

## Thermal Properties, Crystallinity, and Oxygen Permeability of Na-montmorillonite Reinforced Plasticized Poly(lactic acid) Film

Kurniawan Yuniarto<sup>1\*</sup>, Yohanes Aris Purwanto<sup>2</sup>, Setyo Purwanto<sup>3</sup>, Bruce A. Welt<sup>4</sup>, Hadi Karia Purwadaria<sup>2</sup>, and Titi Candra Sunarti<sup>5</sup>

1. Department of Agricultural Engineering, Universitas Mataram, Mataram 83125, Indonesia

2. Department of Machinery and Biosystem, Institut Pertanian Bogor, Bogor 16002, Indonesia

3. National Nuclear Agency, Serpong, Tangerang Selatan 15310, Indonesia

4. Department of Packaging Science, University of Florida, Gainesville 110270, United States of America

5. Department of Agroindustrial Technology, Institut Pertanian Bogor, Bogor 16680, Indonesia

\*e-mail: kurniawan2006@unram.ac.id

---

### Abstract

Introducing unmodified organically clay/Na-montmorillonite (Na-MMT) was applied into plasticized poly(lactic acid) PLA to produce film composites by direct casting. Film composite structure, the crystallinity degree and form, and thermal properties were carried out using X-ray diffraction and differential scanning calorimetry. The effect of Na-MMT to the tortuous path and the crystallinity degree in the plasticized film composites were calculated in oxygen barrier properties. Chromatogram film composites resulted in an intercalated structure that showed peak diffraction angle shift at about  $0.2^\circ$ . Then, a peak diffraction pattern was indicated in  $\alpha$ -form crystal structure. Plasticized PLA has a crystallinity degree at 34%, and the addition of Na-MMT increased to 52%. Glass transition temperature improved from  $53^\circ\text{C}$  to  $57^\circ\text{C}$ , and melting temperature remained stable at  $167^\circ\text{C}$ . Filling Na-MMT into plasticized PLA caused to enhance a tortuous path about 28% and improved the oxygen permeability to 80%. As a result, the addition of Na-MMT of 3% into plasticized PLA during film composite preparation using the mixing method resulted in balancing properties related to the crystallinity degree, thermal properties, and oxygen barrier properties.

### Abstrak

**Sifat Panas, Kristalinitas, dan Permeabilitas Oksigen Film Poly(lactic acid) Terplastisasi diperkuat Na-montmorillonite.** Pembuatan film komposit *poly(lactic acid)* terplastisasi PEG400 dengan bahan penguat Na-montmorillonite (NA-MMT) dilakukan dengan metode *direct casting*. Film komposit PLA terplastisasi dilakukan uji struktur komposit, sifat panas, derajat kristalinitas dan permeabilitas terhadap oksigen. Pengujian sifat panas dan penghitungan derajat kristal diperoleh dari pengukuran *differential scanning calorimetry* (DSC), analisis struktur komposit menggunakan xray diffraction (XRD) dan pengukuran permeabilitas oksigen menggunakan *dynamic accumulation method*. Film komposit PLA terplastisasi dengan bahan penguat Na-MMT menunjukkan terjadinya interkalasi polimer Na-MMT dengan pergeseran sudut difraksi sebesar  $0.2^\circ$ . Struktur kristal yang terbentuk memiliki bentuk alpha dan derajat kristal film komposit meningkat dari 34% menjadi 52%. Parameter sifat panas film PLA terplastisasi dengan bahan penguat Na-MMT mengalami perbaikan suhu transisi gelas dari  $53^\circ\text{C}$  menjadi  $57^\circ\text{C}$  meskipun suhu leleh tidak mengalami perubahan tetap bekisar pada nilai  $167^\circ\text{C}$ . Peran Na-MMT membentuk jalur liku sebesar 20% sehingga terjadi peningkatan daya halang oksigen film komposit PLA terplastisasi yang ditunjukkan dengan penurunan nilai permeabilitas sebesar 80%. Penambahan Na-MMT sebesar 3% dalam pembuatan film komposit PLA terplastisasi cukup untuk mendapatkan keseimbangan perbaikan sifat panas, kristalinitas, dan daya halang oksigen.

*Keywords: crystallinity, Na-MMT, plasticized PLA, permeability, thermal*

---

### 1. Introduction

Poly(lactic acid) or PLA is a biobased thermoplastic which can be produced from an agricultural source by fermentation of lactic acid. Naturally, PLA has good

mechanical properties, such as high strength, high modulus and biocompatibility [1]. However, several researchers emphasized that PLA brittleness and stiffness are limited for wide application use [2]. Thus, many articles have reported applying a plasticizer agent to

improve the mechanical properties. Polyethylene glycol (PEG) is a suitable plasticizer via an hydrophilic interaction group from PEG with a hydrophobic group from PLA [3]. Surprisingly, PEG has a good miscibility with PLA and does not show phase separation [4]. On the other hand, solubility and miscibility of PEG will decrease with increasing molecular weight [5]. Introducing PEG400 at about 5% into PLA created good barrier properties and a morphological structure, although it reduced the thermal properties of plasticized PLA film [6].

Preparation film composites based on PLA has been explored by other researchers. Some filler materials, such as fibers, layered silicates, and nanoparticles, have been reported to partially improve pure PLA composites of the film properties [2,7-10]. Clay based filler, such as organically montmorillonite (NaMMT), is the popular used type of clay as an accepted filler for polymer because the enhanced mechanism is similar to that in function with polymer alone [11]. Promising and efficient MMT for polymers is even less than 10% improved thermal stability and crystallinity [12]. A series of pure PLA with various modified layered silicates have been prepared to achieve important improvement in the mechanical properties [13]. Introducing modified MMT of 5-7% into pure PLA has improved thermo-mechanics due to nucleating agents MMT that promoted crystallinity degree [14]. A series of neat PLA containing MMT of 1-6% showed intercalation and configured a tortuous path in composite structures which resulted in decreasing water vapor permeability [15]. However, research related to the nonmechanical alteration plasticized PLA composited reinforced NaMMT do not explored yet comprehensively. As a reason is the plasticizer of PEG400 can act as a bridge among PLA-NaMMT interaction during composite film preparation. So, it would create a good non mechanical properties for film composite plasticized PLA reinforced NaMMT.

The effect of organically unmodified clay/Na-MMT reinforced the plasticized PLA will be analyzed both the polymer structure and the crystallinity degree for producing plasticized PLA/MMT composite film. Thus, the filling agent of Na-MMT into plasticized PLA composite film that impact to morphological structure as tortuous paths will be investigated to oxygen diffusion effect because it does not any report yet. In hence, thermal properties were also observed for the film composite plasticized PLA reinforced NaMMT.

In this research, we investigated non mechanical properties film composite of plasticized PLA reinforced Na-MMT using direct casting. The aim of this research is to identify the film composite structure and the crystal form. Then, measured thermal properties, the crystallinity degree, the tortuous path, and oxygen barrier property.

## 2. Experiment

**Materials.** Poly(lactic acid) (PLA) A-101 with the molecular weight of 80,000 g/mole and the density 1.24 g/cm<sup>3</sup> was purchased from ShenzenEsun (China). Chlorofom C606-4 HPLC grade was purchased from Fisher Scientific, USA. Polyethylene Glycol-400 was purchased from Fisher Scientific, USA, with the average molecular weight of 380-420, the density of 1.13 g/mol. Unmodified montmorillonite (Na-MMT) was purchased from southern clay products, Gonzales, Texas, USA.

**Plasticized PLA/Na-MMT composites.** Before processing, PLA was dried in the oven for 6 hours at 45 °C. PLA-PEGmatrix films were cast in glass petri dishes by a mixing method. PLA was diluted into chlorofom at 5% of weight (w/v). In detail, 20 grams of PLA was dissolved in 400 mL chlorofom and stirred vigorously at 750 rpm for 60 minutes at 55 °C. Then, PEG was added (5% v/v) and continued to be stirred for 15 minutes. Then, plasticized PLA solution was added with Na-MMT and stirred for 15 minutes. Concentration of Na-MMT was in 1%, 3%, and 5%. The dissolved solution was poured onto a glass petridish. Then, composite solutions were dried into films at 35 °C for 15 hours. Resultant plasticized PLA film composites were peeled from petridishes, and thicknesses were measured in 10 locations using a micrometer.

**Wide angle X-ray diffraction.** The wide angle X-ray diffraction (WAXD) analysis was carried out by XRD Goniometer VG-108R, Shimadzu, Japan. The instrument has a monochromatic source and a Cu radiation source of wave length 1.546 Å operating at 30 kV 30 mA, width step of 0.05 degree/step and scan speed at 3 degree/step. D-spacing was calculated using the Bragg's law equation. Chromatograms were analyzed into two regions, a small angle at 2θ 2-10° and a wide angle at 2θ 5-70°.

**Differential scanning calorimetry (DSC).** The glass transition, crystallization, and melting temperature of neat PLA, PLA-PEG blend samples have been studied using Perkin-Elmer Diamond DSC. Samples of 3.5 mg were heated from 30 to 400 °C at a rate 20 °C/min under a constant flow rate of 20 mL/min nitrogen gas purging through the calorimeter.

The degree of crystallinity can be calculated by using the following equation:

$$X_c \% = \frac{100\Delta H_m}{\Delta H_f W_{FLA}} \quad (1)$$

Where  $\Delta H_m$  is the heat of fusion of samples,  $\Delta H_m$  corresponds to the heat of fusion for 100% crystallized PLA. The crystallinity of PLA in the copolymer was

calculated, where the heat of fusion of crystalline PLA was set equal to 93.6 J/g.

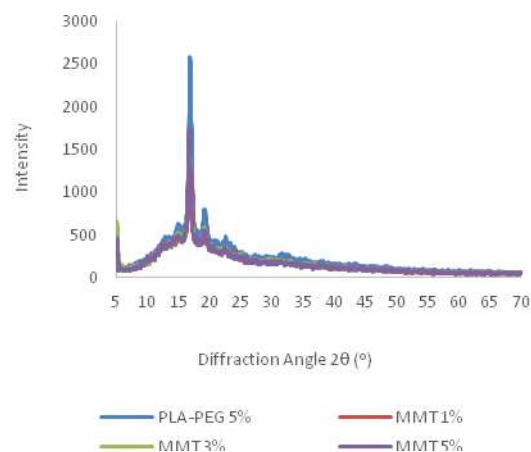
**Permeability analysis. ASTM F3136-15.** The oxygen permeability of the matrix film neat PLA and copolymer PLA-PEG was measured according to a new method “dynamic accumulation”. This method has been established as ASTM F3136-15, and the measurement used the permeation apparatus from OxySense, Inc. 6000 S. Eastern Ave, Suite 14G, Las Vegas, NV 89119, USA. Oxygen transmission rate measurement was done at 23 °C. Thickness variety of matrix film plasticized PLA/MMT composites was in seven different thickness, three replications, and temperature condition of 23 °C.

The oxygen accumulation chamber had a sample area of 16.62 cm<sup>2</sup> and the volume of 8.3 cm<sup>3</sup>. Initially, the cell was purged with more than 10 volumes of industrial grade compressed nitrogen. Purge completeness was followed by monitoring an oxygen concentration decrease to a constant zero level using the OxySense Model 310 device. Next, industrial-grade oxygen (approximately 100%) was used to purge the test-gas chamber. Oxygen concentration in the DA chamber was measured and recorded periodically during the test using the commercially available oxygen fluorescence sensor (Model 310; OxySense, Inc). OTR was subsequently calculated as described [16].

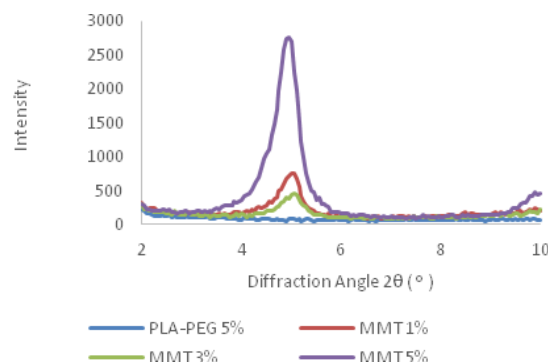
### 3. Results and Discussion

**Morphological structure.** Na-MMT distribution into plasticized PLA can be seen from the chromatogram pattern of XRD analysis results [17]. The distribution pattern can be classified as three structure types: dispersion, intercalation, and exfoliation. The structure of plasticized PLA/Na-MMT composite film was represented the WAXD analysis at a low angle ( $2\theta$  2-10°) to analyze the effect of Na-MMT into plasticized PLA. Then, a wide angle investigation thoroughly measured the composite film at  $2\theta$  5-70°. Wide angle diffraction patterns of plasticized PLA/Na-MMT were shown in Figure 1, whereas a small angle measurement was shown in Figure 2. Chromatograms plasticized exhibited reflection at  $2\theta = 16.9$  and indicated a semi-crystalline structure of PLA [18,19]. Addition of Na-MMT at various concentrations into plasticized PLA does not significantly change the PLA origin peak, although some peak shifted into a lower angle. Generally, Na-MMT was dispersed into plasticized matrix film, although a tiny intercalated structure occurred for Na-MMT addition about 3% and 5% that shows a shift diffraction angle at about 0.25° and 0.18°. Other researchers reported a shift angle diffraction when added MMT of 5% into a pure PLA matrix from  $2\theta$  16.6° to 16.4° [17].

In detail, the effect of Na-MMT shows a different pattern when the diffraction angle ran into a small angle



**Figure 1. The Diffraction Pattern of Plasticized PLA/Na-MMT Film Composites at a Wide Angle**



**Figure 2. The Diffraction Pattern of Plasticized PLA/Na-MMT Film Composites at a Small Angle**

because the main peak of diffraction of Na-MMT can be found clearly at  $2\theta = 2-10^\circ$  with the main peak at  $2\theta$  5° [20]. Other researchers measured the main peak of MMT at  $2\theta$  7-8° and basal spacing 11.7 Å [21]; the main peak was at  $2\theta$  4° and basal spacing 22 Å [17]. From this research, the main peak plasticized PLA was absent at  $2\theta$  2-10°; however, plasticized PLA/Na-MMT composites show the main peak close to  $2\theta$  5°. Then, a basal spacing plasticized PLA/Na-MMT increased for presenting 3% and 5% Na-MMT at 17.6 Å and 17.9 Å, respectively. This condition shows an intercalated structure during the mixing. This suggests that plasticized PLA filled interlayer space of Na-MMT during the mixing [21]. Preparing bioplastic from starch reinforced Na-MMT resulting an increasing basal spacing Na-MMT from 11.7 Å to 17.1 Å followed with an intercalated starch/Na-MMT composites using plasticized PLA/PEG1000 of 20% and MMT of 3% increased basal spacing clay from 12.1 to 17.7 Å [20]. Related to the crystal structure of plasticized PLA/Na-MMT, this shows that the movement remains stable compared to that of plasticized

PLA without MMT addition. From the Figure 1, it is clear that some main peaks appeared to be similar at 2016°, 19°, and 22°. These peaks illustrated a crystal structure in  $\alpha$  form [19]. It means that Na-MMT addition does not change the crystal structure of plasticized PLA.

**Thermal properties.** Thermal properties of plasticized PLA/NA-MMT were measured including glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), enthalpy fusion ( $\Delta H_m$ ) and the crystallinity degree ( $X$ ). Previous research showed that plasticized PLA using PEG400 decreased glass enthalpy fusion ( $\Delta H_m$ ) and the crystallinity degree ( $X$ ). Previous research showed that plasticized PLA using PEG400 decreased glass transition temperature and melting temperature. Neat PLA was recorded having a  $T_g$  about 58.5 °C and plasticized PLA fell to 53.2 °C. Then, melting temperature decreased slightly from 167.72 °C to 167.26 °C. On the other hand, the crystallinity degree of plasticized PLA increased from 17.7% to 34.6% [6].

Thermal properties of plasticized PLA/Na-MMT are shown in Figure 3. It can be seen that the presence of Na-MMT improved the  $T_g$  value of plasticized PLA film composites. It could be related to the molecular chain mobility where Na-MMT has layered silicates enhancing the adhesion degree between plasticized PLA and the layered silicate surface. However, Na-MMT of 5% decreased  $T_g$  because excessing Na-MMT reduced the crosslinking between matrix polymer and MMT. Other researchers reported the reduced  $T_g$  plastic polymer based on polyester because of the crosslinking between MMT and plasticized PLA matrix [22].

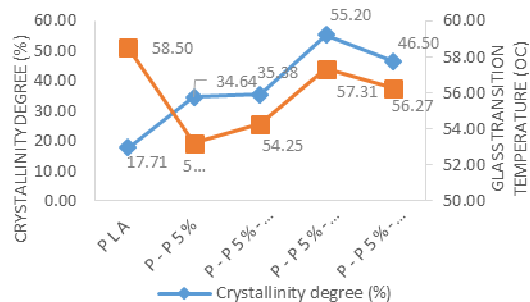
Surprisingly, the melting temperature of plasticized PLA/Na-MMT did not improve. Then, the melting temperature decreased slightly from 167.72 °C to 167.26 °C. On the other hand, the crystallinity degree of plasticized PLA increased from 17.7% to 34.6%. Thermal properties of plasticized PLA/Na-MMT are shown in Figure 3. It can be seen that the presence of Na-MMT improved the thermal properties.

It can be seen that the presence of Na-MMT improved the  $T_g$  value of plasticized PLA film composites. It could be related to the molecular chain mobility where Na-MMT has layered silicates enhancing the adhesion degree between plasticized PLA and the layered silicate surface. However, Na-MMT of 5% decreased  $T_g$  because excessing Na-MMT reduced the crosslinking between matrix polymer and MMT. Other researchers reported the reduced  $T_g$  plastic polymer based on polyester because of the crosslinking between MMT and plasticized PLA matrix [22]. Surprisingly, the melting temperature of plasticized PLA/Na-MMT remained stable at about 167 °C.

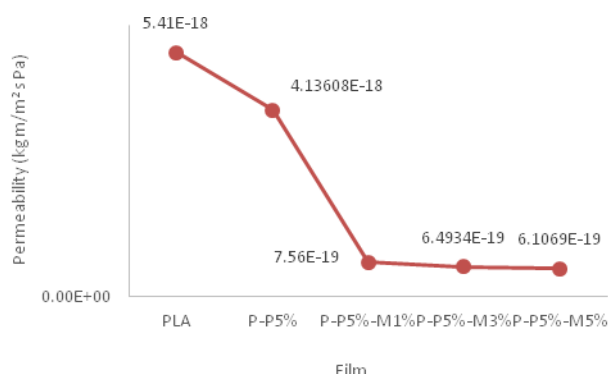
The crystallinity degree of plasticized PLA/Na-MMT increased with addition of Na-MMT of 3% and 5%. The improved crystallinity degree was about 32% to 52% compared to that of plasticized PLA. Crystallinity degree improvement with presenting MMT has been reported for PET/MMT composites and using PLA/MMT [12,23].

**Oxygen permeability.** A new method of permeability measurement was applied to measure barrier properties. Using the dynamic accumulation method, the barrier properties can be obtained by oxygen transmission rate measurement. Oxygen permeability at various Na-MMT concentrations is showed in Figure 3. Some researchers reported the effect of MMT as the filling agent that altered composites morphological like tortuous paths, and the amount of tortuous path formation can be seen in Figure 3. Generally, Na-MMT creates some physical composite alterations because of dispersion, intercalated, and exfoliated structures. In addition, presenting a tortuosity path gave an impact to the oxygen diffusion distance. The diffusion distance length increased between 4.79 and 15.66 micron. Then, the tortuosity path increased into plasticized PLA/Na-MMT from 7.85 to 28.13%. Increasing diffusion distance and a tortuous path is responsible to improve oxygen barrier properties because the amount of oxygen passing through the film composites will decrease. Tortuous paths can be created from the filler agent into composites caused by the tortuous structure in the composite structure that affects the improving barrier properties [24,25]. In addition, silicate addition into film matrix composites enhanced diffusion length which influenced the improved barrier properties [26].

Detail oxygen permeability of plasticized PLA/Na-MMT is shown in Figure 4. Oxygen permeability measurement of plasticized PLA/Na-MMT is not significantly different at various Na-MMT additions from 1% to 5%. In addition, oxygen permeability improved 5 to 7 times or 80% with the addition of Na-MMT into plasticized PLA film composites. Other researchers reported oxygen permeability improvement of composite PLA/clay was about 25% (Picard *et al.*, 2013), 48% [2,27-29]. Introducing Na-MMT into plasticized PLA was



**Figure 3. Thermal Properties Plasticized PLA/Na-MMT Film Composites**



**Figure 4. The Oxygen Permeability of PLA, Plasticized PLA, and Plasticized PLA/Na-MMT Composites**

also increasing the crystallinity degree. It could enhance the oxygen barrier properties because the crystalline structure is present in plasticized PLA/Na-MMT hindering the mobility of the amorphous chain. As mentioned before, the diffusion of gas molecules mainly moves in the amorphous region of the polymer within the free volume among the polymeric molecules [30]. In addition, the effect of the crystalline structure can act as the impermeable structure from penetrating gases [31,32].

#### 4. Conclusions

Characterization structure, thermal properties measurement, and oxygen permeability of plasticized PLA/Na-MMT film composites for film packaging were carried out. Introducing Na-MMT represented an intercalated structure in the morphological composite. Diffractogram peaks show the crystal structure formation of plasticized PLA/Na-MMT in  $\alpha$ -form. Increasing Na-MMT into plasticized PLA improved the crystallinity degree of composite film. Glass transition temperature increased with the presence of NaMMT, although melting temperature remained stable. Na-MMT enhanced oxygen barrier properties on the plasticized PLA of composite film by tortuous path improvement. To sum up, this research would be that Na-MMT is a good filler to enhance crystallinity formation, glass transition temperature, and oxygen barrier properties of plasticized PLA. However, the concentration addition must be conducted carefully because the contrary effect might occur with the largest Na-MMT concentration. Na-MMT can be added into the plasticized PLA composite film to improve non-mechanical properties at concentration between 3 and 5%.

#### Acknowledgements

This work was supported in part by the University of Florida, Agricultural Experiment Stations at the Agricultural and Biological Engineering Department's Packaging Engineering Laboratory and Directorate General of Higher Education (DGHE) of the Ministry of Education of the Republic of Indonesia.

#### References

- [1] B.W. Chieng, N.A Ibrahim, W.M.Z.W. Yunus, M.Z. Hussein, *Polymer*. 6/1 (2014) 93.
- [2] K. Halasz, L. Csoka, *J. Eng.* 1 (2013) 1.
- [3] R.A. Auras, L-T. Lim, S.E.M. Selke, H. Tsuji, *Poly(lactic acid) Synthesis, Structures, Properties, Processing, and Application*. John Wiley & Sons. Inc., Hoboken, New Jersey, 2010, p.528.
- [4] A.K. Mohapatra, S. Mohanty, S.K. Nayak, *Polym. Compos.* 35 (2014) 283.
- [5] M. Baiardo, G. Frisoni, M. Scandola, M. Rimelen, D. Lips, K. Ruffieux, E. Wintermantel, *J. Appl. Polym. Sci.* 90 (2003) 1731.
- [6] K. Yuniarto, B.A. Welt, Y.A. Purwanto, K.P. Purwadari, A. Abdellatif, T.C. Sunarti, S. Purwanto. *J. Appl. Packag. Res.* 6 (2014) 51.
- [7] M. Pluta, J.K. Jeszka, G. Boiteux, *Eur. Polym. J.* 43 (2007) 2819.
- [8] W.M. Chiu, Y.A. Chang, H.Y. Kuo, H. Lin, H.C. Wen, *J. Appl. Polym. Sci.* 108 (2008) 3024.
- [9] H. Balakrishnan, A. Hassan, M.U. Wahit, A.A. Yussu, S.B.A. Razak, *Mater. Des.* 31/7 (2010) 3289.
- [10] E. Fortunati, M. Petzer, I. Armentano, A. Jimenez, J.M. Kenny, *J. Food Eng.* 118 (2013) 117.
- [11] R. Liu, S. Luo, J. Cao, Y. Peng, *Composites Part A*, 51 (2013) 33.
- [12] A. Gonzales, A. Dasan, B. Herrero, E. Plancker, J. Santaren, A. Esteban, *Polym. Degrad. Stab.* 97 (2012) 248.
- [13] S.S. Ray, P. Maiti, M. Okamoto, K Yamada, K. Ueda, *Macromolecules*, 35 (2002) 3104.
- [14] K. Fukushima, D. Tabuani, G. Camino, *Mat. Sci. Eng.* 32 (2012) 1790.
- [15] Z. Duan, N.L. Thomas, W. Huang, *J. Membr. Sci.* 445 (2013) 112.
- [16] A. Abdellatif, B.A. Welt, *J. Packag. Technol. Sci.* 12 (2012) 1.
- [17] S. Huang, J. Hwang, H. Liu, L. Li, *J. Appl. Polym. Sci.* 117 (2010) 434.
- [18] D. Battegazzore, S. Bocchini, A. Frache, *eXPRESS Polym. Lett.* 5 (2011) 849.
- [19] A.L. Nadia, T.M.N. Farah, *Int. J. Appl. Innov. Eng. Manage.* 3 (2014) 77.
- [20] M. Paul, Alexandre, Mi, P. Degee, C. Henrist, A. Rulmont, P. Dubois, *Polymer*. 44 (2003) 443.
- [21] B. Stiller, Master Thesis, Packaging Science, Graduate School of Clemson University, USA, 2008.
- [22] A.B. Inceoglu, U. Yilzamer, *Mat. Res. Soc. Symp. Proc.* 703 (2002) 387.
- [23] C. Fo, T.H. Mong, R.L. Jia, *J. Polym. Res.* 10 (2003) 127.
- [24] J.M. Herrera-Alonso, E. Maran, J.C. Little, S.S. Cox, *J. Membr. Sci.* 337 (2009) 208.
- [25] G. Chaudalakis, A.D. Gotsis, *Eur. Polym. J.* 45 (2009) 967.
- [26] H. Oguzlu, Mater Thesis, The Graduate School of Science and Engineering, Izmir, Turkey, 2011.

- [27] E. Piccard, E. Espuche, R. Fulchiron, *Appl. Clay Sci.* 53 (2011) 58.
- [28] C. Thellen, C. Orroth, D. Froio, D. Ziegler, J. Lucciarini, R. Farrell, N.A. De Souza, J.A. Ratto, *Polym.* 46 (2005) 11716.
- [29] M. Zenkiewicz M, J. Richert, *Polym. Test*, 27 (2008) 835.
- [30] E. Almenar, R. Auras, In: R.A. Auras, L-T. Lim, S.E.M. Selke, H. Tsuji (Eds.), *Poly(lactic acid) Synthesis, Structures, Properties, Processing, and Application: Permeation, Sorption and Diffusion in Poly(lactic acid)*. John Wiley & Sons. Inc., Hoboken, New Jersey, 2010, p.528.
- [31] K. Sungsanit, N. Kao, S.N. Bhattacharya, *Korea-Australia Rheol. J.* 22 (2010) 177.
- [32] A. Guinault, C. Sollogoub, V. Ducruet, S. Domenek, *Eur. Polym. J.* 48 (2012) 779.