Modification of lignin by hexamethylene diisocyanate to synthesize lignin-based polyurethane as an organic polymer for marine polyurethane anticorrosive coatings

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Abstract
A green and facile preparation was used to synthesize modified lignin (ML) from alkaline lignin by using hexamethylene diisocyanate (HDI) as the modifier and tetrahydrofuran as the solvent without a catalyst. Then, the as-synthesized ML was dispersed in hydroxy acrylic resin and used to prepare modified lignin-based polyurethane composites by using HDI trimer as the curing agent and dibutyltin dilauric acid as the catalyst at room temperature. Fourier transform infrared (FTIR) and elemental analysis confirmed that the main chemical in ML was lignin urethane when the amount of HDI was 0.2 g. The tensile strength of the modified lignin-based polyurethane (MLPU-0.2) film using ML-0.2 reached 12.07 MPa, which was improved by 23.2% and 68.3% compared with that of the pure polyurethane (PU) film (9.79 MPa) and lignin-based polyurethane (LPU) film prepared using unmodified lignin (7.17 MPa), respectively. After the addition of lignin or ML, the elongation at break of the polyurethane film increased. The water contact angle of MLPU-0.2 increased up to 96°, which was higher than that of PU (74°) and LPU (68°). The pencil hardness of MLPU-0.2 (3 H) was higher than that of PU (H) and LPU (2 H). Modified lignin-based polyurethane shows promise for marine anticorrosive coatings.

1. Introduction
Lignin is a renewable biomass resource with a reserve second only to cellulose. Approximately 100 million tons of lignin are produced globally each year [1]. However, most of it is used as a low-value fuel to provide heat for industrial production, and only approximately 2% can be used to produce products with high commercial value [2, 3]. Therefore, the conversion of lignin into high-value products has received increasing interest [4]. Due to its rich phenolic hydroxyl and alcohol hydroxyl groups, lignin has been successfully used as a polyol to prepare polyurethane (PU) materials, such as adhesives [5], foams [6], elastomers [7], coatings [8] and other materials. These lignin-based PU materials are promising candidates for potential applications because of the shortage of petroleum resources and environmental pollution caused by petroleum-based materials.

Lignin-based PU (LPU) materials can be directly prepared from lignin and isocyanate. For example, organosolv lignin extracted by the high boiling solvent method was applied to prepare a PU film by reacting with 4,4′-diphenylmethane diisocyanate [9]. Kumari and coworkers [10] prepared PU foam via the reaction between alkaline lignin and 4,4′-diphenylmethane diisocyanate. In the process of reacting with diisocyanate, the hydroxyl groups of lignin showed low reaction activity because of their large steric hindrance. Therefore, when using...
lignin as the sole polyol, the prepared LPU materials presented some shortcomings, such as brittleness and poor mechanical properties [11].

The approach of partially replacing polyols with lignin was applied to prepare LPU materials, which exhibited good ductility because the soft chain segments of polyols provided excellent flexibility [12]. For example, Klein and coworkers [13] used a mixture of lignin extracted from pulping liquor and polyethylene glycol 425 or polypropylene glycol 600 to synthesize a PU coating by using diphenylmethane diisocyanate as a curing agent. The as-synthesized LPU coating presented high homogeneity and flexibility. Although partial substitution of polyols by lignin can improve the performance of LPU materials, the hydroxyl groups of polyols generally present higher activity than those of lignin. Therefore, polyols more easily react with diisocyanate than lignin does, and the competitive reaction between polyols and lignin with diisocyanate can hinder the strong chemical connection between lignin and the PU matrix. Therefore, lignin acts as a filler in the PU matrix, reducing the performance of the LPU.

Chemical modification methods have been used to improve the performance of LPU materials [14]. For example, lignin separated from black liquor was demethylated, mixed with polyethylene glycol 400, and reacted with 4,4’-diphenylmethane diisocyanate to prepare an LPU antibacterial coating. The results indicated that the hydrophobicity of the PU coating prepared with modified lignin was enhanced, and its water contact angle was approximately 23° higher than that of the PU coating prepared without modified lignin [15]. Chen et al [5] used formaldehyde to modify lignin, mixed it with polyethylene glycol 200, and then reacted the mixture with toluene diisocyanate to prepare PU adhesive. The tensile strength and elongation at break of the as-synthesized adhesive were increased by 125% and 151%, respectively. Jang et al [16] prepared PU-based gel coating membranes by grafting lignin with poly(ε-caprolactone), mixing it with acrylic resin, and reacting it with an NCO-terminated urethane prepolymer. The results showed that the as-prepared membranes had similar physical properties and surface characteristics to those prepared from petroleum-based polyols. Cao et al [17] used propylene bromide and 2-mercaptoethanol as modifying agents to convert phenolic hydroxyl groups of enzymatically hydrolysed lignin into alcohol hydroxyl groups, and then the as-modified lignin was reacted with hexamethylene diisocyanate (HDI). When the content of modified lignin or lignin was approximately 41%, the prepared LPU coating films possessed an approximately 41% higher tensile strength than the films prepared without modified lignin. Li and coworkers [18] used oxypropylene to modify lignin extracted from corn straw with 15% ethanol. Then, the modified lignin was mixed with polyether polyol and finally reacted with polymeric diphenylmethane diisocyanate. The as-prepared rigid PU foam exhibited a 17% increase in compressive strength. However, the above chemical modification methods have disadvantages, such as complex preparation processes, high postprocessing costs and poor environmental friendliness.

In this paper, modified lignin (ML) was synthesized from alkaline lignin and hexamethylene diisocyanate (HDI) by using the reaction between the -OH of lignin and -NCO of HDI. The only byproduct was pollution-free water and the experimental conditions of the modification is simple, therefore, the method of preparing modified lignin was green and facile. The as-prepared modified lignin (ML) was dispersed in hydroxy acrylic resin to prepare modified lignin-based polyurethane (MLPU) composites, which are important film-forming materials for marine anticorrosive polyurethane coatings. Furthermore, the effect of HDI dosage on the modification of lignin was studied. The chemical structure and thermal degradation performance of the modified lignin were characterized by Fourier transform infrared spectroscopy (FTIR), elemental analysis and thermogravimetric analysis (TGA). Finally, the effect of modified lignin with different HDI dosages on the properties of lignin-based PU films was characterized by x-ray diffraction (XRD), TGA, differential scanning calorimetry (DSC), tensile tests, water contact angle tests and pencil hardness tests. This paper presents modified lignin-based polyurethane composites developed for the potential application in marine anticorrosive coatings.

2. Experimental section

2.1. Materials

Alkaline lignin was purchased from Tokyo Chemical Industry Co., Ltd (product number: L0082) and dried in a vacuum oven at 60 °C for 24 h. Tetrahydrofuran and butyl acetate were purchased from Sinopharm Chemical Reagent Co., Ltd. HDI was purchased from Shanghai Macklin Biochemical Co., Ltd. Hydroxy acrylic resin (product number: R-48), hexamethylene diisocyanate trimer (HDI trimer) and dibutyltin dilaurate were supplied by Changzhou Paint and Coating Industry Research Institute Co., Ltd.

2.2. Modification of lignin

One gram of lignin and a certain amount of HDI (0.1–0.6 g) were dissolved in 12 g of THF and stirred at 50 °C for 6 h under a nitrogen atmosphere, followed by incubation at room temperature for 24 h to remove the solvent. Finally, the modified lignin was obtained by drying in an oven at 50 °C for 24 h. When the amount of
HDI was 0, 0.1 g, 0.2 g, 0.3 g, 0.4 g, 0.5 g and 0.6 g, the prepared ML was denoted as ML-0.1, ML-0.2, ML-0.3, ML-0.4, ML-0.5 and ML-0.6, respectively.

2.3. Preparation of lignin-based PU films
Lignin or ML (ML-0.1, ML-0.2, ML-0.3 and ML-0.4) was ground and then screened with a 200-mesh screen. One gram of the screened ML or lignin was dissolved in 6.5 g of butyl acetate in a 50 ml beaker, followed by stirring for 1 min. Then, 13 g of hydroxy acrylic resin, 6.5 g of HDI trimer and 1 wt % dibutyltin dilauric acid were added to the above solution under stirring, followed by 10 min of conditioning in which residual bubbles were removed by ultrasound treatment. These reactants were evenly coated on a glass plate using a film applicator with a thickness of 1000 μm and then cured at room temperature for 7 days. The PU films were labelled LPU, MLPU-0.1, MLPU-0.2, MLPU-0.3 and MLPU-0.4. The control sample of the PU film was prepared without lignin or ML.

2.4. Characterization

2.4.1. Characterization of ML
The FTIR spectra of lignin and ML were recorded on a Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific, U.S.A.). The carbon, hydrogen and nitrogen contents of lignin and ML were determined by elemental analysis (PE 2400 II, PE, U.S.A.). The thermal stability of lignin and ML was measured by thermogravimetric analyser (STA2500, NETZSCH, Germany) under the condition of being heated from room temperature to 600 °C at a rate of 10 °C min⁻¹ in a nitrogen atmosphere.

2.4.2. Characterization of PU films
X-ray diffraction (XRD) patterns were recorded by x-ray diffraction spectroscopy (Ultima IV, Rigaku, Japan). Differential scanning calorimetry (DSC) was conducted using a differential scanning calorimeter (DSC 214, NETZSCH, Germany) under a nitrogen atmosphere, and the glass transition temperature (Tg) was determined as the midpoint of the heat capacity change of the second scan at 10 °C min⁻¹. The tensile tests were performed with a universal tensile-compressive tester (TY8000B, TYTESTER, China) according to GB/T2567–2008. Each sample was tested on at least three specimens, and the average values were reported. Water contact angle (WCA) measurements were conducted on a drop shape analyser (KRUSS DSA100, Germany) with deionized water at room temperature. The fractured surface of the samples was observed by scanning electron microscopy (JSM-7600F, Japan Electronics). The FTIR spectra of PU films were recorded on a Nicolet iS5 FTIR spectrometer (Thermo Fisher Scientific, U.S.A.). A penicil hardness tester (QHQ-A, Tianjin Material Testing Machine Factory, China) was used to test the surface hardness of the samples according to ASTM D3359. Adhesion tests of the PU, LPU and MLPU films were performed according to ASTM D3359.

2.4.3. Anti-corrosion performance tests
PU or LPU was coated on a common Q235 carbon steel substrate, and the thickness of the coating was approximately 50 μm. The corrosion resistance of the coating was evaluated by electrochemical impedance spectroscopy (EIS). A three-electrode electrochemical system was used for the test. The prepared electrode was immersed in 3.5 wt% NaCl aqueous solution, and EIS was conducted on a chemistry workstation (CHI660E, Chenhua, China) equipped with a shielding box. The battery was balanced for 90 min before each measurement. EIS was performed in the frequency range of 0.01 Hz–1000 kHz with an amplitude of 5 mV.

3. Results and discussion

3.1. Lignin modification
3.1.1. FTIR
The chemical structures of lignin and ML were characterized by FTIR. As shown in figure 1, the intense stretching vibration peaks at 3420 cm⁻¹ were attributed to hydroxyl groups and water in lignin. However, the above peaks in ML-0.1 and ML-0.2 were shifted to 3397 cm⁻¹ and 3355 cm⁻¹, respectively, because of the influence of the -NH group in the lignin urethane [19]. Furthermore, the stretching vibration peaks of the -NH group at 3344 cm⁻¹ were obviously present in ML-0.3, ML-0.4, ML-0.5 and ML-0.6 [3]. The changes in those peaks indicated that the hydroxyl group in lignin gradually reacted and that the -NH group was gradually generated with the increase in the amount of HDI. On the other hand, the stretching vibration peaks of lignin and ML samples at 2932 cm⁻¹ and 2855 cm⁻¹ were presented with respect to the asymmetric stretching vibration and symmetric stretching vibration of the CH₂ group, respectively. The intensity of these two bands in the ML was increased, which indicated that the hexamethylene chain in the HDI group was successfully introduced into the lignin [20].
The stretching vibration peaks of the ester carbonyl group ($\text{C} = \text{O}$) of ML samples appeared at $1724 \text{ cm}^{-1}$, which indicated that lignin urethane was successfully synthesized from HDI and lignin [21]. In addition, the ML-0.3, ML-0.4, ML-0.5 and ML-0.6 samples exhibited vibration peaks at $1623 \text{ cm}^{-1}$, which were attributed to $\text{C} = \text{O}$ in the urea group (-NHCONH -). When the amount of HDI was as high as 0.3 g, polyurea was unexpectedly generated because excess HDI easily reacted with the strongly adsorbed water in ML and moisture in the air, which could be verified by TG. The ML-0.5 and ML-0.6 samples presented vibration peaks of the -NCO group at $2268 \text{ cm}^{-1}$, which was due to excess polyurea formed in the ML particles hindering the reaction of excess NCO- with adsorbed water. Undesirably, the formation of excessive polyurea led to a large particle size and high hardness of ML, which made it difficult to prepare PU films.

In summary, lignin urethane, as the main chemical, was synthesized from lignin and HDI without a catalyst at room temperature, and polyurea was formed unexpectedly when excess HDI was used.

3.1.2. Elemental analysis

From the FTIR results, the hydroxyl group in lignin almost completely reacted when the amount of HDI was 0.2 g. Based on the molecular structure of the lignin C$_9$ unit shown in figure 2(a), provided by Tokyo Chemical Industry Co., Ltd., the molecular structure of the ML C$_9$ unit is inferred in figure 2(b). According to the hypothetical molecular structure of ML, the theoretical contents of C, H and N elements (shown in table 1) were calculated to be 50.34%, 5.28% and 2.45%, respectively. As shown in table 1, the experimental data of these elemental contents were 52.62%, 5.28% and 2.42%, in which H and N were in agreement with the calculated
values and C was also close to the calculated value. Therefore, elemental analysis further proved that lignin urethane was the main chemical involved in the reaction between lignin and HDI.

3.1.3. Thermal properties

The thermal properties of the lignin and ML were investigated by TGA. As shown in figure 3(a), the mass loss of lignin mainly occurred in two stages. The first mass loss occurred below 100 °C due to the volatilization of solvent and water in lignin. The second mass-loss stage occurred between 200 °C and 500 °C, which was relatively wide because of the cleavage of different chemical bonds at different temperatures [22], such as the cleavage of α- and β-aryl-alkyl-ether linkages at approximately 200 °C, the oxidative cleavage of the side chain of lignin (carbonylation, carboxyl and dehydrogenation, etc) between 300 °C and 400 °C and the cleavage of C-C bonds between the structural units of lignin at approximately 400 °C [23]. Despite having similar mass-loss stages to lignin, the mass-loss rates in both stages of ML were higher than those of lignin. As shown in figure 3(a), the T5% of lignin was 184 °C, while that of ML decreased from 156 °C to 89 °C with increasing HDI, which indicated that ML possessed increased hydrophobicity. As shown in figure 3(b), the Tmax of ML was between 311 °C and 309 °C, lower than that of lignin at 339 °C, which indicated that ML was easier to degrade than lignin because of the cleavage of urethane and polyurea groups between 300 °C and 400 °C [24, 25].

3.2. PU film characterization

All the samples PU, LPU and MLPU films showed good adhesion properties, achieving the best grade of 5B, which all reached the highest of standard of coating adhesion.

3.2.1. XRD and DSC

The hardness and flexibility of PU are related to its degree of crystallinity. The crystal structure of PU is mainly formed by the ordered arrangement of hard segments. The higher the degree of PU crystals, the higher the hardness. The amorphous structure is mainly formed by the disordered arrangement of soft segments. The more amorphous PU, the higher its flexibility [26]. As shown in figure 4(a), samples of PU, films exhibited a diffraction peak at approximately 20° = 20°, which was consistent with the results reported in the literature [27, 28]. Compared with PU films, the diffraction peak of LPU and MLPU films shifted to higher or lower, which was caused by the complex structure of lignin.

The diffraction peak intensity of LPU was slightly lower than that of PU because the content of hard segments of the PU film decreased with the addition of lignin, while the diffraction peak intensity of MLPU increased gradually with increasing amount of HDI due to the increase in ordered hard segments in ML. Therefore, MLPU has higher crystallinity than LPU and PU.
From the DSC curves of PU films, shown in figure 4(b), the glass transition temperature \((T_g)\) of each sample could be determined; for example, the \(T_g\) of PU was 63.1 \(^\circ\)C, the \(T_g\) of LPU dropped to 61.7 \(^\circ\)C, and the \(T_g\) of MLPU-0.1, 0.2, 0.3 and 0.4 decreased to 61.6 \(^\circ\)C, 59.7 \(^\circ\)C, 60.9 \(^\circ\)C and 54.5 \(^\circ\)C, respectively. The results showed that the \(T_g\) of LPU and MLPU decreased after the addition of lignin or ML, which was contrary to previously reported results [5, 24]. In those studies, diisocyanate was generally used as a curing agent; thus, the prepared PU had a low degree of cross-linking, and the density of its network structure was lower than that of lignin. Therefore, the addition of lignin or ML can improve the crosslink density of the PU network structure, and thus, the \(T_g\) of PU increases. However, in this study, an HDI trimer was used as the curing agent; thus, the crosslinking degree of PU was higher than that of lignin and ML. Therefore, the addition of lignin or ML reduced the crosslink density of the PU network structure, leading to a decrease in its \(T_g\).

3.2.2. Mechanical properties
The mechanical properties of the PU, LPU and MLPU films were determined by tensile testing. As shown in figure 5(a), the tensile strength of LPU decreased significantly compared with that of PU because lignin with relatively poor reactivity only played a filling role in the matrix, disrupted the PU networks and thus reduced the integrity of the PU matrix [21]. The MLPU-0.1 sample exhibited a slightly higher tensile strength than that of LPU, but it was still lower than that of PU. The results indicated that partially modifying lignin by using a small amount of HDI improved the interface compatibility between the ML and PU matrix; however, the effect was not obvious. The MLPU-0.2 sample was completely modified and exhibited a high tensile strength of 12.07 MPa, 68.3% higher than that of LPU and 23.2% higher than that of PU because ML contains lignin urethane, which has a similar chemical structure to PU, and thus improves the compatibility between ML and PU [29]. However, the tensile strength of MLPU-0.3 and MLPU-0.4 decreased gradually, which may be due to the polyurea generated by using excess HDI reducing the compatibility between ML and PU. As shown in figure 5(b), the
Elongation at break of LPU and MLPU was higher than that of PU. This was due to the plasticizing effect of lignin and ML on the PU matrix. In addition, lignin and ML dispersed in the PU matrix decreased the crosslink density of the PU matrix and thus increased the flexibility of PU \(^{30}\). Therefore, the MLPU film prepared from ML with an appropriate amount of HDI exhibited a significant improvement in mechanical performance over PU containing unmodified lignin and pure PU without lignin.

3.2.3. SEM of the PU, LPU and MLPU films
As shown in figure 6(a), the fractured surface of the pure PU film was very smooth, and the polyurethane network was evenly distributed, which indicated the formation of homogeneous network systems. As shown in figure 6(b), the evenly distributed polyurethane network was destroyed with the addition of lignin. The phase separation between the particles and the polyurethane matrix was clearly observed, and the fractured surface of the LPU was very rough and looser. As shown in figure 6(c), the fractured surface of MLPU-0.1 was similar to that of the LPU. This indicated that the compatibility of the LPU and MLPU-0.1 polyurethane matrices was poor. With the addition of ML-0.2 and ML-0.3, as shown in figures 6(d) and (e), the connection between the particles and polyurethane matrix was relatively close, and the fractured surface was relatively smooth, indicating that MLPU-0.2 and MLPU-0.3 had good compatibility with the polyurethane matrix. The compatibility of MLPU-0.2 and MLPU-0.3 with PU was better than that of MLPU-0.1 and LPU, which indicated that the addition of lignin with optimal amount was conducive to increase the compatibility. As shown in figure 6(f), the fractured surface of MLPU-0.4 was rough, and the phase separation between the lignin particles and polyurethane matrix was clearly observed, which is caused by the excessive polyurea in ML-0.4 particles. Therefore, the formation of lignin carbamate improved the compatibility of modified lignin with the
polyurethane matrix, whereas the presence of polyurea reduced the compatibility of modified lignin with the polyurethane matrix.

3.2.4. FTIR of the PU, LPU and MLPU films
The FTIR spectra of the PU, LPU and MLPU-0.2 samples are shown in figure 7. Compared to PU, the characteristic peaks of lignin in the LPU and MLPU samples were not obvious due to the relatively low content of lignin in the polyurethane matrix. The absorption peaks of the samples at 2929 cm\(^{-1}\) and 2857 cm\(^{-1}\) were produced by the asymmetric stretching vibration and symmetric stretching vibration of CH\(_2\) in HDI, respectively. The stretching vibration peak of -NH in the carbamate bond appeared at 3363 cm\(^{-1}\). The stretching vibration peak of ester carbonyl C = O appeared at 1717 cm\(^{-1}\) and 1680 cm\(^{-1}\), and the -NH bending vibration peak appeared at 1527 cm\(^{-1}\). These bonds formed the basic unit of carbamate bonds and urea groups [31]. As shown in the FTIR spectra of ML in figure 1, there were excessive -NCO groups in samples ML-0.5 and ML-0.6; however, the -NCO groups in both the MLPU-0.5 and MLPU-0.6 samples disappeared, as shown in figure 7. Hence, we can infer that the -NCO groups in the modified lignin samples of ML-0.5 and ML-0.6 reacted with the -OH group on the hydroxyl acrylic resin during the curing process of polyurethane, which confirmed the presence of crosslinking in PU and MLPU.

3.2.5. Water contact angle and pencil hardness
The hydrophobicity of the PU films was assessed qualitatively by water contact angle measurements. The larger the water contact angle of PU was, the better its hydrophobicity was [31]. As shown in figure 8(a), the water contact angle of PU was 74°. However, the LPU sample prepared by adding lignin presented a low water contact angle of 68°, indicating that the surface hydrophobicity of the material was reduced because lignin in the LPU film was almost unreacted with the HDI trimer and many polar groups, such as hydroxyl groups, on the surface of lignin particles reduced the hydrophobicity of LPU [15]. In contrast, the water contact angles of MLPU-0.1, 0.2, 0.3 and 0.4 were increased to 91°, 96°, 89° and 90°, respectively, which indicated that modifying lignin with HDI could effectively improve the hydrophobicity of PU films because the hydrophilic -OH groups in lignin reacted with HDI to generate lignin urethane [21]. On the other hand, the benzene ring structure of ML could improve the hydrophobicity of MLPU films [32]. Therefore, the modification of lignin with HDI significantly improved the hydrophobicity of the MLPU films.

The pencil hardness of the PUs is an important aspect of their abrasion and scratch resistance. As shown in figure 8(b), the pencil hardness of PU was H, while that of LPU increased to 2 H, which was mainly due to the presence of a rigid benzene ring structure in lignin. Samples of MLPU-0.1, 0.2 and 0.3 exhibited an increased pencil hardness of 3 H because of the better compatibility between the ML and PU matrix [33]. However, the pencil hardness of MLPU-0.4 decreased to 2 H, and this change was mainly caused by the formation of polyurea on the surface of ML-0.4, which disrupted the compatibility of lignin and the PU substrate. Therefore, the pencil hardness of PU films could be effectively improved by ML prepared using an appropriate amount of HDI.
3.2.6. Evaluation of the PU, LPU and MLPU-0.2 coatings corrosion resistance

The corrosion resistance of the LPU and MLPU-0.2 coatings was investigated by EIS. The Bode impedance and Bode phase of the coating after immersion in 3.5 wt% NaCl solution for 1.5 h and 7.5 h are shown in figures 9(a) and (b), respectively. Generally, the magnitude of the impedance modulus at the lowest frequency, |Z₀₀Hz|, was used to estimate the polarization resistance of the system [17]. A high value of |Z₀₀Hz| indicated better corrosion resistance. After 1.5 h, the |Z₀₀Hz| of MLPU-0.2 was 4.61 ohms cm⁻², which was higher than that of LPU (4.27 ohms cm⁻²). The phase angle of MLPU-0.2 was also higher than that of LPU because of the good compatibility between ML-0.2 and the polyurethane matrix, which was conducive to the formation of a uniform
and dense coating and prevented the penetration of the electrolyte solution. However, the $|Z|_{\text{LPU}}$ of LPU and MLPU-0.2 drops sharply to 3.73 ohms·cm$^{-2}$ and 3.83 ohms·cm$^{-2}$ after 7.5 h of immersion, respectively. This was due to the micropores formed by lignin and ML particles, which caused the electrolyte solution to quickly penetrate the coating/metal substrate interface and easily damage the integrity of the coating, thus corroding the metal substrate surface. The Nyquist plots of LPU and MLPU-0.2 are shown in figure 9(c). Both LPU and MLPU-0.2 showed two time constants, indicating that corrosion had occurred on the coating surface [34]. The second capacitive radius of MLPU-0.2 was much larger than that of LPU, which also indicated that the corrosion resistance of MLPU-0.2 was better than that of LPU after 1.5 h of immersion. The second capacitive radius of LPU and MLPU-0.2 decreased sharply after 7.5 h of immersion, indicating that the corrosion resistance of both LPU and MLPU-0.2 decreased. In conclusion, MLPU has better anti-corrosion performance than LPU.

4. Conclusion

In this study, ML was synthesized by using HDI as a modifier to increase the compatibility between lignin and PU. Then, MLPU films were prepared using the as-synthesized ML. It was found that the main chemical in ML was lignin urethane when the amount of HDI was 0.2 g. Nevertheless, polyurea was formed when the amount of HDI was greater than 0.3 g because the excess HDI reacted with water strongly adsorbed by ML and moisture in air. In addition, modifying lignin using HDI reduced the thermal degradation temperature of lignin, which was conducive to the subsequent thermal degradation treatment. Compared with pure PU, the pencil hardness of the LPU film increased, but the tensile strength and hydrophobicity of the LPU film decreased. Compared with lignin without modification, the addition of ML helped to improve the crystallinity, tensile strength, hydrophobicity and pencil hardness of the pure PU film. Therefore, the introduction of HDI-modified lignin into PU films has good potential for the application of lignin-based polyurethane for marine anticorrosive coatings.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflicts of interest

There are no conflicts to declare.

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