Investigation of Jojoba Oil-wax as a Plasticizer for Poly(lactic acid)

MOATAZ A. ELSAWY[a,b], JESPER DECLAVILLE CHRITIANSEN[a], CATALINA-GABRIELA SANPOREAN (PREVIOUSLY POTARNICHE)[a,*]

[a]*Department of Mechanical and Manufacturing Engineering, Aalborg University, Fibigerstraede 16, Aalborg 9220, Denmark*
[b]*Polymer laboratory, Petrochemical Department, Egyptian Petroleum Research Institute, Nasser City 11727, Cairo, Egypt*

This study is dealing with the effect of Jojoba oil-wax on physical properties of polylactic acid (PLA). Mixing of the materials was carried out by the extrusion process. The mechanical and thermal properties of the mixtures were investigated as a function of Jojoba oil content in the mixture. Differential scanning calorimetry (DSC) analysis indicated that the crystallinity of PLA increased with the increasing of the oil percentage in the mixture. Based on the experimental data, there are significant improvements in PLA mechanical properties by the addition of Jojoba oil; this can be observed from an increase in elongation to break. At low concentration of oil-wax the creep properties were not severely affected. The data reveals that the Impact strength reached near its double value at 3% Jojoba when compared with neat PLA.

1. Introduction

Biodegradable polymers made from renewable resources are important materials innovation because it decreases dependence on fossil based resources and reduces the amount of waste material resulting from the use of polymer from petroleum. One of these polymers is polylactic acid (PLA). PLA is a thermoplastic aliphatic polyester that might be derived from agricultural products, such as roots, chips or starch of tapioca, and sugarcane. PLA has several attractive properties such as biocompatibility, high strength, stiffness and thermo-plasticity but low impact strength [1]. In addition, due to its commercial availability at an affordable cost, it has been extensively studied and used for packaging applications as well as biomedical applications including sutures, bone screws, and tissue engineering scaffolds [2, 3]. Literature reports that the maximum PLA crystalline content is around 35-45%, but crystallization kinetic of neat PLA is very slow. Thus processability of crystalline PLA can be difficult for processes like extrusion or injection where solidification of a free surface or a high crystalline content is needed in an injection molded part [4-7]. Mechanical properties of PLA have been modified by several means including copolymerization [8], blending with other polymers [9], or by using additives. Additives are used in PLA to improve its crystalline properties, either by adding a nucleating agent to lower the free surface energy and initiate crystallization [10, 11], or plasticizers to increase chain polymer mobility [12]. Literature reports many plasticizers which can be used to improve PLA properties; the well-known plasticizing agent PEG is the most used and efficient plasticizer for PLA, but has the drawback of promoting polymer degradation during processing [13-15]. Modified vegetable oils are used as plasticizers to improve thermal stability in order to negate this shortcoming.

In this work, PLA was compounded with Jojoba oil-wax with different ratio of Jojoba to modify the mechanical properties. The stress-strain behavior (in uniaxial extension), relaxation, creep and impact strength were investigated for the blends. Thermal investigations were also performed to study the effect of Jojoba oil as a plasticizer for PLA.

Plasticizing materials can be classified into internal and external or in other words chemical and physical plasticizers [17-19]. Internal or chemical plasticizers may be flexible monomers incorporated regularly or irregularly between inflexible monomer of a polymer chain [20], flexible polymers may be copolymerized with rigid polymers [21] or by grafting of monomer onto polymer as side chains which reduce the crystallinity and glass transition by the reduction of the intermolecular forces [22,23]. The other type is external or physical plasticizers which include esters, polyester, solvents and non-solvent. Such a type of plasticizers is interacting physically with polymers through weak interaction by formation of hydrogen bond or by Wan der Waals forces. The primary role of external plasticizers as low molecular weight non-volatile additives is to improve the flexibility and processability of polymers by lowering the second order transition temperature (glass transition temperature, Tg) [24]. Compatibility between polymer and plasticizer is an important factor in choosing the external plasticizer, in

order to produce a homogeneous, stable composition with reduced tendency for plasticizer migration [25, 26].

2. Experimental

2.1 Materials

The PLA polymer (Ingeo™3001D) was purchased from NatureWorks® LLC (Minnetonka, USA) and PLA granules were dried at 100 °C for 3.75 hours before use. The Jojoba oil-wax, a commercial grade, was purchased from Egyptian Natural Oil Company NATOIL (Cairo, Egypt). Table 1 presents several physical and chemical characteristics of the Jojoba oil used in our experiments along with corresponding Jojoba values reported in literature for comparison purposes [27].

Table 1. Physical and chemical characteristics of Jojoba oil compared with literature values.

Characteristic	Value for this study	Corresponding value from literature
Specific gravity at 25 °C	0.860	0.863
Flash point (°C)	295	295
Fire point (°C)	338	338
Freezing point (ºC)	10.6 – 7.0	9.0
Boiling point (°C)	398	398
Ash (%wt)	0.10	0.10
Moisture content (%water)	Less than 0.05	**
Iodine value (g/100 g)	81-82	82
Saponification value	92-95	92
Average molecular weight	606	**
pH	6.7-7.0	7.0–7.3
Refractive index at 25 °C	1.460	1.465

2.2. Preparation PLA with Jojoba oil

PLA was mixed with Jojoba oil-wax with different ratios before extrusion. Extrusion was performed using a Prism Eurolab 16 co-rotating twin-screw extruder from Thermo Scientific with a strong configuration of the screws having 3 mixing zones with 90 degrees spaced mixing disks as part of the zone. Three different PLA/Jojoba blends were obtained which contained 1%, 3% and 7% Jojoba oil. All materials were moulded into dog bones with dimensions of $50 \times 4 \times 2$ mm using a piston type Haake minijet injection moulding machine from Thermo Scientific. The specimens were obtained using an injection pressure set to 800 bar, a melting temperature of 200 °C, a post pressure of 650 bar and the temperature of the mould was set to 25 °C.

2.3. Differential scanning calorimetry

The thermal characterization of extruded PLA and PLA/Jojoba blends was carried out using a DSC Q2000 from TA-Instruments at a constant nitrogen flow of 50 ml/min. The sample's weights were maintained at low levels (5 – 10 mg) for all measurements in order to minimize any possible thermal lag during the scans. The samples were heated from 25 °C to 200 °C with a heating rate of 5 °C/min followed by cooling with the same rate to 25 °C. The glass transition temperature (T_g), melting temperature (T_m), melting enthalpy (ΔH_f), cold crystalline temperature (T_{cc}), and cold crystalline enthalpy (ΔH_{cc}) were determined from the second heating run curve. The degree of crystallinity was calculated using the following equation [28].

$$\chi_c\ (\%) = \frac{(\Delta H_f)-(\Delta H_{cc})}{\Delta H°.w} \times 100 \qquad (1)$$

where $\Delta H°$ is the melting enthalpy per gram of 100% crystallinity and equal 93 J/g, w is the weight fraction of PLA in blends [29].

2.4. Mechanical testing

2.4.1. Tensile Strength, stress relaxation and creep testing

A Universal tensile machine –INSTRON 5944 with a load cell of 2 kN was used to study uniaxial tensile tests, stress relaxation and creep measurements. Five specimens from each material were tested according to the ISO-527 2 tensile test procedure. The tests were performed at room temperature (23 ± 2 °C) with a crosshead speed of 50 mm/min. Stress relaxation test was performed at constant strain of 0.015 mm/mm for 20 min with a crosshead speed of 10 mm/min. Creep tests were conducted at a constant load of 25 MPa with a crosshead speed of 10 mm/min for 20 min. All of the reported data for stress relaxation and creep tests were based on two repetitions.

2.4.2. Impact strength

Izod impact tests were performed on an Instron CEAST 9050 impact tester equipped with a DAS 8000 Junior data-acquisition system, with a sample frequency of 1000 kHz and a 50 J instrumented hammer. Specimens with dimensions of 80×10×3 mm were molded on the Haake minijet described previously. Impact tests were carried out at room temperature and a minimum of 5 specimens were tested for each material.

3. Results and discussion

3.1. Solubility parameters

Compatibility of external plasticizer may be affected by some factors, such as polarity, molecular weight, boiling point, and the solubility parameters. The plasticizer behaves normally as a solvent for the polymer, and the solubility parameter concept has been applied to this solution [30, 31]. Jojoba oil might be an example of external plasticizers; the advantages of Jojoba oil as a plasticizer for PLA emerge from its moderately high molecular weight compared with solvents and low if it compared with polymers, and the high boiling point (398 °C) which mean low volatility [32]. The solubility parameters (δ) of Jojoba oil and PLA can be calculated using Small's equation [33].

$$\delta = \frac{D\sum G}{M} \qquad (2)$$

where D is the density, G is molar attraction constant and M is molecular weight.

By applying the equation, the solubility parameter of jojoba oil and PLA found to be 8.7 $(Cal/cm^3)^{1/2}$ and 9.7 $(Cal/cm^3)^{1/2}$ respectively, so Jojoba might be a fair solvent for PLA.

3.2. DSC Data

The DSC studies were performed to investigate the effect of Jojoba oil on the crystallinity of PLA. Fig. 1 shows the DSC curves of PLA extruded with different amounts of Jojoba oil; 1%, 3% and 7% (w/w). The DSC scans shown were obtained from the second heating run with a heating rate of 5 °C/min. Table 2 shows the numerical values of temperatures, enthalpies and degree of crystallinity χ_c of PLA samples obtained from the DSC measurement. Fig. 1 shows four thermal characteristics; glass transition (T_g), cold crystallization peak (T_{cc}), endothermic fusion peak (T_m), and recrystallization peak (T_c) which appears just before melting. As noticed in table (2) there was a decrease in glass transition value obtained from the first heating run (T_{g1}) when increasing the amount of Jojoba oil in PLA. It is known that the glass transition (T_g) is a complex phenomenon which depends on several factors including intermolecular interactions, steric effects, the chain flexibility, the molecular weight, the branching and the cross-linking density [34]. The presence of the Jojoba oil molecules between the PLA polymer chains' could increase the chains flexibility and that would then be indicated by the decrease of the (T_{g1}) [35]. It can be observed that the cold crystallization peak enthalpy (ΔH_{cc}) decreased and the cold crystallization temperature (T_{cc}) shifted to a lower value with increasing of the Jojoba percentage as compared to the cold crystallization of neat PLA. This indicated that the PLA crystallization was enhanced by the presence of Jojoba oil. An increase of the

degree of crystallinity χ_c (%) from 9.11 to 13.74 can be observed by addition of only 1% Jojoba oil and up to 18.27 when 7% was added. Figs. 2 (a, b) show the first, second and the third run performed for the neat PLA and PLA3%Jojoba respectively. As shown from the figures, the cold crystalline peak for PLA3% Jojoba sample shifted to a higher temperature in the second and third runs than its position in first run and. This was not observed for neat PLA. The difference in T_g value between neat PLA and PLA/jojoba blends becomes lower in second run when compared with the first heating run. The cause of these phenomena may be attributed to the possibility of oil migration during melting of the sample in the first run which in turn leads to decrease the plasticizing effect due to oil migration out of the sample. DSC data correlates with computed solubility parameters, showing that jojoba oil might be a plasticizer for PLA.
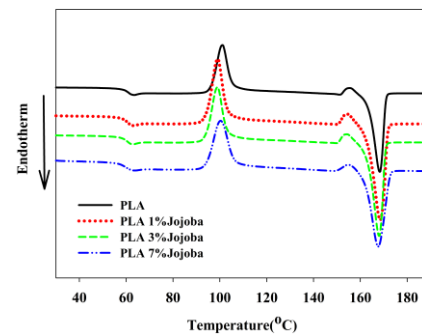

Fig. 1. DSC curve show 2nd up-scan for neat PLA and Jojoba containing PLA samples using 5 ^{o}C/min heating rate.
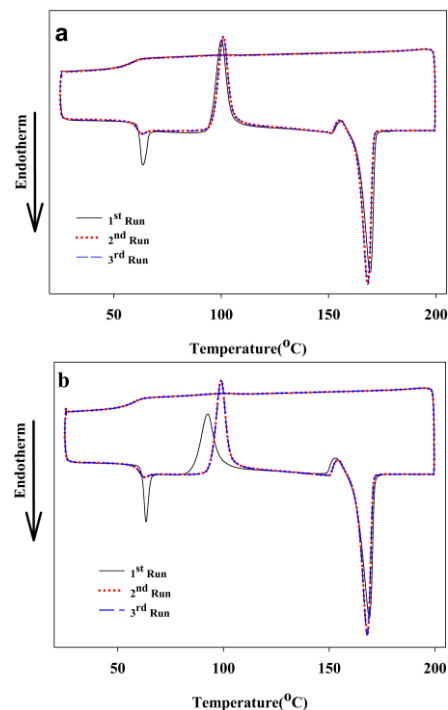

Fig. 2. The three DSC runs using 5 °C/min on a) neat PLA and b) PLA3% Jojoba sample.

Table 2. Thermal characteristics and degree of crystallinity of neat PLA and Jojoba containing PLA samples.

Material	Tg_1	Tg_2	$T_{cc}(^oC)$	$\Delta H_{cc}(J/g)$	$T_c(^oC)$	$\Delta H_c(J/g)$	$T_m(^oC)$	$\Delta H_f(J/g)$	$\chi_c(\%)$
PLA	64.22	61.16	101.01	30.34	3.30	3.30	168.31	38.82	9.11
PLA 1%Jojoba	63.24	60.83	99.05	28.74	153.89	3.88	168.53	41.39	13.74
PLA 3%Jojoba	63.23	60.56	98.88	27.08	154.39	4.059	168.00	40.77	15.18
PLA 7%Jojoba	62.69	60.16	100.38	27.35	154.02	3.671	168.23	43.15	18.27

Tg_1 and Tg_2 are glass transition temperature from first and second heating runs respectively

3.3. Mechanical properties

PLA polymer is a rather rigid polymer, it shows brittle fracture and exhibit limited deformation to breakage. Improving deformation to breakage and impact properties would be the main purpose of modifying PLA with Jojoba oil. Tensile strength, relaxation, creep and impact strength tests were used to investigate the plasticizing effect of Jojoba oil on PLA.

3.3.1. Tensile strength

The results of the tensile tests are shown in Fig. (3). The figure shows the stress–strain curves for neat PLA and PLA-Jojoba blends. It was observed that the tensile strength decreased and elongation at break increased with increasing the Jojoba percentage in the blend. By comparing the test results for PLA and PLA7%Jojoba, elongation to break increased from 3% to 74% and tensile stress was decreased from 77 MPa to 46 MPa, respectively. The experiments showed that PLA exhibited the characteristic of brittle material, this brittleness decreased by addition of Jojoba oil to PLA to provide a ductile behavior. Increasing oil content caused increased deformation to break. For concentrations above 1% necking was observed. The improvement in deformation to breakage when adding a plasticizer was in literature attributed to a crystalline structure caused by the addition of plasticizing oil [12, 36].
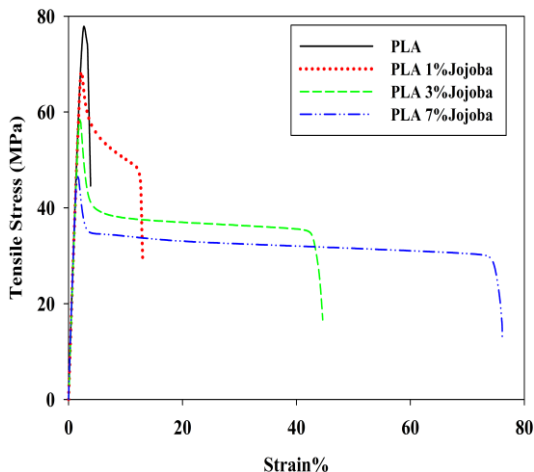

Fig. 3. Show the stress strain curve of PLA and PLA-Jojoba blends.

3.3.2. Relaxation tests

A parameter that provides information about the time dependent properties is the stress relaxation test. It is interesting to investigate as potentially increased mobility of chains would affect this property causing a faster relaxation. Fig. 4 shows the stress relaxation test for the four tested materials. The Jojoba containing samples showed a faster initial relaxation, however the slope of the curves after the initial relaxation remained more or less the same. So, the presence of the Jojoba oil caused higher mobility initially, whereas the relation processes that occurred at lower stress and longer time seemed to remain unaffected.
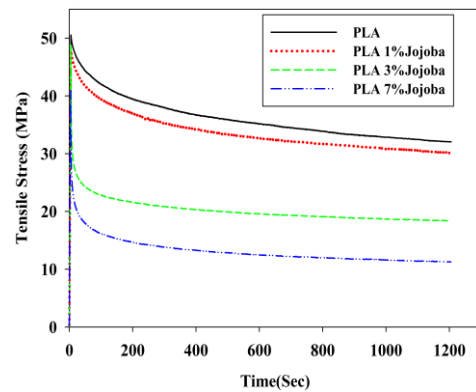

Fig. 6. Stress relaxation curve of curve of PLA and PLA-Jojoba blends.

3.3.3. Creep test

Creep tests were carried out to demonstrate the effect of the addition of Jojoba oil on the creep strain of neat PLA. Fig. 5 represents the creep behavior of neat PLA and PLA-Jojoba blends. As seen in Fig. 5 the deformation increased gradually with increasing Jojoba percentage from 1% to 3%, however the creep rate changed significantly when the percentage was increased to 7. This may be attributed to the extra mobility of the PLA polymer chains gained by increasing the Jojoba content from 3% to 7%.
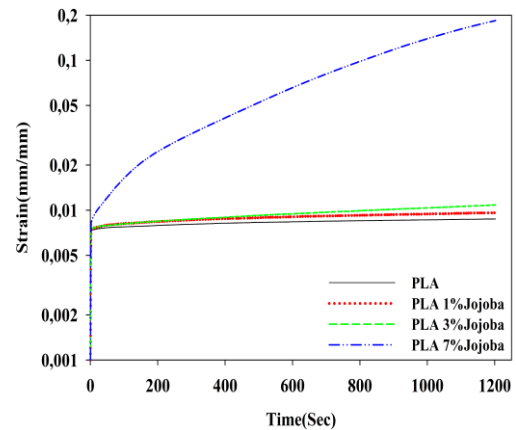

Fig. 5. Creep curve with a load of 25 MPa for 0, 1, 3 and 7% oil.

3.3.4. Impact strength

Impact strength is used to determine the amount of energy absorbed by a material during fracture. This absorbed energy is a measure of a given material's toughness. Fig. 6 shows the unnotched Izod impact strength measurements for neat PLA and PLA-Jojoba samples. A significant increase in impact strength was observed with increasing content of oil. An addition of Jojoba oil up to 3% produced an increase in impact strength to near its double value, but a further increase up to 7% only resulted in a marginal additional improvement in impact strength. The increase in toughness of PLA indicated the flexibility of PLA polymer chains caused by Jojoba oil [37, 38], and in turn it was an evidence for the plasticizing effect of Jojoba oil.
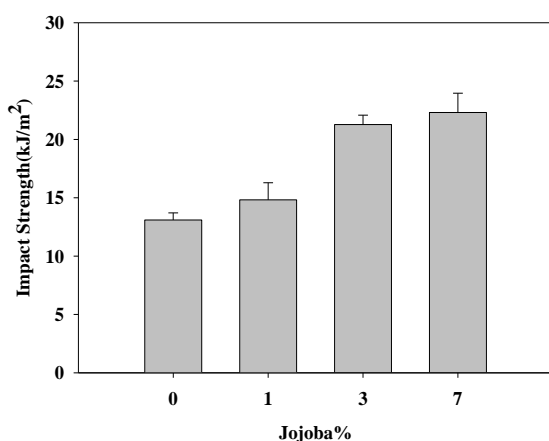

Fig. 6. Impact strength curve of PLA and PLA-Jojoba blends.

4. Conclusions

Jojoba oil-wax was studied as natural plasticizer derived from renewable resource. The choosing of Jojoba as PLA plasticizer was based on its compatibility with PLA, that coming from the close solubility parameters of both materials. The higher degree of crystallinity was an indication that the PLA polymer chain gained mobility by the presence of Jojoba oil between the chains. The plasticizing effect of Jojoba oil on PLA was evidenced through mechanical testing. The results revealed improvement of elongation to break and impact strength properties of PLA containing Jojoba over neat PLA. The overall enhancements in crystallinity and mechanical properties indicated the possibility of using Jojoba oil as a plasticizer for PLA.

References

[1] A. C. (Ed). Albertsson, Adv Polym Sci 157 (2002).
[2] A. Kramschuster, L. S. Turng, J Biomed Mater Res B **92**, 366 (2010).
[3] M. I. Sabir, X. X. Xu, L. Li, J Mater Sci **44**(21), 5713 (2009).
[4] D. Garlotta, Journal of Polymers and the Environment **9**, 63 (2001).
[5] P, Sarazin, L. Gang, J. O. William, B. D. Favis, Polymer; **49**, 599 (2008).
[6] V. M. Correlo, L. F. Boesel, M. Bhattacharya, J. F. Mano, N. M. Neves, R. L. Reis, Mat Sci Eng A **403**, 57 (2005).
[7] H. Li, M. Huneault, Polymer; **48**, 6855 (2007).
[8] D. M. Bigg, Adv Polym Tech **24**(2), 69 (2005).
[9] J. W. Park, S. S.Im, Polym Eng Sci **40**(12), 2539 (2000).
[10] N. Kawamoto, A. Sakai, T. Horikoshi, T. Urushihara, E. Tobita, J App Polym Sci; **103**, 198 (2007).
[11] T. Yokohara, M. Yamaguchi, Eur Polym J **44**, 677 (2008).
[12] H. Xiao, W. Lu, J-T. Yeh, J Polym Sci **113**, 112 (2009).
[13] C. Courgneau, S. Domenek, A. Guinault, L. Averous, V. Ducruet, J Polym Environ **19**, 362 (2011).
[14] S-H. Hyon, K. Jamshidi, Y. Ikada, Biomaterials **18**, 1503 (1997).
[15] L. T. Lim, R. Auras, M. Rubino, Prog. Polym. Sci. **33**, 820 (2008).
[16] P. M. Daugherty, H. H. Sineath, T. A. Wastler, Engin Exp Sta Ga Inst Techn Bul **17**, 1 (1953).
[17] H. F. Mark, N. G. Gaylord, Encyclopedia of Polymer and Technology: Plastics, Resins, Rubbers, Fibers. Interscience Publisher NewYork (1964).
[18] L. I. Nass, C. A. Heiberger. Encyclopedia of PVC: Resin Manufacture and Properties. Marcel Dekker Inc 1,702 (1986).
[19] A. S. Wilson. Plasticizers: Principles and Practice. The Institute of Materials, (1995).
[20] R. W. Venderbosch, H. E. H. Meijer, P. J. Lemstra, Polymer **35**, 4349 (1994).
[21] D. M. Panaitescu, P. V. Notingher, M. Ghiurea, F. Ciuprina, H. Paven, M. Iorga, D. Florea, J. Optoelectron. Adv. Mater. 9(8), 2524 (2007).
[22] S. W. Hwang, S. B. Lee, C. K. Lee, J. Y. Lee, J. K. Shim, S. E. M. Selke, H. Soto-Valdez, L. Matuana, M. Rubino, R. Auras, Polym Test **31**, 333 (2012).
[23] F. Hassouna, J. M. Raquez, F. Addiego, V. Toniazzo, P. Dubois, D. Ruch, Eur Polym J **48**, 404 (2012).
[24] S. L. Rosen, Fundamental Principles of Polymeric Materials, John Wiley & Sons, New York, NY, USA, (1993).

[25] J. K. Sears, J. R. Darby, The Technology of Plasticizers. Wiley, New York 1982.

[26] F. Cakar, O. Yazici, O. Cankurtaran, F. Karaman, Optoelectron. Adv. Mater. -Rapid Comm. **6**(11-12), 1153(2012).

[27] Al-Widyan, A. Mu'taz, Al-Muhtaseb, Energy Conversion and Management **51**, 1702 (2010).

[28] S. B. Roy, B. Ramaraj, S. C. Shit, S. K. Nayak, J App Polym Sci **120**, 3078 (2011).

[29] M. Mihai, M. A. Huneault, B. D. Favis, H. B. Li, Macromolecular Bioscience **7**, 907 (2007).

[30] L. A. Chen, J Appl Polym Sci **15**, 1247 (1971).

[31] J. J. Bernardo, H. Burrell, in "Polymer Science", A. D. Jenkins, Ed., North-Holland Publishing Co. Amsterdam, Chapter 8 (1972).

[32] L. Canoira, R. Alcantara, M. J. García-Martínez, J. Carrasco, Biomass and Bioenergy **30**, 76 (2006).

[33] P. A. Small, J Appl Chem **3**, 71 (1953).

[34] P. Krishnamachari, J. Zhang, J. Lou, J. Yan, L. Uitenham, polym anal charact **14**, 336 (2009).

[35] K. Q. Yu, Z. S. Li, J. Sun, Macromol Theo Sim **10**, 624(2001).

[36] A. M. Harris, E. C. Lee, J Appl Polym Sci **107**, 2246 (2008).

[37] Z. Xiong, C. Li, S. Ma, J. Feng, Y. Yang, R. Zhang, J. Zhu, Carbohydr Polym **95**, 77 (2013).

[38] M. Murariu, A. Da Silva Ferreira, M. Pluta, L. Bonnaud, M. Alexandre, P. Dubois, Eur Polym J, **44**, 3842 (2008).

_____

[*]Corresponding author: gabi@m-tech.aau.dk