

1
2
3
4
5

Development of thermal properties and surface morphology of Poly(L-lactic)/Chitosan blend with Microcrystalline cellulose obtained from natural jute fiber

13

ABSTRACT

This research is a systematic study of how Microcrystalline cellulose (MCC) affects the thermal properties and surface morphology of Poly(L-lactic acid)(PLLA)/Chitosan blend by acting as reinforcement agent. MCC has high strength, high stiffness and high strain used for this work, has been obtained by acid (sulfuric acid) hydrolysis of α -cellulose extracted from jute fiber. Blends were prepared with constant percentage (20 percent) of Chitosan and different percentage of PLLA and MCC by solution casting methods. Then samples of those blends have been characterized by Fourier-transform infrared spectroscopy (FTIR) for the confirmation of blending, Thermo-gravimetric analysis (TGA) & Differential thermal analysis (DTA) for the thermal properties measurement and Scanning electron microscope (SEM) for measuring element distribution and surface morphology. FTIR Analysis curves showed that there is no new characteristic absorption peaks appeared in the spectrum except slight shifting due to hydrogen bond and confirmed a formation of suitable blends. TGA and DTG results indicated that MCC can improve the heat resistivity of the PLLA/Chitosan blends by increasing its degradation temperature upto 5%. Comparison of DTA peaks also ensured developed thermal properties. Image of SEM show the improvement of surface morphology.

Keywords: Blends, Microcrystal, Reinforcement agent, Acid hydrolysis, Thermal resistivity.

1. INTRODUCTION

1 In recent years, Poly(L-lactide) or Poly(L-lactic acid) (PLLA) is approaching to the centre of
2 polymer composites research depending upon its attractive properties and application
3 [1][2][3]. Because of some excellent properties i.e. natural degradability at room
4 temperature, non-toxicity and biocompatibility with human body, it is playing a vital role in
5 both medical and industrial purposes [4][5]. In medical science & tissue engineering, PLLA
6 can be used as degradable sutures, drug releasing particle and porous scaffolds for human
7 body cell [6]. To be implanted into the tissue engineering, it should have resistivity against
8 some bacterial or microbial infection [7]. Numerous studies have been performed for
9 developing the antibacterial activity of PLLA by blending with other natural antibacterial
10 agents. Among them, PLLA/Chitosan show stronger activity against the growth and activity
11 of some bacteria such as *Staphylococcus aureus* and *Escherichia coli* [8]. In order to
12 develop the thermal and mechanical properties of PLLA/Chitosan di-blend, is being used
13 with some functional additives by fabricating PLLA based composites and tri-blends [9]. In

14 this research we investigated the effects of microcrystalline cellulose (MCC) on the thermal
15 properties and surface morphology on PLLA/Chitosan blends. According to the previous
16 research, natural fiber has high mechanical performance to act as a reinforcing agent in
17 different polymeric composites [10]. MCC can form very strong particle–particle interactions
18 between polymer matrix because of their length, flexibility, and strong hydrogen bonds,
19 provide a better thermal resistivity [11][12]. Good dispersion with minor agglomeration
20 provides a better surface morphology and can improve mechanical properties [13]. To the
21 best of our knowledge, the effects of MCC on the properties of PLLA/Chitosan/MCC ternary
22 blends have not been reported so far. The objective of this study is to develop PLLA based
23 ternary blends with extended physical properties and also to investigate the effects of small
24 percentages of MCC on the properties of PLLA/Chitosan/MCC blends.

25

26 **2. EXPERIMENT**

27

28 PLLA, used as a blend matrix, was collected from Mitsubishi Chemical Corporation,
29 UNITIKA Plastics Division, Japan. Micro Crystalline Cellulose (MCC) was prepared from jute
30 fiber by conventional acid hydrolysis [14]. Chitosan was derived from the partial
31 deacetylation of chitin extracted from chemical treatment of shrimp shell [15][16]. Tossa jute
32 (*Corchoru solitorius*) and shrimp (*Penaeus monodon*) shell was collected from southern part
33 of Bangladesh as a raw jute and raw shell respectively.

34

35 **2.1 Extraction of Chitosan from shrimp shell**

36

37 Washed and dried raw shrimp shell was crushed to small size (approximately
38 0.5cmx0.5cm). Crushed shell was dipped into 1.57M HCl solution in 1gm:10ml (w/v) ratio for
39 6-8 hrs at ambient temperature under constant stirring for removing mineral [17]. After
40 washing & filtering with vacuum pump, demineralized shell, it was treated with 0.5% KMnO₄
41 in the presence of aq. H₂C₂O₄ for 2-3 hrs at 60-70°C with a ratio 1g:15ml (w:v), to remove
42 the color from the demineralized shell [18]. To separate the chitin from the protein complex it
43 was treated with 1.25M NaOH at 100°C for 30 mins [19]. Deacetylation process was carried
44 out by 50% NaOH at 100°C for 4-5 hours at a ratio between shell & solution is 1g:20ml (w:v)
45 to obtain pure chitosan from chitin [20].

46

47 **2.2 Extraction of Micro Crystalline Cellulose from Jute Fiber**

48

49 Washed raw jute fibers were dried and cut into small length (approximately 2cm) and
50 bleached with 0.08M sodium chlorite (NaClO₂) solution along with 2M CH₃COOH, at pH 4
51 [21]. Bleaching was conducted at temperature 85°C-90°C for 90 mins with a ratio 1g:80ml
52 (w:v). Prior to bleach, acetic acid and sodium acetate buffer solution was used to maintain
53 constant pH. After washing and drying at 105°C for 24 hrs, bleached fiber was treated with
54 17.5% NaOH for removing of β and γ cellulose [22]. NaOH was removed from α-cellulose by
55 washing several times with distilled H₂O and dried at 75°C for 48 hrs using vacuum drier.

56

57 MCC was prepared from previously prepared α-cellulose by acid hydrolysis process using
58 64 wt% H₂SO₄. H₂SO₄ was used to break down glycoside bonds of the cellulose polymeric
59 chain [23]. α-cellulose was treated by acid solution for 25–30 mins at 35°C-40°C in a ratio
60 1g:10ml (w:v) with constant stirring. The reaction was immediately stopped by quenching
61 with ice cool water to obtain gel type MCC [24]. H₂SO₄ was completely removed by washing
62 with distilled H₂O. MCC was stored in acetone, as dispersion, by replacing H₂O by acetone
63 with centrifugation.

64

65 2.3 Sample Preparation

66

67 Five samples of different composition were made by well-known solution casting method.
 68 Chloroform, a suitable solvent for PLLA, was used to prepare PLLA solution with continuous
 69 stirring [25]. Because of -OH group, hydrophilic property and reactivity of MCC can be
 70 increased. Therefore, it was dispersed in a non-aqueous solvent acetone with 90 mins
 71 sonication [26]. 1-2% acetic acid was used as a solvent for dissolving Chitosan [27]. To
 72 obtain the blend film, calculated amount of these three solutions were casted on petri dishes.
 73 Prior to cast, it was blended with vigorously stirring with magnetic stirrer until homogenous
 74 solutions were obtained [28]. Films, obtained on petri dishes were evaporated at room
 75 temperature for 3-4 days under vacuum [29]. Sample codes were designed as LCMC-X,
 76 where L, C and MC-X mean PLLA, Chitosan and MCC with X, stand for percentages of MCC
 77 in the blend respectively, are as follows:

78

79

80

Table 1: Sample code and composition of different blends for the experimental purposes

Sample Code	Composition of Blend
LCMC-0	PLLA 80% + Chitosan 20%+ MCC 0%
LCMC-1	PLLA 79% + Chitosan 20%+ MCC 1%
LCMC-3	PLLA 77% + Chitosan 20%+ MCC 3%
LCMC-5	PLLA 75% + Chitosan 20%+ MCC 5%
LCMC-10	PLLA 70% + Chitosan 20%+ MCC 10%

81

82

83

82 2.4 Sample Characterization

84

85

86

87

88

89

90

91

92

93

94

95

95 3. RESULT DISCUSSION

96

97

98

99

100

101

102

96 3.1 FT-IR Spectroscopy Analysis

98 FTIR spectroscopy technique was used to investigate intermolecular and intramolecular
 99 interactions. The absorption peak shifting in specific regions was monitored to determine the
 100 functional group interactions due to hydrogen bonding between PLLA, chitosan and MCC.
 101 The FTIR spectrum of neat PLLA, Chitosan, MCC and LCMC-0 and LCMC-5 are depicted in
 102 Figure 1.

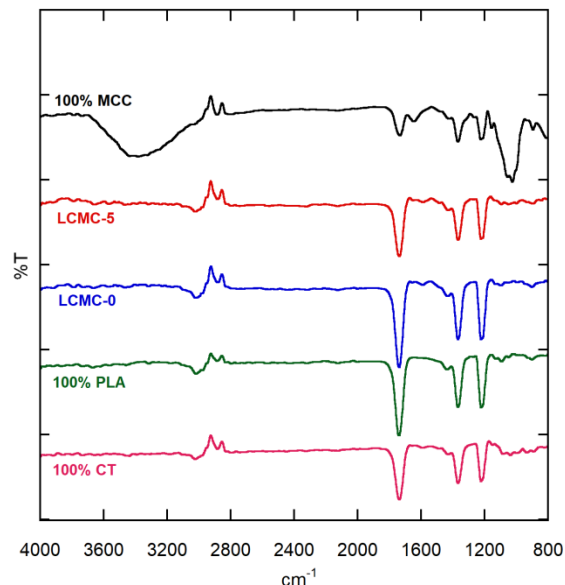


Figure 1: Comparison of FT-IR spectra of different blends and pure components

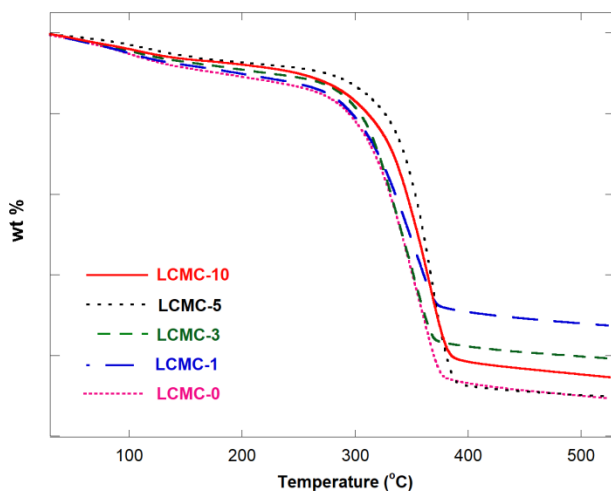
Table 3.1: Assigned Peak and Accounted Bond for LCMC-0 & LCMC-5

LCMC-0 Assigned Peak (cm ⁻¹)	LCMC-5 Assigned Peak (cm ⁻¹)	Accounted Bond for the Absorption
3652.13	3653.18	-OH stretching overlapping with N-H stretching
3017.34	3021.53	-CH stretching (Asymmetric)
2878.79	2881.68	-CH stretching (symmetric)
1735.86	1735.03	-C=O stretching
1365.65	1365.65	-CH bending
1220.96	1213.30	-C-O- stretching for Acid
1094.67	1092.73	-C-O- stretching for Alcohol

In LCMC-0 and LCMC-5, a small peak was observed at 3652.13cm⁻¹ & 3653.18cm⁻¹ can be originated from overlapping of OH stretching N-H stretching. Broad O-H stretching band of MCC was changed to a small peak in blends [30]. Same as symmetric, Peak for O-H bond stretching (asymmetric) shifted to higher wave number from 3017.34 cm⁻¹ to 3021.53cm⁻¹ indicating that bond energy increases after adding MCC. In case of C=O stretching from ester group of PLLA shifted from high region 1737.79cm⁻¹ to lower 1735.86cm⁻¹ in LCMC-0 and 1735.03cm⁻¹ in LCMC-5 confirmed that, MCC and CS produce intermolecular hydrogen bond between O-H and C=O group to weaken the C=O in ester group in PLLA. Similarly, other bending peaks shifted to the lower wave number caused by the intermolecular hydrogen bonding. Therefore characteristic absorption peaks were obtained from the LCMC-5, are nearly the same as LCMC-0. This can be explained based on a hypothesis that MCC is just combined with PLLA and CS by hydrogen bonding interactions without forming new functional groups. Therefore, this information can provide a confirmation of a good blend formation [31].

3.2 Thermal Stability Analysis

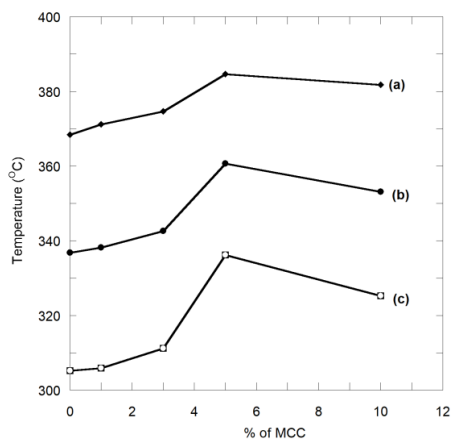
Thermal stability was observed by Thermogravimetric analysis (TGA).



125
126

Figure 2: Comparison between TGA curves of different blends

127 TGA data was obtained by measuring the weight loss due to degradation as a function of
128 temperature.



129
130
131

Figure 3: Relation between % of MCC and degradation point (a) Final degradation point (b) Half degradation point (c) Initial degradation point

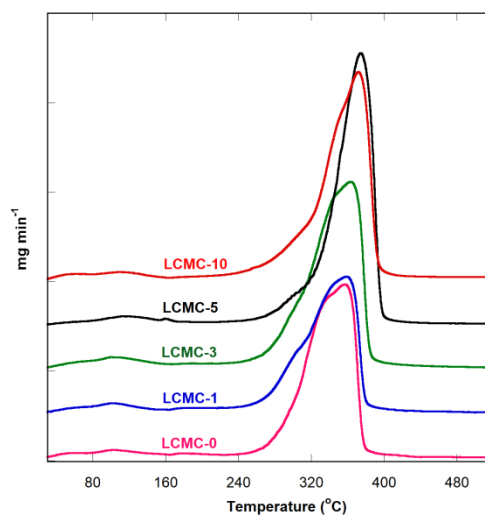
132

Table3: Initial, half and final degradation points of different blends

SAMPLE NAME	INITIAL DEGRADATION POINT (°C)	HALF DEGRADATION POINT (°C)	FINAL DEGRADATION POINT (°C)
LCMC-0	305.3	336.8	368.4
LCMC-1	306.8	338.2	371.2
LCMC-3	311.3	342.6	374.7
LCMC-5	337.2	360.7	384.6
LCMC-10	325.5	353.1	381.8

133

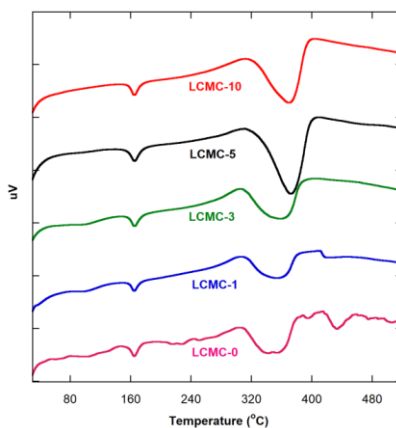
134 TGA curves have shown in Figure 2 are the comparison of different blends with different
 135 compositions. At 80°C to 160°C, initial loss of moisture and desorption of gases took place,
 136 also provided information about the percentage of moisture present in the blends. Major
 137 degradation was started at approximately 300°C and finally ended up to 390°C. TGA
 138 analysis shows a sharp increase of initial degradation point from LCMC-0 to LCMC-5. In
 139 case of LCMC-10, each degradation point decreased with the increase of the percentage of
 140 MCC. Initial degradation point shifted from 305.3°C to 306.8°C, 311.3°C and 337.2°C for
 141 LCMC-1, LCMC-3 and LCMC-5 respectively. MCC can act as filler in the PLLA/chitosan
 142 matrix and decrease flexibility and mobility of polymeric chain by holding them tightly [32].
 143 Therefore, more compact composite structure can be formed with better heat resistivity. In
 144 case of LCMC-10, MCC has a tendency to accumulate by hydrogen bonding in higher
 145 percentage and caused sudden drop in heat degradation point to 325.5°C [33].
 146



147
 148

Figure 4: Comparison between DTG curves of different blends

149 Half degradation point and final degradation point also showed the same pattern has given
 150 in figure 3. DTG data was used to determine the maximum degradation point has shown in
 151 figure 4. Maximum degradation point (T_{max}) increased similarly up to LCMC-5 and decreased
 152 for LCMC-10. For LCMC-0, LCMC-1, LCMC-3 and LCMC-5 the T_{max} are 357.0°C, 358.8°C,
 153 362.8°C & 374.3 respectively, and for LCMC-10 the T_{max} is placed on 371.2°C.
 154



155
 156

Figure 5: Comparison between DTA curves of different blends

157 Figure 5 shows the change in melting point (T_m) for different blends composition depending
 158 upon the DTA curves. DTA data shows similar trend in shifting of T_m with the addition of
 159 MCC into the blends. T_m of LCMC-0 is 162.6°C, shifted gradually up to 165.2°C in LCMC-5
 160 and then similarly dropped down to 164.9°C in LCMC-10.

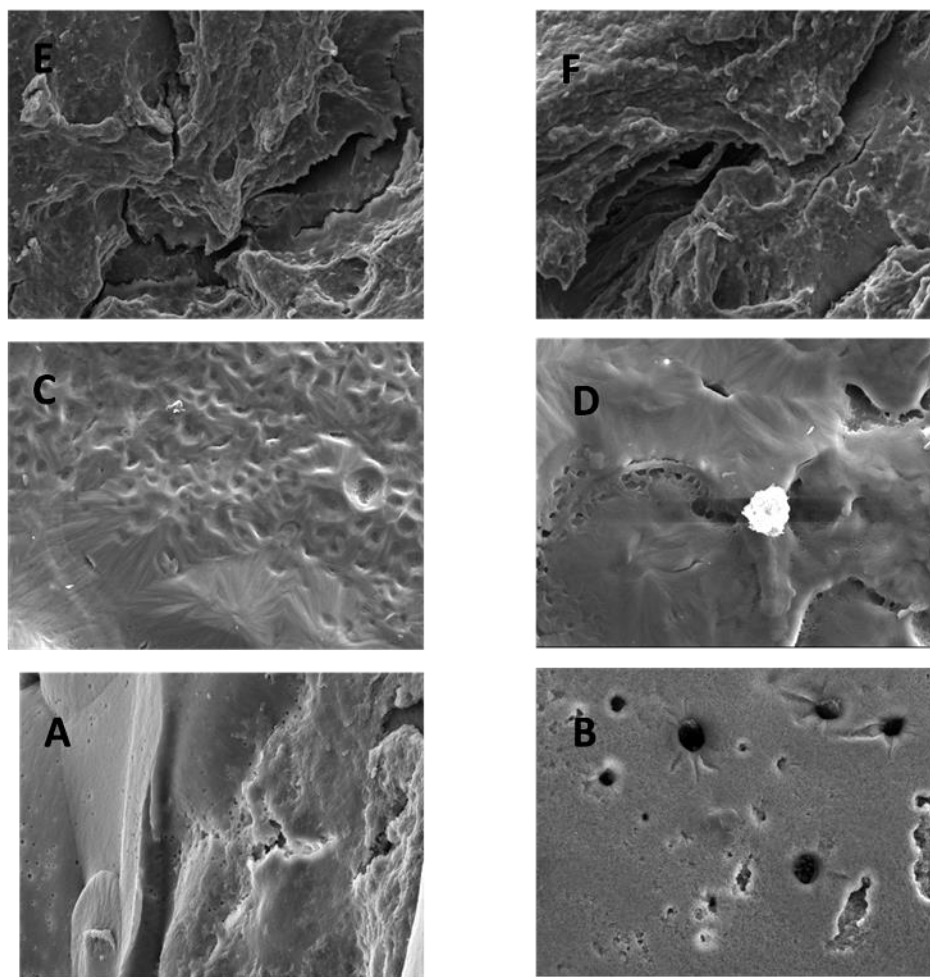
161

162 T_m has been positively changed with introduction of MCC, can be described based on their
 163 intermolecular attraction between PLLA, chitosan and cellulose. Due to the formation of
 164 hydrogen bonding among PLLA, chitosan and MCC, distance between the molecules
 165 decreases alternatively increases the molecular attraction caused high T_m [34]. However, in
 166 case of LCMC-10, low T_m may be due to the increasing of amorphous region provided by
 167 MCC or intermolecular bond formation between consecutive cellulose units.

168

169 3.3 Surface Morphology Analysis

170



171

172 **Figure 6: SEM micrograms for surface morphology analysis (A) LCMC-0 at 500X, (B)**
 173 **LCMC-0 at 1000X, (C) LCMC-5 at 500X, (D) LCMC-5 at 1000X, (E) LCMC-10 at 500X, (F)**
 174 **LCMC-10 at 1000X.**

175 Figure 6 shows the surface morphology of LCMC-0, LCMC-5 and LCMC-10 obtained from
 176 SEM microscopy. However, the surface is smoother than the other two types; relatively a
 177 large number of voids and cracks presents in the LCMC-0 caused relatively low melting point

178 and heat degradation point. After insertion of MCC in LCMC-5, it is clearly observed that the
179 number of pores dramatically reduced and surface looked more compact. MCC can be found
180 inside the matrix as filler and tightly attached with the matrix caused high heat resistance
181 capability. However with the increase of MCC, in LCMC-10, the surface was compacted but
182 fractured can be ascribed as the accumulation of MCC can make that fosse structure and
183 results the low heat degradation temperature and low melting point.
184

185 **4. Conclusion**

186
187 In this work we studied the influence of the addition of small amounts of MCC over the
188 thermal properties and surface morphology of PLLA/chitosan blend. After increasing the
189 thermal properties i.e. heat degradation temperature, melting point with the initial addition of
190 MCC up to 5%, it decreased with the 10% of MCC and showed maximum thermal property
191 at %5. Surface morphology also observed and can be concluded as the surface of LCMC-5
192 has less pores and cracks then the other compositions; however LCMC-0 showed the
193 smoother and plain surface comparing with the other.
194

195 **REFERENCES**

- 196 1. Macromol. Rapid. Commun, 2000;21: 117–132
- 197 2. Vert M., Schwarch G., Coudane J., J Macromol. Sci. A Pure Appl.Chem., 1995;32:787-96.
- 198 3. Thomson R.C., Yaszemski M.J., Powers J.M., Mikos A.G. J. Biomater.Sci.Polym. Ed
199 1995;7:23-38.
- 200 4. Hamad et al. – eXPRESS Polymer Letters, 2015; 9(5): 435–455
- 201 5. Coombes A.G.A., Meikle M.C., Clin. Mater., 1994;17: 35-67.
- 202 6. Lasprilla A. J. R., Martinez G. A. R., Lunelli B. H., Jardini A. L., Filho R. M., Poly-lactic acid
203 synthesis for application in biomedical devices – A review. Bio - technology Advances, 2012
204 ; 30: 321–382
- 205 7. X. Chen and H. J. Schluesener, “Nanosilver: a nanoprodukt in medical application,”
206 Toxicology Letters, 2008, 176(1), 1– 12
- 207 8. Maria C., Li’via C., Nelson D., Lucia M., Macromol. Symp., 2006; 245-246: 515-518,
208 DOI:10.1002/masy.200651373
- 209 9. Jour. of Chem. and Pharmac. Resear., 2014; 6(5):734-738
- 210 10. Aji P. M., Kristiina O., Mohini S., App. Poly. Scien., 2005; 97: 2014–2025, DOI:
211 10.1002/app.21779
- 212 11. Fatemeh S., Davood B., Pierre J. C., Marie C. H., Musa R. K., polym. compos., 2016,
213 DOI 10.1002/pc.24127
- 214 12. Nakagaito A.N., Fujimura A., Sakai T., Hama Y., and Yano H., Compos. Sci. Technol.,
215 2009; 69: 7
- 216 13. Kowalczyk M., Piorkowska E., Kulpinski P., and Pracella M., Compos. Part A: Appl. Sci.,
217 2011; 42: 10
- 218 14. Sarwar M. J., Abrar S., Zhibin H., Yonghao N., Cellulose, 2011; 18(2): 451–459
- 219 15. Varshosaz J., Exper. Opin. on Drug Del., 2007; 4: 263-273
- 220 16. Tarun K. V., Swaraj S., Natasha J., Jayaram C., Sohini R., Vijay B. T., Mayank G., and
221 Narender K., Vet World., 2017; 10(2): 170–175.
- 222 17. Laila M., Olfa G. B., Kemel J., Islem Y. & Moncef N., Appl. Biochem. Biotechnol. 2010;
223 162: 345–357, DOI 10.1007/s12010-009-8846-y
- 224 18. Yuegang Z., Jian Z., Nuno C., Environmen. Consci. Manufact., 2001: 4193: doi:
225 10.1117/12.417286
- 226 19. Peesan, M., Supaphol, P., Rujiravanit R., Preparation and characterization of hexanoyl
227 chitosan/ polylactide blend films, Carbohydr. Polym., 60; 2005: 343–350

- 228 20. Seiichi M., Masaru M., Reikichil w., Susumu Y., *Journ. Appl. Poly. Scien.*, 1983; 28:
229 1909–1917
- 230 21. Morán J. I., Alvarez V. A. , Cyras V. P. , Vázquez A., *Cellulose*, 2008; 15(1): 149–159
- 231 22. Cao X., Ding B., Yu J., Al-Deyab S.S., *Carbohydr. Polym.*, 2012; doi:
232 10.1016/j.carbpol.2012.06.046
- 233 23. Vedernikov N. A. and Kalnina V. K., *Wood Cell Wall and Its Changes at Chemical*
234 *Treatments*, Chem., Riga, Latvia, 1972
- 235 24. Thomas M.G. , Abraham E. , Jyotishkumar P. , Maria H.J. , Pothen L.A. , Thomas S.,
236 *Internat. Journ. of Biolog. Macromol.*, 2015; 81: 768-777
- 237 25. *Bioresour. Techn.*, 2010; 101(22): 8493-8501
- 238 26. Mehdi J. ,Jalaluddin H., Aji P. M., Mohd Z. B. H., Kristiina O., *Cellulose*, 2010; 17: 299–
239 307,DOI 10.1007/s10570-009-9387-9
- 240 27. Hong K. N., Na Y. P., Shin H. L., Samuel P. M., *Intern. Journ. of Food Microb.*, 2002;
241 74(1–2); 65-72
- 242 28. Hideto T., Suong H. H., Yoshito I., *Macromol.*, 1991; 24 (20): 5651–5656 DOI:
243 10.1021/ma00020a026
- 244 29. H Tsujia, Ikada Y., *Polymer*, 1999; 40(24): 6699-6708
- 245 30. Person F.G., Marchessault R.H., Liang C.Y., *J Polym. Sci.*, 1960; 43: 101-107
- 246 31. Ping Q., Yuan G., Guo-feng W., and Li-ping Z., “PLA/cellulosenanocomposites,” *Bio*
247 *Resour.* 2010; 5(3): 1811-1823
- 248 32. Khoo R.Z., Ismail H., Chow W.S., *Procedia. Chem.*, 2016; 19: 788 – 794
- 249 33. Fortunati E., Armentanoa I., Zhouc Q., Iannoni A., Sainoe E., Visaie L., Berglundd L.A.,
250 J.M. Kenny, 2014; 23(8): 1957-63, doi: 10.1093/hmg/ddt588
- 251 34. Lin Dai, Dan Li, Jing He, *J. Appl. Polym. Sci.*, 2013; DOI: 10.1002/APP.3945.
- 252