

Electronic Supplementary Information

Novel Catalytic Two-Step Process for Preparation of Rigid Polyurethane Foams: Synthesis, Mechanism and Theoretical Studies.

Loredana Maiuolo,^{*a} Fabrizio Olivito,^{*a} Fortuna Ponte,^{*a} Vincenzo Algieri,^a Matteo Antonio Tallarida,^a Antonio Tursi,^a Giuseppe Chidichimo,^a Emilia Sicilia,^a Antonio De Nino^a

^a Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, 87036, Rende (CS), Italy.

Corresponding authors: *E-mail address* maiuolo@unical.it (L. Maiuolo); fabrizio.olivito@unical.it (F. Olivito); fortuna.ponte@unical.it (F. Ponte).

Table of Contents

1.	Reagents	S3
2.	Catalysts	S4
3.	FT-IR spectra of the reagents (1-4) and the relative prepolymers (7-9)	S5
4.	FT-IR spectra of polyurethanes extended with 1,2-ethylene glycol (10-12)	S12
5.	FT-IR spectra of polyurethanes extended with 1,4-butanediol (13-15)	S15

1. 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[®]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'-methylenedicyclohexyl diisocyanate H₁₂MDI (EVONIK INDUSTRIES, Code: VESTANAT[®]H₁₂MDI)

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

Appearance (Colour): Clear colourless

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

2,2,4-Trimethylhexamethylene diisocyanate TMDI (EVONIK INDUSTRIES, Code: VESTANAT[®]TMDI)

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

Appearance (Colour): Clear colourless

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

2. Catalysts

Sodium Chloride NaCl (Sigma Aldrich, 99%)

Sodium bromide NaBr (Sigma Aldrich, 99.9%)

Sodium iodide NaI (Sigma Aldrich, 99.9%)

Sodium acetate NaOAc (Sigma Aldrich, 99%)

Sodium sulphate Na₂SO₄ (Sigma Aldrich, Anhydrous, 99%)

Magnesium Chloride MgCl₂ (Sigma Aldrich, 98%)

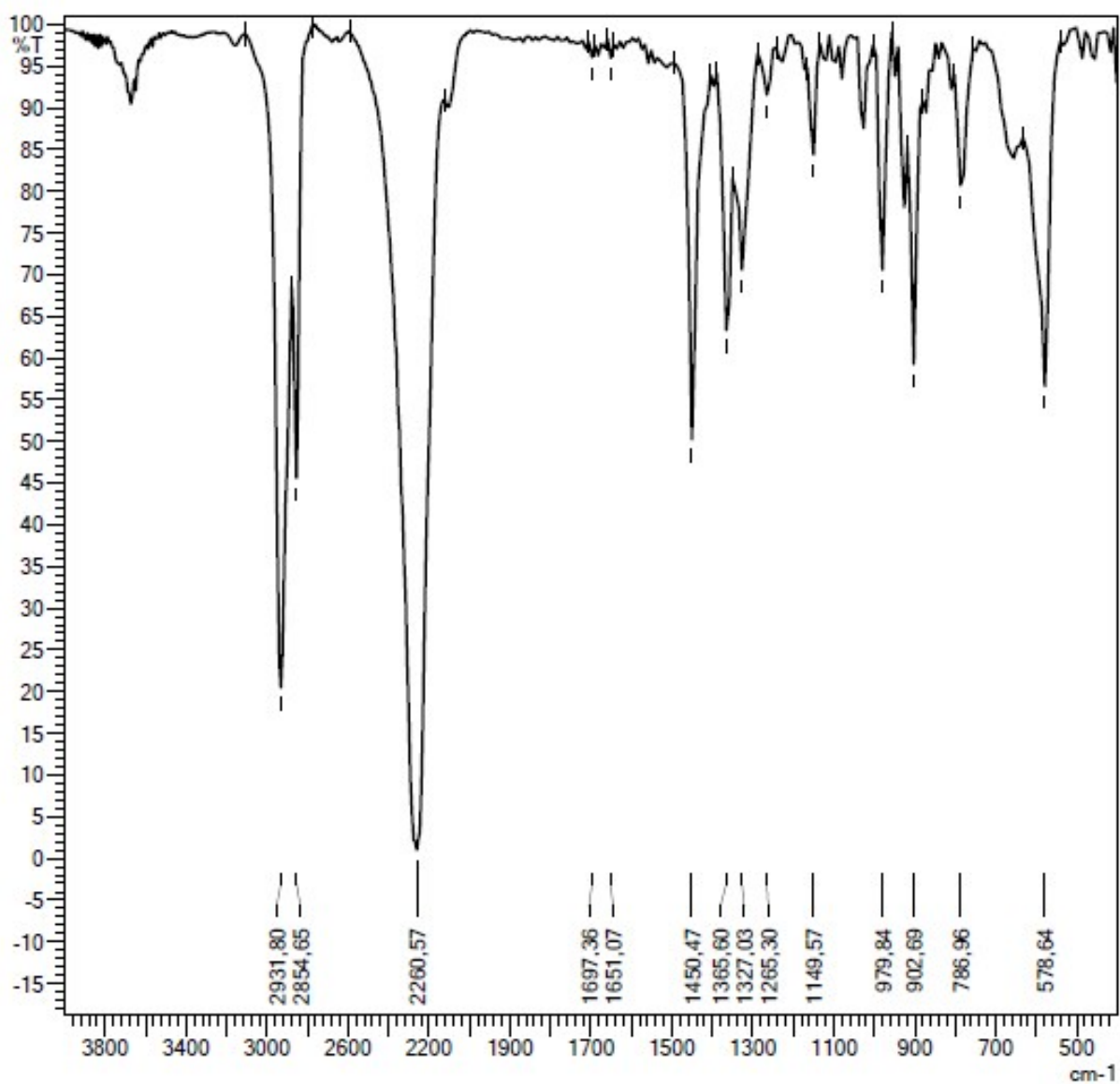
Magnesium Sulphate MgSO₄ (Sigma Aldrich, 99.5%)

Calcium chloride CaCl₂ (Sigma Aldrich, 99.9%)

Calcium sulphate CaSO₄ (Sigma Aldrich, 99.9%)

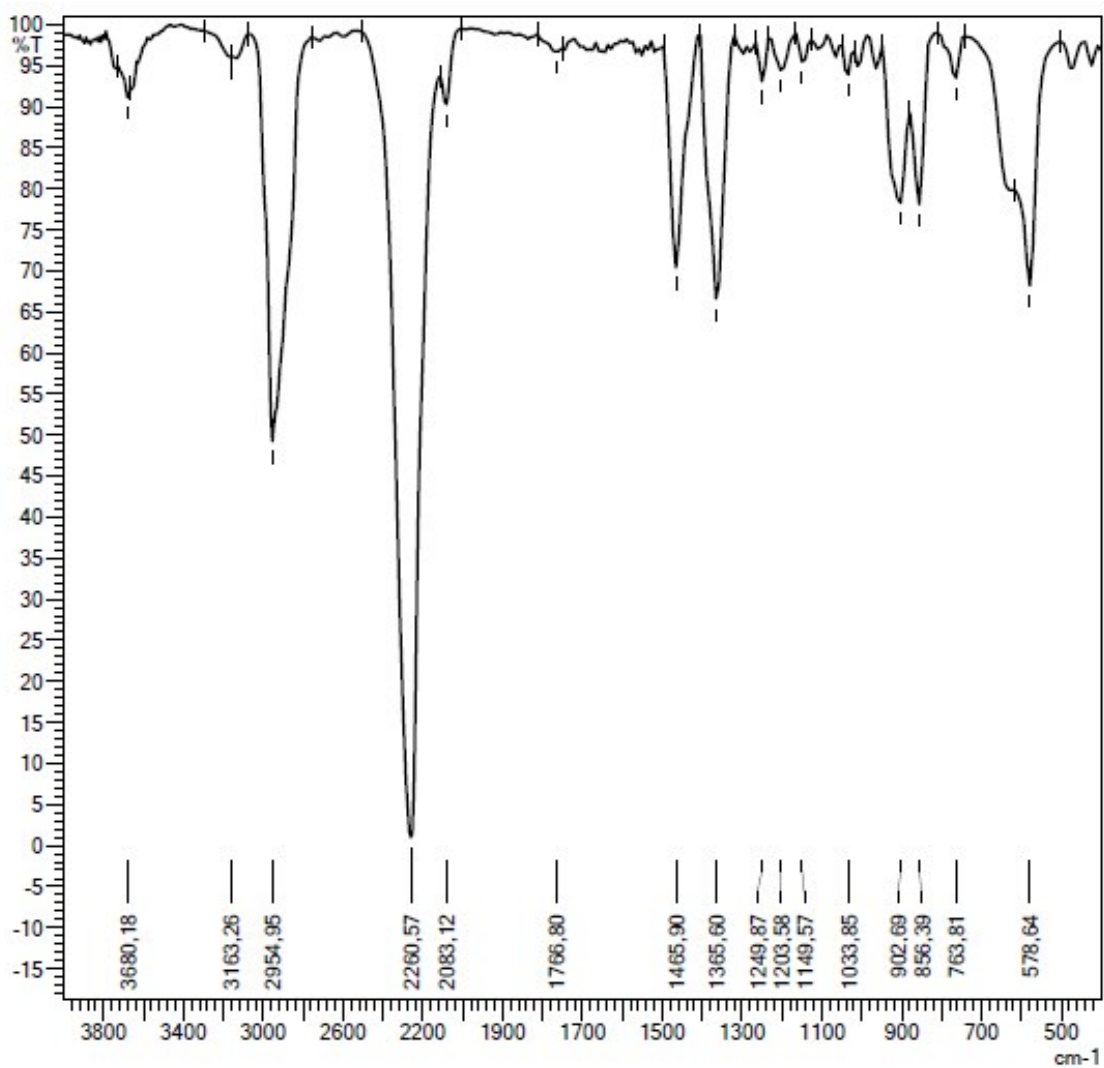
3. FT-IR spectra of the reagents and the relative prepolymers

FT-IR spectrum of 4,4'-methylenedicyclohexyl diisocyanate H₁₂MDI (1)



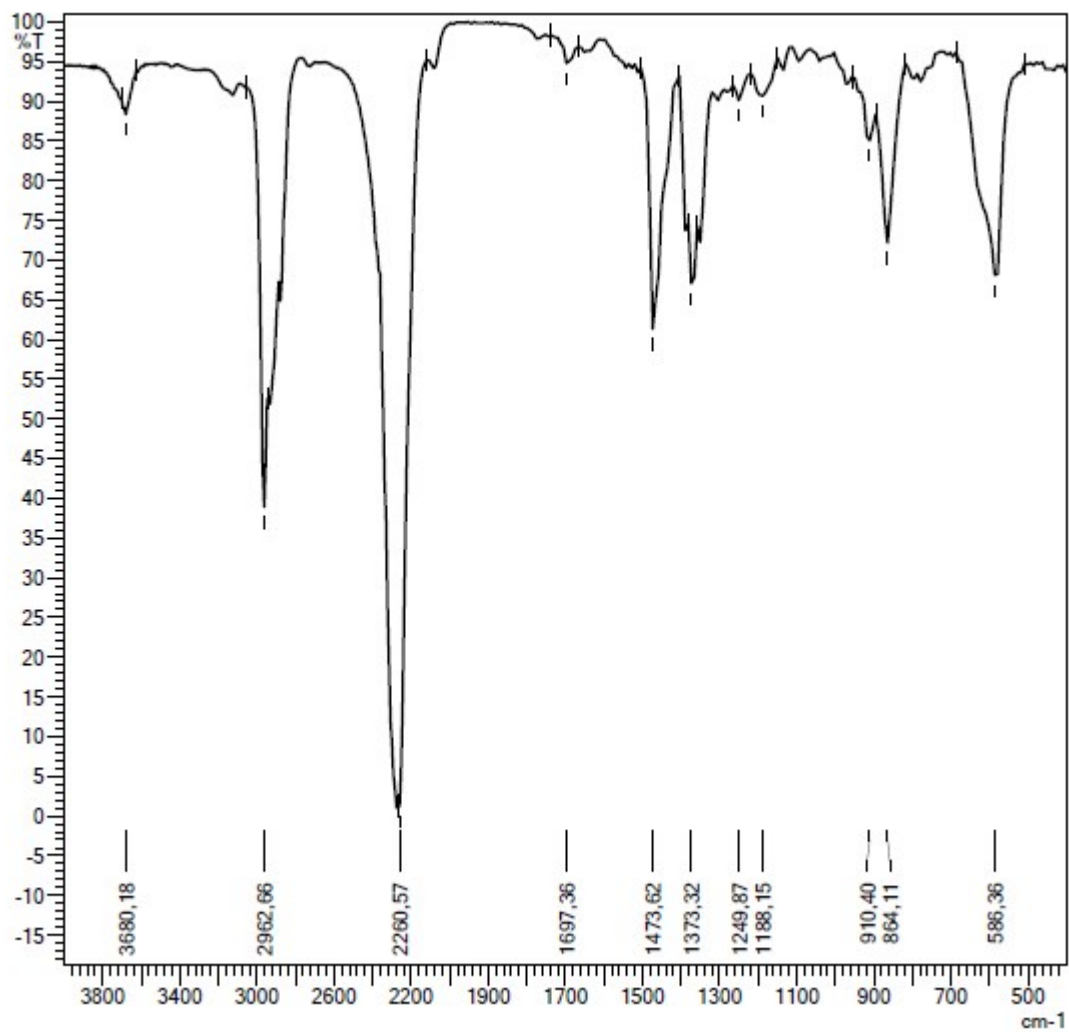
Group (stretching)	Absorption peak (cm ⁻¹)
Aliphatic C-H	2854-2931
N=C=O	2260

FT-IR spectrum of isophorone diisocyanate IPDI (2)



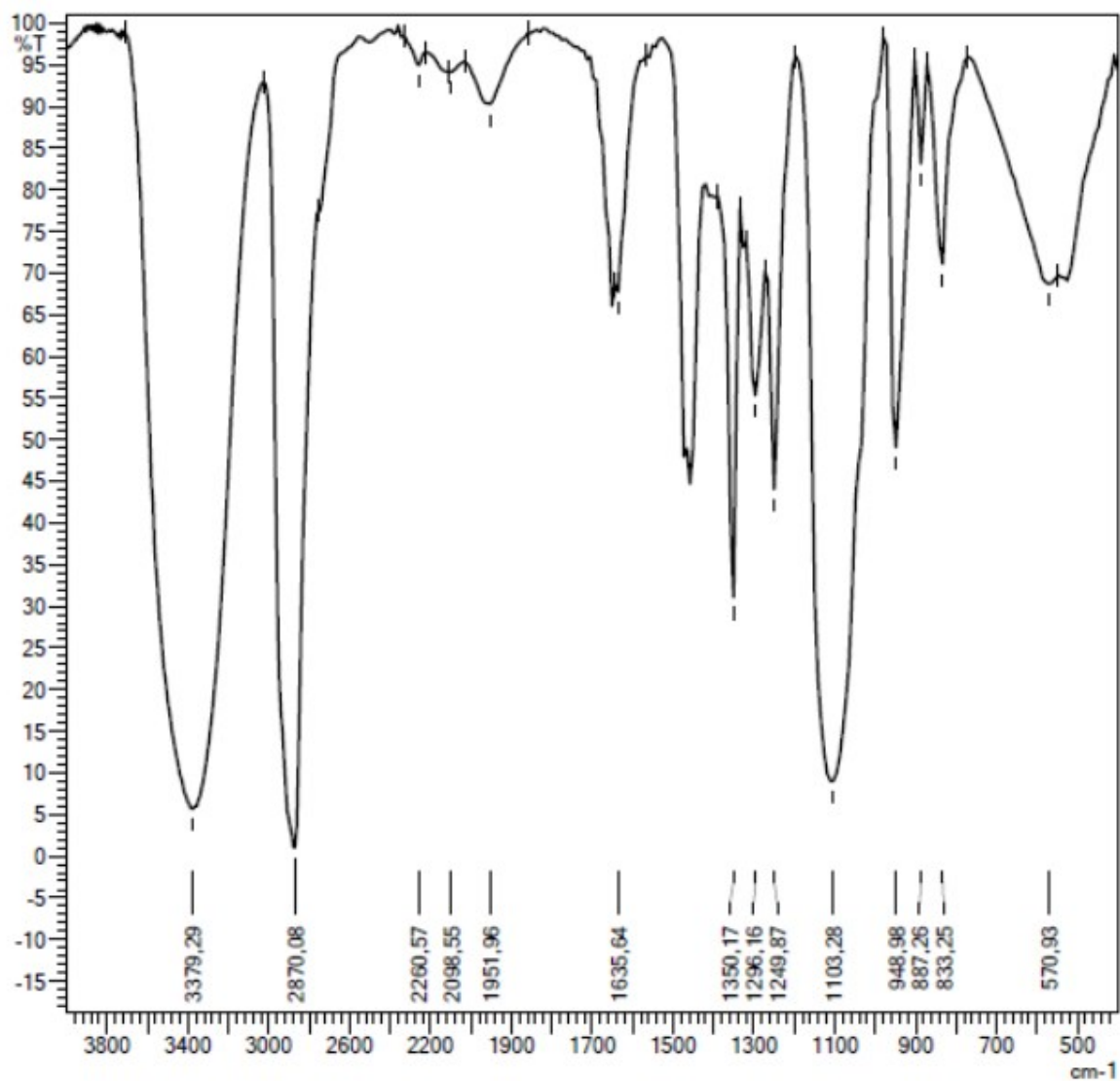
Group (stretching)	Absorption peak (cm ⁻¹)
Aliphatic C-H	2954
N=C=O	2260

FT-IR spectrum of 2,2,4-trimethylhexamethylene diisocyanate TMDI (3)



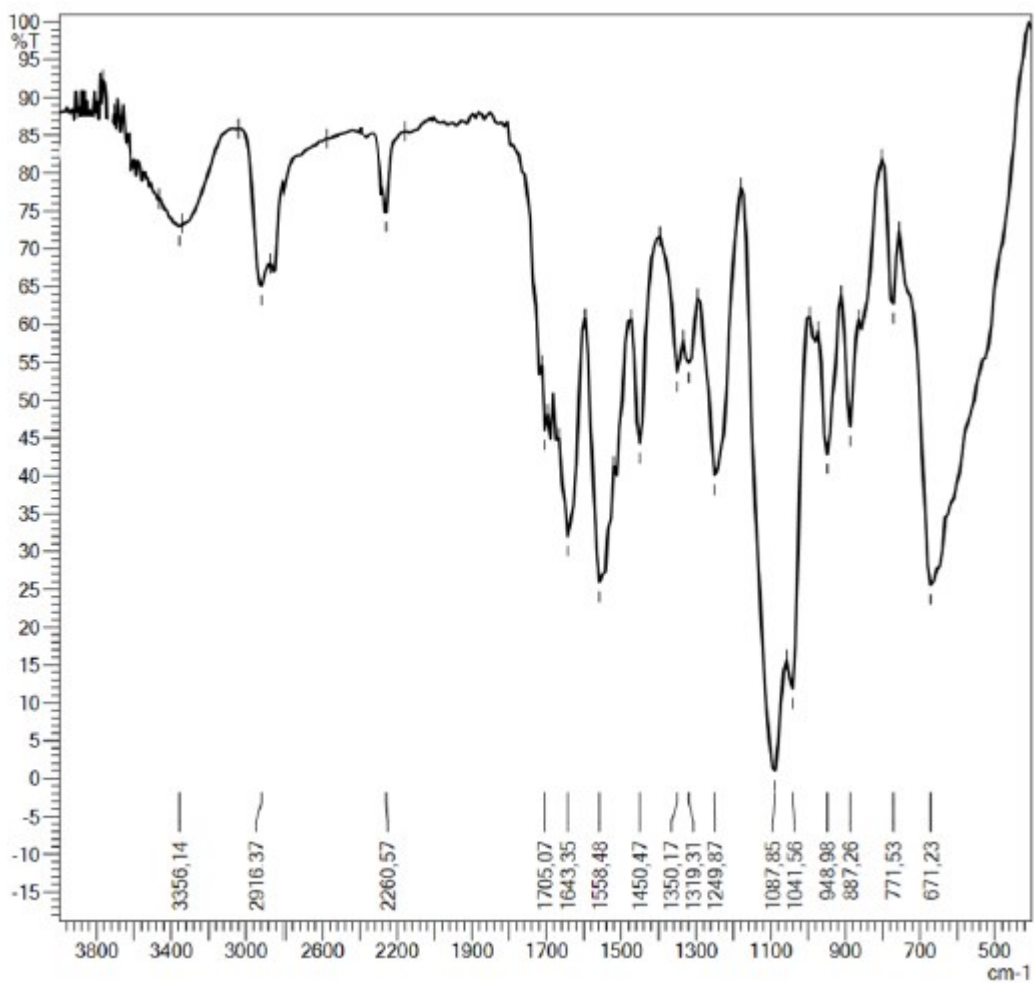
Group (stretching)	Absorption peak (cm ⁻¹)
Aliphatic C-H	2962
N=C=O	2260

FT-IR spectrum of PEG 400 (4)



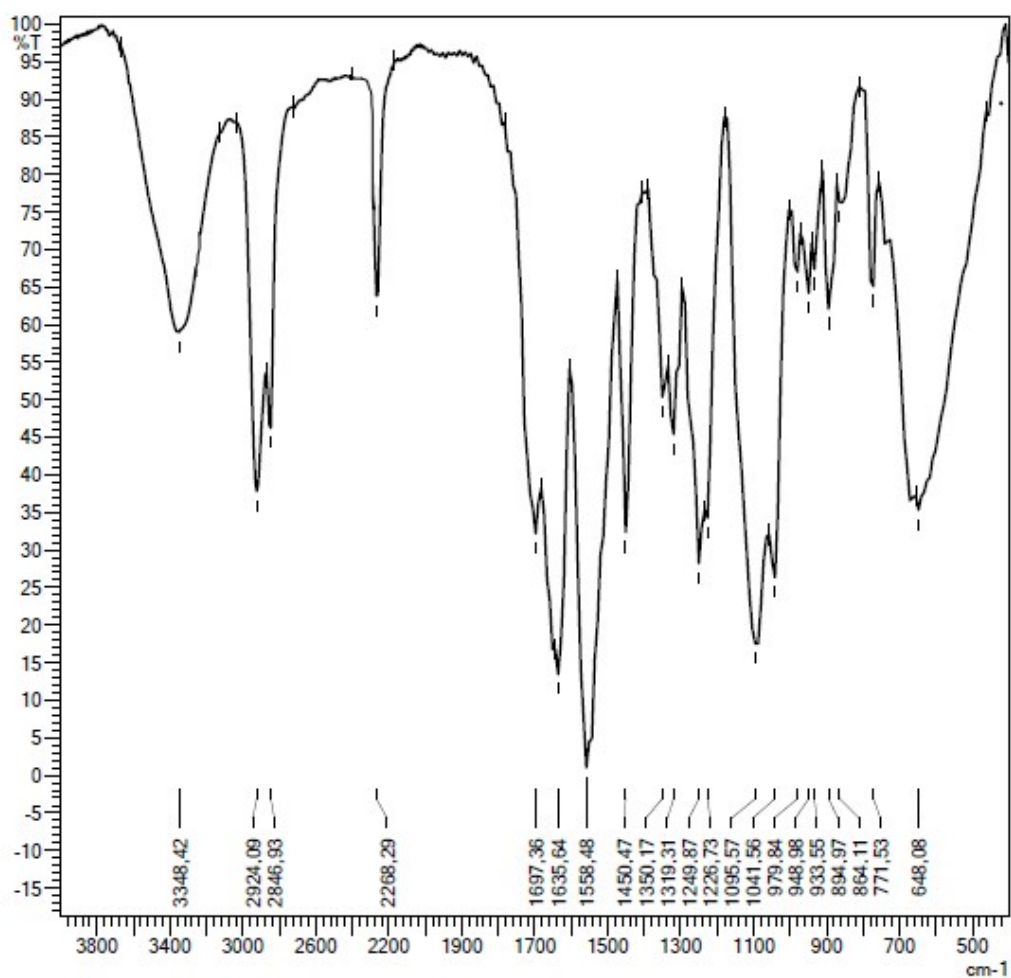
Group (stretching)	Absorption peak (cm ⁻¹)
O-H	3379
Aliphatic C-H	2870
C-O-C and C-O-H	1103

FT-IR spectrum of the prepolymer 7



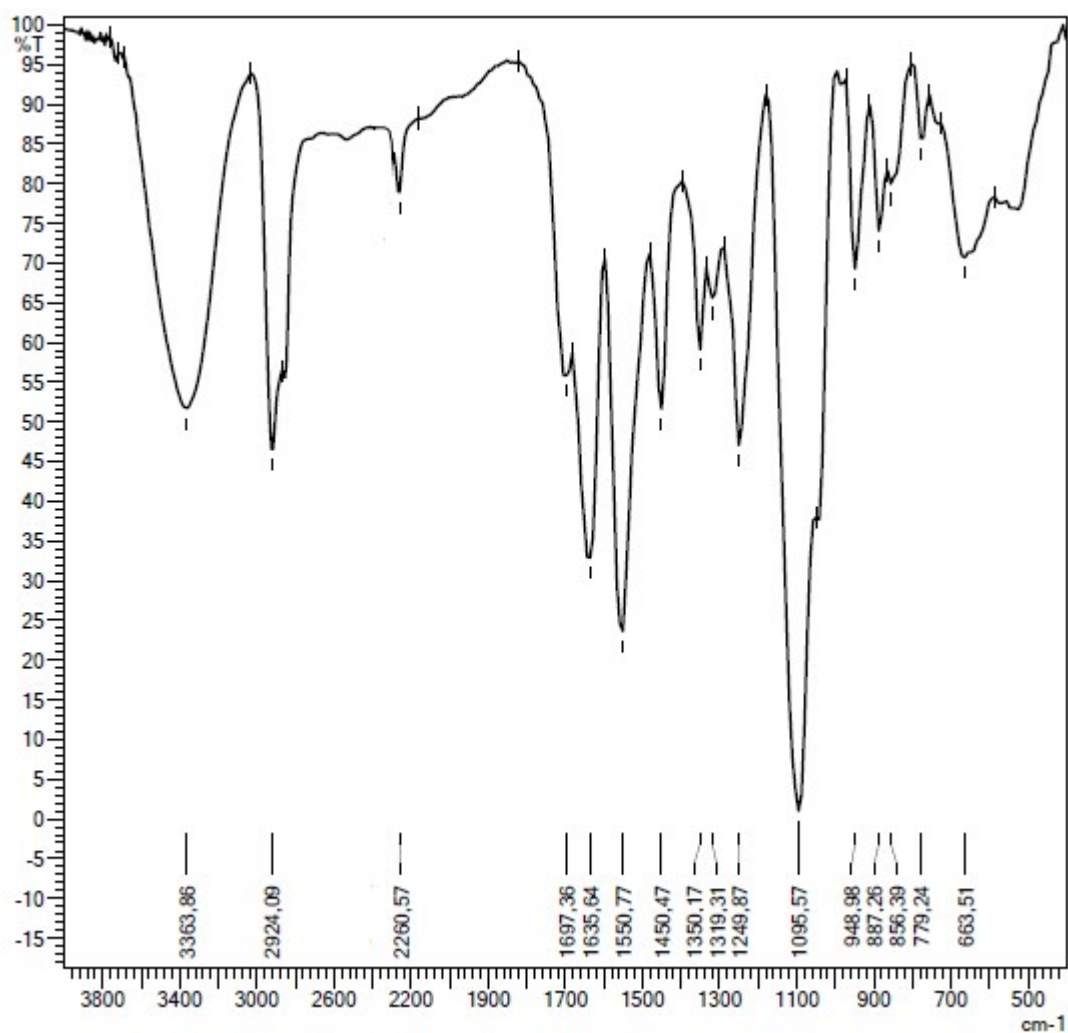
Group (stretching)	Absorption peak (cm ⁻¹)
N-H	3356
Aliphatic C-H	2916
N=C=O	2260
C=O (urethane)	1705
C=O (urea)	1643
CO-NH	1558
C-O	1249
C-O-C	1087

FT-IR spectrum of the prepolymer 8



Group (stretching)	Absorption peak (cm ⁻¹)
N-H	3348
Aliphatic C-H	2864-2924
N=C=O	2268
C=O (urethane)	1697
C=O (urea)	1635
CO-NH	1558
C-O	1249
C-O-C	1095

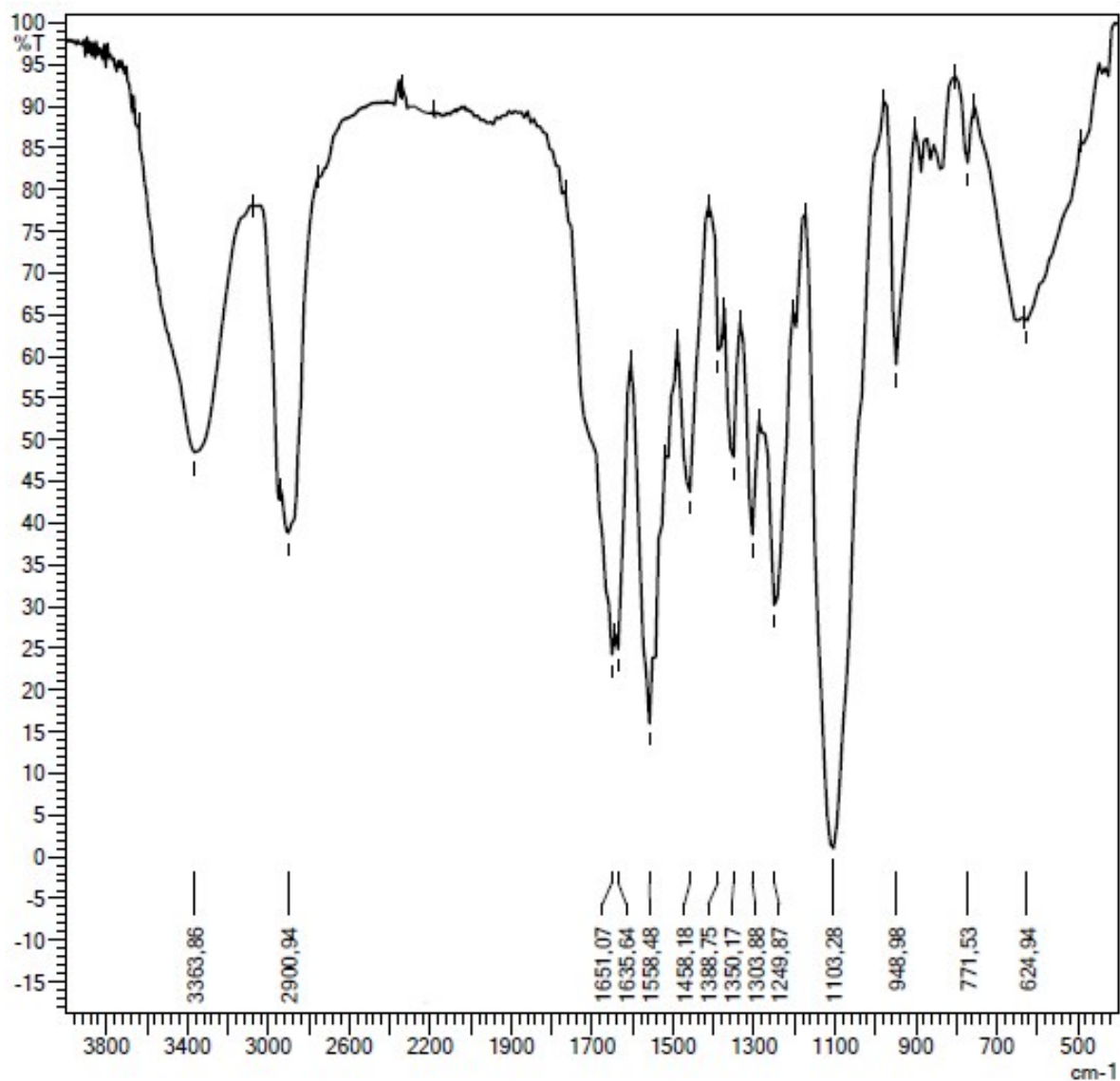
FT-IR spectrum of the prepolymer 9



Group (stretching)	Absorption peak (cm ⁻¹)
N-H	3363
Aliphatic C-H	2924
N=C=O	2260
C=O (urethane)	1697
C=O (urea)	1635
CO-NH	1550
C-O	1249
C-O-C	1095

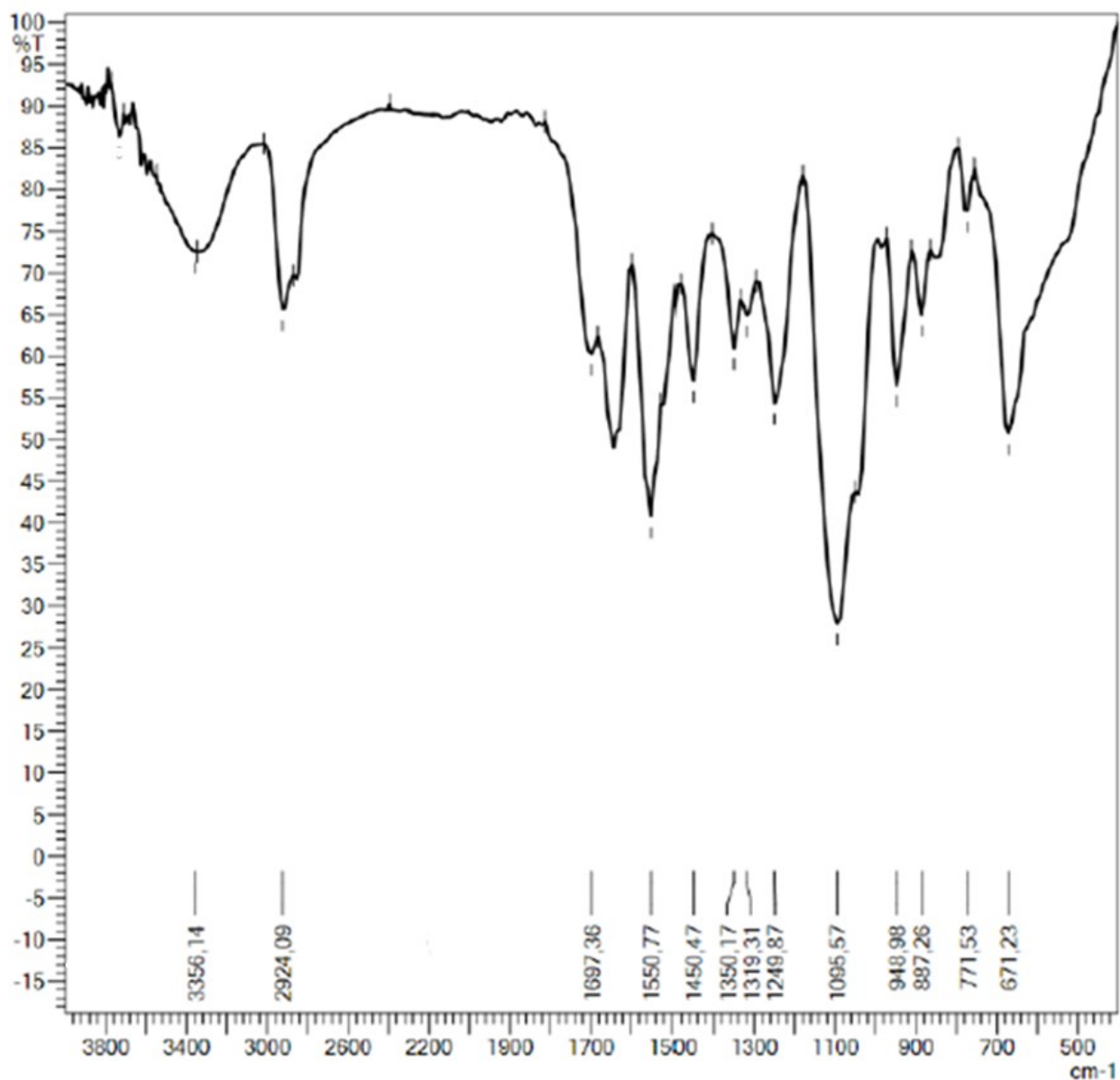
4. FT-IR spectra of polyurethanes extended with 1,2 ethylene glycol (10-12)

FT-IR spectrum of polyurethane 10



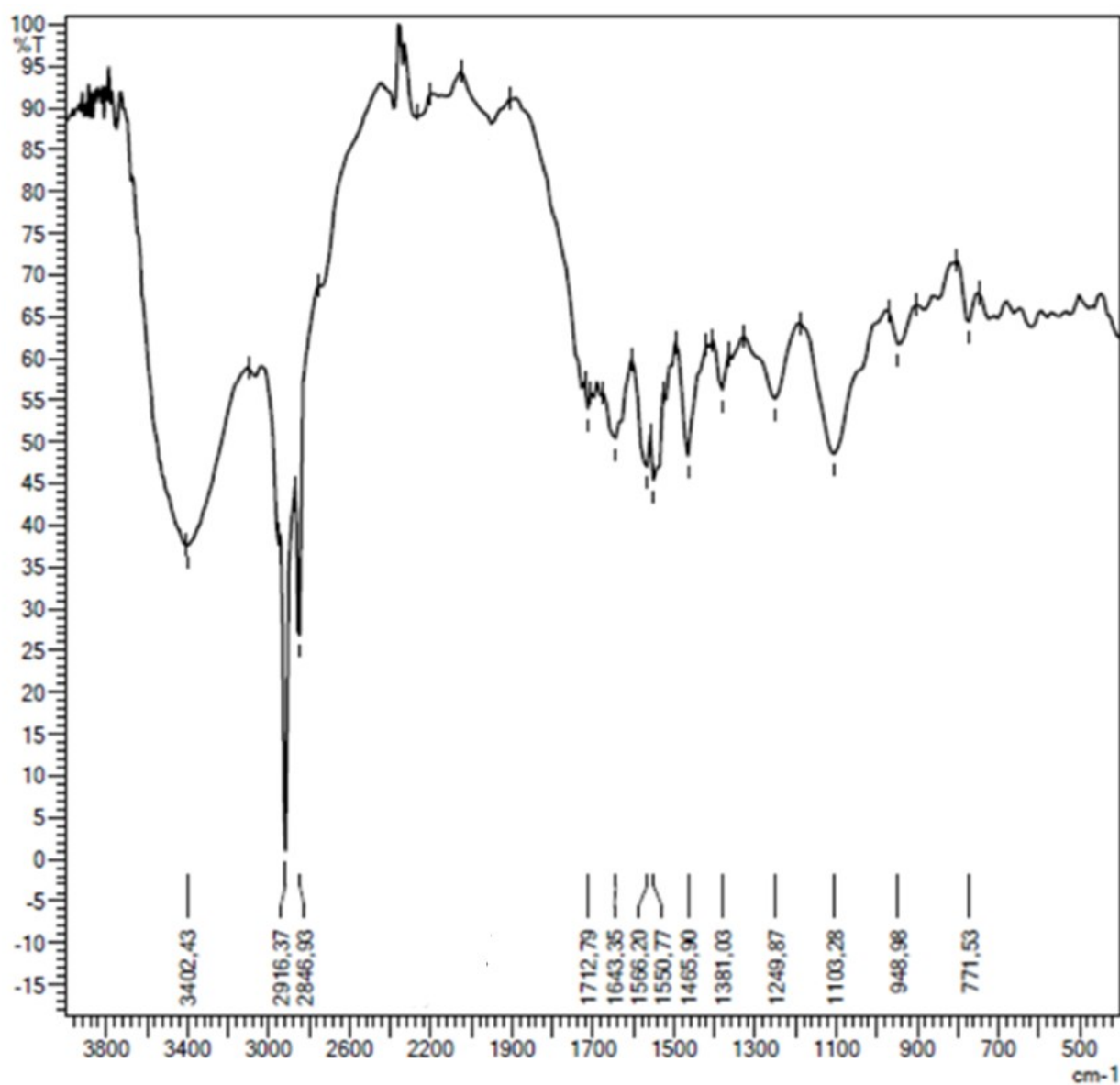
Group (stretching)	Absorption peak (cm ⁻¹)
N-H	3363
Aliphatic C-H	2900
N=C=O	2260
C=O (urethane)	1651
C=O (urea)	1635
CO-NH	1558
C-O	1249
C-O-C	1103

FT-IR spectrum of polyurethane 11



Group (stretching)	Absorption peak (cm ⁻¹)
N-H	3356
Aliphatic C-H	2924
C=O (urethane)	1697
C=O (urea)	1635
CO-NH	1550
C-O	1249
C-O-C	1095

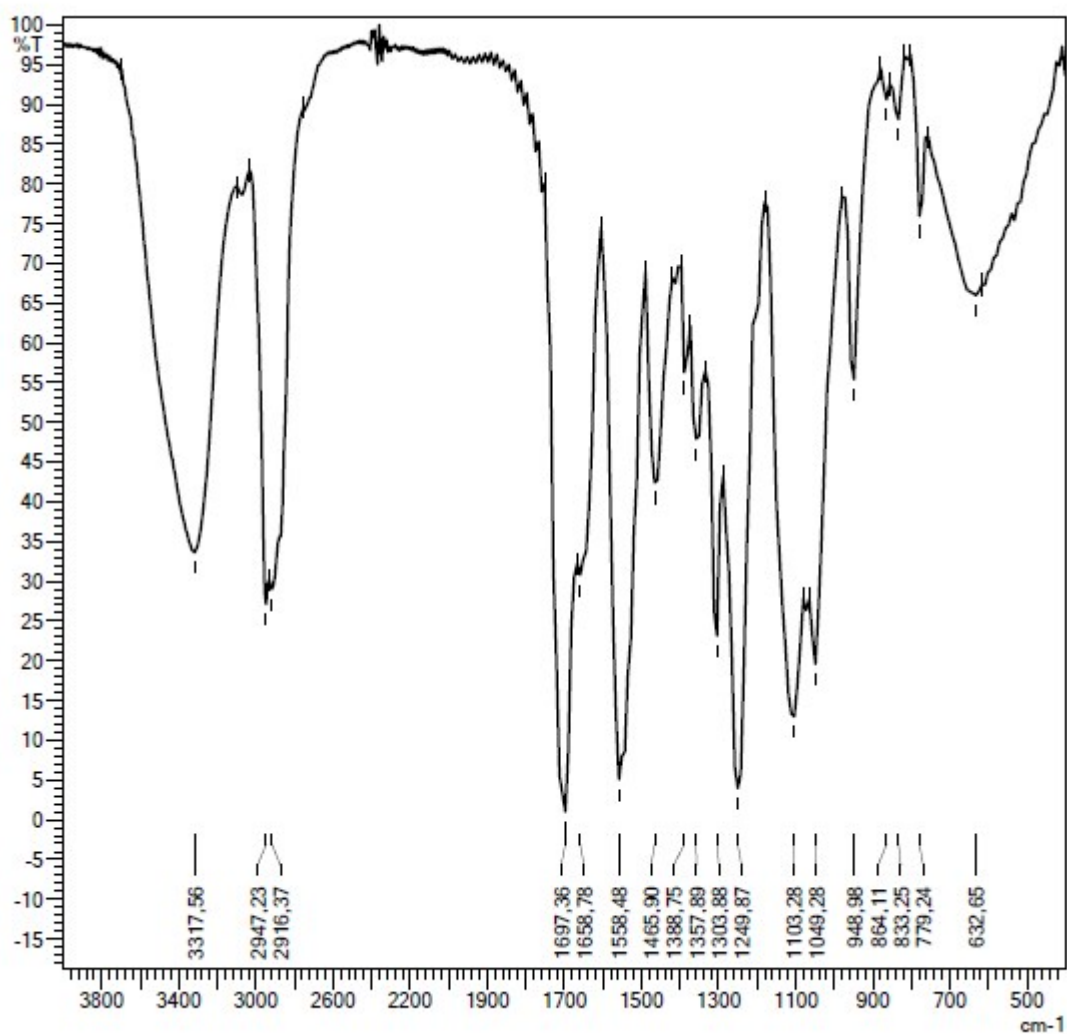
FT-IR spectrum of polyurethane 12



Group (stretching)	Absorption peak (cm ⁻¹)
N-H	3402
Aliphatic C-H	2846-2916
C=O (urethane)	1712
C=O (urea)	1643
CO-NH	1550
C-O	1249
C-O-C	1103

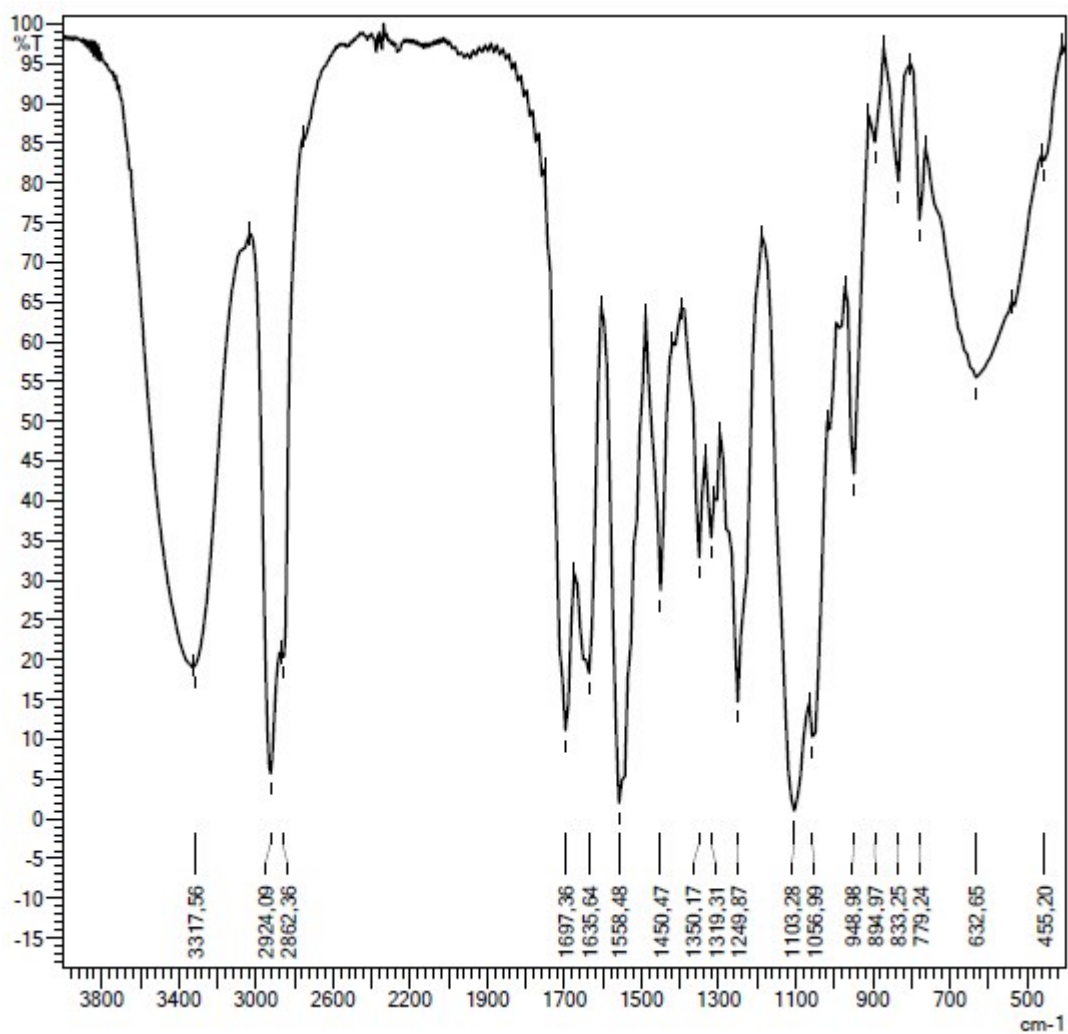
5. FT-IR spectra of polyurethanes extended with 1,4 butanediol (13-15)

FT-IR spectrum of polyurethane 13



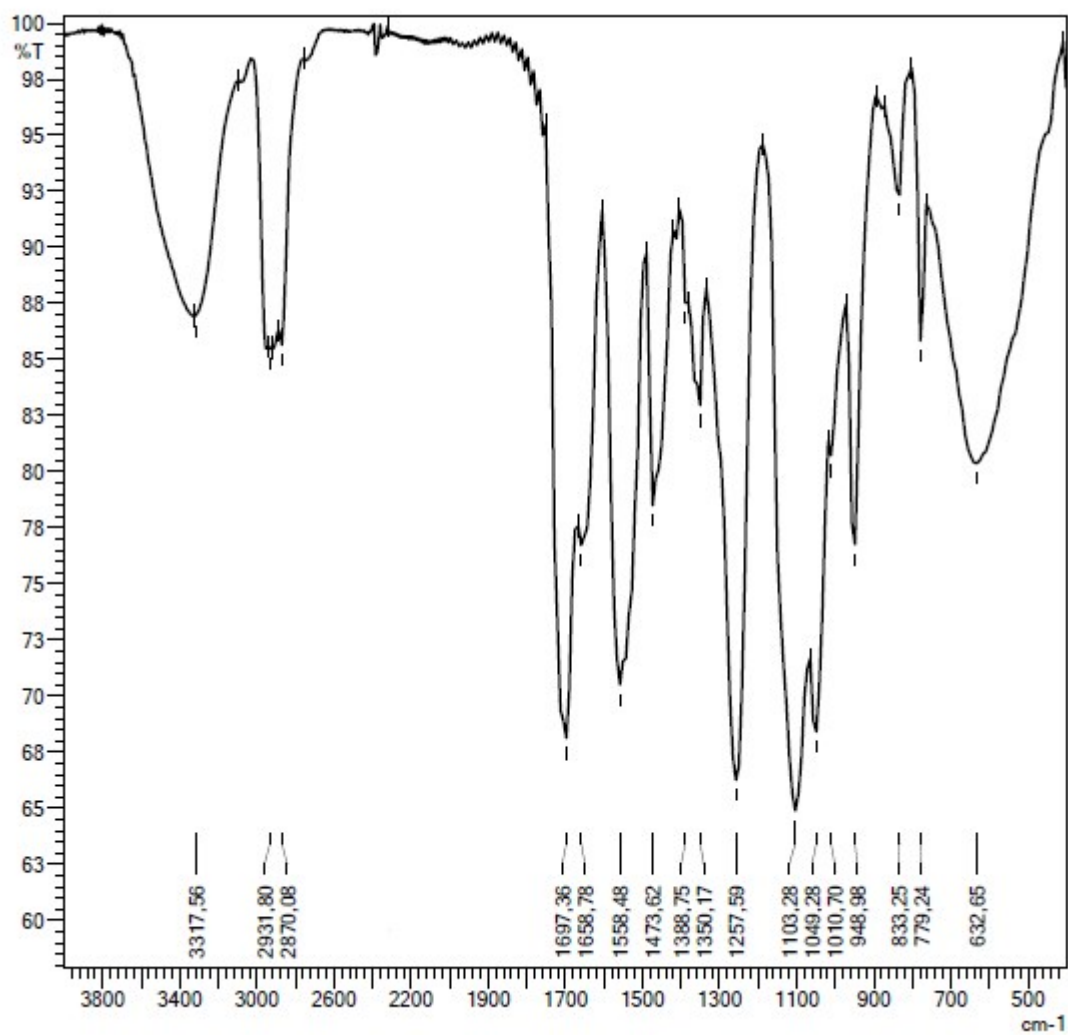
Group (stretching)	Absorption peak (cm ⁻¹)
N-H	3317
Aliphatic C-H	2916-2947
C=O (urethane)	1697
C=O (urea)	1658
CO-NH	1558
C-O	1249
C-O-C	1049-1103

FT-IR spectrum of polyurethane 14



Group (stretching)	Absorption peak (cm ⁻¹)
N-H	3317
Aliphatic C-H	2862-2924
C=O (urethane)	1697
C=O (urea)	1635
CO-NH	1558
C-O	1249
C-O-C	1056-1103

FT-IR spectrum of polyurethane 15



Group (stretching)	Absorption peak (cm ⁻¹)
N-H	3317
Aliphatic C-H	2870-2931
C=O (urethane)	1697
C=O (urea)	1658
CO-NH	1558
C-O	1257
C-O-C	1049-1103