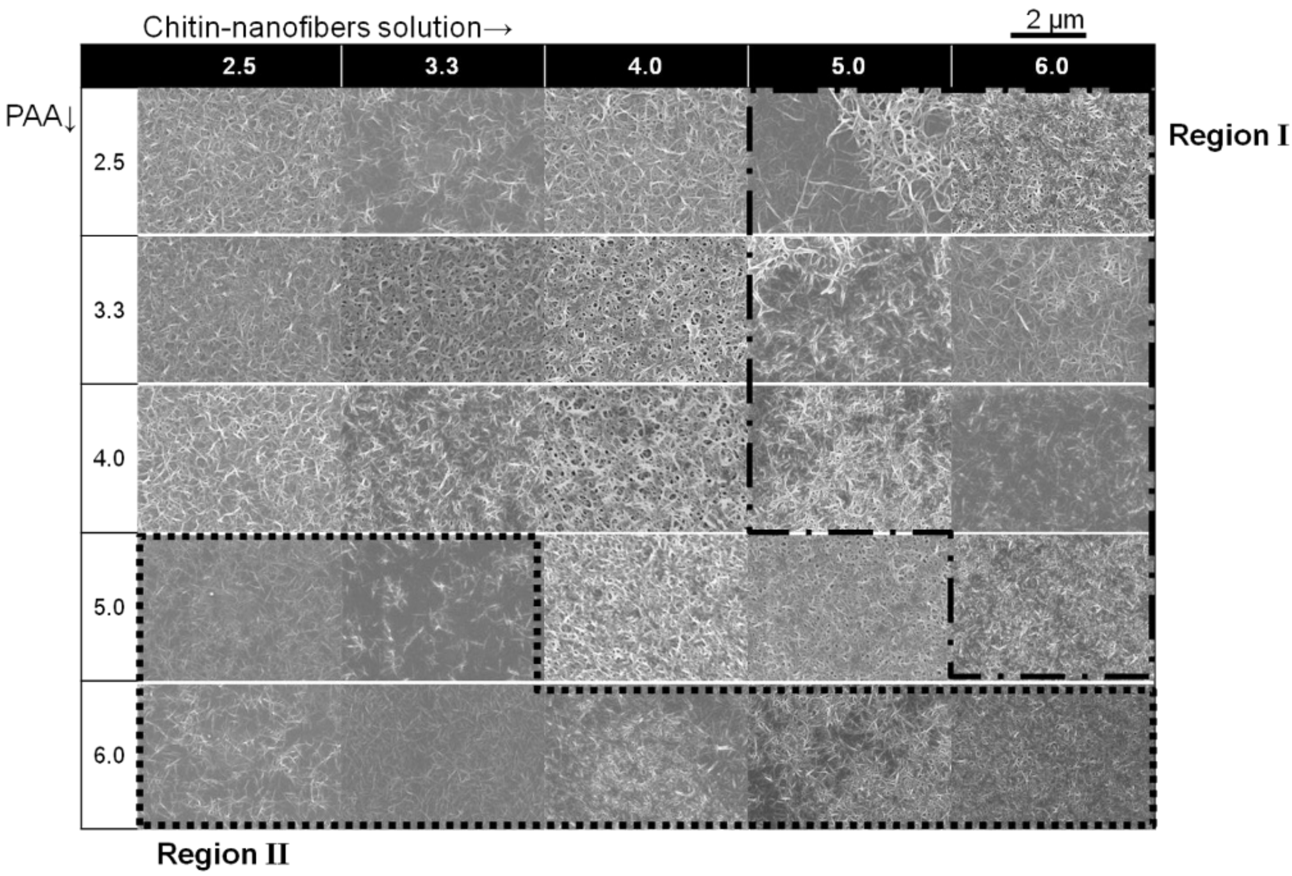


Fig. 3. SEM images showing effects of changing pH in the CHINF and PAA solutions. The vertical column (white region) shows the pH values for PAA, and the horizontal row (black regadvion) shows the pH values of the chitin-nanofiber solutions.

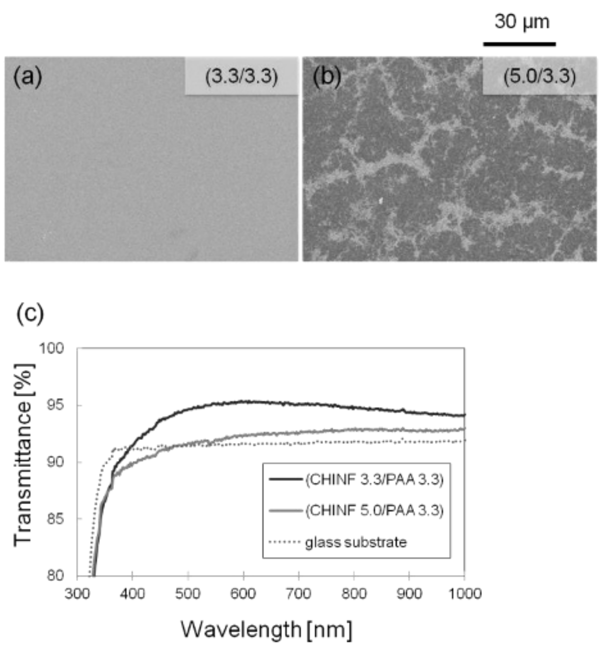


Fig. 4. SEM images illustrating the effects of changing the pH in the CHINF solutions. The left image shows (a) a (CHINF 3.3/PAA 3.3) film, and the right image shows (b) a (CHINF 5.0/PAA 3.3) film. (c) Transmittance of (a), (b), and the glass substrate.

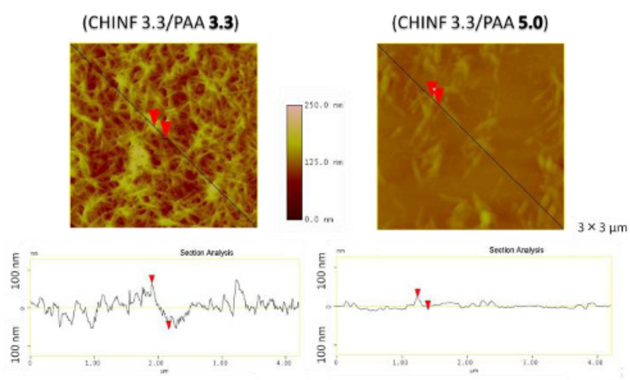


Fig. 5. AFM images and section analysis of (CHINF 3.3/PAA 3.3) and (CHINF 3.3/PAA 5.0).

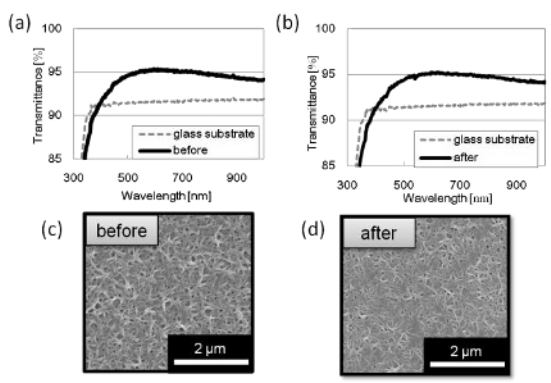


Fig.6. Transmittance of (a) before and (b) after abrasion test, SEM images of (c) before and (d) after abrasion test.

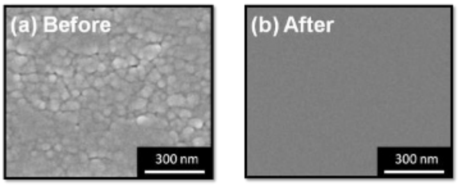


Fig.7. SEM images of $(PAH/SiO_2)_3$ (a) before and (b) after abrasion tests performed for 10 cycles.

Fig. 8. Photo of the cooled glass slide at room temperature.

4 Conclusion

From the TEM and AFM observations, it was found that each of CHINF was completely separated one by one. High quality antireflection (AR) film was successfully fabricated by LbL method because of the low refractive index. Porous surface was formed like flattened matchsticks pile with CHINF. High transmittance, homogeneous film was fabricated by adjustment of the pH. Refractive index and transmittance of the fabricated film is 1.29 and 95.07% (at 550nm), respectively. The durability tests demonstrated that the durability was drastically improved even in the wet process. The structure of the surface and transmittance were maintained after abrasion tests performed for 100 cycles, and the fabricated thin films had antifogging properties, due to their hydrophilicity. Because the CHINF had high mechanical strength, low refractive index films with high durability could be successfully fabricated using nanofibers of natural origin.

References

1. Ifuku, S.; Nogi, M.; Abe, K.; Yoshioka, M.; Saimoto, H.; Yano, H. *Biomacromolecules 10* (6), 1584-1588, (2009)
2. Chen, P.; Lin, A. Y.; McKittrick, J.; Mayer, M. A. *Acta Biomater 4* (3), 587-596, (2008)
3. Fan, Y.; Saito, T.; Isogai, A. *Carbohydr. Polym 79* (4), 1046–1051, (2010)
4. Hiller, J. A.; Mendelsohn, J. D.; Rubner, M. F. *Nature Mater. 1*, 59-63, (2002)
5. Wu, Z.; Walish, J.; Nolte, A.; Zhai, L.; Cohen, R. E.; Rubner, M. F. *Adv. Mater. 18*, 2699–2702, (2006)
6. Cho, J.; Hong, J.; Char, K.; Caruso, F. *J. Am. Chem. Soc. 128* (30), 9935–9942, (2006)
7. Xu, L.; He, J.; *Appl. Mater. Interfaces. 4* (6), 3293–3299, (2012)
8. Han, J. B.; Dou, Y. B.; Wei, M.; Evans, D. G.; Duan, X. *Chem. Eng. J. 169* (1) 371–378, (2011)
9. Cebeci, F. C.; Wu, Z. Z.; Zhai, L.; Cohen, R. E.; Rubner, M. F. *Langmuir 22*, 2856−2862, (2006)
10. Ariga, K.; Hill, J. P.; Ji, Q. *Phys. Chem. Chem. Phys. 9*, 2319-2340, (2007)
11. Kim, J. H.; Fujita, S.; Shiratori, S. *Colloids Surf. A: Physicochem. Eng. Aspects. 284,* 290-294, (2006)
12. Zhang, L.; Li, Y.; Sun, J.; Shen, J. *J. Colloid Interface* 319 *(1),* 302‑308, (2008)
13. Bravo, J.; Zhai, L.; Wu, Z. Z.; Cohen, R. E.; Rubner, M. F. *Langmuir* 23 *(13)*, 7293-7298, (2007)
14. Hattori, H. *Advanced Materials* 13 (1), 51‑54, (2011)
15. Süheyla Kas, H. *Journal of Microencapsulation 14* (6), 689-711, (1997)
16. Nuraje, N.; Asmatulu, R.; Cohen, R. E.; Rubner, M. F. *Langmuir 27* (2), 782– 791, (2011)
17. Qi, Z.-D.; Saito, T.; Fan, Y.; Isogai, A. *Biomacromolecules 13* (2), 553-558, (2012)
18. Shams, M. I.; Ifuku, S.; Nogi, M.; Oku, T.; Yano, H. *Appl. Phys. A: Mater. Sci. Process. 102* (2), 325–331, (2011)
19. Fan, Y.; Saito, T.; Isogai, A. *Biomacromolecules 9* (1), 192–198, (2008)
20. Fan, Y.; Saito, T.; Isogai, A. *Biomacromolecules 9* (7), 1919–1923, (2008)
21. Ifuku, S.; Nogi, M.; Yoshioka, M.; Morimoto, M.; Yano, H.; Saimoto, H. *Carbohydr. Polym. 81* (1), 134–139, (2010)
22. Shams, MI.; Nogi, M.; Berglund, LA.; Yano, H. *Soft Matter 8* (5), 1369-1373, (2012)
23. Ifuku, S.; Morooka, S.; Nakagaito, A. N.; Morimoto, M. Saimoto, H. *Green Chemistry 13* (7), 1708–1711, (2011)
24. Ifuku, S.; Ikuta, A.; Hosomi, T.; Kanaya, S.; Shervani, Z.; Morimoto, M.; Saimoto, H. *Carbohydrate Polymers 89* (3), 865–869, (2012)
25. Yoo, D.; Shiratori, S.; Rubner, M. F. *Macromolecules 31* (13), 4309–4318, (1998)
26. Shiratori, S.; Rubner, M. F. *Macromolecules33* (11), 4213–4219, (2000)
27. Mendelsohn, J. D.; Barret, C. J.; Rubner, M. F. *Langmuir 16* (11), 5017–5023, (2000)
28. Nair, K. G.; Dufresne, A. *Biomacromolesules 4* (3), 657-665, (2003)
29. Kim, S. J.; Kim, M. S.; Kim, S. I.; Spinks, G. M.; Kim, B. C.; Wallace, G. G. *Chem Mater, 18* (24), 5805-5809, (2006)
30. Guzmán, J.; Saucedo, I.; Navarro, R.; Revilla, J.; Guibal, E. *Langmuir 18* (5), 1567–1573, (2002)
31. Hedborg, F.; Lindstrom, T. *Nord Pulp Pap Res J.* 8(2), 258-263, (1993)
32. Guan, Y.; Qian, L.; Xiao, H.; Zheng, A.; He, B. *Cellulose* 15 (4), 619–629, (2008)