

## Supplementary Material

# Synthesis, Characterization and Mechanical Properties of Novel Bio-based Polyurethane Foams Using Cellulose-derived Polyol for Chain Extension and Cellulose Citrate as a Thickener Additive

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## Section S1. Reagents

### **Polyethylene glycol PEG 400 (Thermo Fisher Scientific)**

Molecular formula:  $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ ,  $n = 8-9$  (average)

Appearance (Color): Clear colorless

Form: Viscous liquid

Identification (FTIR): Conforms

Molecular Weight: Average mol weight 380-420 (based on OH value)

Hydroxyl Value: 267- 295 mg KOH/g

pH: 4.5-7.0 (10%, demin water)

Viscosity: 104-140 mPa·s at 20°C

### **Isophorone diisocyanate IPDI (EVONIK INDUSTRIES, Code: VESTANAT<sup>®</sup>IPDI)**

Molecular formula:  $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_2$

Appearance (Color): Clear colorless

Form: liquid

Identification (FTIR): Conforms

Molecular Weight: 222.3 g/mol

NCO content: 37.5- 37.8 %

Viscosity: 14 mPa·s at 20°C

Density: 1.058 g/ml

### **4,4'-dicyclohexylmethane diisocyanate H<sub>12</sub>MDI (EVONIK INDUSTRIES, Code: VESTANAT<sup>®</sup>H<sub>12</sub>MDI)**

Molecular formula:  $\text{C}_{15}\text{H}_{22}\text{N}_2\text{O}_2$

Appearance (Color): Clear colorless

Form: liquid

Identification (FTIR): Conforms

Molecular Weight: 262.35 g/mol

NCO content: 31.8- 32 %

Viscosity: 35 mPa·s at 20°C

Density: 1.07 g/ml

### **Trimethylhexamethylene diisocyanate TMDI (EVONIK INDUSTRIES, Code: VESTANAT<sup>®</sup>TMDI)**

Molecular formula:  $\text{C}_{11}\text{H}_{18}\text{N}_2\text{O}_2$

Appearance (Color): Clear colorless

Form: liquid

Identification (FTIR): Conforms

Molecular Weight: 210.27 g/mol

NCO content: 39.7- 40 %

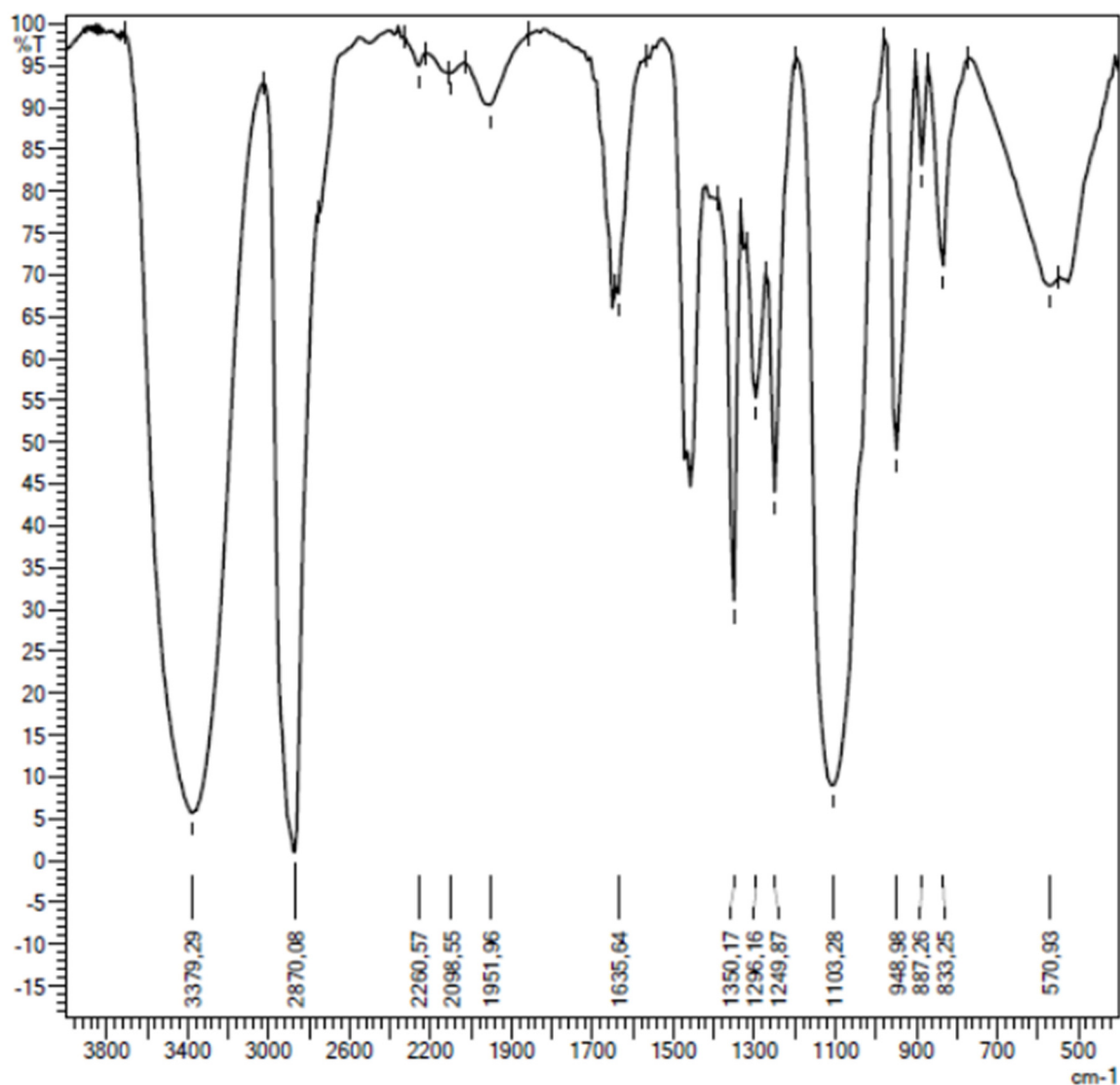
Viscosity: 5-8 mPa·s at 20°C

Density: 1.01 g/ml

### **Sodium Chloride NaCl (Sigma Aldrich, 99%)**

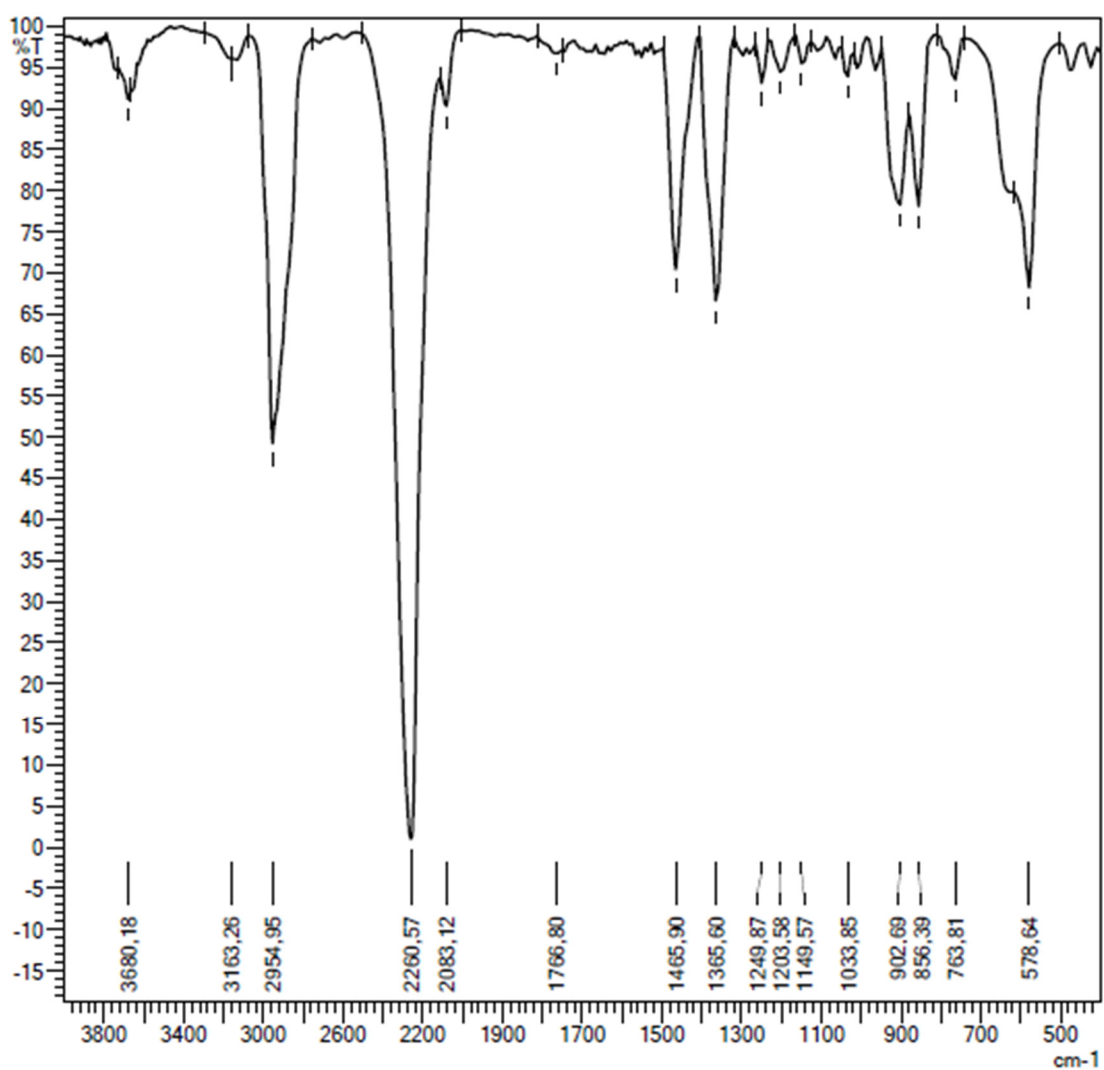
## Section S2. FT-IR spectra of PEG 400, isocyanates and the relative prepolymers

### FT-IR spectrum of PEG 400 (2)



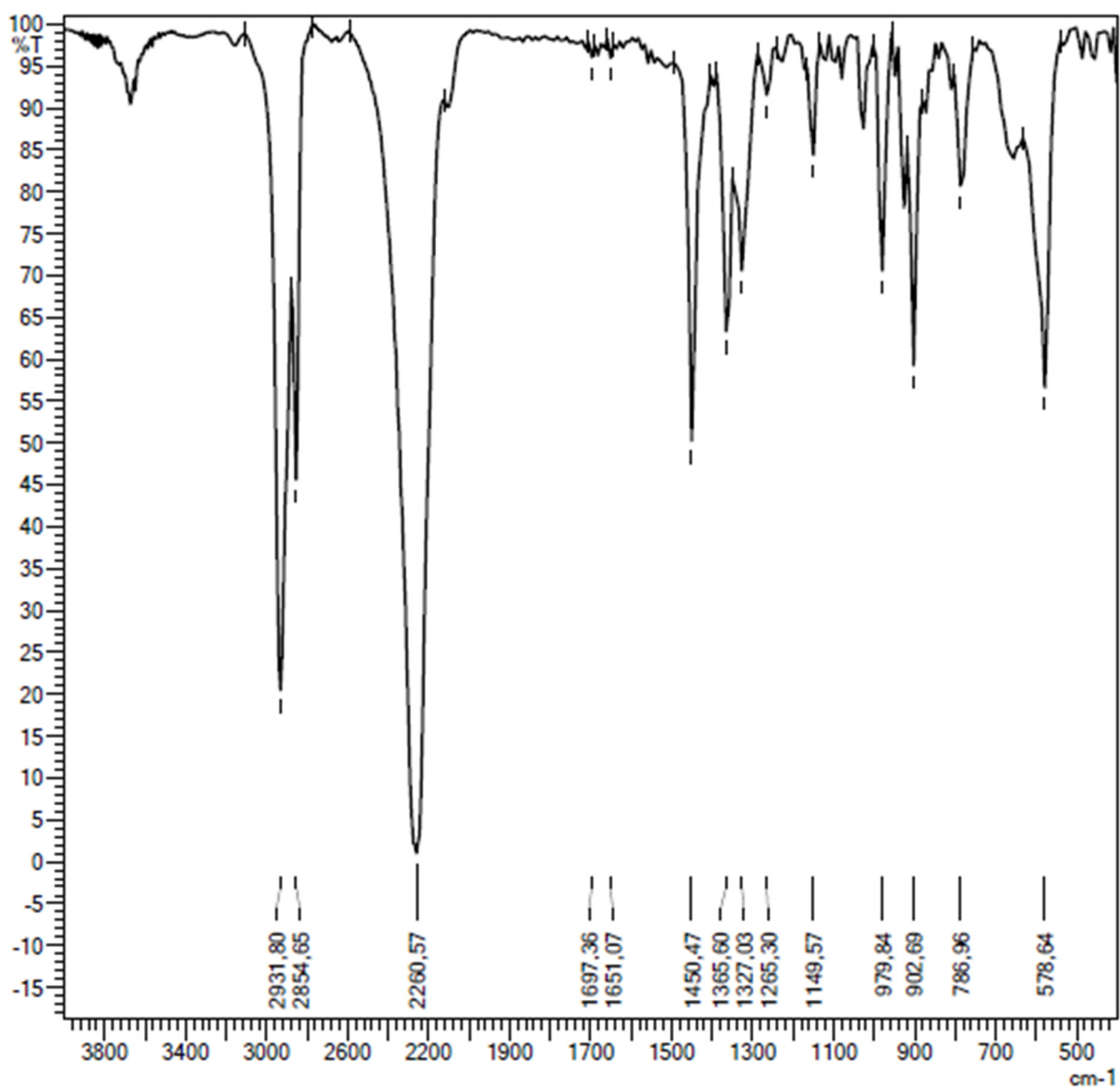
| Group (stretching) | Absorption peak (cm <sup>-1</sup> ) |
|--------------------|-------------------------------------|
| O-H                | 3379                                |
| C-H                | 2870                                |
| C-O-C and C-O-H    | 1050-1180                           |

**FT-IR spectrum of isophorone diisocyanate (IPDI) (3)**



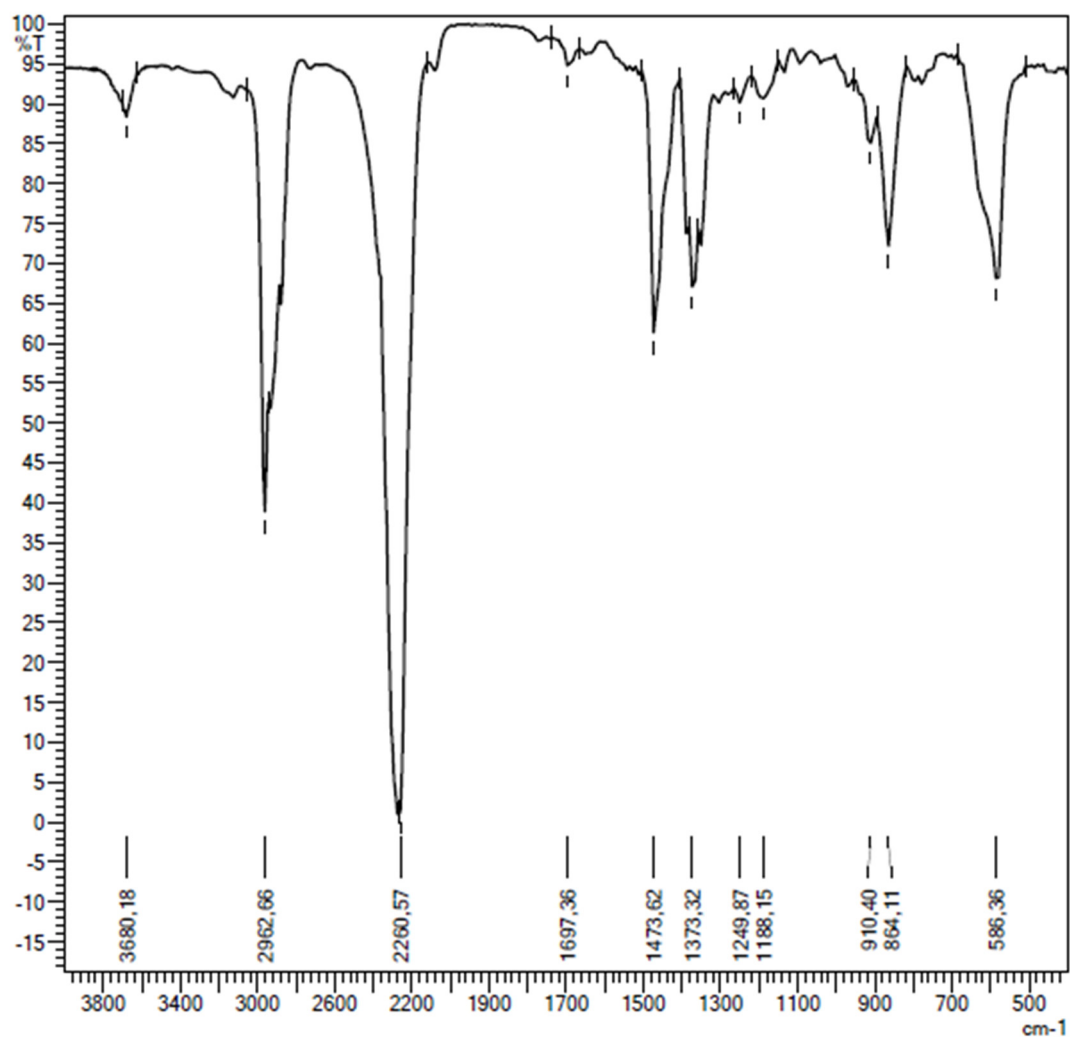
| Group (stretching) | Absorption peak (cm <sup>-1</sup> ) |
|--------------------|-------------------------------------|
| C-H                | 2954                                |
| N=C=O              | 2260                                |

FT-IR spectrum of 4,4'-methylenedicyclohexyl diisocyanate (H<sub>12</sub>MDI) (4)



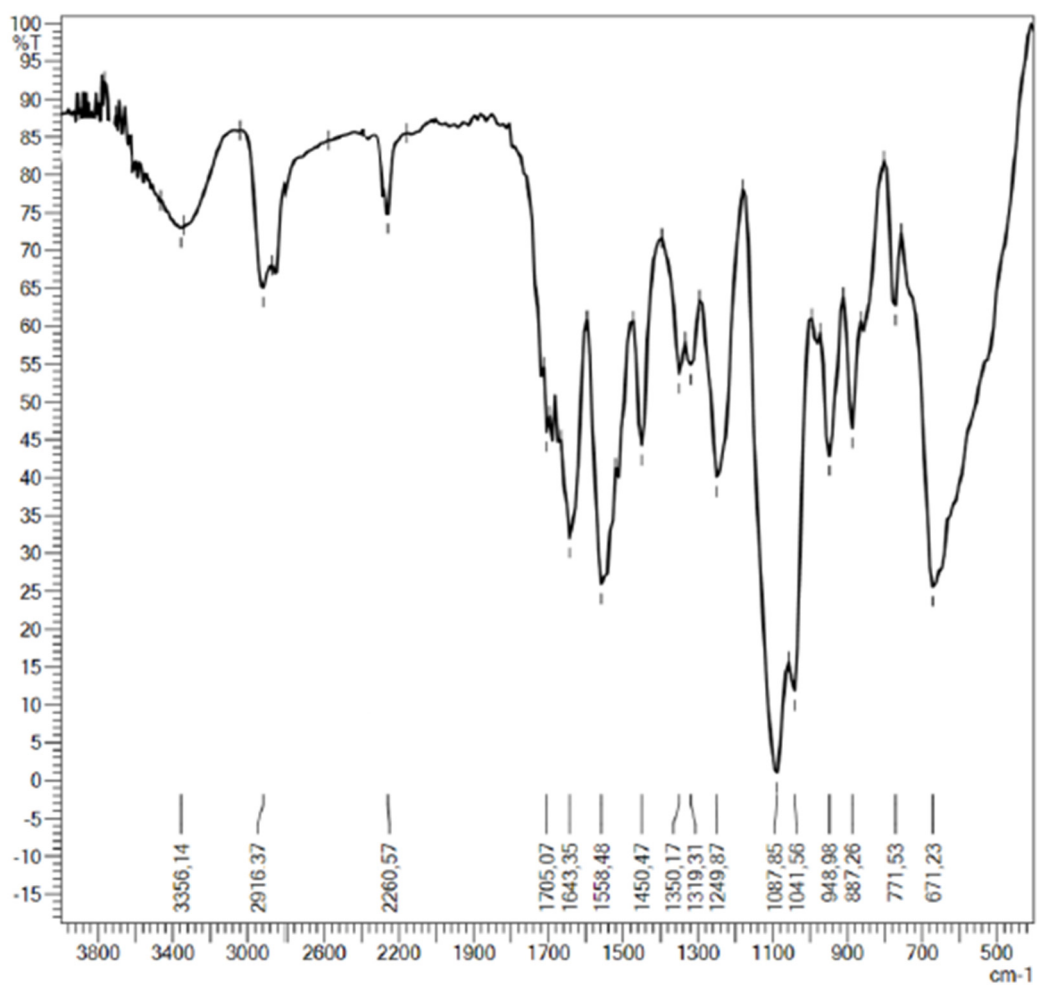
| Group (stretching) | Absorption peak (cm <sup>-1</sup> ) |
|--------------------|-------------------------------------|
| C-H                | 2854-2931                           |
| N=C=O              | 2260                                |

**FT-IR spectrum of 2,2,4-trimethyl hexamethylene diisocyanate (TMDI) (5)**



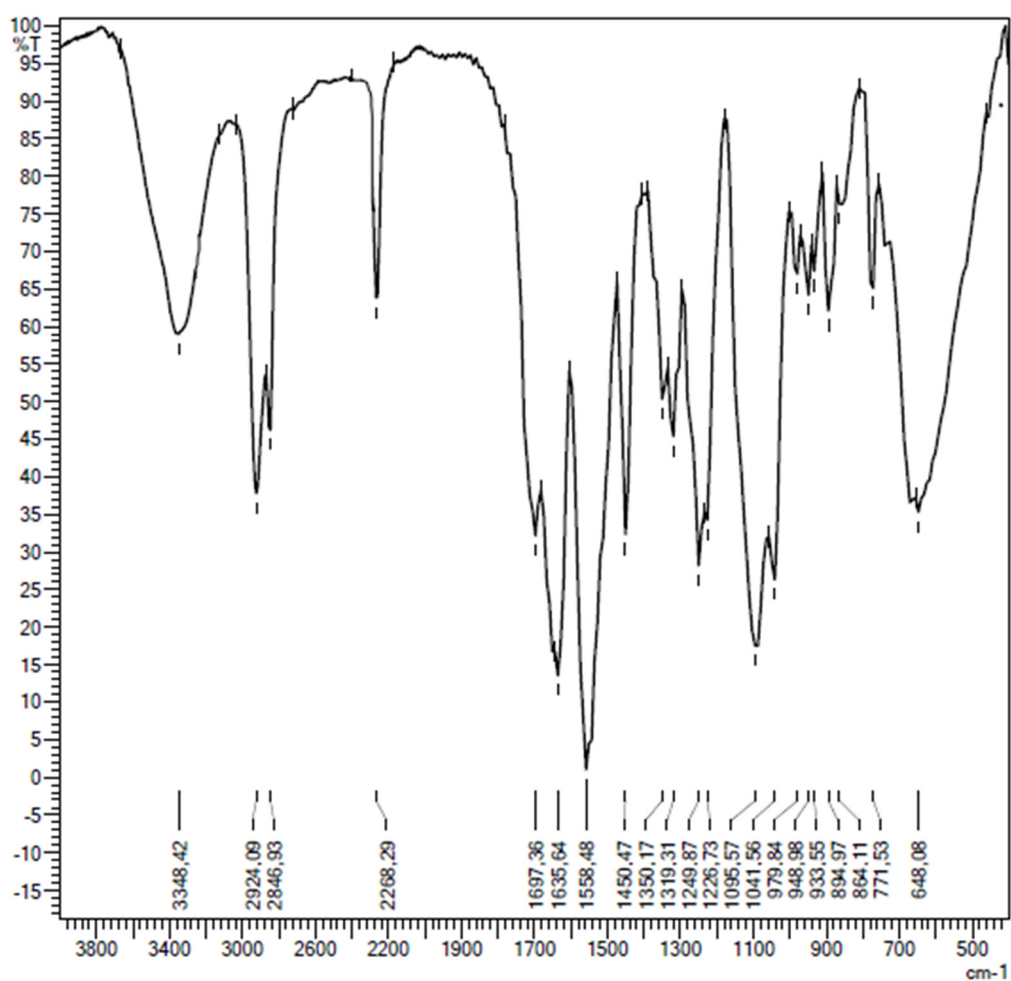
| Group (stretching) | Absorption peak (cm <sup>-1</sup> ) |
|--------------------|-------------------------------------|
| C-H                | 2962                                |
| N=C=O              | 2260                                |

### FT-IR spectrum of the prepolymer (6)



| Group (stretching)       | Absorption peak (cm <sup>-1</sup> ) |
|--------------------------|-------------------------------------|
| N-H                      | 3356                                |
| C-H                      | 2916                                |
| N=C=O                    | 2260                                |
| C=O (urethane)           | 1705                                |
| C=O (disubstituted urea) | 1643                                |
| CO-NH                    | 1558                                |
| C-O                      | 1249                                |
| C-O-C                    | 1087                                |

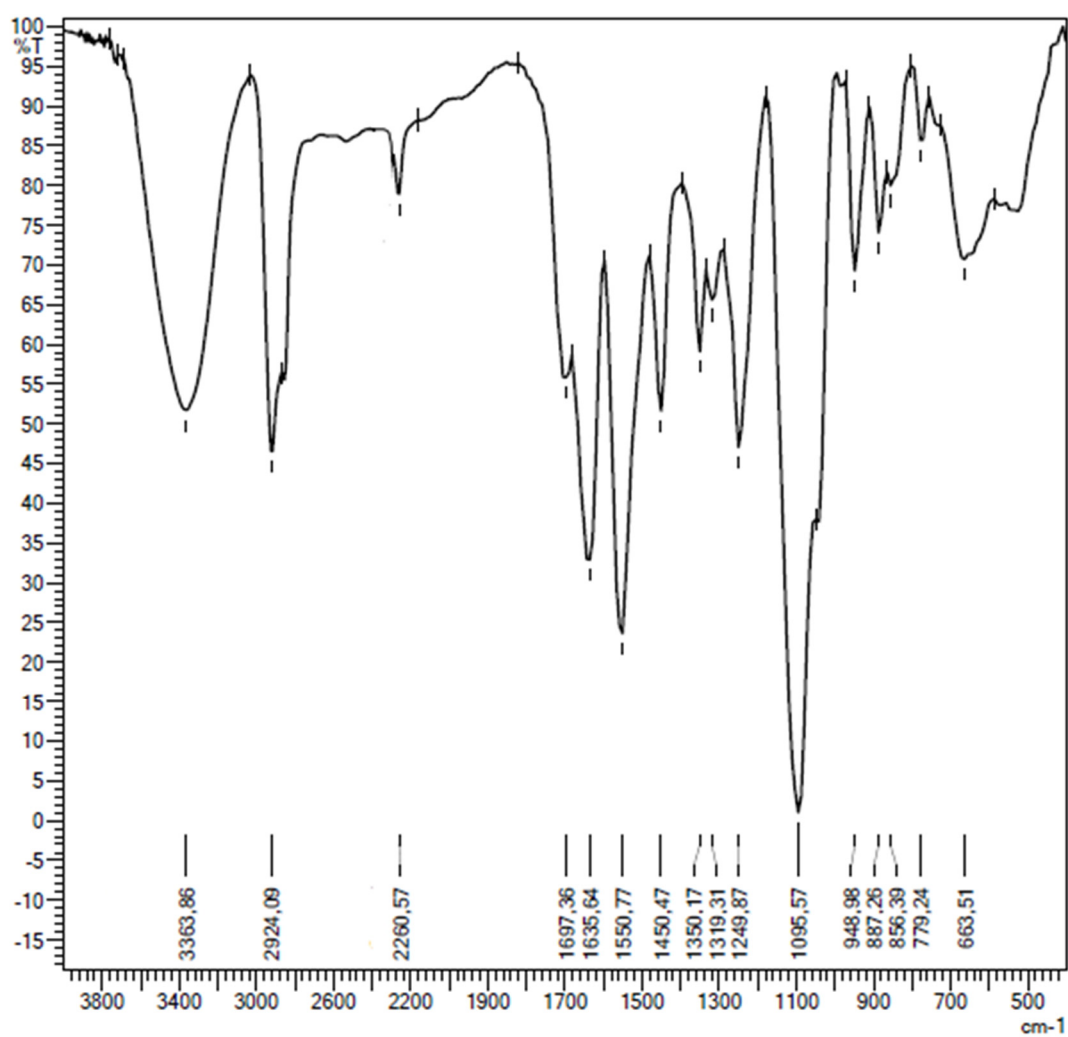
### FT-IR spectrum of the prepolymer (7)



| Group (stretching)       | Absorption peak (cm <sup>-1</sup> ) |
|--------------------------|-------------------------------------|
| N-H                      | 3348                                |
| C-H                      | 2864-2924                           |
| N=C=O                    | 2268                                |
| C=O (urethane)           | 1697                                |
| C=O (disubstituted urea) | 1635                                |
| CO-NH                    | 1558                                |
| C-O                      | 1249                                |
| C-O-C                    | 1095                                |

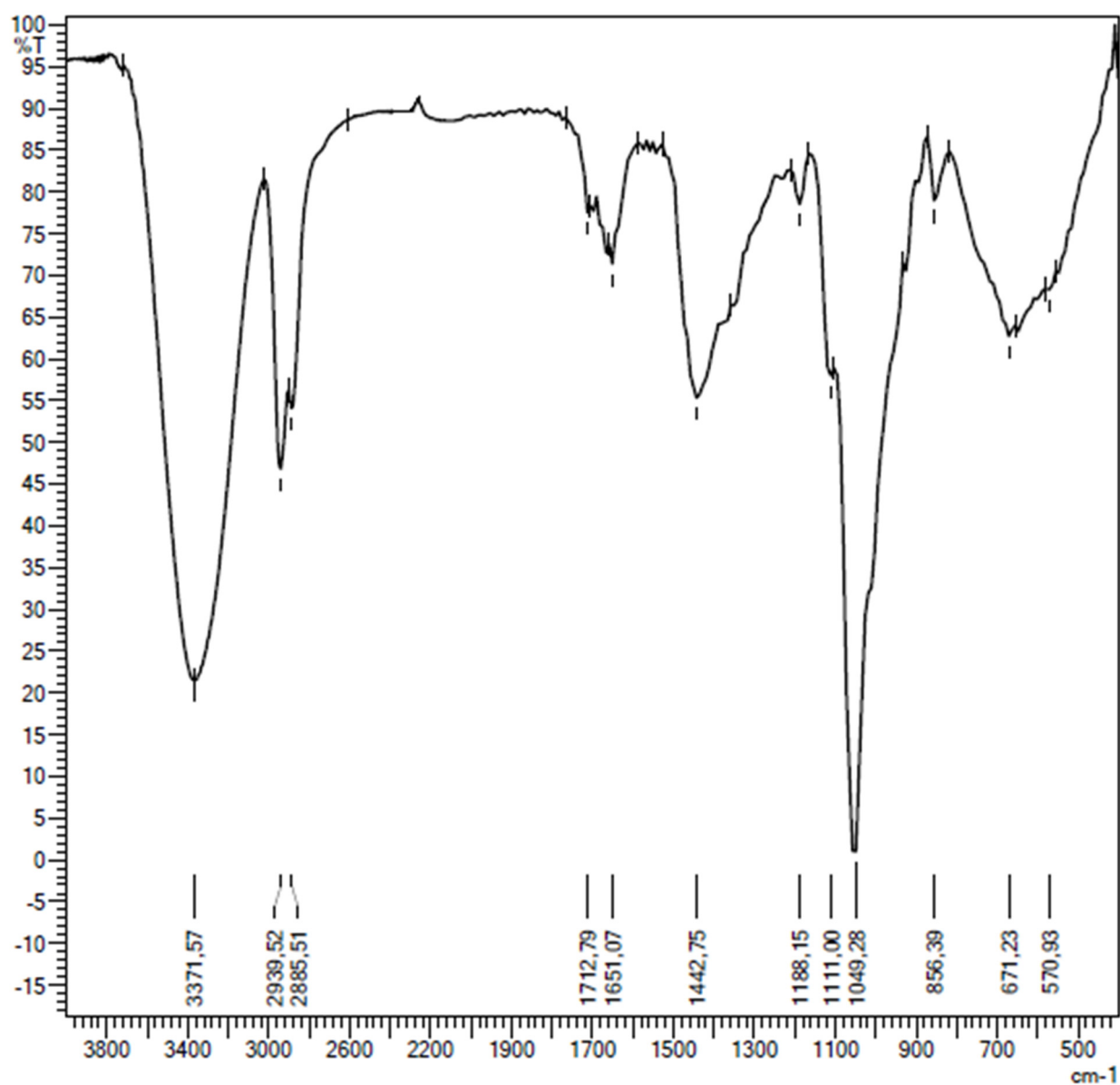


### FT-IR spectrum of the prepolymer (8)



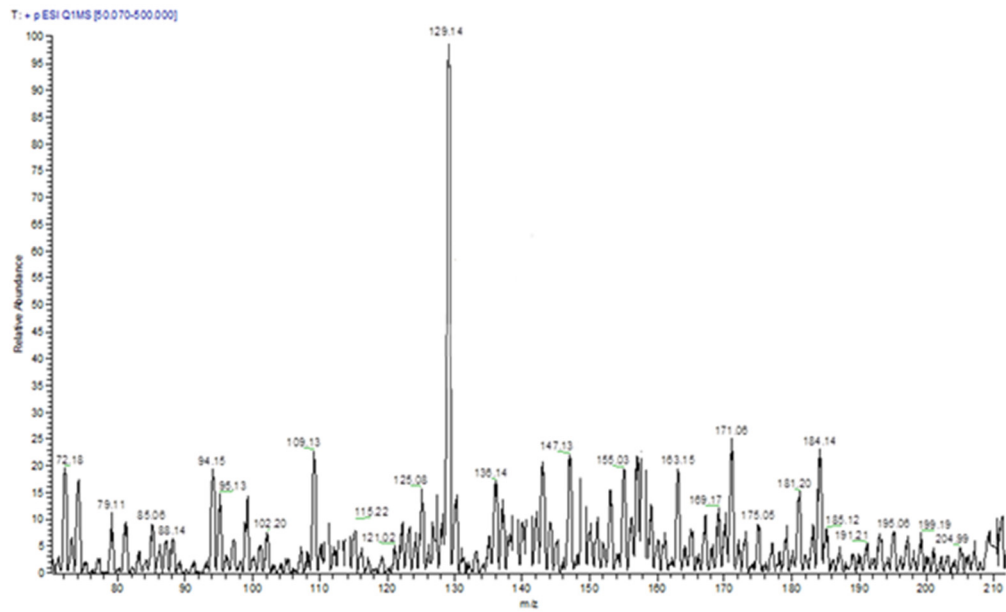
| Group (stretching)       | Absorption peak (cm <sup>-1</sup> ) |
|--------------------------|-------------------------------------|
| N-H                      | 3363                                |
| C-H                      | 2924                                |
| N=C=O                    | 2260                                |
| C=O (urethane)           | 1697                                |
| C=O (disubstituted urea) | 1635                                |
| CO-NH                    | 1550                                |
| C-O                      | 1249                                |
| C-O-C                    | 1095                                |

### Section S3. FT-IR spectra of biomass derived polyol (1)



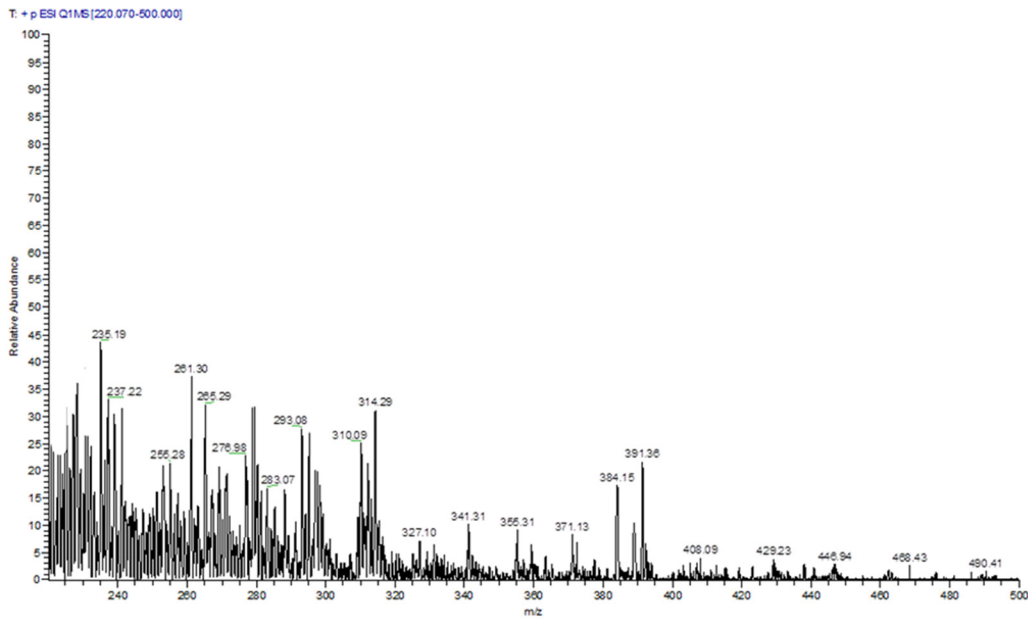
**Section S4.** LC-MS spectrum of polyol (1)

Full scan 70-210



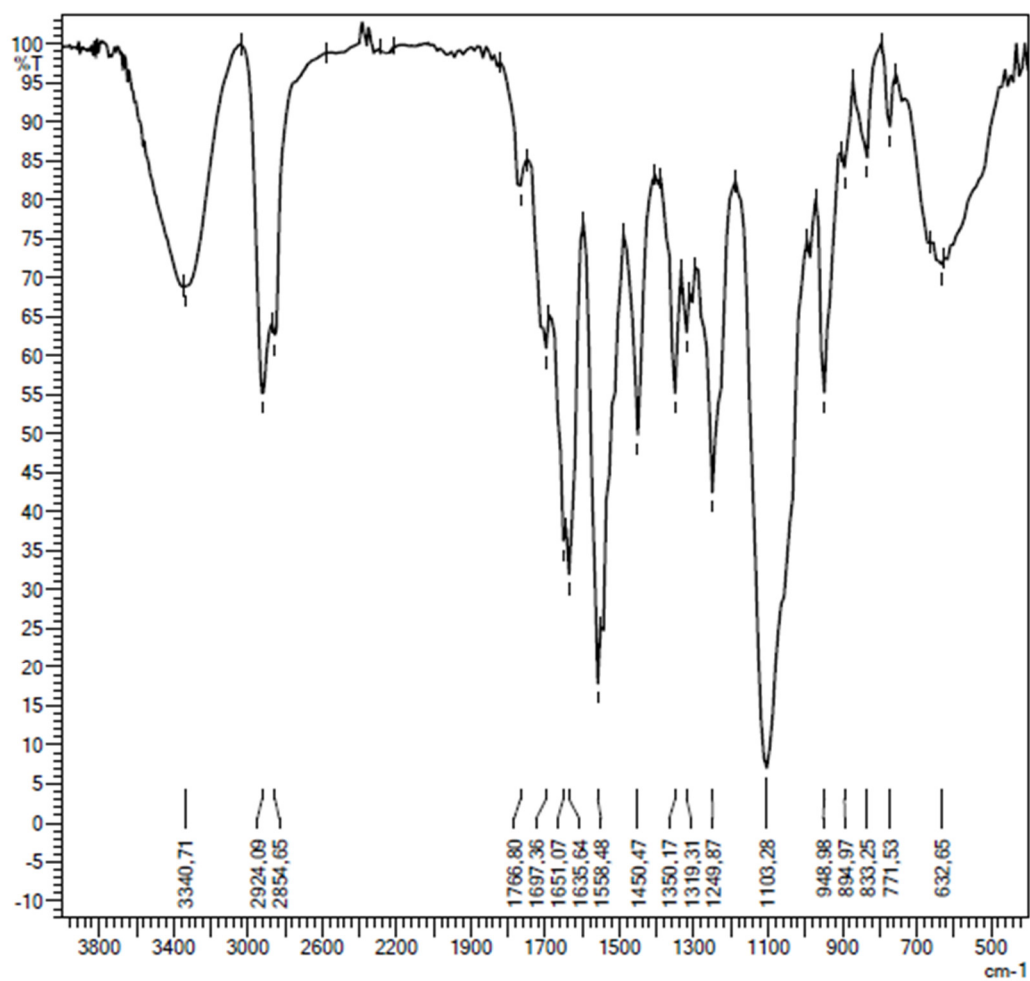
|           |        |
|-----------|--------|
| Structure |        |
| m/z + 1   | 129.14 |

Full scan 220-250



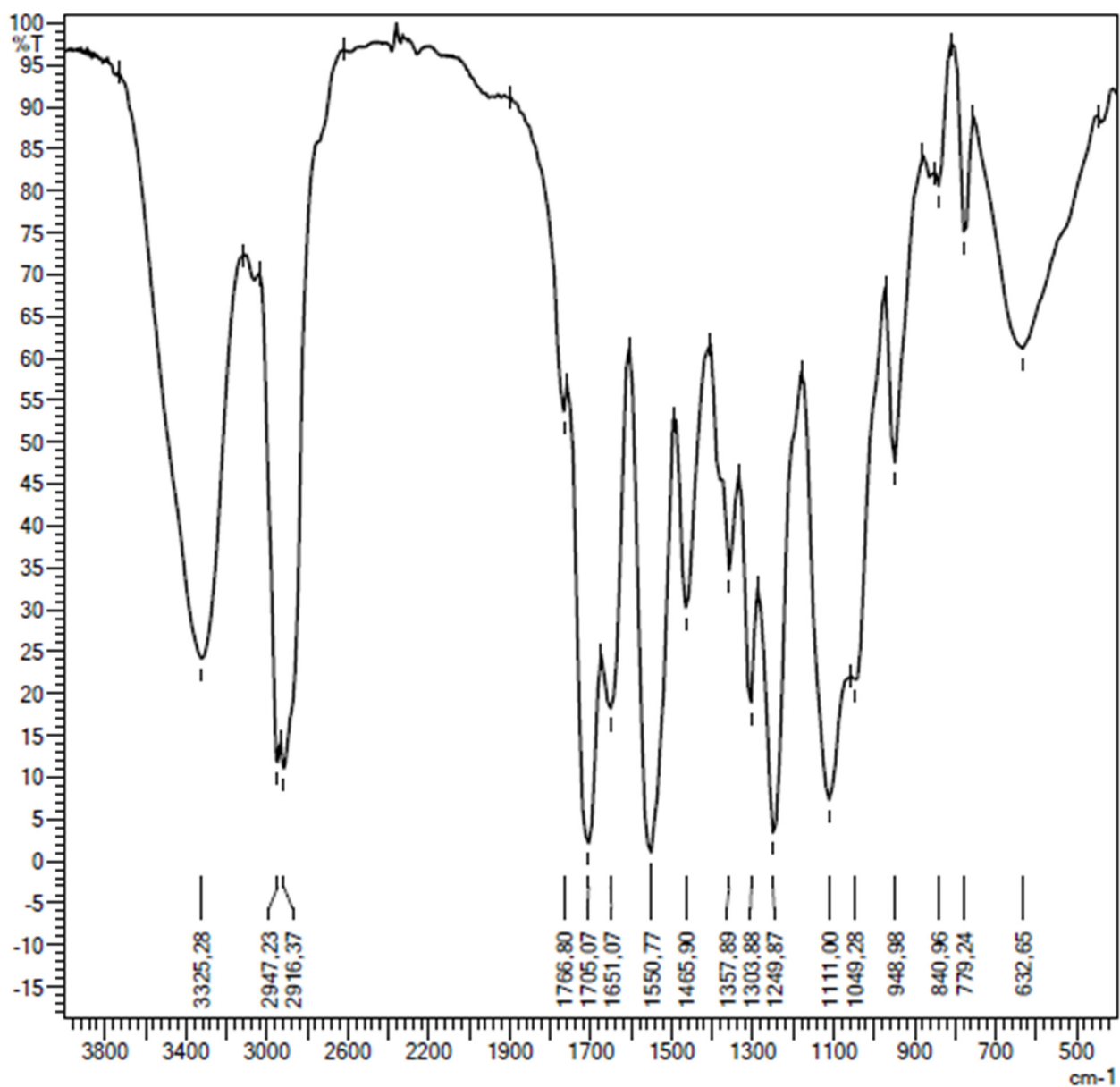
## Section S5. FT-IR spectra of biomass-based polyurethanes

### FT-IR spectrum of polyurethane (9)



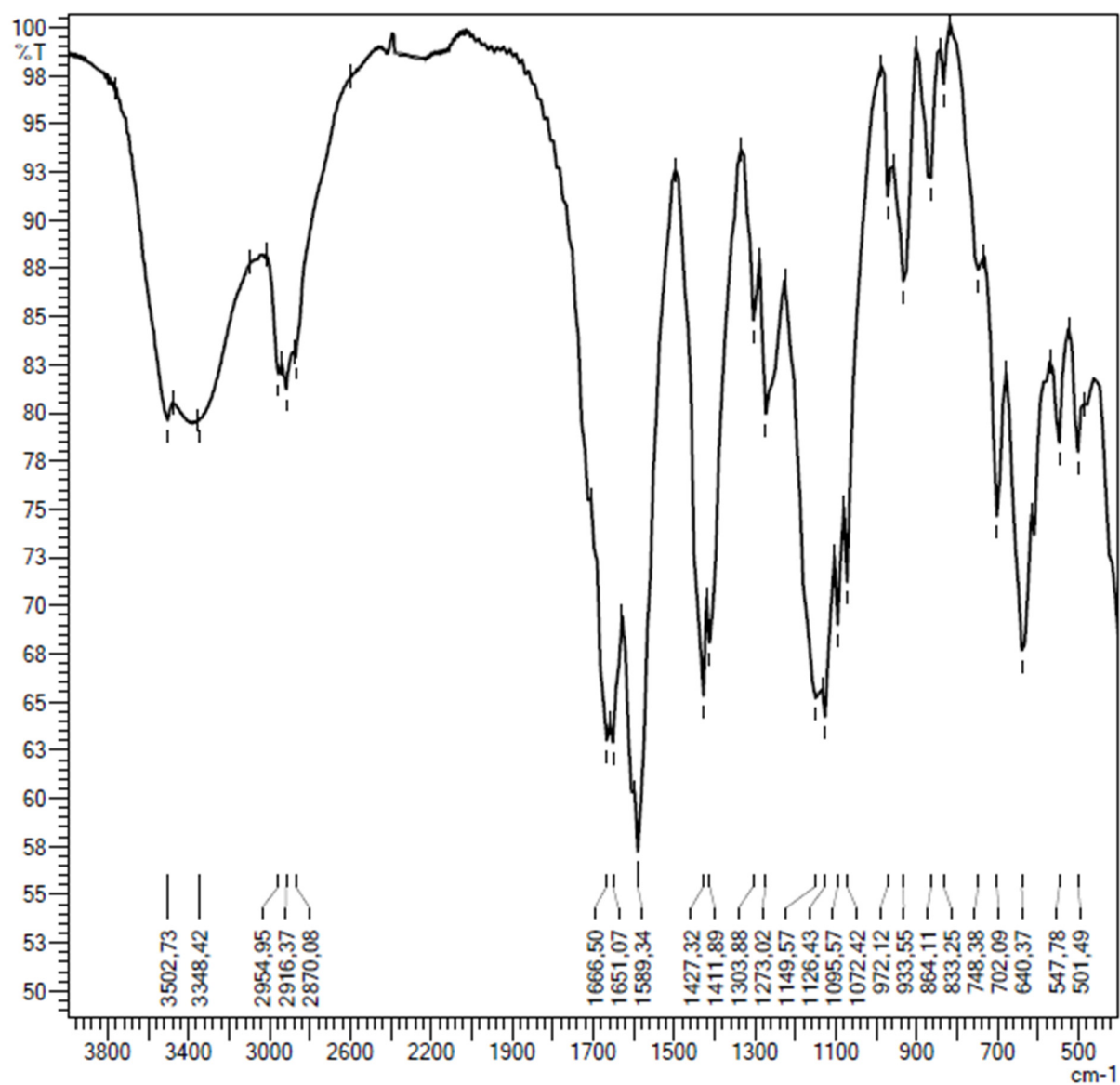
| Group (stretching) | Absorption peak (cm <sup>-1</sup> ) |
|--------------------|-------------------------------------|
| N-H                | 3340                                |
| C-H                | 2854-2924                           |
| C=O                | 1651-1712                           |
| C-O                | 1188-1049                           |

FT-IR spectrum of polyurethane (10)



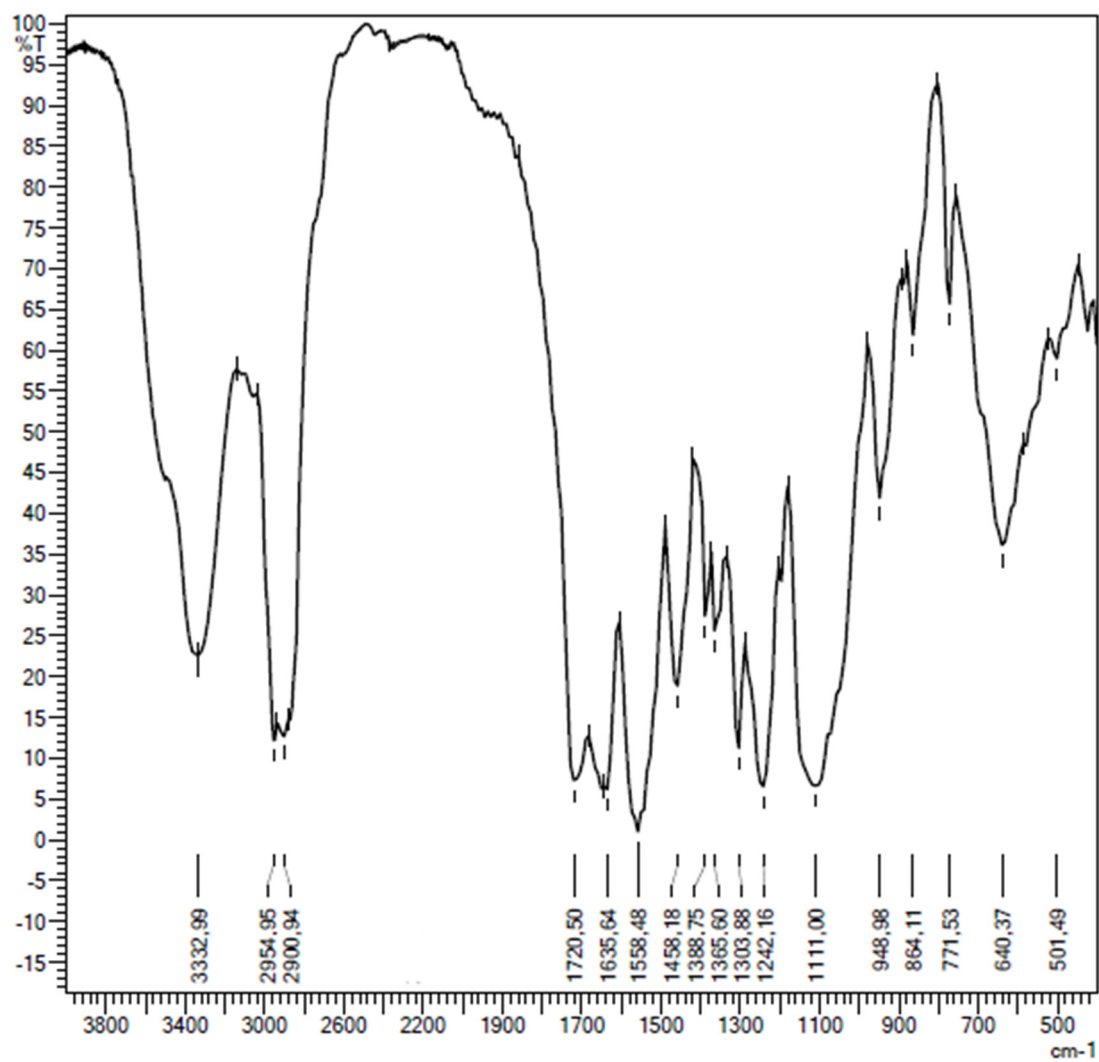
| Group (stretching) | Absorption peak (cm <sup>-1</sup> ) |
|--------------------|-------------------------------------|
| N-H                | 3325                                |
| C-H                | 2947-2916                           |
| C=O                | 1651-1712                           |
| C-O                | 1188-1049                           |

FT-IR spectrum of polyurethane (11)



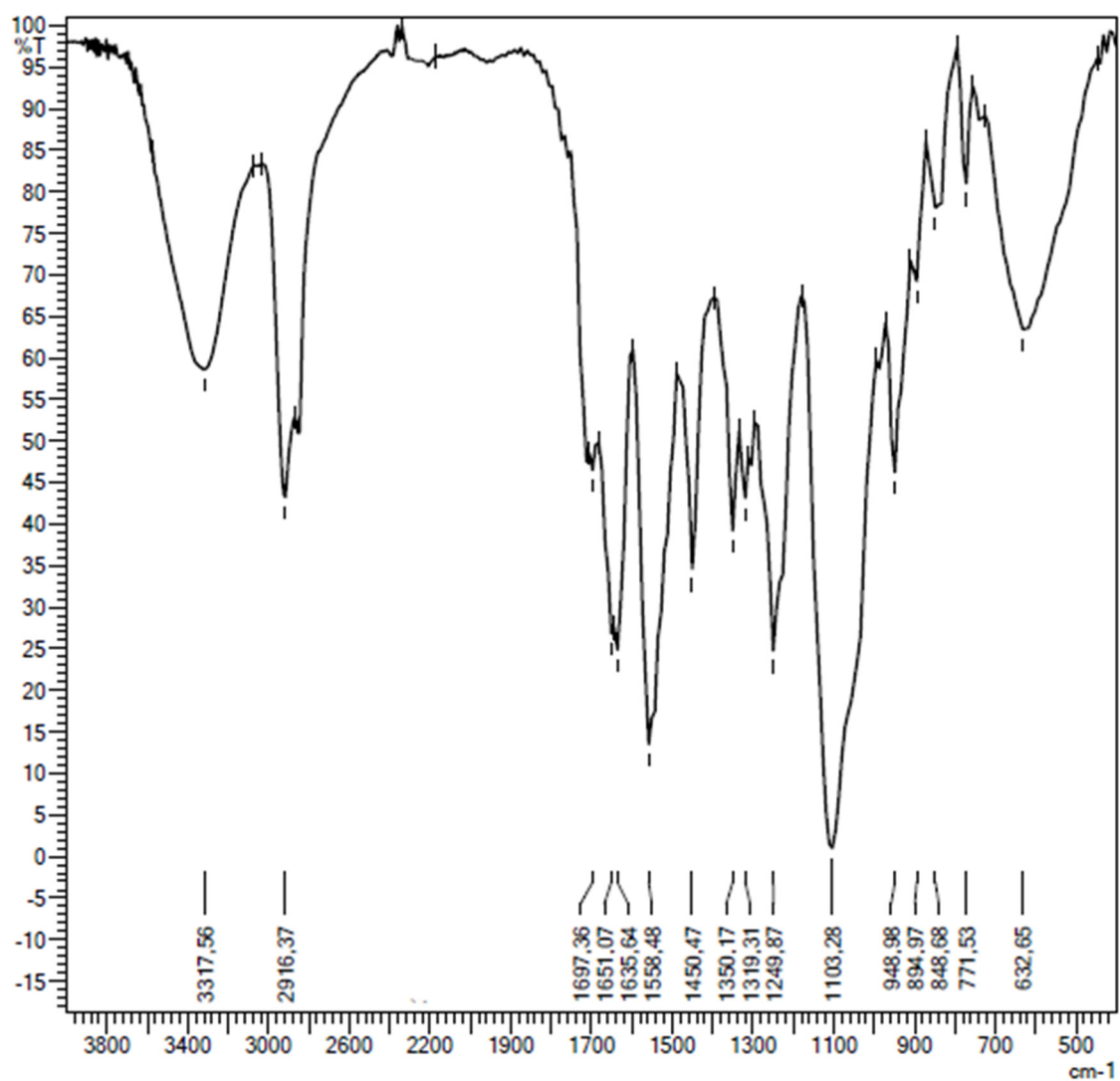
| Group (stretching) | Absorption peak (cm <sup>-1</sup> ) |
|--------------------|-------------------------------------|
| N-H                | 3348-3502                           |
| C-H                | 2870-2954                           |
| C=O                | 1651-1712                           |
| C-O                | 1188-1049                           |

# FT-IR spectrum of polyurethane (12)



| Group (stretching) | Absorption peak (cm <sup>-1</sup> ) |
|--------------------|-------------------------------------|
| N-H                | 3332                                |
| C-H                | 2900-2954                           |
| C=O                | 1630-1735                           |
| C-O                | 1188-1049                           |

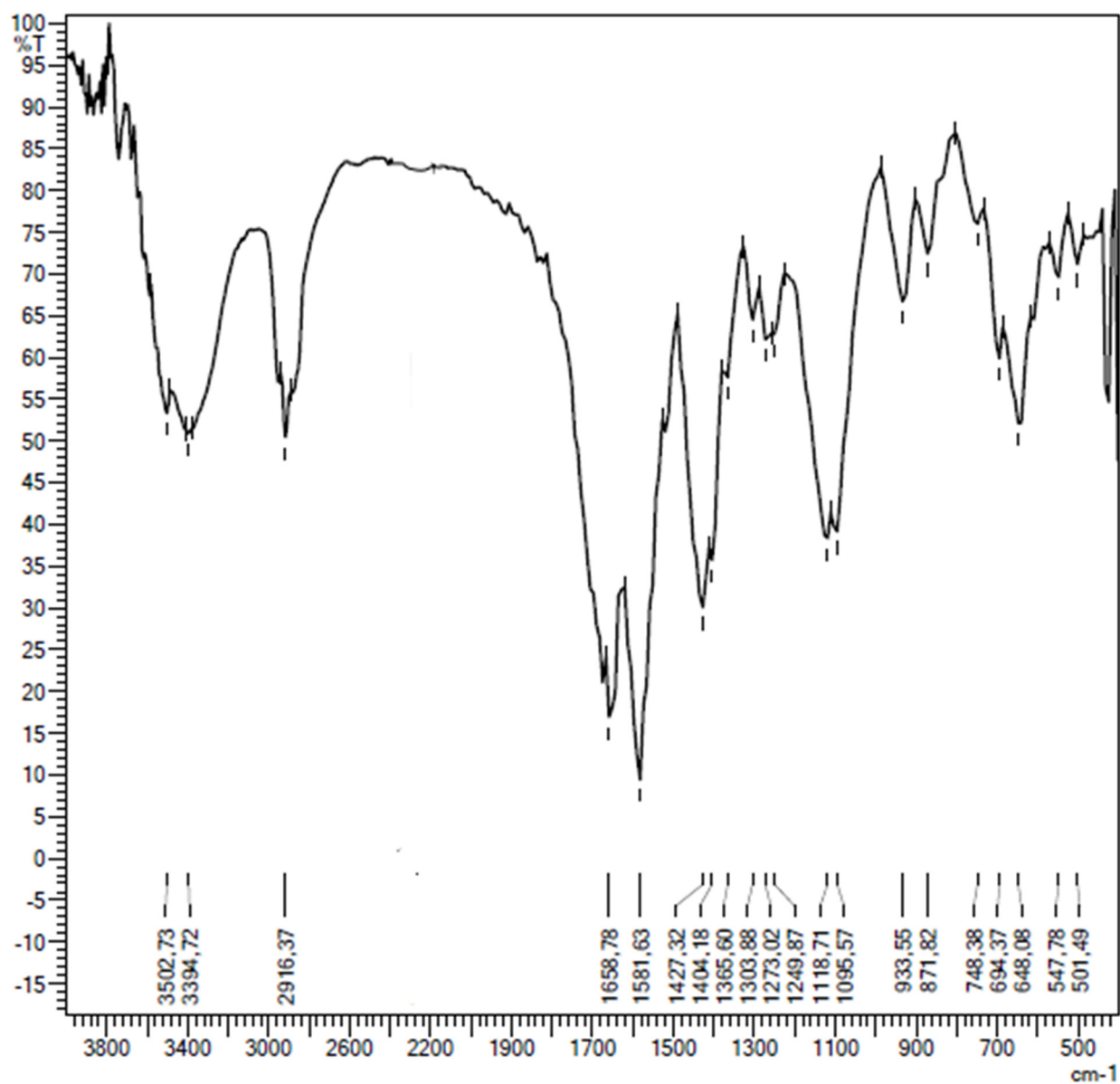
FT-IR spectrum of polyurethane (13)



| Group (stretching) | Absorption peak (cm <sup>-1</sup> ) |
|--------------------|-------------------------------------|
| N-H                | 3317                                |
| C-H                | 2916                                |
| C=O                | 1630-1720                           |
| C-O                | 1188-1049                           |



FT-IR spectrum of polyurethane (14)



| Group (stretching) | Absorption peak (cm <sup>-1</sup> ) |
|--------------------|-------------------------------------|
| N-H                | 3394-3502                           |
| C-H                | 2916                                |
| C=O                | 1651-1720                           |
| C-O                | 1188-1049                           |

**Section S6. Composite material processing equipment**



**Section S7. Photographs of bio-based polyurethanes**



**9** (rigid foam)



**10** (rigid foam)



**11** (flexible foam)

**Section S8. Photographs of bio-based composite materials**



**12 (rigid foam)**



**13 (rigid foam)**



**14 (flexible foam)**