Supporting Information

Hydrothermal Liquefied Bio-oil from Municipal Sewage Sludge as a Reactive Filler in Polymeric Methylene Diphe-nyl Diisocyanate (p-MDI) Wood Adhesives

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Number of Figures: 2

Number of Equations: 6

Table S1: Composition Details of MSS-Bio-oil and pMDI

Compound / Chemical	Compound/ Chemical	Equivalent Ratio	OH and NCO Groups eq/g	Molecular Weight (g/mol)	Equivalent Weight g/eq
Polyol	MSS-Bio-oil	0.0007	0.00157		638.57
Isocyanate	P-MDI (Rubinate M)	0.0189	2.7	364.5	135

Equivalent weight of MSS Bio-oil = 638.57 g/eq

Equivalent weight of pMDI = 135 g/eq

For each molar ratio, the mass ratio is calculated as:

$$Mass\ Ratio = \frac{Molar\ Ratio\ of\ MSS{-}Bio{-}oil \times Equivalent\ Weight\ of\ MSS\ {-}Bio{-}oil}{Molar\ Ratio\ of\ pMDI \times\ Equivalent\ Weight\ of\ pMDI} \quad \text{Eq. S1}$$

1. Molar Ratio 1:1

$$Mass\ Ratio = \frac{1 \times 638.57}{1 \times 135} = 4.73:1 \quad \text{Eq. S2}$$

2. Molar Ratio 2:1

$$Mass\ Ratio = \frac{2 \times 638.57}{1 \times 135} = 9.46:1 \quad \text{Eq. S3}$$

3. Molar Ratio 4:1

$$Mass\ Ratio = \frac{4 \times 638.57}{1 \times 135} = 18.92:1 \quad \text{Eq. S4}$$

4. Molar Ratio 1:2

$$Mass\ Ratio = \frac{1 \times 638.57}{2 \times 135} = 2.37:1 \quad \text{Eq. S5}$$

5. Molar Ratio 1:4

$$Mass\ Ratio = \frac{1 \times 638.57}{4 \times 135} = 1.18:1 \quad \text{Eq. S6}$$

These calculations yield the mass ratios based on equivalent weights for each specified molar ratio.

Commented [AB1]: Reviewer #3 (Comment #6): Line 200, any reason for using molar ratio? I think the weight ratio is more straightforward.

Response to Reviewer #3 (Comment #6): Thank you for your comment regarding the use of molar ratios. Molar ratios were chosen because they provide a precise stoichiometric comparison of the reactive groups in MSS-bio-oil and pMDI. This ensures accuracy in representing the proportions of reactive components used. To address your suggestion, the mass ratios corresponding to the molar ratios have been added to Supporting Information (Table S1) for additional clarity.

^{31}P NMR spectrum of municipal sewage sludge bio-oil (MSS-Bio-oil)

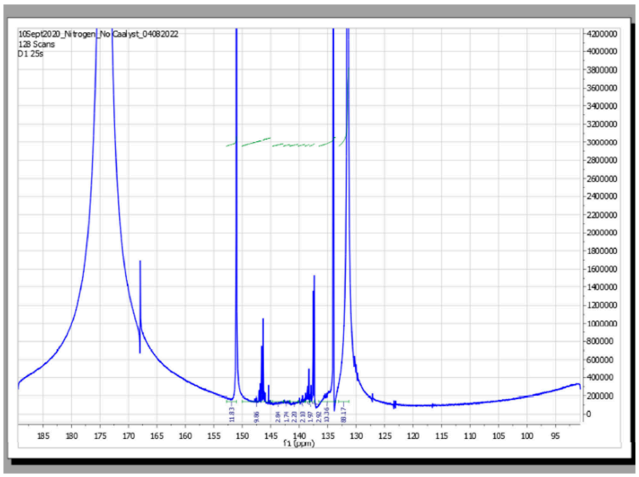

Figure S1. ^{31}P NMR spectrum of municipal sewage sludge bio-oil (MSS-Bio-oil)

Commented [AB2]: Reviewer #3 (Comment #7): Where is the ^{31}P NMR spectrum? Without it the whole analysis is dubious.
Response to Reviewer #7 (Comment #3): Thank you for your suggestion regarding the inclusion of the 31P NMR spectrum. We have now added the 31P NMR spectrum to the Supporting Information (Figure S1). Initially, we did not include the spectrum in the manuscript because the data it provides is already summarized in the table presented in the main text.

FTIR analysis of MSS Bio-oil/pMDI adhesive

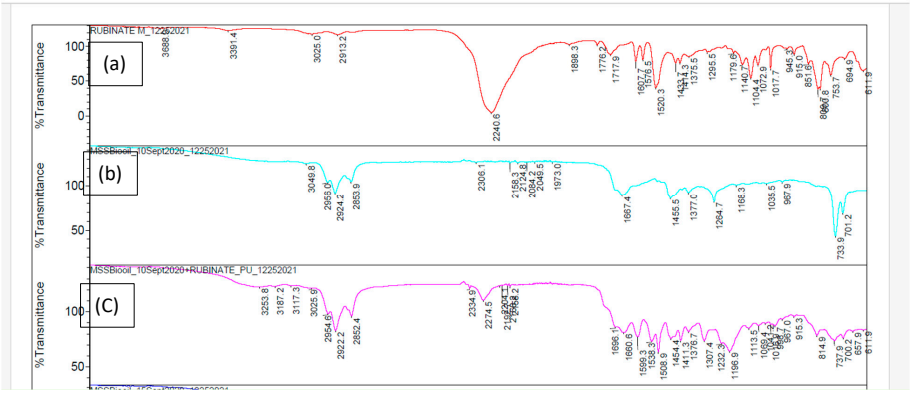

Figure S2. FTIR spectra of (a) p-MDI (Rubinate M) (b) Municipal sewage sludge bio-oil (MSS-Bio-oil, and (c) MSS Bio-oil/pMDI adhesive

The FTIR spectra provided in Figure S2 indicate the chemical interactions occurring in the MSS Bio-oil/pMDI adhesive system, as detailed below:

1. **Spectrum (a) - pMDI (Rubinate M):** The FTIR spectrum of pure pMDI reveals a distinct peak at approximately 2270 cm^{-1}, corresponding to the isocyanate functional groups (−N=C=O). Other peaks around 1595 cm^{-1} and 1410 cm^{-1} are attributed to the aromatic C=C stretching vibrations from the phenyl ring in pMDI.
2. **Spectrum (b) - MSS Bio-oil:** The MSS bio-oil spectrum shows the presence of hydroxyl (−OH) groups in the broad peak region of 3300–3500 cm^{-1}, as well as carbonyl (C=O) functional groups near 1700 cm^{-1}. Additionally, peaks near 1600 cm^{-1} suggest aromatic structures. These functional groups are potential reaction sites for interaction with pMDI.
3. **Spectrum (c) - MSS Bio-oil/pMDI Adhesive:** The spectrum of the MSS Bio-oil/pMDI adhesive shows a noticeable reduction in the isocyanate peak at 2270 cm^{-1} compared to pure pMDI, suggesting partial consumption of −N=C=O groups. New peaks observed around 1700 cm^{-1} and 3300 cm^{-1} indicate the potential formation of urethane (−NH−CO−O−) linkages. These changes align with chemical reactions between the −N=C=O groups of pMDI and the hydroxyl and carbonyl groups in MSS bio-oil.

The FTIR data support the assertion that MSS bio-oil interacts chemically with pMDI, contributing to the adhesive system by forming crosslinked structures.

Commented [AB3]: Reviewer #1 (Comment #5): Line 365-367, the interaction between -OH in MSS bio-oil and -N=C=O in pMDI (figure 3b) is proved by any experimental results or from references?

Response to Reviewer #1 (Comment #5): Thank you for raising this point. We acknowledge the importance of providing experimental evidence or references to support the interaction between the −OH groups in MSS bio-oil and the −N=C=O groups in pMDI, as depicted in Figure 3b. To address this, we have included FTIR analysis in the Supporting Information (Figure S2) to demonstrate the chemical interaction. The FTIR spectra show a reduction in the intensity of the isocyanate peak at 2270 cm^{-1}, indicating the consumption of −N=C=O groups, and the appearance of new peaks associated with urethane and urea linkages. These observations confirm the chemical reaction between the −OH groups in MSS bio-oil and the −N=C=O groups in pMDI. We have also added a reference to this data in the manuscript.

Commented [AB4R3]: Reviewer #1 (Comment #6): Line 379-381, any experimental results or references can prove that.

Response to Reviewer #1 (Comment #6): Thank you for your thoughtful comment. We understand the need to provide experimental evidence to support the statement regarding the interaction between MSS bio-oil and pMDI. To address this, we have added the FTIR analysis that we performed to evaluate the reactivity of MSS bio-oil toward pMDI. The FTIR spectra demonstrates the consumption of isocyanate groups (−N=C=O) from pMDI and the formation of urethane linkages, confirming the chemical interactions between MSS bio-oil and pMDI.
The FTIR spectra and their detailed explanation are included in the Supporting Information (Figure S2), and a reference to this data has been added to the manuscript.