

Synthesis and Properties of Waterborne Polyurethane (WBPU)/Modified

Lignin Amine (MLA) Adhesive: A Promising Adhesive Material

Mohammad Mizanur Rahman^{1*}, Md. Hasan Zahir², Han Do Kim³

(1) Center of Research Excellence in Corrosion, King Fahd University of Petroleum & Minerals
Dhahran 31261, Kingdom of Saudi Arabia

(2) Center of Research Excellence in Renewable Energy, King Fahd University of Petroleum &
Minerals, Dhahran 31261, Kingdom of Saudi Arabia

(3) Department of Organic Material Science and Engineering, Pusan National University, Busan
608-739, Republic of Korea

ABSTRACT

A series of waterborne polyurethane (WBPU)/modified lignin amine (MLA) adhesives was prepared using modified lignin amine (MLA) as a chain extender by a prepolymer mixing process. A successful Mannich reaction was achieved during the synthesis of MLA by reacting lignin with bis(3-aminopropyl)amine. Higher tensile strength, Young's modulus and thermal stability were recorded for WBPU/MLA adhesives with higher MLA contents. The WBPU/MLA adhesive materials were used to coat PVC substrates. The adhesive strength increased with increasing MLA content. More importantly, the MLA also enhanced the WBPU/MLA coating in terms of adhesive strength at moderately high temperatures as well as under natural weather exposed conditions. The adhesive strength was essentially unaffected with 6.48 mole% MLA in the WBPU/MLA coating after exposure to natural weather conditions for 180 days.

Keywords: waterborne polyurethane; adhesive; lignin

*To whom correspondence should be addressed. E mail: mrahman@kfupm.edu.sa Phone 966138607210, Fax. 966138603996

1. INTRODUCTION

Loosening of adhesion of a coating from a substrate over time is a common phenomenon that leads to changes in the overall coating protection. These changes will induce corrosion (for metals), fouling or failure of the overall system, particularly in outdoor use where coatings are exposed to weathering, oxidation from the effects of UV radiation, and variation in temperature. Therefore, strong adhesive strength of a coating is crucial for long lasting applications [1, 2].

Most polymeric coatings and adhesives are generally based on fossil feedstocks. However, increasing oil prices and global warming demands a change from fossil feedstocks to renewable resources. Recently, researchers are increasingly devoting their efforts to the possible use of renewable feedstocks as raw materials for the production of monomers and their polymeric coatings and adhesives. Vegetable oils and animal fats play an important role in renewable resources because of their ready availability and many versatile applications. There have been many studies of polymers based on vegetable oils, such as vinyl polymers, epoxy resins, alkyd resins, polyamides, and polyurethanes [3-7].

Polyurethane (WBPU) is one of the most useful coating and adhesive materials because it exhibits superior adhesive strength, mechanical strength, and UV resistance [8-18]. Earlier interest was solvent based PU, in which different organic solvents were used to synthesize PU. However, the rapid rise of solvent price and increased environmental concerns are pressuring the scientists for the use of water as the main solvent in PU applications. In this regard, waterborne

polyurethane (WBPU) can be a good choice due to using water as a main solvent during their synthesis. There are different monomers to prepare WBPU dispersions using mainly polyols, diisocyanates, hydrophilic agents with pendant acid group, neutralizing agents and chain extenders [16-18]. Most of the monomers are petroleum-based. Only few researchers have successfully used plant-resourced monomer to synthesize PU without sacrificing their properties [19]. One of the important monomers in WBPU is chain extender. The mechanical strength highly depends on the chain extender. Ethylenediamine (EDA) is a widely used chain extender. The properties changed dramatically using different EDA content [17]. Unfortunately EDA has toxic nature and scientists are trying to replace it by naturally resourced monomer.

The properties can also be further improved by using proper renewable resource fillers, such as tannins and lignins [20–22]. Lignin, a promising renewable resource filler for PU, is composed of phenolic units and is the second most abundant plant biomass component after cellulose. In industry, lignins are typically obtained as by-products or waste from papermaking and emerging cellulosic ethanol production. The rigid structure of lignin allows for its utilization as a low-cost reinforcement filler. The properties of PU, epoxy, and acrylate have been improved by using proper lignin contents. A homogeneous lignin-PU material exhibits enhanced mechanical properties, thermal stability and UV protection [23].

Unfortunately, the use of lignin in WBPU coating and adhesive materials is very scarce. One of the challenges of WBPU/lignin dispersion is its stability and shelf life. To improve the stability of WBPU/lignin dispersion, J. Liu et al. modified lignin using diethylenetriamine through a Mannich reaction [19]. Superior mechanical and anti aging properties were recorded following the above technique. Typically, an alkyl group in the coating can improve the

hydrophobicity and thermal resistance [24]. Although there have been some attempts to use larger alkyl chains in different ways, the larger alkyl groups lead to WBPU dispersion challenges. Increasing the DMPA content is one way to use larger alkyl chains in WBPU. Another way to modify the monomer is by reacting the targeted alkyl group. In this study, the lignin was modified by using bis(3-aminopropyl)amine to make MLA as a chain extender. Three different chain extenders (single EDA, single MLA and mixture of EDA and MLA) were used in dispersions and their performances were compared. The MLA was used up to 6.48 mole%. The dispersions were used to coat a PVC surface, and the adhesive strength after exposure for a defined interval to both a hot chamber and natural weather conditions (separately) was evaluated. The outside exposure time was 180 days. Here, the PVC was considered a base specimen to avoid corrosion during the exposure time. The thermal properties of the coatings were analyzed by thermogravimetric analysis (TGA) and differential scanning calorimetry. The mechanical properties were evaluated through tensile tests. XPS analysis was conducted for analysis of degraded coatings.

2. EXPERIMENTAL

2.1 Materials

Poly(tetramethyleneoxide glycol, PTMG Mn=2000, Sigma Aldrich) was vacuum dried at 90°C for three hours prior to use. Dimethylolpropionic acid (Sigma Aldrich, DMPA), triethylamine (TEA, Sigma Aldrich), *N*-methyl-2-pyrrolidone (NMP, Sigma Aldrich), 4,4-dicyclohexylmethane diisocyanate (H₁₂MDI, Sigma Aldrich) and ethylene diamine (EDA, Sigma Aldrich) were used after dehydration with 4 Å molecular sieves for seven days. Dibutyltindilaurate (DBTDL, Sigma Aldrich), lignine (Sigma Aldrich) and bis(3-aminopropyl)amine (BAPA, Sigma Aldrich) were used as received.

2.2 Preparation of Lignin Amine

The lignin amine was synthesized according to the modified method of Liu et al [19]. Lignin (5 g) and BAPA (7.5 g) were mixed in 50 mL of distilled water. The pH of the mixture was maintained at 10–10.5 with 0.1 M NaOH and HCl solutions. The mixture was added to a three-necked flask, to which 5 g of formaldehyde solution (37 wt %) was added stepwise while stirring at room temperature. Next, the mixture was heated to 50 °C for 6 h. Afterward, the solution was added to approximately 350 mL of isopropyl alcohol to precipitate the lignin amine. The resulting light brown precipitate was recovered using suction filtration, washed with isopropyl alcohol four times, and then dried in a vacuum oven at 50 °C.

2.3 Preparation of WBPU dispersion

This dispersion was prepared by a prepolymer process following our previous report [18]. The prepolymer was prepared by charging polyol, 2, 2-dimethylol propionic acid, and H₁₂MDI for 3 h at 85 °C. The prepolymer was neutralized using proper amount of TEA. Water was added in the dispersion step, whereas EDA was added in the chain extension step.

2.4 Preparation of WBPU/MLA dispersions

The sample designation and composition of the WBPU/MLA dispersions are summarized in Table 1. WBPU/MLA dispersions were prepared using the prepolymer process. Initially, MLA was mixed with H₁₂MDI using sonication. This mixture was added to another vessel containing a mixture of PTMG/DMPA/NMP/DBTDL solution to make NCO-terminated prepolymer, followed by neutralization with TEA. A calculated amount of water (30 wt%) was added to the mixture to disperse the prepolymer in water. In the last step, EDA/MLA was added to the

mixture. The residual NCO group reacted with the amine group and terminated the reaction, which was confirmed by the disappearance of the NCO group by FT-IR analysis.

2.5 Preparation of the films

The films were prepared by pouring aqueous dispersions (10 g) onto a Teflon disc (diameter of 7 cm), followed by drying under ambient conditions for 48 hours. The films (typically ~0.5 mm thick) were also dried at 60 °C for 6 hours and vacuum dried at 80 °C for 6 hours. The vacuum dried films were stored in a desiccator at room temperature.

2.6 Mounting of coatings onto the PVC solid supports

The dispersion was mounted onto flat PVC solid supports with an applicator. The coated samples (200 µm under wet conditions) were dried under ambient conditions for 48 hours.

2.7 Curing of the coatings

Both curing temperature and time are important factors in the adhesive strength of the coatings. To avoid any unwanted reaction, the optimum curing time and temperature were determined to be 5 min and 100 °C, respectively.

2.8 Characterization

FTIR spectroscopy (Impact 400D, Nicolet, Madison, WI) was used to identify the composite structure. The dispersion was coated on a thalliumbromide/ thalliumiodide crystal surface as a thin liquid film and dried for analysis. For each sample, 32 scans at a resolution of 4cm⁻¹ were collected in transmittance mode.

The mechanical properties (tensile strength, Young's modulus and elongation at break) were measured at room temperature using a United Data Systems tension meter (SSTM-1 United Data Systems, Japan) according to the ASTM D 638 specifications. A crosshead speed of 50 mm/min was used throughout these studies. The values quoted are the means of five measurements.

Thermal gravimetry analysis was performed in a Pyris 6 TGA (Perkin Elmer, USA). 5.0 mg film sample was placed in a platinum pan and heated from 30 to 500°C in a nitrogen atmosphere, at a heating rate of 10°C/min

The thermal behavior of the WBPU film was analyzed by differential scanning calorimetry (DSC; TA). 3–4 mg WBPU film was placed in an aluminum pan and the experiment was carried out under nitrogen gas atmosphere at a heating rate of 10 °C/min.

The adhesive properties (peel resistance of the adhesive, i.e. T-peel strength) were measured using a universal testing machine according to ASTM D 1876-01. A peel rate of 100 mm/min was used. The values quoted are the means of five measurements.

The polymer surface was analyzed by X-ray photoelectron spectroscopy (XPS) (ESCA 250 XPS, UK).

3. RESULTS AND DISCUSSION

The lignin was modified as in previous report [19]. Fig. 1 shows that the FT-IR peaks correspond to the pristine lignin, MLA and WBPU/MLA respectively. Pristine lignin shows a broad band at 3500 - 3000 cm^{-1} , which is attributed to the hydroxyl groups. The bands centered approximately 2925 and 2843 cm^{-1} arise from CH₂ stretching. In the carbonyl region, medium bands observed near 1710 cm^{-1} are associated with conjugated carbonyl stretching and the three

bands at 1606, 1515 and 1425 cm^{-1} are characteristic of aromatic rings from aromatic skeleton vibrations. The FTIR spectrum of MLA showed that the relative intensity of the broad peak at 3500 - 3000 cm^{-1} increased, this was attributed to the introduction of amino groups. Besides, the greatly weakened band of aromatic stretching vibrations at 817 and 856 cm^{-1} confirmed that the benzene ring of lignin was functionalized via the reaction [25].

A minimum DMPA content is required for the formation of stable conventional WBPU dispersions. A higher DMPA content is typically needed to disperse cross linker or additional nano particles. However, the dispersion with MLA was stable as with pristine WBPU with the same DMPA content. Different MLA contents were used in the WBPU/MLA dispersions which were stable like their respective pristine WBPU dispersions. The synthesis of the WBPU/MLA dispersions was confirmed using FT-IR analysis (see Fig. 1). The absence of a peak within the 2000–2300 cm^{-1} range indicates that all of the isocyanate groups reacted [18, 19]. All of the spectra exhibit the characteristic bands at 3150–3600, 2800–3000, 2795, 1600–1760, and 1109 cm^{-1} , which correspond to NH, CH, O-CH₂, C=O, and C-O-C stretching in the ether group, respectively [17, 18]. These peaks are identical for PU and confirm the preparation of the WBPU/MLA dispersions.

The mechanical properties of the WBPU/MLA films were evaluated using tensile tests. The corresponding Young's modulus, tensile strength, and elongation at break (%) of the films are summarized in Table 2. The mechanical properties of the films varied slightly according to the low MLA content (1.39 mole%). Significant mechanical changes were recorded when the MLA content exceeded (4.63 mole%). The tensile strength and Young's modulus of the WBPU/MLA films increased with increasing MLA content. Maximum tensile strength and

Young's modulus were observed at an MLA content of 6.48 mole%. The tensile strength and Young's modulus increased 38% and 240%, respectively, using only MLA (sample WBPU/MLA-4) comparing to those for using EDA (sample WBPU/MLA-0). This observation can be ascribed to the insertion of an ideal amount of the MLA into the matrices, resulting in the formation of strong interfacial interactions between the flat MLA and the polymer chains. This restricts the mobility of the polymer chains and creates a compact structure, which requires high energy input for elongation, which is reflected in the higher tensile strength and Young's modulus of the films.

Thermal stability of polymers is typically determined using TGA analysis (see Fig. 2). TGA curves indicate the weight loss (%) of materials with respect to the temperature of thermal degradation [18]. The thermal degradation of pristine WBPU can be divided into main two stages. The first stage at 250 °C corresponds to the urethane group, whereas the second stage at 390 °C mainly accounts for the urea group [18]. Using different chain extenders did not alter the stages, all degradation were two stages. However, the addition of MLA increased the thermal stability in both stages. This thermal stability continued to increase with increasing MLA content. The stiff aromatic ring as well as direct linkage of the MLA group into the PU chain enhanced the overall thermal stability.

The thermal properties of the WBPU/MLA films were studied using differential scanning calorimetry (DSC), the results of which are summarized in Fig. 3. All of the samples containing MLA were shown to almost same melting peaks for the soft segment (T_m SS) at approximately 19 °C (see Fig. 3). The heat of fusion (18.5 mJ/mg) remained nearly unchanged for different MLA contents. The melting temperature of the hard segment was not observed, indicating the

amorphous structure of the hard segment regions of the WBPU/MLA coatings. One possible explanation for this observation is that the MLA disrupts the hard segment crystallinity and that the peak for the hard segment was not observed.

The coating properties were evaluated by adhesive strength and mechanical damage. Visually, there was no mechanical damage to the coatings before exposure to a hot chamber or to outside conditions. The adhesive strength gradually increased with increasing MLA content before exposure, which may be attributed to the higher mechanical strength with increasing MLA content. The aromatic planar lignin made the coating very stiff and improved the adhesive strength. The mean adhesive strength value is shown in Fig. 4. The adhesive strength changed after exposure to different defined temperatures (see Fig. 5). For all samples, the adhesive strength decreased with increasing temperature. However, the decreased rate of the adhesive strength was different for all coatings; the rate decreased with increasing MLA content. This implies that the degradation rate might be decreased with increasing MLA content. The coating with 6.48 mole% MLA exhibited the lowest decreased rate of approximately 30% at 100 °C; whereas, the coating without MLA (only EDA) exhibited the highest decreased rate of 67% at 100 °C. These results imply a moderately resistant adhesion of WBPU/MLA with 6.48 mole% MLA at moderately high temperatures. A good combination of high thermal stability and mechanical strength of the WBPU/MLA coatings made the difference in adhesive strength compared to WBPU without lignin at moderately high temperatures.

The adhesive strength was also evaluated after exposure of coating to natural weather conditions for 180 days. The adhesive strength of exposed coatings is summarized in Fig. 6. This was recorded that the adhesive strength decreased with increasing exposure time. However, the

adhesive strength was less affected in the WBPU/MLA coatings. The adhesive strength decreased only 3% after 180 days of exposure of the WBPU/MLA (6.48 mole%) coatings. The adhesive strength of the exposed coating might be depends highly on the coating degradation rate. A degraded coating has less resistivity of barrier, allowing for more facile passing of water, air and other unwanted dusts, which help to decrease the bond strength of the coating. In this case, the MLA acted as a UV absorber and protected the coating from degradation. Visually, the change in coatings was very minor. However, a large degradation was recorded through the XPS technique. The peaks for certain atoms were found to be nearly identical in all exposed coatings (see Fig. 7). The peaks at 531, 285 and 400 eV attributed to oxygen (1s), carbon (1s), and nitrogen (1p), respectively [24], were observed in the survey spectra for all the exposed coatings. Because the oxygen (1s), carbon (1s), and nitrogen (1p) atoms have different binding energies, their peaks are observed at different values. However, for the carbon atoms in different environments with different functional groups, the C1s binding energies of these functional groups are very close to each other and their original functional groups can be determined using curve fitting analysis. The C1s peaks are classified into five groups: C=O carbon atom appearing at 289.7–285.8 eV, C–C or C–H appearing at 282.0–285.9 eV, C–O appearing at 284.1–286.1 eV, C–N appearing at 284.5–287.1 eV, aromatic ring appearing at 283.20–285.68 eV (see Fig. 8) [24, 26]. With the inclusion of MLA, the area at 289.7–285.8 eV (for the carbonyl groups) decreased (not shown). As reported elsewhere, the carbonyl contribution is attributed to the urethane/urea groups of WBPU. A smaller carbonyl area implies a lower content of urethane/urea groups on the surface. The lowest carbonyl area was determined for the highest MLA content of 6.48 mole% (not shown), implying that the maximum amount of buried urethane/urea groups by MLA on the surface was found at this composition. Usually the coatings

exposed to open air atmosphere are susceptible to degradation, leading to eventual loss of adhesion. Carbon dioxide and carbon monoxide are two prominent degrading products, which can be detected by the presence of carbonyl groups through XPS analysis. The increased carbonyl content of the exposed coatings implies the degradation of the coatings and eventually effects the adhesive strength of the coatings. The carbonyl contents of all the exposed coatings are shown in Fig. 9. The carbonyl content changed significantly for the pristine WBPU exposed coating, which further increased with time. This degradation resulted in the facile passing of water/air through the coating into the PVC and directly impacted the adhesive strength of the coating. Very low adhesive strength was observed in this case. However, the carbonyl content was different when 4.63 mole% or higher MLA content was used in the coatings. The carbonyl content was observed to be lowest for the WBPU/MLA coating with 6.48 mole% MLA (see Fig. 9). This result can be ascribed to the lowest chain scission of urethane/urea groups in the presence of UV (sunlight). Herein, the MLA acted as a UV absorber, which protected the chain scission of urethane/urea groups, eventually decreasing the degradation of the coating. Hence, the adhesive strength was nearly unaffected, especially at 6.48 mole% MLA content.

4. CONCLUSIONS

Naturally resourced lignin was modified through Manich reaction using bis(3-aminopropyl)amine to made modified lignin amine (MLA) as a chain extender used in WBPU/MLA dispersions. The thermal stability, UV degradation resistivity and adhesive strength all increased using MLA as a chain extender. Regarding the adhesive strength at moderately high temperatures and under exposed conditions, the WBPU coating with EDA showed very less resistance; whereas, the WBPU with MLA showed high resistance. The adhesive strength of the

WBPU/MLA coating (using 6.48 mole% MLA, without EDA) decreased 30% and 3 % at 80 °C and under exposed conditions, respectively. Considering the good adhesive strength at different conditions, the MLA can be considered an alternative to the current toxic EDA in WBPU materials, which will create a new branch of application of green products.

Acknowledgement

This study was supported by Center of Research Excellence in Corrosion (CoRE-C), King Fahd University of Petroleum and Minerals (KFUPM), Dhahran 31261, Saudi Arabia.

References

1. Li, A.; Li, K. Pressure-Sensitive Adhesives Based on Epoxidized Soybean Oil and Dicarboxylic Acids. *Sustain. Chem. Eng.* **2014**, *2*, 2090–2096.
2. Ratna, D.; Banthia, A. K. Epoxidized soybean oil toughened epoxy adhesive. *J. Adhes. Sci. Technol.* **2000**, *14*, 15–25.
3. Meier, M.A.; Metzger, J.O.; Schubert, U.S. Plant oil renewable resources as green alternatives in polymer science. *Chem. Soc. Rev.* **2007**, *36*, 1788–1802.
4. Sharma, V.; Kundu, P. P. Addition polymers from natural oils-A review. *Prog. Polym. Sci.* **2006**, *31*, 983–1008.
5. Williams, C. K.; Hillmyer, M. A. Polymers from Renewable Resources: A Perspective for a Special Issue of Polymer reviews. *Polym. Rev.* **2008**, *48*, 1–10.

6. Elena, O.C.; Franciska A.A.; Ana, M.T.; Enrique M.P.; Cesar O.B. Synthesis of polyurethanes from CO₂-based polyols: A challenge for sustainable adhesives. *Int. J. Adhes. Adhes.* **2016**, *67*, 63–68.
7. Corcuera, M.A.; Rueda, L.; Saralegui, A.; Martín, M.D.; Fernández-D'Aras, B.; Mondragon, I.; Eceiza, A. Effect of diisocyanate structure on properties and micro-structure of polyurethanes based on polyols derived from renewable resources. *J. Appl. Polym. Sci.* **2011**, *122*, 3677–3685.
8. Chattopadhyay, D.K.; Raju, K.V.S.N.; Structural engineering of polyurethane coatings for high performance applications. *Prog. Polym. Sci.* **2007**, *32*, 352-418.
9. Madbouly, S.A.; Otaigbe, J.U. Recent advances in synthesis, characterization and rheological properties of polyurethanes and POSS/polyurethane nanocomposites dispersions and films. *Prog. Polym. Sci.* **2009**, *34*, 1283-1332.
10. Chattopadhyay, D.K. Webster, D.C. Thermal stability and flame retardancy of polyurethanes. *Prog. Polym. Sci.*, **2009**; *34*: 1068-1133.
11. Rahman, M.M.; Kim, E.Y.; Lim, K.T.; Lee, W.K. Morphology and properties of waterborne polyurethane/CNT nanocomposite adhesives with various carboxyl acid salt groups *J. Adhesion Sci. Technol.* **2009**, *23*, 839-850.
12. Gorrasi, G.; Tortora, M.; Vittoria V. Synthesis and physical properties of layered silicates/polyurethane nanocomposites. *J. Polym. Sci. Part B: Polym. Phys.* **2005**, *43*, 2454-2467.
13. Rahman, M.M.; Kim, H.D.; Lee, W.K. Preparation and characterization of waterborne polyurethane/clay nanocomposite: Effect on water vapor permeability. *J. Appl. Polym. Sci.* **2008**, *110*, 3697-3705.

14. Sin, S.L.; Kumar, J.N.; Tan, H.R.; He, C.; Liu, Y.; Xu, J. The effect of different clay dispersion methods on the properties of polyurethane/clay nanocomposites. *Aus. J. Chem.* **2013**, *66*, 1039-1047.
15. Zhao, C.X.; Zhang, W.D. Preparation of waterborne polyurethane nanocomposites: Polymerization from functionalized hydroxyapatite. *E. Polym. J.* **2008**, *44*, 1988-1995.
16. Kwon, J.Y.; Kim, H.D. Preparation and properties of acid-treated multiwalled carbon nanotube/waterborne polyurethane nanocomposites. *J. Appl. Polym. Sci.* **2005**, *96*, 595-604.
17. Rahman, M.M.; Kim, H.D.; Lee, W.K. Properties of Waterborne Polyurethane Adhesives: Effect of Chain Extender and Polyol Content. *J. Adhes. Sci. Tech.* **2009**, *23*, 177-193.
18. Rahman, M.M.; Kim, H.D. Synthesis and Characterization of waterborne polyurethane adhesives containing different amount of ionic groups (I). *J. Appl. Polym. Sci.* **2006**, *102*, 5684-5691.
19. Liu, J.; Liu, H.F.; Deng, L.; Liao, B.; Guo, Q.X. Improving Aging Resistance and Mechanical Properties of Waterborne Polyurethanes Modified by Lignin Amines. *J. Appl. Polym. Sci.* DOI: 10.1002/app.39267.
20. Khan, M.A.; Ashraf, S.M.; Malhotra, V.P. Eucalyptus bark lignin substituted phenol formaldehyde adhesives: a study on optimization of reaction parameters and characterization. *J Appl Polym Sci* **2004**, *92*, 3514–3523.
21. Danielson, B.; Simonson, R. Kraft lignin in phenol formaldehyde resin. Part 2 Evaluation of a industrial trial. *J Adhes Sci Technol* **1998**, *12*, 941–946.
22. Khan, M.A.; Ashraf, S.M.; Malhotra, V.P. Development and characterization of a wood adhesive using bagasse lignin. *Int J Adhes Adhes* **2004**, *24*, 485–493.

23. Zhang, C.; Wu, H.; Kessler, M.R. High bio-content polyurethane composites with urethane modified lignin as filler. *Polymer* **2015**, *69*, 52-57.
24. Rahman, M.M.; Kim, H.D.; Chun, H.H.; Lee, I.W.; Park, H. Properties of waterborne polyurethane coatings: Effect of alkyl chain length of tertiary amines of carboxyl acid salt groups. *Fib. Polym.* **2013**, *14*, 886-894.
25. Yue, X.P.; Chen, F.G.; Zhou, X.S. Improved interfacial bonding of PVC/wood-flour composites by lignin amine modification. *Bioresources* **2011**, *6*, 2022-2034.
26. Yeo, J.S.; Seong, D.W.; Hwang, S.H. Chemical surface modification of lignin particle and its application as filler in the polypropylene composites. *J. Indus. Engin. Chem.* **2015**, *31*, 80-85.

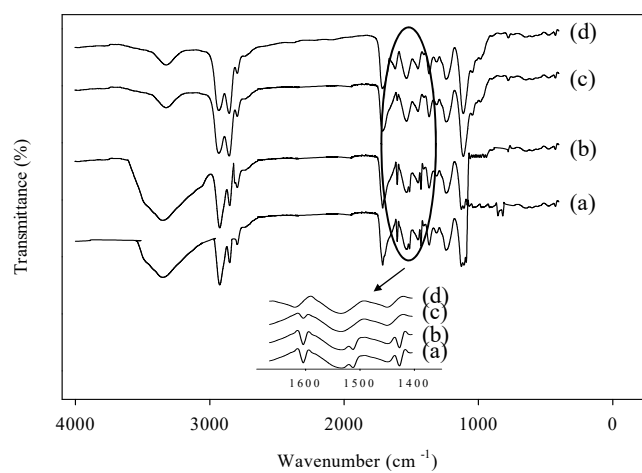


Figure 1. FT-IR spectra of (a) lignin (b) modified lignin amine (MLA) (C) WBPU/MLA-3 (lignin 4.63 mole%) and (d) WBPU/MLA-0 (without lignin)

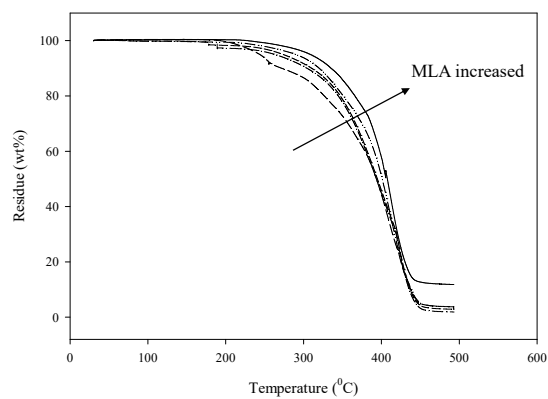


Figure 2. TGA of WBPU/MLA films with different MLA content

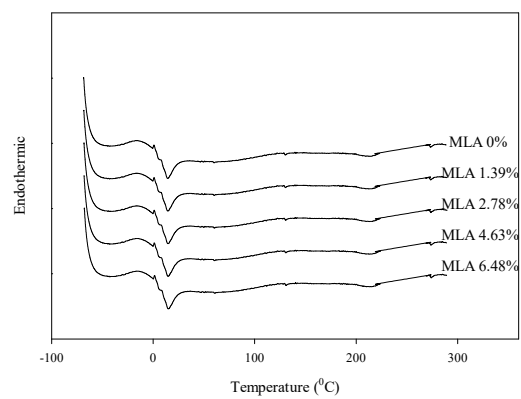


Figure 3. DSC of WBPU/MLA films with different MLA content

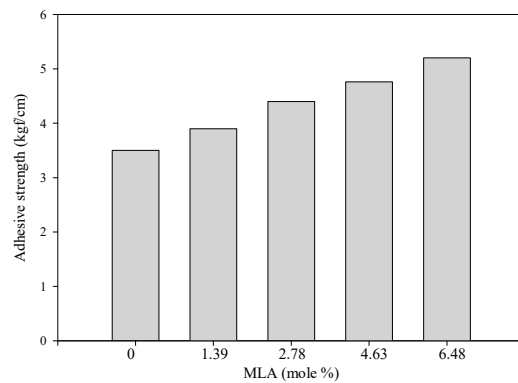


Figure 4. Effect of MLA content on adhesive strength of coatings at ambient condition

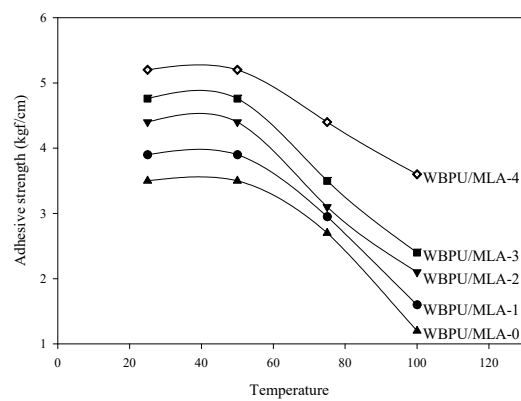


Figure 5. Adhesive strength of WBPU/MLA coatings at different temperature

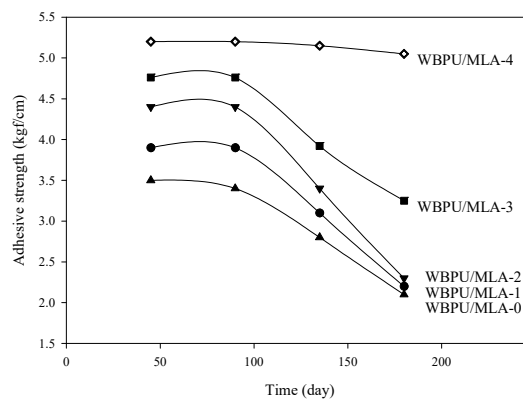


Figure 6. Adhesive strength of WBPU/MLA coatings at different exposure time

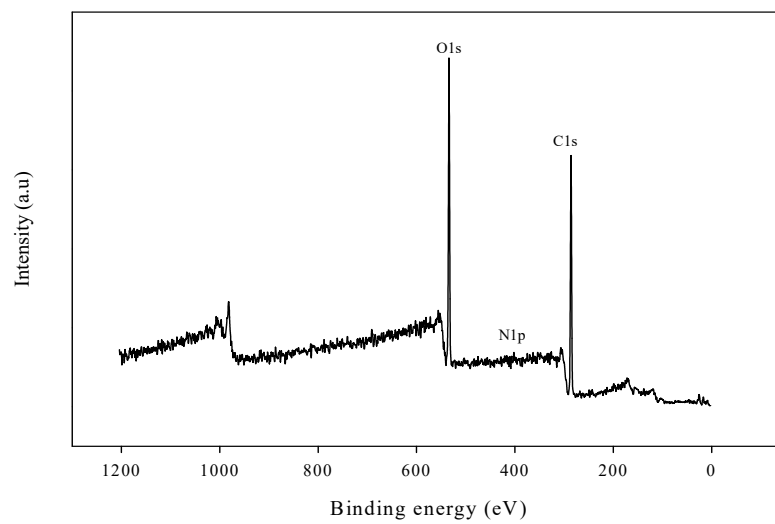


Figure 7. XPS spectra of WBPU/MLA-4 coating

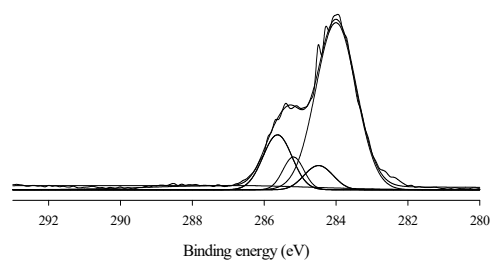


Figure 8. Deconvoluted spectra of WBPU/MLA-4 coating

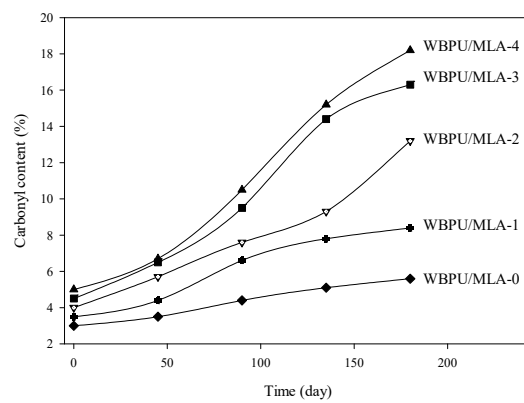


Figure 9. Carbonyl content of exposed WBPU/MLA coatings

Table 1. Composition of WBPU/MLA dispersions

Sample	Mole ratio					MLA (mole %)
	PTMG	H12MDI	DMPA	TEA	EDA/MLA	
WBPU/MLA-0	0.040	0.108	0.054	0.054	0.014/ 0	0
WBPU/MLA-1	0.040	0.108	0.054	0.054	0.011/ 0.003	1.39
WBPU/MLA-2	0.040	0.108	0.054	0.054	0.008/ 0.006	2.78
WBPU/MLA-3	0.040	0.108	0.054	0.054	0.004/ 0.010	4.63
WBPU/MLA-4	0.040	0.108	0.054	0.054	0/ 0.014	6.48



© 2016 by the authors; licensee Preprints, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons by Attribution (CC-BY) license (<http://creativecommons.org/licenses/by/4.0/>).