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Synthesis, Characterization, and Performance Evaluation of Highly Reactive and Sustainable Hot-Melt Polyurethane Adhesives Derived from Lignin-Based Polyols

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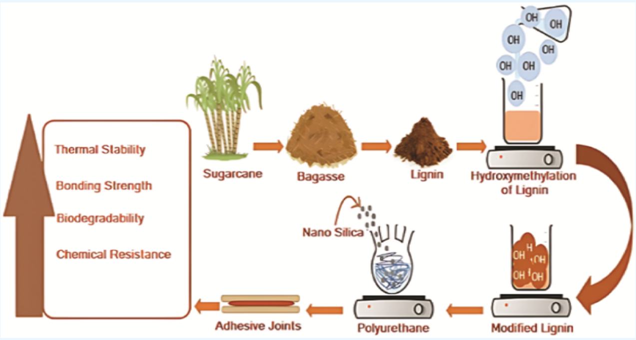

ABSTRACT: The current research was conducted to study the use of waste materials to isolate lignin, which was further used to prepare polyurethane hot-melt adhesives. To enhance the reactivity of lignin, its hydroxyl content was increased by hydroxymethylation, and then it was polymerized with 4,4′-methylenediphenyl diisocyanate (MDI), polyethylene glycol (PEG), and 1,4-butanediol (BDO) to prepare polyurethane hot-melt adhesives. SiO_2 nanoparticles were added to provide mechanical strength to the final polymer. The structure of the final polymer was confirmed by FT-IR spectroscopy. Morphological behaviors were analyzed by using SEM and XRD. Thermomechanical characteristics were studied by using thermogravimetric analysis (TGA\DSC). Finally, the adhesion properties were analyzed by using melting viscosity, softening temperature, and a T-peel strength test. The absence of the -NCO peak of monomers in the FT-IR spectra confirmed the completion of the reaction. The gradual decrease in thermal transition and increasing crystallinity in the DSC\TGA thermograms represent its stable thermal behavior. SEM and XRD show that the prepared hot-melt polyurethane adhesives have distinct crystallinity and peaks. Melting viscosity, softening temperature, and T-peel strength test exhibit the strong adhesive behaviors of the prepared biobased polymers in different time intervals under stress and heating conditions. HMPUA-4 with optimum values of lignin and SiO_2 nanoparticles is considered to be the best product due to its high adhesive properties and sustainability. Lignin's strong antibacterial activity is also evidence that a promising polymeric adhesive was prepared that can be used in various fields.

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1. INTRODUCTION

Over the recent decades, reactive hot-melt polyurethane adhesive (RHMPUA), due to its exceptional features compared to other kinds of adhesives, has attracted increasing attention for its applications,.[1,2] These features include excellent adhesion to a multitude of substrates, high initial adhesion strength, high mechanical strength, good resistance to chemicals, heat, aging, environmental friendliness, and easy processing.[1−5] Compared to other adhesives, hot-melt adhesives are promising as green adhesives due to their solvent-free nature. They also avoid the emission of volatile organic compounds (VOCs).[6] Basically, RHMPUA is an isocyanate-terminated linear polyurethane prepolymer with low molecular weight, which is then, upon reaction with ambient moisture, can be cured and converted to high-molecular-weight polymer. The resulting polymer can be obtained with great adhesion strength and superior resistance to heat and solvent.[6−8]

In polyurethane synthesis, polyol plays a certain role; it has a direct impact on the properties and morphology of polyurethane. Studies have been conducted to generate polyols from renewable sources in light of the need to develop sustainable materials to replace petroleum-based polyurethane.[9,10] Green carbon content in polyurethane materials is rising as a direct consequence of using biobased polyols. A new perspective on the quality of polyurethanes was brought about by the significant advancement in the synthesis of biobased polyols, such as ester-based polyols.[11] In terms of adhesive technology, this has resulted in the application of more modern technology like the use of modified vegetable oils or lignin derivatives for binder synthesis.[12,13]

Nowadays, lignin is attracting the attention of researchers as it is a suitable starting material to be used in polymer products.[14] To improve the sustainability of polyurethane products, biobased materials are incorporated as polymer

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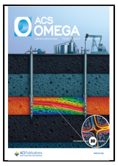

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precursors. Lignin incorporation in addition to increased biobased content in polyurethane products also provides several advantages such as improved biodegradability, antioxidant properties enhancement in cross-linking density, and ultraviolet (UV) stability. It also improves the thermal stability and mechanical strength of the final product.[15,16] Studies have been reported with the high potential applications of lignin in RHMPUA as the adhesive strength of cardboard bonding is increased after the addition of lignin-based polyol.[17−1819] One of the drawbacks associated with lignin as an adhesive is its least functionality due to the lack of active groups to overcome this problem. Modifications including (hydroxy methylation, phenylation, and demethylation) have been performed to introduce new active groups or to increase the number of existing groups.[20,21]

In addition to lignin's environmental advantages, incorporating lignin into polyurethane synthesis offers various functional benefits that enhance the overall performance of the final product. By integrating lignin, the biodegradability of polyurethane is improved, promoting an eco-friendly breakdown in natural environments. By optimizing lignin's structure and its interactions within the polyurethane matrix, additional performance enhancements are achievable, including mechanical strength improvement and chemical resistance. The natural rigidity of lignin can contribute to more durable PU materials, making them suitable for a broader range of applications. The hydroxyl groups in lignin can actively participate in the urethane reaction with isocyanates, promoting a more robust polymer network with increased cross-linking. This results in polyurethane materials with enhanced thermal stability, which can withstand higher temperatures without compromising their structural integrity.[22−25]

Over the last decades, significant attempts have been made to enhance the properties of RHMPUA. Nanomodification is worthy to mention, it was regarded as a promising technique in improving physiochemical properties, adhesiveness, mechanical strength, and thermal stability.[26] The research on nanocomposite-based polyurethane hot-melt adhesive has been carried out for years.[27,28] The incorporation of nanofillers such as SiO_2 has been widely used for many years to produce a better version of the existing polymer as it not only improves radiation resistance and heat resistance but also provides mechanical strength to the prepared polymer.[26,27,29] Nano-SiO_2 gives highly impactful results when dispersed in polyurethane hot-melt adhesives. It works with the mechanical properties of the adhesive and provides bond shear strength. Studies have proved that the incorporation of SiO_2 accelerates the adhesive property as compared to adhesives without any fillers.[30]

Polyurethane, due to its comfort, environmental soundness, and cost benefits, has been widely used nowadays with a variety of applications in many fields.[31] In the field of adhesives, polyurethane-based hot-melt adhesives are now extensively used due to their excellent durability, heat resistance, and water resistance properties. HMPUAs are now considered promising agents to be used for various applications at the industrial level.[5,6]

Lignin is used as a polyol because of its renewable nature, high hydroxyl group concentration, and aromatic structure. These properties improve the adhesive's mechanical strength, sustainability, and thermal stability.[32,33] Moreover, lignin's hydroxyl groups enable good mixing with polyurethane components, ensuring homogeneous dissolution.[34] This research introduces an innovative method for developing hot-melt polyurethane adhesives by incorporating lignin as a sustainable polyol and uniformly dispersing silica (SiO_2) nanoparticles into the polymer matrix. Lignin contributes to the environmental benefits and structural integrity due to its aromatic and hydroxyl-rich composition, while SiO_2 nanoparticles improve the adhesive's bonding capability. As compared to earlier studies, which focused on each additive independently[19,35−37] this combined approach delivers enhanced overall performance and structural uniformity, supporting the creation of eco-friendly adhesives suited for industrial uses.

Herein, we aim to synthesize reactive polyurethane hot-melt bioadhesives based on lignin polyols derived from renewable sources. In addition to obtaining sustainable polyurethane adhesives from biobased raw materials, nontoxic and highly reactive polyurethane adhesives can be formed by using biobased raw materials. For this purpose, the different mole ratio of lignin was used to synthesize HMPUAs, and MDI was used as the diisocyanate. Furthermore, the properties of new adhesives were evaluated by using techniques such as FTIR, TGA, and DSC. Finally, softening temperature, melting viscosity, and T-peel test were used to measure the adhesion property of the biobased adhesive. Lignin′s antibacterial property is also proof of its durability as an adhesive.

2. EXPERIMENTAL SECTION

2.1. Materials. Lignin was isolated from sugarcane bagasse, which was obtained from a local sugar factory. Methylene diphenyl diisocyanate (MDI), 1,4-butanediol (BDO), and polyethylene glycol (PEG) were purchased from Sigma-Aldrich Chemical Co. Prior to the use of the chemical reagents for the purpose of moisture removal, they undergo a drying process at temperature reaching up to 80 °C. SiO_2 nanoparticles were provided by the National Institute of Biotechnology and Genetics Engineering (NIBGE), Faisalabad. NaOH, H_2SO_4, and all other reagents used in this work were of analytical grade. These chemicals were placed in a vacuum for 24 h.

2.2. Isolation, Purification, and Surface Modification of Lignin. The bagasse raw materials undergo a crushing process and are subsequently subjected to filtration to remove undesirable components, such as soluble tannins, resins, and pigments. Bagasse from sugarcane was cut into small pieces (1−2 cm), crushed, and screened such that it could pass through a 1.0 mm sieve after being air-dried at room temperature for a period of 3 days. The dry powder undergoes a treatment process involving the addition of hot water at a temperature range of 70−80 °C for a duration of 2 h. After cooling at 25 °C and centrifuging for 10 min at 90−80 °C. Sodium hydroxide solution (2−4% concentration) at 140 to 160 °C for 1−3 h was used to separate the pulp and washed with deionized water. The resulting black liquor was acidified to precipitate out lignin from the solution by adding conc. H_2SO_4 until the pH of the black liquor drops below 2. The mixture was stirred for 1−2 h at room temperature to allow lignin to fully precipitate. Next, lignin was fractionated and hydroxymethylated when heated under alkaline conditions. Lignin was dissolved in an aqueous NaOH solution, and formaldehyde (lignin/NaOH/HCHO molar ratio 1/1/2.4) was added for hydroxymethylation.[38]

2.3. Synthesis of Polyurethane Prepolymer and Final Polymer. Polymer synthesis was based on two major steps.

According to the recommended method, reactions are processed.[39] First, polyethylene glycol (PEG) was placed in an electric oven at 45 to 50 °C to remove moisture from it. Then, lignin concentrations mentioned in Table 1 were added in 0.8 mol of polyethylene glycol in a four-neck round-bottom flask and mechanically stirred for 2 h at 100 °C and refluxed until the lignin was fully dispersed in PEG after lignin nano-SiO_2 was added and further stirred for 1 h until the complete dispersion of nano-SiO_2 in PEG. Then, 2 mol of methylene diphenyl diisocyanate (MDI) was added and the reaction was processed for a further 2 h at 80 °C to get isocyanate-terminated (−NCO) polyurethane prepolymer (Figure 1a). Synthesis of prepolymer was confirmed by FTIR (Figure 2c). The lignin-based polyurethane final polymer was attained by adding 1.2 mol of 1,4-butanediol (BDO) chain extender in

Table 1. Sample Codes and Chemical Composition of the Synthesized Polyurethane Hot-Melt Adhesives

Samples Code	Molar ratio of PEG[a]	Molar ratio of Lignin	Nano-SiO_2 [d]% by weight	Molar ratio of (MDI[b]/BDO[c])
HMPUA-1	0.8	-	-	2:1.2
HMPUA-2	0.8	0.1	-	2:1.2
HMPUA-3	0.8	0.2	0.1	2:1.2
HMPUA-4	0.8	0.3	0.3	2:1.2
HMPUA-5	0.8	0.4	0.5	2:1.2

[a] Polyethylene glycol (PEG). [b] 4,4′ methylenediphenyl diisocyanate (MDI). [c] 1,4-butanediol (BDO), silicon dioxide (SiO_2).

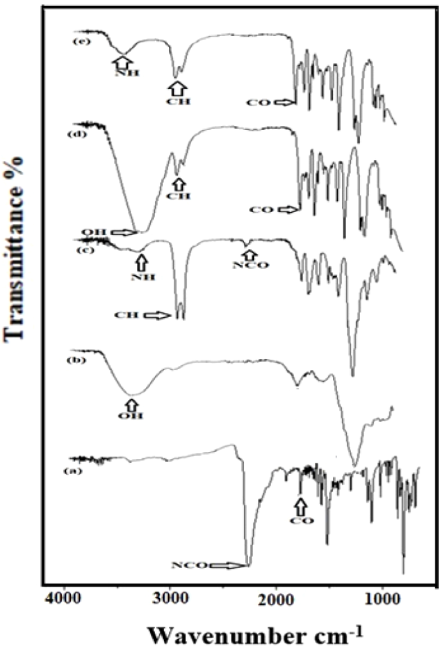

Figure 2. FT-IR spectra: (a) 4,4′-methylenediphenyl diisocyanate (MDI); (b) lignin; (c) NCO-terminated polyurethane prepolymer; (d) 1,4-butanediol (BDO); (e) final biobased hot-melt polyurethane adhesive (HMPUA).

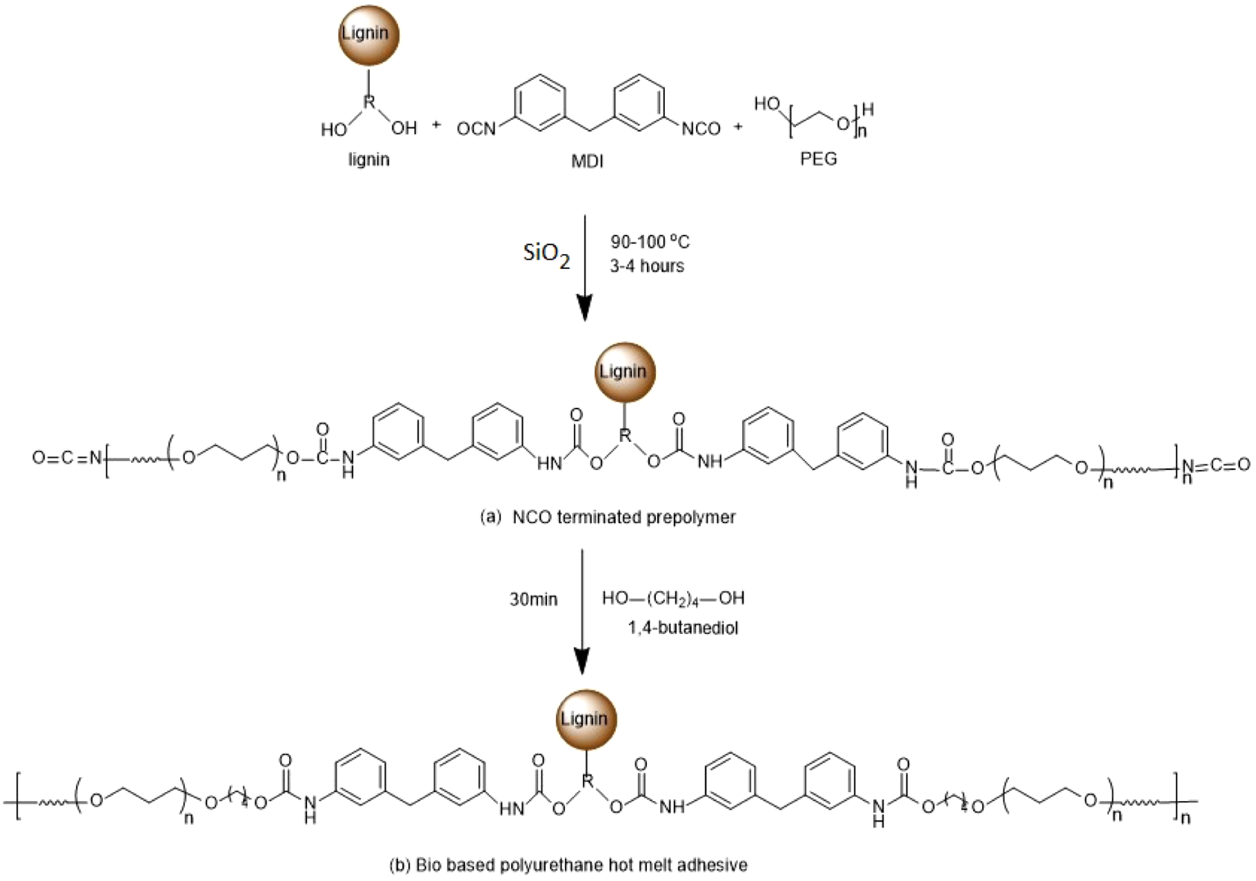

Figure 1. Synthesis of biobased hot-melt polyurethane adhesive. (a) Step 1: Preparation of the NCO-terminated prepolymer. (b) Step 2: Biobased polyurethane hot-melt adhesive.

polyurethane prepolymer, heating at 90 °C, and stirring for 30 min. The visual aspect of uniformity and the achievement of a fully distributed state of BDO in the reaction mixture are shown in Figure 1b. Samples were subjected to characterization before use.

Following the above procedure, a series of biobased polyurethane adhesives were prepared with different mole ratios of lignin. The mole ratios of all of the samples are given in Table 1. The chemical route for the sample preparation is given in Figure 1a,b).

3. CHARACTERIZATION

3.1. Morphological Analysis. The surface examination of the prepared samples with different mole ratios of lignin was done by using scanning electron microscopy (SEM) and powder X-ray diffraction (XRD). Fractured surface samples were analyzed using an FEI NOVA 450 NanoSEM instrument for SEM and a Bruker D2 Phaser instrument for XRD analysis.

3.2. Fourier Transform Infrared (FTIR) Spectroscopy. Molecular structure analysis of the hot-melt polyurethane adhesives was obtained by FTIR. The IR peaks of the prepared HMPUAs were obtained by Equinox 55 Fourier transform infrared (FT-IR) spectrometer, Bruker, equipped with the ATR assembly.

3.3. Thermogravimetric Analysis (TGA). Thermogravimetric analysis (TGA) was conducted to find the decomposition temperature of the prepared samples by using a TGA/DSC 1 analyzer (Mettler-Toledo, Switzerland). Prior to TGA, the prepared samples were dried in an oven to remove moisture. In the TGA, samples (about 10−20 mg) were heated from 0 to 400 °C at a rate of 10 °C/min.[40]

3.4. Differential Scanning Calorimetry (DSC). The transitions including glass transition (Tg), melting (Tm), and crystallization (Tc), under the nitrogen purge (50 mL/min) were measured using DSC (Mettler-Toledo, Switzerland). The formation of polymers was brought about in a sealed aluminum pan by encapsulation of the specific weight (11 mg). The samples were heated from room temperature to 400 °C at a rate of 10 °C/min. Thermal characteristics of various HMPUAs have been discussed by varying molar ratios of lignin.[40]

4. TEST FOR ADHESION

4.1. Softening Temperature. The softening temperature of the reactive hot-melt polyurethane adhesives was determined according to standard.[41] The temperature above which the viscous properties of the adhesives become dominant is termed the softening temperature of the adhesive. According to a standard test, the softening temperature is determined by measuring the point at which a steel ball, submerged in either mineral oil, glycerol, or water, passes through an adhesive-filled ring.

4.2. Melting Viscosity. The melting viscosity of the RHMPUA was evaluated by using the BDV-4N viscometer, Biobase Biosoon Co. Ltd., China, according to the standard test procedure.[41] The viscosity was measured at about 25 °C.

4.3. T-Peel Strength Test. A 180° peel test was used to assess the initial and final bonding strength of the prepared polyurethane hot-melt adhesive. Bonding strength was measured according to the standard method.[41] Standard materials were used as substrates, such as 25 × 100 mm area of rigid polycarbonate plate (PC) and 25 × 20 mm of soft polyvinyl chloride (PVC). Prior to the application of HMPUAs, they were heated to 120 °C, with a 3 mm thickness and a coverage area of 25 × 60 mm applied between the two surfaces. The specimens were stored at room temperature, and bonding strength was measured at different time intervals at a 25 mm/min peel rate.

5. ANTIBACTERIAL ACTIVITY

Antibacterial activity is the measure of potential against bacteria for a given material. The disk diffusion method was performed in triplicate for the determination of the antibacterial potential. For this purpose, 6 mm diameter filter paper disks were formed by a punch machine and sterilized by autoclave at 121 °C in a sealed bottle. 10 μL of the compound was applied to a sterilized filter paper disk. Pathogenic bacterial test strains (10^8 CFU/ML) (*E. coli*and *S. aureus*) were spread over nutrient agar plates, and compound-impregnated disks were placed in agar plates using forceps. The plates were incubated for 24 h at 37 °C. Antibacterial potential was determined as inhibition zones around the disk by using a ruler in millimeters (mm). This activity makes the materials useful in medical and food applications of adhesives. Antibacterial activity was measured via the disk diffusion method according to standard.[42]

5.1. Minimum Inhibitory Concentration (MIC) and Minimum Bactericidal Concentration (MBC). The antibacterial evaluation revealed that the H-3, H-4, and H-5 samples exhibited the most significant activity against *E. coli*. Among these, only the H-4 sample demonstrated antibacterial effects against *S. aureus*. Therefore, we checked the MIC of H-3, H-4, and H-5 against *E. coli* and only H-4 MIC against *S. aureus*.

The MIC of the bioactive samples (H-3, H-4, and H-5) was determined by using the standard 96-well microdilution method. A series of 2-fold serial dilutions (1000, 500, 250, 125, 62.5, 31.2, 15.6, 7.8, 3.9, and 1.9 μg/mL) of each sample was prepared. From each dilution, 130 μL was added to the wells of a 96-microtiter plate. Afterward, 20 μL of bacterial culture was introduced into each well. Nutrient broth served as a negative control. The plate was then incubated at 37 °C for 24 h, and bacterial growth was measured by recording the absorbance at 600 nm using a spectrophotometer. Additionally, the minimum bactericidal concentration (MBC) was determined by subculturing the contents from the well showing no visible growth onto nutrient agar plates, followed by incubation at 37 °C for another 24 h.[43]

6. STATISTICAL ANALYSIS

The experiments were performed in triplicate ($n = 3$), mean ± standard deviation/error.

7. RESULTS AND DISCUSSION

7.1. FT-IR Study. The FT-IR spectra of the monomers 4,42032-methylenediphenyl diisocyanate (MDI); lignin; NCO-terminated polyurethane prepolymer; 1,4-butanediol (BDO); and final biobased hot-melt polyurethane adhesive (HMPUA) were taken in the range of 1000−4000 cm^{-1}, as can be seen in Figure 2. Figure 2a shows the spectra of MDI with a strong peak at 2264 cm^{-1} for the isocyanate (−NCO) attached to 4,4′-methylenediphenyl diisocyanate. In the FT-IR spectra of lignin (Figure 2b), strong peaks can be seen at 3354.4 cm^{-1} (OH stretching vibrations); 2903.6 cm^{-1} (CH stretching);

1653.3 cm^{-1} (CO stretching); and 1034.4 (C−O−C stretching). FT-IR spectrum of −NCO-terminated polyurethane-terminated prepolymer is represented in Figure 2c. The spectrum showed the disappearance of OH group signal, with the intensity of the −NCO group also reduced along with the appearance of NH group at 3321.3 cm^{-1}, which is strong evidence for the formation of prepolymer. Other peaks for CH at 2853.3 cm^{-1} and CO at 1725.4 cm^{-1} also appear in the spectra. For the final product, biobased polyurethane hot-melt adhesives BDO were added as chain extender. The spectra for BDO in (Figure 2d) indicate that the chain extender works properly as a broad peak for OH stretch 3363.2 cm^{-1} can be seen in the spectra, where other peaks for CH at 2948.4 cm^{-1} and CO at 1720 cm^{-1} are also present. The FT-IR spectra of the final HMPUA are represented in Figure 2e. The appearance of the NH peak at 3340.1 and the disappearance of the -NCO peak confirmed the formation of final biobased polyurethane hot-melt adhesives.[39] Figure 3 represents the IR spectra for the final polyurethane hot-melt adhesives. NH stretching at 3349−3352.2 cm^{-1}; CH stretching at 2920.4 and 2853.3 cm^{-1}; and the appearance of CO group at 1721−1725.4 cm^{-1} confirm the formation of polyurethane linkage and final polymer with different mole ratios of lignin. In the hot-melt polyurethane adhesives when polyols obtained from lignin were incorporated, a decrease in free isocyanate content was observed. This decrease became more prominent when more lignin-based polyols were added.[41,44]

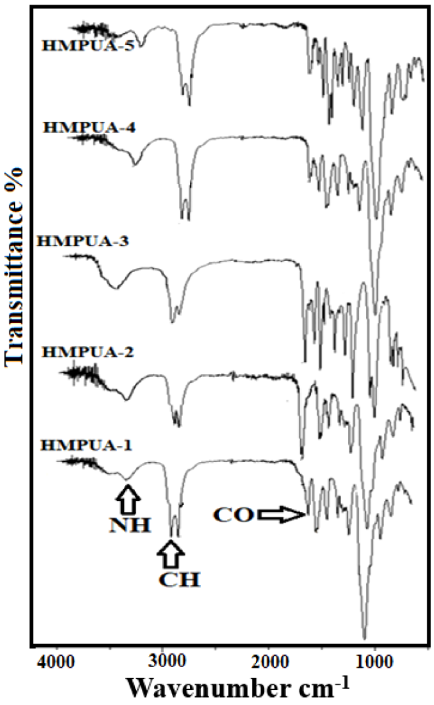

Figure 3. FT-IR spectra of HMPUAs with varying mole ratios of lignin (bottom to top) HMPUA-1, HMPUA-2, HMPUA-3, HMPUA-4, and HMPUA-5.

7.2. Morphological Study. The phase morphology of the polyurethane hot-melt adhesives and the impact of lignin-based polyol distribution within the polyurethane matrix were revealed via SEM images. Figure 4 represents SEM images of prepared polyurethane hot-melt adhesives. All images were taken with (magnification × 10,000) (Figure 4a): HMPUA-1 with no lignin and nano-SiO$_2$ incorporated into (Figure 4b), HMPUA-2 with just lignin-based polyol incorporated into hot-melt adhesives. Figure 4c with HMPUA-3 (Figure 4d) represents HMPUA-4 (Figure 4e) and HMPUA-5. Samples with the presence of lignin showed that it has a high effect on pore size, distribution, and connectivity due to the presence of a large number of OH moieties on the lignin-based polyols. These parameters overall enhance the adhesive properties of the hot-melt adhesives. The sample with the absence of lignin (Figure 4a) lacks the above-mentioned morphological characteristics. Moreover, the presence of lignin also provides strong connectivity for the dispersed nano-SiO$_2$, which in return enhances the mechanical strength and sustainability of the prepared product. HMPUA-4 with both lignin and nano-SiO$_2$ after incorporation of optimal amounts is considered as best final product.[14,15,1745] Samples without lignin (HMPUA-1) exhibit a smoother surface, whereas those containing lignin (HMPUA-2 and HMPUA-3) display a rougher texture. This roughness arises from the phase separation induced by the hydroxyl groups in lignin, which enhances the adhesive properties. The addition of nano-SiO$_2$, as seen in HMPUA-4 and HMPUA-5, further amplifies surface roughness by introducing a reinforcing particulate structure.[46]

The crystallinity of the prepared adhesives was investigated by XRD. Figure 5 represents the XRD curves of HMPUAs. The pattern shows peaks of approximately 2θ = 20.85 ° and 23.9 ° for all the prepared samples. These values are responsible for the crystallinity of soft and hard segments sharply increasing (bottom to top) peaks at 23.9 ° representing the PU/lignin/SiO$_2$ hybrid. The hybrid peaks are typical semicrystalline or amorphous materials. The absence of sharp peaks for HMPUA-1 and HMPUA-2 represents the absence of lignin/SiO$_2$ and SiO$_2$, respectively. Results further depict that the addition of lignin and SiO$_2$ is successfully cross-linked with the polyurethane matrix and does not significantly affect the crystallinity of the PU matrix. HMPUA-4 with lignin and silica ideal value represent a sample with good performance. The results are consistent with previous studies.[47−4849]

7.3. DSC Analysis. DSC analysis was used to measure the thermal properties of HMPUAs prepared with lignin-based polyols. Figure 6 represents the DSC thermograms of the prepared samples; with the addition of an increased amount of lignin-based polyols, a decrease in glass transition temperature (Tg) can be noticed, which is due to the incorporation of cold crystallization to hot-melt polyurethane adhesives after the rearrangement of soft segments. Due to the crystalline nature of lignin-based polyol, a higher enthalpy of crystallization is observed. The melting of different crystalline fractions present in soft segments results in a corresponding endothermic peak of melting temperature (Tm). With the increasing amount of lignin-based polyols (bottom to top), glass transition temperatures decrease. This can be associated with the decrease in the amorphous chains with the increasing amount of lignin. The samples with very low melting indicate the absence of crystallinity in their structures. This can be related to the fact that they increase their viscosity.[40] Lignin reduces the glass transition temperature (Tg) by disrupting the polymer chain interactions, while its crystalline nature promotes cold crystallization, leading to shifts and broadening of the melting temperature (Tm) peaks. In sample HMPUA-1, the absence of lignin and nanosilica did not show clearly distinguishable Tg as compared to other samples. This is due to the homogeneity and high flexibility of the base polymer matrix, which leads to

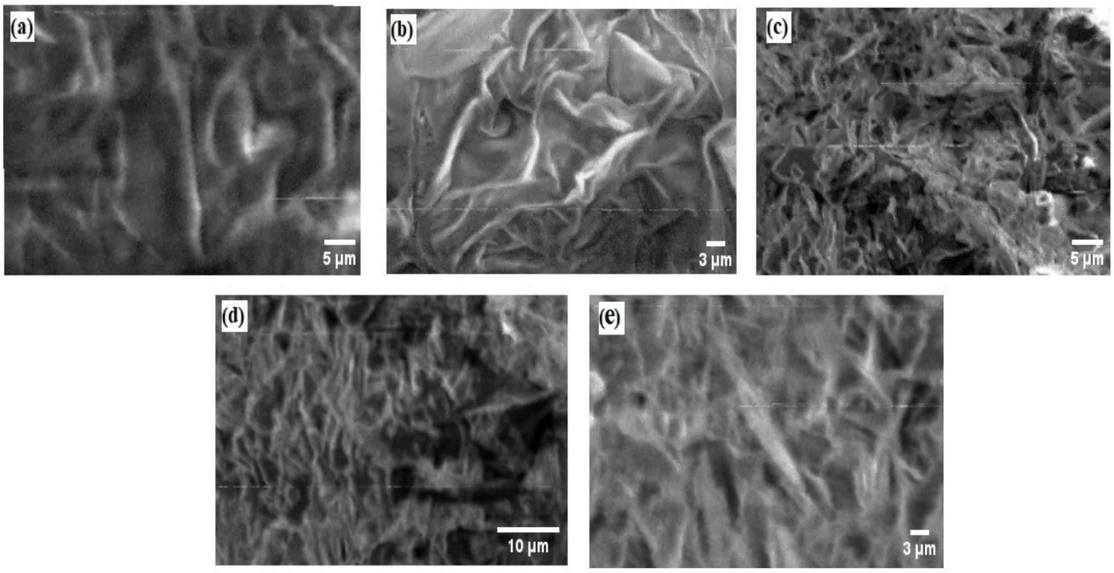

Figure 4. SEM images of (a) HMPUA-1, (b) HMPUA-2, (c) HMPUA-3, (d) HMPUA-4, and (e) HMPUA-5.

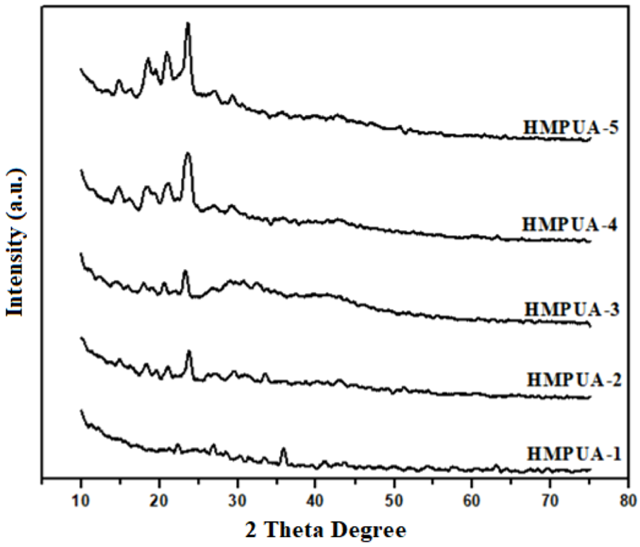

Figure 5. XRD analysis of HMPUA-1, HMPUA-2, HMPUA-3, HMPUA-4, and HMPUA-5.

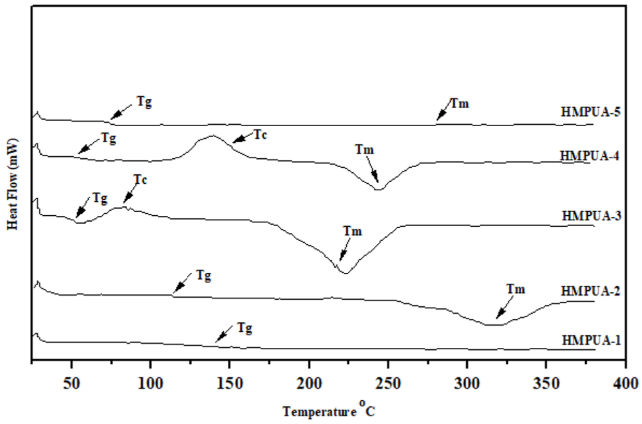

Figure 6. DSC thermograms for the prepared polyurethane hot-melt adhesives.

weak Tg signals. The introduction of lignin likely contributes to showing a more defined Tg by increasing the rigidity of the polymer matrix due to its aromatic and cross-linked nature, while nanosilica further intensifies this effect by strong interfacial interactions with the polymer chain. Silica, as reinforcing, increases viscosity, which restricts polymer chain mobility, potentially increasing the Tg and contributing to broader peaks due to inhomogeneous polymer dynamics. The combination of lignin and silica also induces heterogeneous crystallization, with different crystalline fractions melting at distinct temperatures, further broadening the peaks. The viscosity changes along with variations in the crystallinity and dispersion of both lignin and silica, lead to shifts and broadening in both Tg and Tm across the 0 to 400 °C range.[50−5152]

7.4. TGA. The thermal stability of the prepared HMPUAs was analyzed by a thermogravimetric analysis. In different temperature ranges, PU/lignin decomposition varies, as observed in (Figure 7). The temperature range from 22.89 °C to 185.76 °C is associated with the urethane bonds breakage, leading to the release of small volatile products. The damage of different soft segments in the range of 185.67−

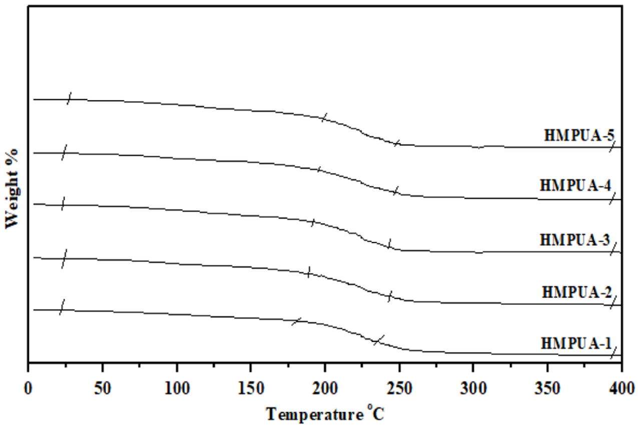

Figure 7. Effect of the temperature on the weight percentages of the prepared HMPUAs.

245.98 °C depends upon the three-dimensional arrangements, which are influenced by the chemical structure, molecular weight, and lignin content. The leftover temperature range from 245.98 °C to 400 °C indicates the further maximum degradation of the prepared HMPUAs including carbon—carbon bond linkages and different functional groups. Compared to the samples with no lignin\SiO_2, i.e., HMPUAs-1 and 2, the percentage weight loss in HMPUA-3, HMPUA-4, and HMPUA-5 was reduced due to the presence of lignin's aromatic rings, and high cross-linking in PU matrix acts as a barrier against heat and prevents degradation. The presence of lignin enhances the thermal stability of the HMPUAs. HMPUA-4, due to the optimum values of lignin/SiO_2, was a more thermally stable sample due to the strong bonding of lignin with the polyurethane matrix.[40,53,54] After the complete degradation of the polyurethane matrix (400 °C), the residual mass observed in the TGA of lignin silica containing inorganic materials (such as silica) and carbonaceous char was left from the lignin decomposition. For HMPUA-4, a higher residual mass as compared to other samples was observed as both lignin with aromatic nature and cross-linked structure, and silica contribute to the mass that does not decompose at high temperatures.[54]

It was observed that the incorporation of lignin polyols and nanosilica into hot-melt polyurethane adhesives (HMPUAs) improves their heat resistance and bonding strength.[55] This is due to lignin enhancing structural stiffness and polarity, while nanosilica limits chain flexibility, reinforcing the overall network. This combined approach results in a more durable and thermally stable adhesive. Compared to traditional or single-additive systems, it offers better performance as compared to the system already reported in the literature.[15]

7.5. Adhesion Strength of the Lignin/SiO_2-Based HMPUAs. After the addition of lignin polyol, the viscosity of the HMPUAs increased. With the higher content of lignin polyol, a trend in the increase of viscosity was noticed. This trend is attributed to the increase in the molecular weight of polyurethane after the addition of lignin polyol. However, this increase in viscosity does not affect the adhesive flow property as the content of lignin polyol was optimized, and the best result is shown by HMPUA-4, as the addition of a large amount of lignin will give brittleness, and as a result, its adhesive property will be affected.[42,43,56]

Furthermore, the softening point of the HMPUAs was the same as that of the sample without lignin polyol, around 67 °C. The results show that there is no significant effect of lignin on the softening point of the prepared HMPUAs.[43] Table 2 represents the viscosities and softening points of the HMPUAs calculated at a controlled temperature range.

Table 3 presents the bonding strength of the prepared HMPUAs. The bonding strength was measured through the T-peel strength test at different time intervals; with the increase in time, bonding strength increased. Different parameters are here responsible for the increasing bonding strength of the hot-melt adhesives; after the application of HMPUAs onto the substrate, interactions such as hydrogen bonding, van der Waals forces, mechanical interaction between the samples and substrate, and covalent interactions increase with time and the adhesion strength increases.

Table 2. Measured Viscosities and Softening Points of the Prepared HMPUAs

Sample Code	Viscosity (mPa·s)	Softening Points
HMPUA-1	1124 ± 0.25	67 °C
HMPUA-2	1234 ± 0.25	69 °C
HMPUA-3	1525 ± 0.57	71 °C
HMPUA-4	1632 ± 0.15	72 °C
HMPUA-5	1745 ± 0.56	73 °C

In the case of hot-melt adhesive with moisture curing, proper interactions between isocyanates groups (−NCO) and moisture are necessary during the initial timing. This interaction was low, which caused the poor adhesion of the HMPUAs with the substrate.[56] Furthermore, when bonding strength of different samples with the increased content of lignin was analyzed, then the PU incorporated with lignin polyol results in the formation of strong interfacial interactions between the polymer matrix and lignin, which in turn increases the shear resistance of the adhesives. It is well known that the adhesion strength of the polymer is related to its glass transition temperature (Tg). Glassy polymers have higher mechanical energy and cohesive strength, as the increase in hydroxyl-enriched lignin enhances the Tg value of the polymer, so in Table 3, a trend of increasing adhesion strength values is noticed with the increase in lignin content. HMPUA-1 with the absence of lignin and a low Tg value also has lower adhesion strength compared to the sample with high lignin content and Tg values. HMPUA-4 with the ideal amount of lignin and high Tg value gives high initial and final strength between the polymer and substrate. HMPUA-C represents the values of a commercial adhesive. It was found that the commercial values were comparatively better. All adhesives showed a lower adhesive strength than the commercial ones. This may be due to the biobased nature of the synthesized samples. With the increase in bonding strength from HMPUA-1 to HMPUA-5, the increased trend in toughness is noticed; this can be attributed to the presence of SiO_2 nanoparticles and increasing lignin content. The average of toughness values was measured by using the corrected beam theory (CBT) as 2.4 ± 0.56, which was in accordance with polyurethane adhesive.[57]

7.6. Antibacterial Activity of HMPUAs. The antibacterial activity of the prepared HMPUAs was evaluated by the disk diffusion method against bacterial strains of *Escherichia coli* and *Staphylococcus aureus*. Cultures of bacteria were spread on agar plates. 5 mm samples of HMPUAs were placed over the plates. Each plate was divided into 5 counterparts with H1−H5 representing the samples HMPUA-1 to HMPUA-5. These plates were incubated for 24 h at 37 °C. The results are shown in Figure 8a against Gram-negative bacteria and in Figure 8b against Gram-positive bacteria. Resistance of HMPUAs against *E. coli* and *S. aureus* is shown in the zone of inhibition. In the case of *S. aureus*, an 11.6 ± 0.56 mm zone of inhibition was observed in the H-4 section; however, no inhibitory potential was observed for other samples.

In the case of *E. coli*, inhibition zone was observed in H-3, H-4, and H-5 with 7.6 ± 0.25 mm, 14.6 ± 0.25 mm, and 8.3 ± 0.25 mm inhibitory potential, respectively. H-4 showed the highest inhibitory potential against *E. coli*. It was observed that the presence of lignin and SiO_2 is responsible for the antibacterial activity of the samples. The interaction of hydroxyl groups of lignin with the bacterial cell membrane causes the rupture of cell structure and infiltration of cell components following the release of bacterial cell contents.[50] Results depict that the samples without lignin and silica content have low antibacterial activity.[58] The minimum

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Table 3. Bonding Strengths of the HMPUAs at Different Time Intervals

	Bonding strength (N/25 mm) over time					
Sample Code	10 min	20 min	30 min	40 min	50 min	6 days
HMPUA-C	27.34 ± 0.07	35.56 ± 0.12	70.98 ± 0.15	82.45 ± 0.76	95.78 ± 0.32	Fractured
HMPUA-1	14.49 ± 0.03	20.29 ± 0.05	46.29 ± 0.75	60.21 ± 0.34	87.43 ± 0.56	Fractured
HMPUA-2	18.69 ± 0.13	26.46 ± 0.06	47.39 ± 0.34	62.74 ± 0.56	88.24 ± 0.57	Fractured
HMPUA-3	20.89 ± 0.07	28.57 ± 0.15	49.32 ± 0.19	68.24 ± 0.26	89.26 ± 0.76	Fractured
HMPUA-4	21.79 ± 0.12	30.67 ± 0.13	68.37 ± 0.17	70.24 ± 0.29	62.36 ± 0.59	Fractured
HMPUA-5	22.57 ± 0.18	30.29 ± 0.24	65.26 ± 0.57	69.39 ± 0.21	90.24 ± 0.54	Fractured

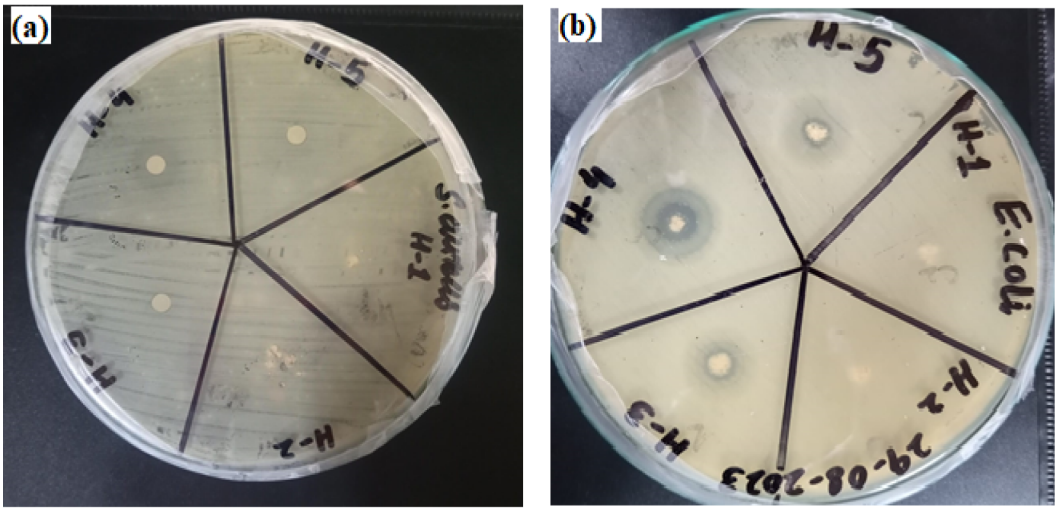

Figure 8. Antibacterial activity of HMPUAs (a) against *S. aureus* and (b) against *E. coli*.

inhibitory concentration (MIC) values for the H-3, H-4, and H-5 samples against *E. coli* were found to be 500, 62.5, and 500 μg/mL, respectively. For *S. aureus*, only the H-4 sample showed activity with an MIC of 250 μg/mL.

Regarding the minimum bactericidal concentration (MBC), the values for H-3, H-4, and H-5 against *E. coli* were 500, 125, and 1000 μg/mL, respectively. The MBC of the H-4 sample against *S. aureus* was determined to be 500 μg/mL.

8. CONCLUSIONS

The reactivity was increased by hydroxymethylation providing the strong interfacial interactions between lignin and the polymer matrix. The increasing content of lignin polyol in the polyurethane matrix provides adhesion strength with decreased Tg values and provides thermal stability to the prepared HMPUAs. HMPUA-1 with no lignin content has a low adhesion strength with a low Tg and thermal stability. HMPUA-4 with the optimized value of lignin gives the best adhesion strength and stability to the hot-melt adhesive. Furthermore, the incorporation of SiO_2 in the presence of lignin polyol enhances the thermal, physical, and mechanical properties of the prepared hot-melt adhesive. Lignin's antibacterial activity further supports its adhesive application in sensitive areas. We can infer that lignin, a natural polyol with its effectiveness as an adhesive and stability as well as a cheaper source, can replace the petro-based polyol. Lignin is a promising bio-polyol in a polyurethane matrix to be used in a wide range of applications as a hot-melt adhesive.

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Notes

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