Effect of a novel coupling agent, alkyl ketene dimer, on mechanical properties of wood/polypropylene composites

HONGLI ZHANG*
College of Chemistry & Life Science, Weinan Teachers University, Weinan 714000, Shaanxi, P.R. China

The objective of this study was to investigate the incorporation of poplar wood fibers both with and without a novel coupling agent, alkyl ketene dimer (AKD), on the mechanical properties of wood fiber/polypropylene (PP) composites. The resulting properties were compared to those obtained with the most commonly used coupling agent, maleic anhydride grafted PP (MAPP). Tensile and impact strengths of the composites decreased with increasing poplar wood fibers content. Tensile modulus of the composites increased by the incorporation of the wood fibers content up to 70 wt% but further increment in the wood fibers decreased the tensile modulus. At the constant content of poplar wood fibers (70 wt%), the tensile strength determined for the coupled composites with 5% AKD increased by 41% in comparison with the non-coupled composites while the tensile modulus increased by 45%, the impact strength of the coupled composites increased by 38%. The performance of 5% AKD on the mechanical properties of the composites is a little better than 3% MAPP. The good performance of 5% AKD is attributed to the enhanced compatibility between the poplar wood fibers and the polymer matrix. The increase in mechanical properties of the composites demonstrated that AKD is an effective coupling agent for wood fiber/PP composites.

(Received September 26, 2013; accepted January 22, 2014)

Keywords: Alkyl ketene dimer, Coupling agent, Mechanical properties, Wood-plastic composites

1. Introduction

Wood-plastic composites (WPCs) have been given considerable interest by researchers and industrialists in recent years because of the increasing price of petroleum, ecological concerns, and the impending depletion of fossil fuels [1]. WPC is a product which could be made from thermoplastic polymers and small wood particles. WPCs have been widely used for windows, door frames, interior panels in cars, railings, fences, landscaping timbers, cladding and sliding, park benches, molding and furniture due to its many advantages, such as stiffness, low cost, resistance to water, rot, decay and termite, good workability, sustainability, recyclability and so on [2-4]. The main problem of WPCs is the incompatibility between hydrophilic wood fibers and hydrophobic thermoplastics, which results in the weak adhesion at the two-phase interface and leads to the poor mechanical and physical properties.

To improve the interfacial adhesion between hydrophilic wood fibers and hydrophobic thermoplastics, several methods have been reported in literature [5-9]. Some methods are based on the physical or chemical modification of wood fibers or thermoplastics. Mueller et al. [10] investigated the influence of wood modification by aminosilane, melamine and acetic anhydride on the water absorption and mechanical properties of polyvinyl chloride (PVC)/wood flour composites. The results showed that the equilibrium moisture content and the water absorption speed of composites with modified wood flour are lower than those with unmodified wood-flour. Tensile strength, elongation at break and unnotched impact strength were considerably improved by the aminosilane treatments. Zhang et al. [11] used acrylic acid/poly(methyl methacrylate) and acrylic acid/silanization (AAS) to treat wood fibers. The results showed that the AAS composites possessed the optimum comprehensive mechanical properties. Lou et al. [12] studied the effect of alkali treatment on coir fibers/polypropylene (PP) composites and found that alkali treatment can increase the mechanical property of the resulting WPC. Ozmen et al. [13] investigated the effect of Scots pine wood acetylation with vinyl acetate and acetic anhydride on the properties of WPCs. It was observed that wood acetylation allowed a significant increase in both the mechanical properties and thermal stability of WPCs, which indicated the improved compatibility.

Another effective method is adding a coupling agent into the composite system. Nourbakhsh et al. [14] reported polybutadiene isocyanate (PBNCO) as a coupling agent for WPCs and studied the effect of PBNCO on the mechanical properties of hardwood aspen fiber/PP composites. The increase in mechanical properties demonstrated that PBNCO is an effective coupling agent for wood fiber/PP composites. Nachtigall et al. [15] analyzed the suitability of using PP modified with vinyltriethoxysilane (PPVTES) as coupling agent for PP/wood-flour composites. The results indicated that PPVTES increased the interfacial adhesion between the fibers and the polymer matrix and this effect was better than that obtained for the composites using maleic anhydride grafted PP (MAPP) as coupling agent, which is

the most popular coupling agent for WPCs [3, 12, 16, 17]. Shah et al. [18] used chitin and chitosan as coupling agents for PVC/wood-flour composites, the addition of chitin and chitosan to PVC/wood-flour composites increased their flexural strength by ~20%, their flexural modulus by ~16%, and their storage modulus by ~33-74% compared to PVC/wood-flour composite without the coupling agent. The optimum content for chitin and chitosan was 0.5 wt% of chitin and 6.67% chitosan. Rozman et al. [19] investigated the effect of hexamethylene diisocyanate (HMDI) modified ALCELL® lignin as a coupling agent on the flexural properties of oil palm empty fruit bunch (EFB)-PP composites. The results showed that the HMDI-modified lignin was able to impart greater compatibility between EFB and PP. This was reflected in the greater flexural strength shown by the composites with HMDI-modified lignin than those with the unmodified lignin. Scanning electron microscopy studies showed that HMDI-modification of lignin results in a better blending and compatibility between lignin and PP matrix. Although many coupling agents have been reported for WPCs, most of the coupling agents reported are very expensive. Developing cost-effective coupling agents for WPCs is still an important and attractive topic.

Alkyl ketene dimer (AKD) has been widely used as a sizing agent in neutral/alkaline papermaking. The reaction of AKD with cellulose to form the β-keto ester is the primary mechanism by which AKD sizes paper. If AKD is used as a coupling agent for WPCs, its strained lactone ring can react with cellulose forming the β-keto ester, and its long carbon chain can interact with macromolecules of the polymer by an entanglement mechanism. Based on this assumption, the objective of this study is to investigate the suitability of using AKD as a coupling agent for poplar wood/PP composites. The results were compared with those obtained for similar composites coupled with MAPP. A systematic investigation on the effect of fiber content and coupling agent concentration was undertaken to obtain optimum mechanical strength.

2. Experimental

2.1 Materials

Polypropylene (PP) was purchased from PetroChina Company Ltd. under the trade name K8003 with a density of 0.91 g/cm3, and a melt index 2-3 g/10 min at 190 °C. The poplar wood fibers were provided by a local sawmill, manually screened to choose 60-80 mesh and oven-dried at 105 ºC for 24 h to a moisture content of less than 3%. Maleic anhydride grafted PP (MAPP) was supplied by Shandong Dawn Polymer CO., Ltd. with a grafting ratio of 0.8-1.0% and a melt index 50-80 g/10 min at 190 ºC. Alkyl ketene dimer (AKD) (R=C14-C16) was obtained from Shandong Tralin Group. N-hexane was bought from Xi'an Sanpu Chemical Plant.

2.2 Modification of wood fibers with AKD

1) AKD was dissolved in n-hexane at 3% and 5% (w/w) concentration. 2) 1 kg poplar wood fibers were impregnated in 5 L 3% or 5% AKD solution for 1 h. 3) The poplar wood fibers were taken out from the AKD solution by filtration and the treated poplar wood fibers were put in fume hood where the n-hexane was allowed to evaporate overnight. 4) The treated poplar wood fibers were put in oven at 105 ºC for 3 h to allow the reaction of AKD with wood fibers. 5) The modified poplar wood fibers were cooled to room temperature and kept in bags for end-use.

2.3 Sample preparation

A series of wood fibers/PP composites containing 50, 60, 70, 80 and 90 wt% of untreated poplar wood fibers or WPCs containing 70 wt% of treated poplar wood fibers with AKD or MAPP were prepared. The composites were compounded in an M-101 high-intensity laboratory mixer for about 5 min. Then the mixture was processed with a Giant SHJ-72B co-rotating twin-screw extruder to make composite pellets. The temperatures of the first to the last chambers were 150, 155, 160, 160, and 150 °C, respectively. The rotational speed was 30 rpm. And the composite pellets were extruded in a Giant SJ-120 single-screw extruder with a die. The temperatures of the first to the last chambers were 170, 175, and 180 °C, and the die was 170 °C. The screw rotational rate was 20 rpm. The test specimens were conditioned before testing at 23±2 °C, 50±5% RH for at least 40 h according to ASTM D 618.

2.4 Mechanical properties test

The tensile strength and modulus of the specimens were carried out on a computer-controlled INSTRON testing machine (Model 4486) in accordance with ASTM Standards D 638. The crosshead speed of tension test was set at 5 mm/min. The Charpy impact strength was tested as per ASTM D 256 using an Impact Pendulum Tester (Model KRT-2050) supplied by Kunshan Creator Testing Instrument Co., Ltd. In each series of treatments, tensile strength, modulus and impact strength were reported after taking statistical average of six measurements.

3. Results and discussion

In practical applications, the mechanical properties of composites are very important. For WPCs, the interfacial adhesion between the fiber and the matrix plays a key role in achieving good mechanical properties. In this study, the strength properties of pure PP, modified and unmodified poplar wood fibers/PP composites were determined.

3.1 The effect of fiber content on the mechanical properties of WPCs

The tensile strength of pure PP and poplar wood fibers reinforced PP composites is summarized in Fig. 1. The tensile strength of pure PP was 29.78 MPa, adding poplar wood fibers to PP significantly decreased the tensile strength of the specimens. The reduction in the tensile strength was attributed to the weak interfacial adhesion between the poplar wood fibers and the plastic matrix, as reported in previous studies [3, 20, 21]. The tensile strength of the WPCs decreased by 50% when poplar wood fibers content increased from 50 to 90 wt%. The decrease in the tensile strength of wood fibers filled thermoplastics was reported in previous studies [3, 16, 22, 23, 24]. These results show that poplar wood fibers behave merely as filler when incorporated into PP matrix without coupling agents. No reinforcing effect was observed in this case.

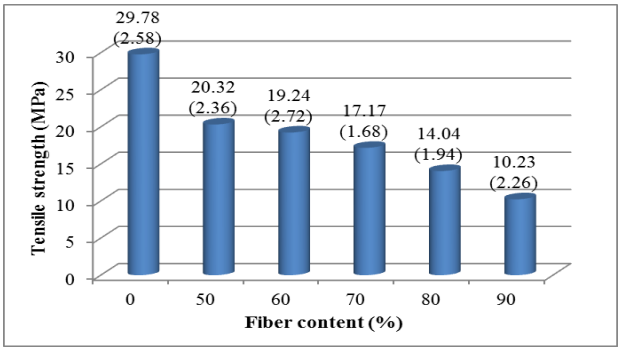

Fig. 1. The relationship between wood fiber content and tensile strength of WPCs (the values in parentheses are standard deviations).

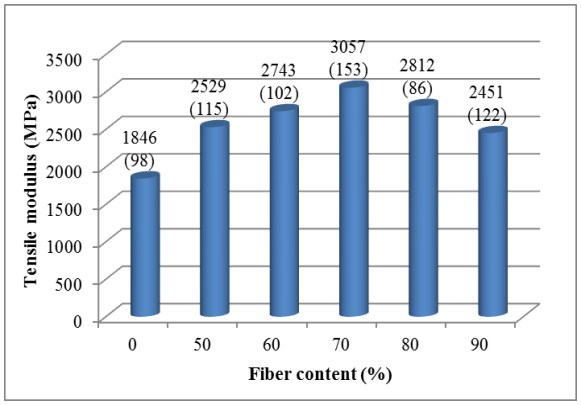

Fig. 2. The relationship between wood fiber content and tensile modulus of WPCs (the values in parentheses are standard deviations).

The results shown in Fig. 2 indicate that the tensile modulus of WPCs increased to some extent as compared to pure PP and then decreased. The tensile modulus of PP filled with 70% poplar wood fibers was almost 65% higher than unfilled PP. As expected wood fibers lead to PP tensile modulus increase in spite of poor fiber-matrix adhesion. The tensile modulus of natural fibers was much higher than that of PP [25]. As a result, when the fiber content of WPCs increased from 50 to 70 wt%, the tensile modulus of WPCs increased. However, in WPCs with higher loadings of fiber content, plastic is utilized as adhesive for bonding wood fibers together [26]. When the fiber content increased from 70 to 90 wt%, no sufficient adhesive boding was present to achieve higher tensile modulus.

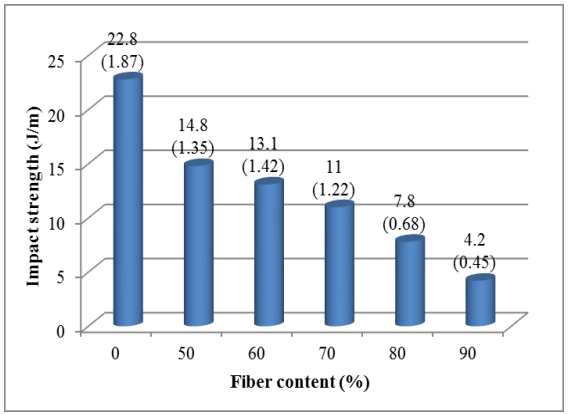

Fig. 3. The relationship between wood fiber content and impact strength of WPCs (the values in parentheses are standard deviations).

Fig. 3 shows the relationship between the impact strength and the fiber loading for the composites prepared without coupling agents. It was found that the impact strength of WPCs decreased with increasing the wood fibers content. The impact strength of the uncoupled specimens decreased by 72% when poplar wood fibers content increased from 50 to 90 wt%. The incorporation of wood fibers into the thermoplastic composite creates the regions of stress concentration that require less energy to initiate a crack in the composite, thereby decreasing the impact strength [27]. For example, the impact strength of the uncoupled specimens containing 90 wt% poplar wood fibers was 4.2 J/m while it was 22.8 J/m for the neat PP. The wood fibers filler reduces the polymer chain mobility and therefore its ability to absorb energy during fracture propagation. The poor interfacial adhesion between the wood fibers filler and polymer matrix causes micro-cracks to occur at the point of impact, which cause cracks to easily propagate in the composite [28]. As compared to the neat PP, the impact strength was decreased by 81% by adding 90 wt% poplar wood fibers to the PP.

3.2 The effect of coupling agents on the mechanical properties of WPCs

Fig. 4 and Fig. 5 illustrate the results of tensile strength and tensile modulus of WPCs reinforced with 70 wt% treated poplar fibers, respectively. The highest tensile strength and tensile modulus for WPCs containing 70 wt% poplar wood fibers were obtained with 5% AKD. The

tensile strength determined for this sample increased by 41% in comparison with the non-coupled WPCs while the tensile modulus increased by 45%. The improvement in the mechanical properties due to the treatment of poplar wood fibers by 5% AKD solution suggests an increased compatibility between the hydrophilic cellulose and hydrophobic polymer. The performance of 5% AKD on the mechanical properties of WPCs is a little better than 3% MAPP, which has been reported by many studies [29-33] as a good compatibilizing agent for WPCs. Although the tensile strength of WPCs with a high content (70 wt%) of treated poplar wood fibers was less than that (29.78 MPa) of the neat PP, the tensile modulus of the WPCs was significantly higher than that (1846 MPa) of the neat PP.

The better performance of AKD is attributed to the higher surface area coverage of the wood fibers surface by the lactone groups and the long carbon chain which enhances the interfacial adhesion between wood fibers and plastics. The four-membered strained lactone ring in AKD can react with cellulose hydroxyl groups forming the β-keto ester. The covalent bond provides immobilization and orientation of the hydrophobic tail outward, away from the surface [34]. And the long hydrophobic carbon chain can interact with macromolecules of the polymer by entanglement. The chemical reaction between AKD and cellulose forming the β-keto ester is shown in Fig. 6.

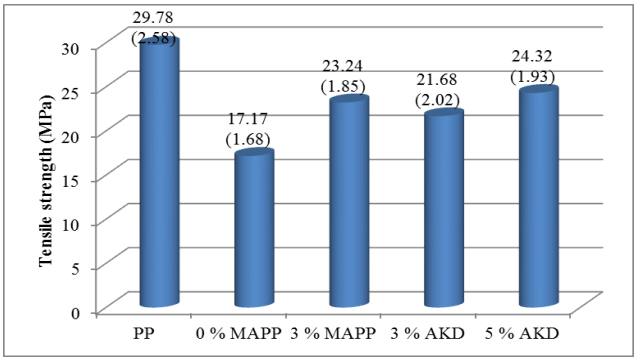

Fig. 4. The relationship between coupling agents and tensile strength of WPCs (the values in parentheses are standard deviations).

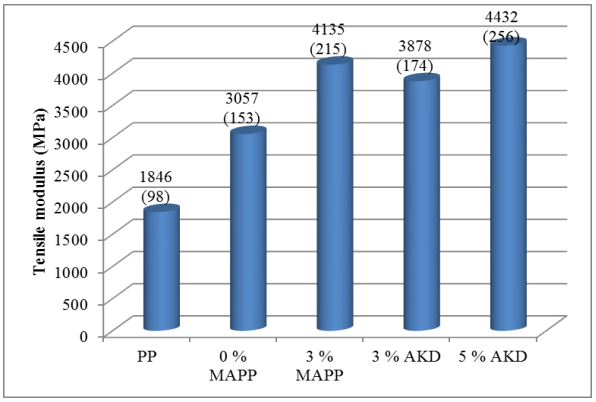

Fig. 5. The relationship between coupling agents and tensile modulus of WPCs (the values in parentheses are standard deviations).

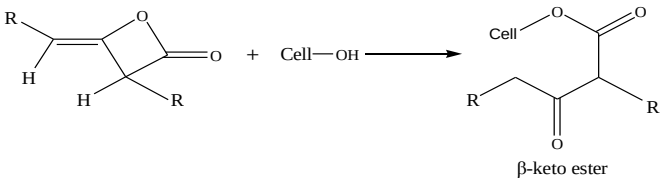

Fig. 6. Alkyl ketene dimers react with cellulose forming the β-keto ester.

The impact strengths of WPCs with 70 wt% treated or untreated poplar wood fibers are shown in Fig. 7. The WPCs coupled with MAPP or AKD showed higher impact strength than the uncoupled ones because the debonding behavior between the interface of wood fibers and PP absorbs larger impact energy in modified composites before break than the unmodified ones [35]. The impact strength values of the WPCs with 70 wt% poplar wood fibers increased by 38% when the poplar wood fibers was treated by 5% AKD solution. The presence of AKD improves the wood fibers dispersion and leads to a more uniform distribution of the applied stress. Therefore, more energy for debonding and fiber pullout is required and thus the impact strength increases.

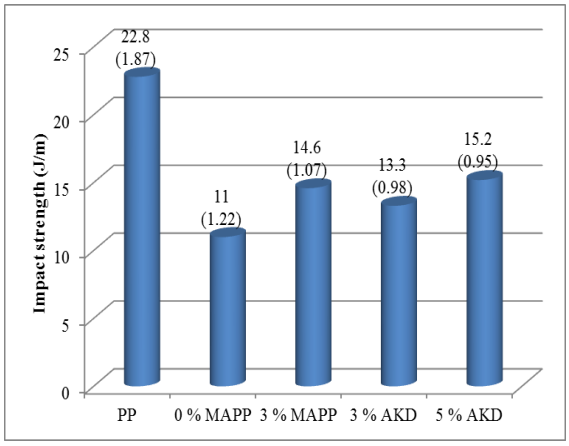

Fig. 7. The relationship between coupling agents and impact strength of WPCs (the values in parentheses are standard deviations).

4. Conclusions

In this study, the effects of the incorporation of poplar wood fibers both with and without a coupling agent on the mechanical properties of WPCs were investigated. Tensile and impact strengths of the WPCs decreased with increasing poplar wood fibers content. Tensile modulus of the WPCs increased by the incorporation of the wood fibers content up to 70 wt% but further increment in the wood fibers decreased the tensile modulus. Adding 3% MAPP or 5% AKD significantly improved the mechanical properties of the WPCs. At the constant content of poplar wood fibers (70 wt%), the tensile strength determined for the coupled WPCs with 5% AKD increased by 41% in comparison with the non-coupled WPCs while the tensile

modulus increased by 45%, the impact strength of the coupled WPCs increased by 38%. The performance of 5% AKD on the mechanical properties of WPCs is a little better than 3% MAPP. The good performance of 5% AKD is attributed to the enhanced compatibility between the poplar wood fibers and the polymer matrix. The four-membered strained lactone ring in AKD can react with cellulose hydroxyl groups forming the β-keto ester while the long hydrophobic carbon chain can interact with macromolecules of the polymer by entanglement. In general, the increase in mechanical properties of the WPCs demonstrated that AKD is an effective coupling agent for wood fiber/PP composites.

Acknowledgements

Financial support (2012JCY-2 & 12YKF020) from Weinan Municipal Bureau of Science & Technology and Weinan Teachers University is gratefully acknowledged.

References

[1] M. Farsi, J. Reinf. Plast. Compos. **29**(24), 3587 (2010).
[2] M. A. Syed, Siddaramaiah, R. T. Syed, A. A. Syed, Polymer-Plastics Technology and Engineering **49**(6), 555 (2010).
[3] Y. Li, Int. J. Polymer. Mater. **61**(11), 882 (2012).
[4] R. Bouza, A. Lasagabaster, M. Jose Abad, L. Barral, J. Appl. Polym. Sci. **109**(2), 1197 (2008).
[5] L. Wei, A. G. Mcdonald, C. Freitag, J. J. Morrell, Polym. Degradation Stab. **98**(7), 1348 (2013).
[6] C. Piao, Z. Cai, N. M. Stark, C. J. Monlezun, J. Appl. Polym. Sci. **129**(1), 193 (2013).
[7] C.-W. Lou, C.-W. Lin, C.-H. Huang, C.-T. Hsieh, J.-H. Lin, J. Reinf. Plast. Compos. **32**(11), 802 (2013).
[8] N. Ozmen, N. S. Cetin, F. Mengeloglu, E. Birinci, K. Karakus, Bioresources **8**(1), 753 (2013).
[9] C. Jinxiang, W. Yong, G. Chenglong, L. Jianxun, L. Yufu, L. Min, et al., Materials **6**(6), 2483 (2013).
[10] M. Mueller, I. Radovanovic, T. Grueneberg, H. Militz, A. Krause, J. Appl. Polym. Sci. **125**(1), 308 (2012).
[11] H. H. Zhang, Y. H. Cui, Z. D. Zhang, J. Vinyl Addit. Techn. **19**(1), 18 (2013).
[12] C. W. Lou, C. W. Lin, C. H. Huang, C. T. Hsieh, J. H. Lin, J. Reinf. Plast. Compos. **32**(11), 802 (2013).
[13] N. Ozmen, N. S. Cetin, F. Mengeloglu, E. Birinci, Bioresources **8**(1), 1361 (2013).
[14] A. Nourbakhsh, B. V. Kokta, A. Ashori, A. Jahan-Latibari, J. Reinf. Plast. Compos. **27**(16-17), 1679 (2008).
[15] S. M. B. Nachtigall, G. S. Cerveira, S. M. L. Rosa, Polym. Test. **26**(5), 619 (2007).
[16] D. Kurniawan, B. S. Kim, H. Y. Lee, J. Y. Lim, J. Adhes. Sci. Technol. **27**(12), 1301 (2013).
[17] H. Gao, Y. J. Xie, R. X. Ou, Q. W. Wang, Composites Part a-Applied Science and Manufacturing **43**(1), 150 (2012).
[18] H. L. Shah, L. M. Matuana, J. Vinyl Addit. Techn. **11**(4), 160 (2005).
[19] H. D. Rozman, K. W. Tan, R. N. Kumar, A. Abubakar, Polym. Int. **50**(5), 561 (2001).
[20] C. Clemons, Forest Products Journal **52**(6), 10 (2002).
[21] J. Z. Lu, Q. L. Wu, Negulescu, Ii, J. Appl. Polym. Sci. **96**(1), 93 (2005).
[22] M. Zahedi, T. Tabarsa, A. Ashori, M. Madhoushi, A. Shakeri, J. Appl. Polym. Sci. **129**(3), 1491 (2013).
[23] M. Poletto, M. Zeni, A. J. Zattera, J. Thermoplast. Compos. Mater. **25**(7), 821 (2012).
[24] P. Threepopnatkul, W. Teppinta, N. Sombatsompop, Fibers and Polymers **12**(8), 1007 (2011).
[25] K. Jayaraman, D. Bhattacharyya, Resources Conservation and Recycling **41**(4), 307 (2004).
[26] M. Chaharmahali, M. Tajvidi, S. K. Najafi, Polym. Compos. **29**(6), 606 (2008).
[27] W. Gacitua Escobar, Influence of wood species on properties of wood/HDPE composites [Ph.D.], Ann Arbor: Washington State University (2008).
[28] A. Nourbakhsh, A. Hosseinzadeh, F. Basiji, J. Polym. Environ. **19**(4), 908 (2011).
[29] N. Ayrilmis, A. Kaymakci, Industrial Crops and Products **43**, 457 (2013).
[30] Y. Kazemi, A. Cloutier, D. Rodrigue, Polym. Compos. **34**(4), 487 (2013).
[31] S. Jarusombuti, N. Ayrilmis, European Journal of Wood and Wood Products **69**(3), 375 (2011).
[32] H. Z. Tabari, A. Nourbakhsh, A. Ashori, Polym. Eng. Sci. **51**(2), 272 (2011).
[33] U. Buyuksari, N. Ayrilmis, T. Akbulut, J. Appl. Polym. Sci. **123**(3), 1740 (2012).
[34] T. Lindstrom, P. T. Larsson, Nordic Pulp & Paper Research Journal **23**(2), 202 (2008).
[35] A. Ashori, A. Nourbakhsh, J. Appl. Polym. Sci. **111**(5), 2616 (2009).

*Corresponding author: zhanghlwnu@gmail.com