

RESEARCH ARTICLE | APRIL 19 2016

Infrared and Raman studies on polylactide acid and polyethylene glycol-400 blend

Kurniawan Yuniarto; Yohanes Aris Purwanto; Setyo Purwanto; Bruce A. Welt; Hadi Karia Purwadaria; Titi Candra Sunarti



AIP Conf. Proc. 1725, 020101 (2016)

<https://doi.org/10.1063/1.4945555>



View
Online



Export
Citation

CrossMark

Articles You May Be Interested In

Determination of thermodynamic properties of polysulfone/PEG membrane solutions based on Flory-Huggins model

AIP Conference Proceedings (May 2017)

Influence of MnC_2O_4 microadditives on combustion characteristics of CuO/Al nanoenergetics

AIP Conference Proceedings (May 2016)

Effect of oxidizer morphology on combustion characteristics of nanoenergetic materials of CuO/Al

AIP Conference Proceedings (June 2013)

500 kHz or 8.5 GHz?
And all the ranges in between.

Lock-in Amplifiers for your periodic signal measurements



Find out more

 Zurich
Instruments

Infrared and Raman Studies on Polylactide Acid and Polyethylene Glycol-400 Blend

Kurniawan Yuniarto^{1, a)}, Yohanes Aris Purwanto², Setyo Purwanto³, Bruce A Welt⁴, Hadi Karia Purwadaria⁵, Titi Candra Sunarti⁶

¹Department of Agricultural Engineering, University of Mataram

²Department of Mechanical and Biosystem Engineering, Bogor Agricultural University

³National Atomic Energy Agency, Indonesia

⁴Department of Packaging Science, Agricultural and Biological Engineering, University of Florida

⁵Retired Professor, Department of Mechanical and Biosystem Engineering, Bogor Agricultural University

⁶Department of Agroindustrial Technology, Bogor Agricultural University

^{a)}Corresponding author: kurniawan2006@unram.ac.id

Abstract. As a biodegradable plastic, polylactide acid (PLA) can be blended with polyethylene glycol (PEG) to form a polymer blend because PEG has a good miscibility with PLA. Furthermore, this paper study the functional groups of PLA-PEG400 blend using direct casting to produce matrix film. Fourier Transform Infrared (FTIR) and Raman spectroscopy was used to identify alteration of functional group PLA-PEG400 blend. Absorbance and frequency wavenumber were used to observe any changing among functional group. In general, PLA-PEG blend did not produce a new configuration or chemical properties although some functional groups tended to decrease. PLA-PEG400 film spectra showed a similarity compared to those of neat PLA because of each pristine polymer. However, FTIR and Raman investigated reducing carbonyl group of PLA with PEG400 addition and followed improving CH-COC bonding. Methyl group represented CH_3 symmetric changed both the shift and absorbance. FTIR and Raman spectroscopy observed increasing hydrogen bonding with increasing PEG400 addition where a largest was found at PEG 10% and appeared at frequency range from 3400 cm^{-1} to 3600 cm^{-1} . According to PEG400 addition, a FTIR measured enhancing crystalline region.

INTRODUCTION

Infrared (IR) is a nondestructive analytical technique widely used to identify mainly organic materials. There are two instruments are very important for characterization both the chemical and physical nature of polymer using IR and Raman spectroscopy. Due to the high sensitivity of IR spectroscopy to changes in the dipole moment of given vibrating group, this method is intensively used for polar group measurement. On the contrary, Raman spectroscopy is specifically useful in the characterization of the homonuclear polymer backbone due to its sensitivity to changes in polarizability. The characterization of polymer using vibrational spectroscopy is based on empirical interpretation of IR or Raman spectra, since the bands are assigned to the independent vibration of atomic group in the macromolecule and give information about the structural features of the polymer such as chemical composition, configuration, conformation and crystallinity [1].

Recently, *poly (lactic acid)* (PLA) has attracted the attention of biopolymer researchers because it is one of the most promising biodegradable thermoplastic polymers [2, 3]. PLA has been used intensively in food and industrial packaging [4]. Surprisingly, PLA has the potential to replace conventional petroleum-based plastics such as polystyrene, polyethylene, polypropylene, polyethylene terephthalate in many disposable or short-term applications [5]. Naturally, PLA has a good mechanical properties such as high strength, high Young modulus, and high biocompatibility [6]. However, PLA has some drawbacks such as its ductility at ambient temperature. To improve its intrinsic properties, blending is applied using other polymer such as some plasticizers [7].

Copolymerization is used to improve some characteristics that is limited in pure polymer. Blending PLA with plasticizer impact to the mechanical, optical, physical, thermal, and barrier properties [7]. It must be noticed that copolymerization occurs between two or more blended materials that have some compatibility. PEG has been used widely for plasticizing PLA because it has good compatibility and miscibility. Interestingly, PEG do not show separation phase at certain concentration [8]. Furthermore, PEG can act to increase chain mobility of PLA polymer [9].

As a plasticizer, polyethylene glycol (PEG) is a suitable plasticizer agent because its hydrophilic group interacts with the hydrophobic group on PLA, as shown in Fig 1. Solubility and miscibility of PEG will decrease with increasing molecular weight [10]. Addition of low molecular PEG is most suitable to improve miscibility [11] and create homogenous blended and even matrix of PLA [7, 12]. However, if the amount of PEG exceeds a specific limit, a basic problem in polymer blends is created. In addition, PEG exhibits phase separation with PLA when its concentration is above 10% [10].

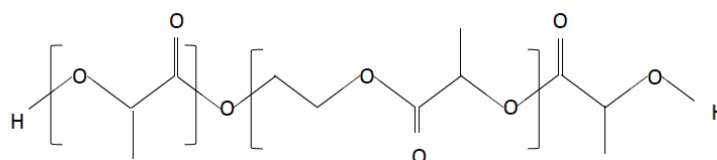


FIGURE 1. Copolymer of LA-PEG-LA.

Generally, hydroxyl terminal group from PEG will react with carboxyl group of PLA [13]. PEG molecules enter the PLA macromolecules, creating physical interaction in the form of hydrogen bonding or dipole atoms. As result, cohesion bonding PLA-PLA will be replaced with adhesion PLA-PEG bond [8]. Based on the chemical structure, PLA has many polar groups, mainly the carbonyl (C=O) groups. This group can interact with hydroxyl group from PEG resulting in hydrogen bonding. Low molecular weight PEG is more recommended than higher molecular weight PEG. Study related to PEG addition into PLA has been widely explored, especially to the mechanical and thermal properties. However, optical properties study polymer blend of PLA-PEG film involves chemical functional group that influences primary group configuration is desirable.

In detail [14, 15], some researcher reported the general IR band assignments for pure PLA-based polymers are as follows. The strong wavenumber at 2997, 2946 and 2887 cm^{-1} are assigned to the CH stretching region ($-\text{CH}_3$ asymmetric, $-\text{CH}_3$ symmetric and CH modes). The C=O stretching region appears in IR spectra at about 760 cm^{-1} as a broad asymmetric band. The CH_3 is responsible for the appearance of the band at 1456 cm^{-1} . The CH deformation and asymmetric bands appear at 1382 cm^{-1} and 1365 cm^{-1} . Furthermore, the CH bending modes result in the band at 1315-1300 cm^{-1} . Then, the C-O stretching modes of ester group appear at 1255 cm^{-1} while the C-O-C asymmetric mode appears at 1090 cm^{-1} . Characteristic of the helical backbone vibration with CH_3 rocking mode can be found at 956 and 921 cm^{-1} . At 871 and 756 cm^{-1} , two bands that can be attributed to the amorphous and crystalline phases, respectively. Therefore [6], the reported band assignments for PEG are as follows. Hydroxyl group appears at 3446 cm^{-1} with broadening peak, then C-O-C groups can be seen at about 1090 cm^{-1} . CH groups can be found at wavenumbers ranging from 1270 to 1360 cm^{-1} . Furthermore, CH_3 groups appeared at wavenumber of 1452 cm^{-1} .

This research argued that functional group characterization PLA-PEG400 polymer blend for film plastic production was important and did not describe clearly. Therefore, this study aims to investigate the interaction functional group and crystallinity formation between the PLA and PEG400 blend for a matrix film production using direct mixing. The Fourier Transform Infrared (FTIR) and Raman spectroscopy were applied to observe functional group alteration and crystallinity region of the PLA-PEG400 film blend.

METHOD

Materials

Polylactic acid (PLA) AI-101 pellets with molecular weight of 80,000 g/mole and density of 1.24 g/cm^3 were purchased from Shenzhen Esun (China). Chlorofom C606-4 HPLC grade, was purchased from Fisher Scientific, USA. Polyethylene Glycol-400 was purchased from from Fisher Scientific, USA with average molecular weight 380-420, density 1.13 g/mol .

Preparation of PLA-PEG400 Polymer Blend

The Matrix film of PLA-PEG400 production was applied by casting method [16]. Before processing, PLA was dried in the oven for 6 hours at 45°C to remove unwanted water content. PLA was diluted into chlorofom at 5% weight (w/v). In detail, 20 gram of PLA was dissolved in 400 ml of chlorofom and stirred vigorously for 60 minutes at 55°C. Then, PEG400 was added and

stirring was continued for 15 minutes. Amount of PEG400 that was added into PLA solution at different concentrations: 0, 1, 5 and 10% (w/w). The dissolved solution was poured onto a glass petridish. Then, solutions were dried into films at 35°C for 15 hours. Resultant PLA-PEG films were peeled from petridishes for optical properties investigation.

Measurements

FTIR and Raman Spectroscopy

FTIR spectra was measured using Perkin Elmer USA with wavenumber range of 400-4000 cm^{-1} . Raman spectra was measured using Opus Braker Raman Spectroscopy with wavenumberrange of 200-2600 cm^{-1} . Detailed band assignments for IR and Raman are shown in Table 1.

TABLE 1. Wavenumber assignment of FTIR and Raman spectroscopy of PLA

Assignment IR		Assignment Raman	
Wavenumber (cm^{-1})	Assignment	Wavenumber (cm^{-1})	Assignment
695	C=O	675, 711	wC=O
715		736, 760	mC=O
740		873	vsC-COO
760	s C=O	1042	s sC-CH3
1045	C-CH3	1092	s C-O-C
1090	C-O-C	1128	as sCH3
1130	Ras CH3	1179, 1216	as mC-O-C
1270	CH + COC	1293, 1302, 1315	CH + COC
1300	CH + COC	1356, 1363, 1371	CH - CH3
1360	CH - CH3	1384-1388	s mCH3
1452	CH3	1452	as sCH3
1747	C=O	1749, 1763, 1773	C=O
2882	CH	2943	vs sCH3
2947	CH	2960, 2970	as sCH3
2997	CH3	2995	as sCH3

RESULTS AND DISCUSSION

FTIR PLA-PEG 400

Fourier Transform Infrared (FTIR) was used to analyze polymer structure by spectra technique. Some information can be read from the sample spectra including isomer configuration from wavenumber frequency. Crystallinity degree and amorphous polymer chain can be predicted using intensity of wavenumber frequency[14]. Spectra polymer blend PLA-PEG can be seen on Fig. 2.

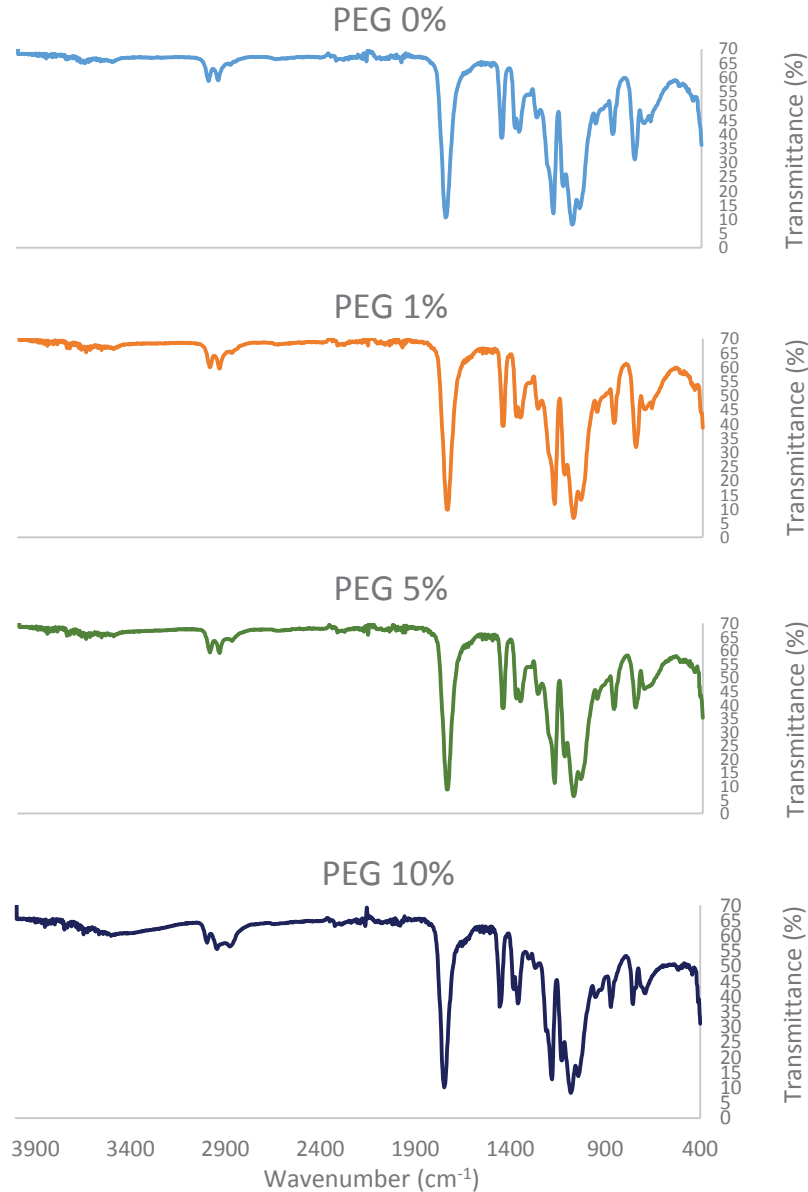


FIGURE 2. FTIR spectra of copolymer PLA-PEG400

FTIR measurement was focused on peak positions and the frequency involved. Basically, PLA is from lactic acid which is rich of carbon chain as C=O groups while PEG400 configures from C-O-C bonding. Main functional group of PLA appeared at the frequency region of 695-760 cm^{-1} and 1740-1750 cm^{-1} which is assigned to the C=O group. Then, PEG has an assignment frequency at 1090 cm^{-1} . In Figure 2, the results of this investigation shows that the PLA-PEG400 blend spectra patterns appeared the same as those of pure PLA. As a reason, a similarity natural structure of PLA and PEG consist of carbon and oxygen atoms. It seems that PLA-PEG film has same absorption peaks as pristine PLA[17]. However, this research has found slightly differences between intensity and shift between PLA and PLA-PEG400 film.

This research confirmed that carbonyl group the PLA-PEG400 film absorption decreased from 0.442 cm^{-1} to 0.375 cm^{-1} ; then, shift peak moved from 750 cm^{-1} to 754 cm^{-1} . This finding of this study suggest that some PLA interacted with the PEG400 because the C-O-C band shifted to 1080 cm^{-1} . It proved that PEG400 has a good miscibility with PLA[8] and low molecular weight PEG improved miscibility into PLA[11]. In addition, a PEG400 5% showed better miscibility during PLA/PEG400 film¹⁷. Hence, FTIR spectra showed the absorbance of CH-COC bonding increased with PEG400 addition at frequency 1270 cm^{-1} that

supported a binding process occurred during PLA-PEG400 blending. A crystalline region at wavenumber of 864 cm^{-1} resulted increasing with addition PEG400. As a plasticizer PEG has a function to promote crystallization [8] and plasticized PLA with PEG400 improved crystallinity degree PLA from 17% to 34%[17].

Related to the hydroxyl group, presenting of PEG 400 showed a broaden peak, especially hydroxyl group which was appeared at frequency range from $3400\text{ to }3600\text{ cm}^{-1}$. It cleared that introducing PEG400 at 10% resulted in broadened spectra compared to other PEG concentration due to providing a largest $-\text{OH}$ group. This assignment band occurred hydrogen bonding which is shown a broadened peak and the hydrogen bonding of PLA-PEG400 polymer blend were more intensive. Hence, functional group such methyl can be found at frequency range from $2800\text{ to }3000\text{ cm}^{-1}$ represented of $\text{CH}_{3\text{asymmetric}}$, $\text{CH}_{3\text{symmetric}}$ and $-\text{CH}$ groups. CH stretching was found at wavenumber of 3000 cm^{-1} that showed characteristic of polymer of PLA[18]. Methyl group which are represented $\text{CH}_{3\text{asymmetric}}$, $\text{CH}_{3\text{symmetric}}$ and $-\text{CH}$ decreasing however CH_2 groups increased as followed by addition of PEG400.

Raman

Raman spectroscopy of pure PLA can be seen in Fig. 6. Pure PLA spectra can be characterized with stretching $\text{C}=\text{O}$ groups which are present at many wavenumber values. Weak $\text{C}=\text{O}$ groups are present at frequency range from 675 cm^{-1} to 711 cm^{-1} while moderate groups can be found between 736 cm^{-1} and 760 cm^{-1} . Strong $\text{C}=\text{O}$ groups in PLA polymer can be found at frequency range between 1749 cm^{-1} , 1643 cm^{-1} and 1773 cm^{-1} . $\text{C}=\text{O}$ groups broadened at frequency range from $1700\text{ to }1800\text{ cm}^{-1}$. Surprisingly, stereo complex did not appear. Stereo complex can usually be seen at 1745 cm^{-1} .

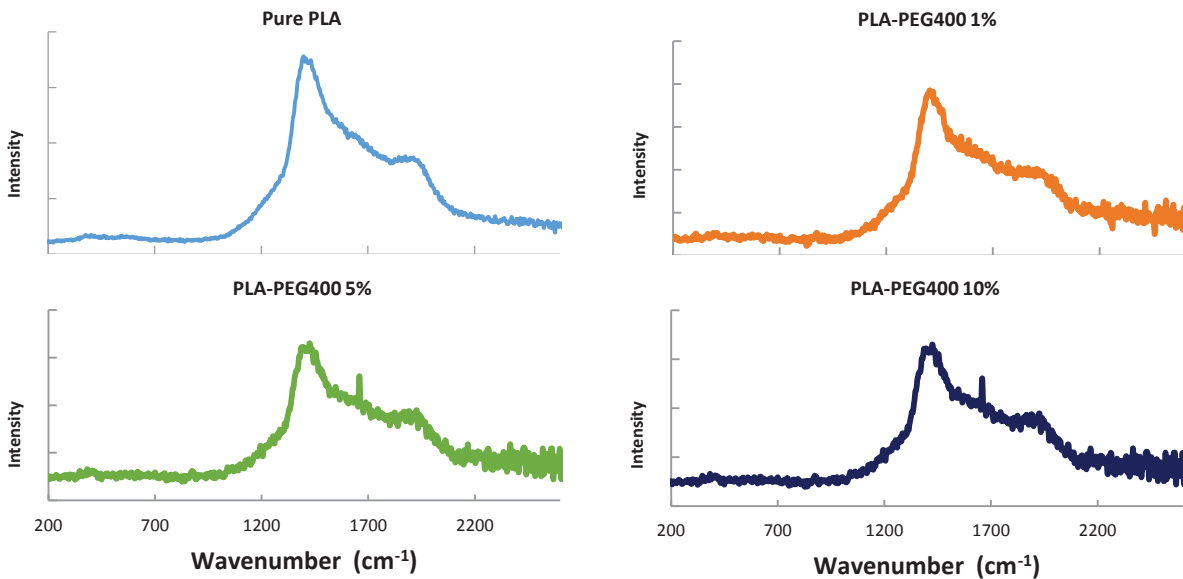


FIGURE 3. Raman spectra of PLA-PEG400 blend.

Specific peak group of PLA polymer appeared at 1450 cm^{-1} which declared asymmetric CH groups. On the other hand, deformation asymmetric CH_3 group of PLA shifted at wavenumber of 1406 cm^{-1} . Functional $\text{CH}_{3\text{symmetric}}$ group used to appear at frequency range between 1384 and 1388 cm^{-1} shifted to 1390 cm^{-1} . Then, $\text{CH}_{3\text{asymmetric}}$ groups are usually found at 1128 cm^{-1} , this measurement remained stable at 1129 cm^{-1} . Raman spectra at frequency range of 1179 and 1216 cm^{-1} were moderate $\text{C}-\text{O}-\text{C}_{\text{asymmetric}}$ group and very strong $\text{C}-\text{O}-\text{C}_{\text{symmetric}}$ at wavenumber 1092 cm^{-1} .

Introducing PEG400 into PLA shifted the $\text{C}=\text{O}$ group from 760 cm^{-1} to 765 cm^{-1} and strong $\text{C}=\text{O}$ groups frequency shifted from 1749 cm^{-1} to 1757 cm^{-1} . Raman observed a decreasing $\text{C}=\text{O}$ group from PLA-PEG400 film. This result proved an interaction between PLA and PEG400 occurred during mixing process. This interaction can be supported with $\text{C}-\text{O}-\text{C}$ absorbance of PEG400; the intensity $\text{C}-\text{O}-\text{C}$ decreased when PEG400 introduced to PLA. Hence, a Raman spectra investigated decreasing CH group and improving $\text{CH}-\text{COC}$ bonding. It assumed that decreasing CH group intensity at 1295 cm^{-1} which is originally from PLA contributed to interaction with PEG400.

CONCLUSION

Introducing PEG400 changed absorbance and frequency some functional group for matrix film PLA-PEG400 blend. FTIR and Raman observed a good interaction between PLA with PEG400 that resulted CH-COC bonding improvement. In addition, main functional group of PLA as carbonyl group reduced with presenting PEG400. Then, addition PEG400 enhanced hydrogen bonding that appeared a broaden peak at frequency 3400-3600 cm^{-1} . On the other hand, methyl groups represented as CH and CH_3 remained stable although CH_3 symmetric frequency changed significantly. FTIR investigated an improving crystalline region PLA-PEG400 blend.

ACKNOWLEDGEMENTS

This study was supported by Directorate General Higher Education, Ministry of Research, Technology and Education, Republic of Indonesia. This research was supported by Advance Material Laboratory, National Atomic Energy Agency of Indonesia. Special thanks to Dr Salim Mustofa for conducting Raman spectroscopy measurement.

REFERENCES

1. M. Carla, B. Goncalves, A. Joao, P. Coutinho and I. M. Marrucho, "Optical properties" in Poly(Lactic Acid) Synthesis, Structures, properties, processing, and application, edited by R. Auras, L-T. Lim, E.M. Susan and H. Tsuji (John Wiley & Sons. Inc., Hoboken, New Jersey 2010), pp. 97-110.
2. R. M. Rasal, A.V. Janorkar and D.E. Hirt, *Prog. Polym. Sci* **35**, 338-356 (2010).
3. S. Slomkowski, S. Penczek and A. Duda, *Polym. Adv. Technol* **25**, 436-447 (2014).
4. S. Saeidlou, M.A. Huneault, H.B. Li, C.B. Park, *Prog. Polym. Sci* **37**, 1657-1677 (2010).
5. C. P. Martino, A. Jimenez, R.A. Ruseckai and L. Averous, *Polym. Adv. Technol* **22**, 2206-2213 (2011).
6. B. Chieng, N.A. Ibrahim, W. Yunus, M.Z. Hussein, *Polymer* **6**, 93-104 (2014).
7. R. Auras, L-T. Lim, E.M. Susan and H. Tsuji. Poly (Lactic Acid) Synthesis, Structures, properties, processing, and application (John Wiley & Sons. Inc., Hoboken, New Jersey, 2010), pp. 158-162.
8. A. K. Mohapatra, S. Mohanty and S.K. Nayak, *Polym. Compos* **35**, 283-293 (2014).
9. K. Sungsanit, N. Kao and S.N. Bhattacharya, *Korea-Australia Rheology J.* **22**, 177-185 (2010).
10. M. Baiardo, G. Frisoni, M. Scandola, M. Rimelen, D. Lips, K. Ruffix and E. Wintermantel, *J Appl Polym Sci* **90**, 1731-1738 (2001).
11. Z. Kulinski and E. Piorowska, *Polymer* **46**, 10290-10300 (2005).
12. J. Ahmed, K.V. Sunil and R. Aura, *J Food Sci* **75**, 17-24 (2010).
13. F. Li, S. Zhang, J. Ling and J. Wang, *Polymer. Adv. Tech.* **26**, 465-475 (2015).
14. G. Kister, G. Cassanas and M. Vert, *Polymer* **39**, 267-273 (1998).
15. D. Garlott, *J Polym Environ* **9**, 63-84 (2001).
16. K. Yuniarto, B.A. Welt, Y. A. Purwanto, K. P. Purwadaria, A. Abdellatief, T. C. Sunarti, and S. Purwanto, *J Appl Packaging Res* **6**, 51-57 (2014).
17. K. Yuniarto, B.A. Welt, Y.A. Purwanto, K.P. Purwadaria, A. Abdellatief, T.C. Sunarti, and S. Purwanto, *J Polym Res*, (2015).
18. K. Boua-in, N. Chaiyut and B. Ksapabutr, *Optoelectron Adv Mat Rapid Commun* **4**, 1404-1407 (2010).
19. M. Tanaka and R.J. Young, *Macromolecules* **39**, 3312-3321 (2006).