Thesis for the Degree of Master of Engineering

Synthesis and properties of bio-based waterborne polyurethanes with 1,5-pentamethylene diisocyanate

by

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(1,5-pentamethylene diisocyanate을 이용한 바이오 기반 수분산 폴리우레탄의 합성 및 특성)

Advisor: Prof. Won-Ki Lee

by
Do Hyeok Lee

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이도혁

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요 약

최근 세계적으로 휘발성 유기화합물(VOCs) 사용 및 석유 기반 폴리올과 이소시아네이트 사용으로 발생되는 여러 가지 문제로 인해 신재생 에너지에 대한 관심이 증가하고 있으며, 바이오 산업에 대한 연구도 활발하게 증가하고 있다. 따라서, 현재 고분자 소재는 유용성과 더불어 환경에 대한 배려가 요구되고 있으며, 이러한 상황에 적합한 소재로서 바이오 매스를 이용한 바이오 고분자가 주목을 받고 있다.

본 연구에서는 친환경 폴리우레탄 접착제를 합성하기 위해 옥수수 전분을 추출하여 만든 바이오 기반 isosorbide carbonate diol 및 1,5-pentamethylene diisocyanate를 이용하였다. 바이오 기반 폴리올 및 이소시아네이트를 이용하여 합성한 친환경 폴리우레탄 접착제는 그 특성이 기존의 상용화된 접착제들에 비해 현저히 떨어졌다. 따라서, 오직 이소시아네이트만을 바이오 기반으로 하는 추가적인 실험을 진행하였고, 특성들이 향상된 접착제를 합성할 수 있었다. 합성한 바이오 폴리우레탄 접착제를 FT-IR 과 ^{1}H-NMR을 통해 합성 유무를 확인하였고, 분자량, 기계적 물성 및 접착 특성을 평가하였으며, DSC 및 TGA를 통해 열적 특성을 분석하였다.

사슬연장제의 함량에 따른 시험 결과, 분자량의 경우 사슬연장제의 함량이 작을수록 분자량이 높게 측정됐으며, 기계적 물성, 접착 특성 및 열적 특성은 사슬연장제의 함량이 증가할수록 대부분 같이 증가하는 것을 확인할 수 있었다. 하지만, 접착 특성의 경우 특정 r값 이후(r=1.3)에 오히려 그 특성이 감소하는 것을 확인할 수 있었다. 이러한 특성들 대부분은 가교밀도와 관련된 것으로 판단되어진다.

1. Introduction

Polyurethanes comprise a polymers containing a urethane (-NHCOO-) bond formed by the polymerization reaction between the -OH compound of a polyol and the -NCO compound of a diisocyanate. They are used in many fields such as architecture, automobiles, electronics, and adhesives. There are two main types of polyurethane adhesives: solvent-based polyurethane adhesives and water-based polyurethane adhesives. Conventionally, solvent-based polyurethane adhesives were mainly used because of their excellent adhesive properties and mechanical properties[1,2]. They have recently been replaced by water-based polyurethane adhesives because of restrictions on the use of volatile organic compounds (VOCs) owing to environmental regulations[3-5]. In addition, not only restrictions on the use of organic solvents, but also problems such as the spread of carcinogens and germ cell mutagenicity associated with the use of petroleum-based polyols and diisocyanates have led to research on more environmentally friendly biomass-derived polyurethane adhesives. Furthermore, biopolyols are already produced on a commercial scale.

Development of polyurethane adhesives using these biopolyols is ongoing. However, the development of polyurethane using bioisocyanate or biopolyol and bioisocyanate is progressing slowly[6-11].

Therefore, in this study, bio-based isosorbide carbonate diol and 1,5-pentamethylene diisocyanate were used together or only bio-based 1,5-pentamethylene diisocyanate was applied to new eco-friendly biopolyurethane adhesives (WPIPs) with varied monomer contents, which were compared based on their structural analysis, molecular weights, and thermal, mechanical, and adhesive properties.

2. Theoretical background

Due to population growth and industrial development, the demand for energy has been increasing constantly. Currently, oil and natural gas are the most frequently used energy resources. However, their supply is not infinite or stable, and they pose major issues such as global warming due to the emission of carbon dioxide[12]. To resolve these problems, various renewable energy technologies have been developed using biomass, one of the applications of which is in the field of adhesives[13].

2.1. Biomass

Biomass refers to parts of a plant that receive solar energy, a plant produced by photosynthesis undertaken by microorganisms, a microbial cell, and a biological organic matter including an object that eats and lives. Currently, all biomass on the earth comprise a mass of approximately 1.7 to 2 trillion tons, and approximately 200 billion tons of biomass equivalent to 10 % of the total is created every year. Bioenergy generated by converting biomass resources into energy is an alternative energy that can solve the crisis presented by depletion of fossil fuels such as gas, oil, and coal and serious environmental problems arising from the use of these resources. It has therefore been receiving great attention. Biomass can be roughly classified into five types, according to the types of raw materials used: (1) starch-based resources such as cereals and potatoes, (2) sugar-based resources including sugarcane and sugar beet, (3) cellulosic resources such as forest trees and straw, grass and rice husks, (4) animal protein-based resources such as livestock manure, microorganisms, and carcasses, and (5) food residue and paper oily waste resources obtained from these resources[14-16].

2.1.1. Biomass industry

The biomass industry is not only a necessity in the market, but also an industry in which research and development and commercialization are under way due to social, political, and environmental factors. The biomass industry has already seen commercialization, notable examples being the use of landfill gas or biodiesel. It is at the stage of research and development in terms of aspects such as the production of hydrogen from biomass or thermogas gasification. The success of the biomass industry depends on the price competitivenessof fossil fuels, such as oil, which is used as the primary energy source currently. Therefore, economic efficiency is affected by fluctuations in the oil prices. Starting with the first and second oil shocks, interest in biomass as an alternative energy resource has increased, and many economists generally find that if the price of oil is above $ 30 per barrel, biomass can offer sufficient price competitiveness. However, since the second oil shock, the price of oil has been stable for about 20 years, and research and development of alternative energy has thus been stagnant.

The biomass industry is an eco-friendly industry that does not increase the overall carbon dioxide production in the process of reforming raw materials for use as energy resources. Additionally, theoretically, all products created using petrochemistry can also be produced from biomass, so if technological progress is sufficient, the biomass industry can cause a great ripple effect in everyday life and the overall industry.

Therefore, the production of mixtures and biofuels such as bioethanol and biodiesel using biomass is being researched and for the development of renewable energy as the most economical and realistic alternative to fossil fuels for transportation[7-8].

2.1.2. Commercialization of biomass

Outside of this country, Dow and Cargill launched biopolyol products using soybean oil, and BASF announced a castor oil-based biopolyol. Bayer has also launched bio-polyols that use woody biomass in addition to existing natural fats and oils obtained from plants, and Maskimi has announced bio-polyol products based on palm oil. As for domestic developments, KTX chemical launched biopolyol products using castor oil, and Samyang manufactured and commercialized an isosorbide-based biopolyol using starch extracted from plant resources[13].

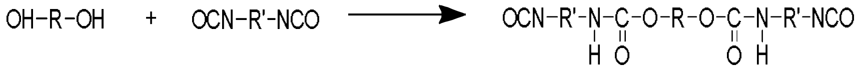
The development of bioisocyanates using biomass is more difficult to manufacture than biopolyols, and research and development in this context has not been active due to the difficulty of packaging existing physical properties.

2.2. Polyurethane

2.2.1. Summary

Polyurethane was first developed in 1849 by Germany's Hoffman and Wurtz, and in 1937 it was industrialized by Germany's Otto Bayer. Polyurethane is a polymer compound containing a certain number of urethane (-NHCOO-) bonds produced by the reaction of a polyol having an active hydrogen group (-OH) and a diisocyanate having an isocyanate group (-NCO). Here, the polyol and diisocyanate correspond to the soft and hard parts of polyurethane, respectively[17].

There are two main methods for producing polyurethane: the prepolymer method and the one-shot method[18]. In the case of the former, the reaction proceeds in two steps. First, polyisocyanate is excessively reacted to generate a prepolymer, and the generated prepolymer is extended to be synthesized. This method has the advantage that the soft and hard part of polyurethane can be adjusted, and it is generally used when the difference between the reaction rates of the polymeric glycol and isocyanate is large. In the case of the one-shot method, the reaction proceeds in one step, and the polymeric glycol, polyisocyanate and chain extender are reacted simultaneously. Because of the high convenience, this technique is used in most industries that require mass production.



$$\mathrm{OH{-}R{-}OH} + \mathrm{OCN{-}R'{-}NCO} \longrightarrow \mathrm{OCN{-}R'{-}}\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}{-}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{{-}O{-}R{-}O{-}}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}{-}\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}\mathrm{{-}R'{-}NCO}$$

1. Prepolymer

Polyol + Diisocyanate → Prepolymer --------> PU
↑
Chain extender

2. One-shot

Polyol + Diisocyanate ------------> PU

Figure 1. PU production process.

2.2.2. Polyol

A polyol is a polymer compound having two or more active alcohol groups (—OH) that can react with isocyanate to produce polyurethane. The two active hydrogen groups lead to the nomenclature of a “diol” or “glycol”. A glycol is a raw material for polyols. Polymeric glycol is a component of polyurethane and corresponds to the soft segment, which affects the flexibility and elasticity. Common polyols are classified as polyesters or polyethers, the characteristics of which are listed in Table 1 and Table 2[19-21].

The physical properties of polyurethane are determined according to the molecular weight of the polyol used. When a polyol having a low molecular weight is used, the concentration of urethane bonds increases in the chain, and the overall urethane chain length is shortened to form a hard segment. When a high-molecular-weight polyol is used, the concentration of urethane bonds in the chain is lowered, and the overall urethane chain length increases to form a more soft segment compared to that formed when a low-molecular-weight polyol is used[22].

Polyols are used in various applications depending on their molecular weights. Low-molecular-weight polyols such as butanediol, glycerine, ethylene glycol, and trimethylol propane are used as crosslinking agents and chain extenders. High-molecular-weight polyols with an average molecular weight of up to 8000 are used in the production of PU for varied applications[23].

Table 1. Types of polyols

Polyol type	종류
Polyether Polyol	PPG (Polypropylene Glycol) Modified PPG PTMG
Polyester Polyol	Polyester Polyol (Adipate) Polyester Polyol (Lactone)
others	polycarbonate Polyol Polybutandiene Polyol Acryl Polyol Flame resisting Polyol

Table 2. Characteristics of various polyols

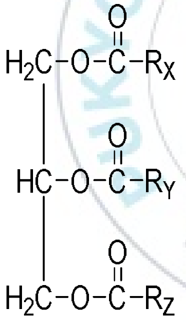
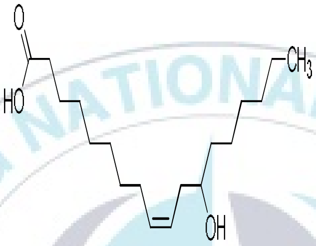
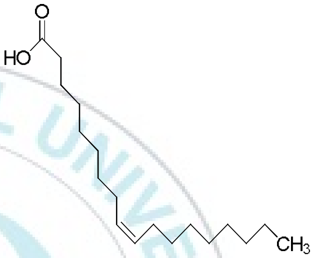
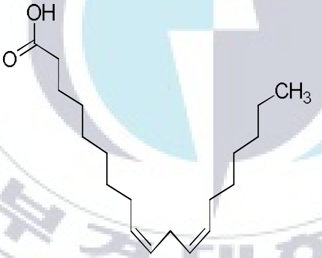
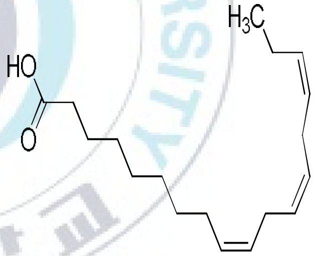
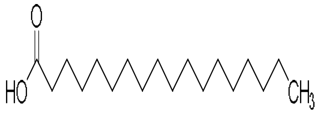
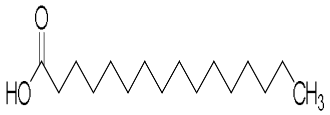
Polyol type	Advantages	Disadvantages
Polyether	flexibility hydrolytic stability solvent resistance low cost low available molecular-wieght	low energy surface → poor adhesion poor weatherproof (≒ polyester) poor toughness (≒ polyester or polycarbonate) physical properties (≪ polyester)
Polyester	toughness abrasion resistance low available molecular-wieght	poor hydrolytic stability low solvent resistnace high cost (≫ polyether)
Polycarbonate	flexibility hydrolytic stability abrasion resistance	high cost soluble

2.2.2.1. Biopolyol

Currently, research is underway to replace many petroleum-based POs and EOs used in most industries with biopolyols. Polyurethanes using biopolyols have the advantage that biomass-derived eco-friendly monomers can be used up to about 70% (w/w) in terms of dry weight. Biopolyols can be produced using vegetable natural oils and fatty lignin and woody biomass such as cellulose and waste glycerol.

Castor oil, rapeseed oil, soybean oil and the like are used as natural vegetable oils. The natural fat of such substances is composed of a triglyceride structure in which three fatty acids are bound to a glycerol molecule. Castor oil was developed as a biopolyol prior to other vegetable natural oils, and polyurethane synthesis using it has also been attempted. The reason is that ricinoleic acid, the main component of castor oil, already contains hydroxyl groups (-OH), and there are about 2.7 hydroxyl groups per molecule of triglyceride[14]. Since the hydroxyl groups of castor oil are distributed throughout the triglyceride molecules, it is possible to synthesize a polyurethane that can form a crosslinked structure and has good mechanical properties. Table 3 below mentions a few typical fatty acids that make up triglycerides.

Table 3. Triglyceride and the type of fatty acids

Triglyceride	Fatty acid	
	Ricinoleic 	Oleic 
	Linoleic 	Linolenic 
	Stearic 	Palmitic 

2.2.2.2. Manufacture of biopolyols

In the manufacture of biopolyols, in order to use most vegetable natural oils that do not contain ricinoleic acid as biopolyols, the step of adding a hydroxyl group must be performed. Most vegetable oil-based biopolyols are manufactured through a process using epoxidation/ring opening (Figure 2). In the first step, epoxidation is facilitated by producing peracid using hydrogen peroxide and acetic acid or formic acid at the carbon double bond of natural vegetable fats and oils. When using this method, the epoxidation can achieve a yield of about 75 − 90 % [24]. In the next step, several proton donors are used for the epoxide ring-opening reaction, but alcohol is mainly used as the proton donor. Various alcohols such as n-butanol and n-propanol can be used, but methanol is preferred because of its low price, molecular weight and boiling point, and fluoroboric acid is commonly used as a catalyst[25]. The hydroxyl group produced through epoxidation is a secondary alcohol. This process suffers from the disadvantage of its reactivity with isocyanate being lower than that achieved when a primary alcohol is used. However, it is currently the most preferred method because of its relative simplicity and the high price competitiveness it offers[26]. The polyol synthesized by epoxidation and castor oil containing the original hydroxyl group are composed of secondary alcohols, which need to be modified to primary alcohols with good reactivity with isocyanates. In this modification method, a transesterification is involved: a biopolyol can be produced by transesterifying a vegetable natural oil with various polyols[27,28].

In this study, bio-based isosorbide carbonate diol (ICD-44220) was used with isosorbide. Isosorbide is a non-toxic, environmentally friendly and renewable biomaterial that provides high stiffness and improved thermal stability.

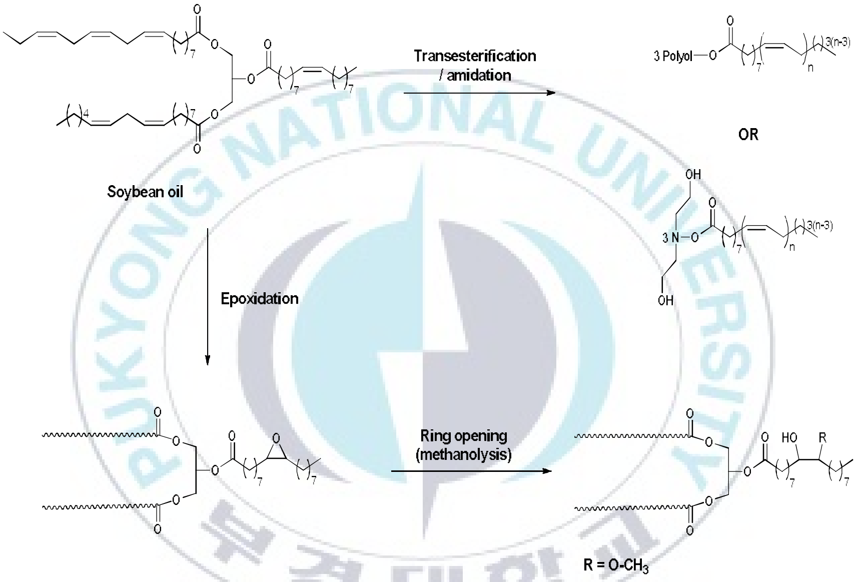


Figure 2. Preparation of biopolyols from soybean oil by epoxidation/methanolysis, transesterification of amidation.

2.2.3. Isocyanate

Isocyanate is a compound having an isocyanate group (—NCO) and has at least two or more isocyanate groups capable of reacting with species such as a polyol, a chain extender, a crosslinking agent, and water. In general, isocyanates used for polyurethane synthesis form the hard segment part and are roughly divided into aromatic and aliphatic isocyanates[18].

Typical aromatic isocyanates include MDI, TDI, etc., which form a chromophore depending on the structure of the benzene component and easily cause yellowing, resulting in lower stability to light than aliphatic isocyanates. Therefore, compounds using aromatic isocyanate are used after coloring with other additives or are used in polyurethane products that have not been exposed to light and do not significantly affect the value of the product even if yellowing occurs.

Typical aliphatic isocyanates include HDI, H12MDI, TMXDI, and IPDI, which exhibit excellent light stability and can be applied even in cases of extensive exposure to discoloration such as in paints and coatings. The advantages and disadvantages of several isocyanates and some characteristics are listed in Table 4.

Table 4. Characteristics of various isocyanates

Isocyanate type	Material	characters
Aromatic	TDI (2,4-toluene-diisocyanate)	First commercialization low cost toxicity have an aromatic ring good heat-resistance good strength yellowing by light → not used exteriorly
	MDI (4,4′-di-phenyl-methane-diisocyanate)	good reactivity have an aromatic ring good heat-resistance good strength yellowing by light → not used exteriorly
	XDI (xylene-di-isocyanate)	have an aromatic ring since the isocyanate is not directly bonded to the aromatic ring, it have a non-yellowing
Aliphatic	IPDI (isophorone-di-isocyanate)	have an aliphatic ring low reactivity high cost non-yellowing
	HDI (hexa-methylene-di-isocyanate)	good reactivity high cost low heat-resistance non-yellowing

2.2.3.1. Bioisocyanate

Bioisocyanate can be produced using natural oils and fats of plants, woody biomass such as lignin and cellulose, waste glycerol, etc., similar to biopolyols. Currently, not many reports are available on the production of poly or diisocyanates using biomass, but the production of biodiisocyanates based on vegetable natural oils is currently the the most commercially utilized. Isocyanates used in the industry are aromatic such as 2,4-toluene diisocyanate, 4,4′ -diphenylmethane diisocyanate, while plant oil-based isocyanates are essentially aliphatic compounds. When producing a polyurethane foam, very high reactivity is required, but aliphatic diisocyanate has the disadvantage that it is less reactive than aromatic diisocyanate. As for application, polyurethanes utilizing aliphatic diisocyanates are mostly used for coatings. However, when an isocyanate is synthesized using the lignin of woody biomass, it is possible to synthesize an aromatic diisocyanate that could not be synthesized with plant natural fats and oils. If research on isocyanate synthesis using lignin is actively promoted, the issue of conventional biomass-derived isocyanates being limited to aliphatic isocyanates can be overcome[29].

2.2.3.2. Manufacture of bioisocyanate

Industrially petroleum-derived isocyanates are made by the phosgenation of primary amines. Vegetable natural oils do not readily undergo this reaction, so other methods of introducing isocyanates are needed. In the most commercially applicable method, isocyanate is introduced to the triglyceride through a reaction empolying N-bromosuccinimide and AgNCO. First, if triglyceride reacts with N-bromosuccinimide, the aryl group is modified with the highly reactive bromine. Then, when reacted with AgNCO, it is converted to triglyceride containing the isocyanate group (Figure 5). This reaction produces about 2.1 isocyanate groups per triglyceride. This process has the disadvantage that the cost incurred is very high due to the use of AgNCO, but it has the advantages that the nitrogen of isocyanate combined with silver has a higher reactivity than that of oxygen and that the silver used can be reused (Figure 3)[30].

In this study, bio-based 1,5-pentamethylene diisocyanate (PDI) was used as the bioisocyanate. PDI has a biomass content of 60 % or more and a high NCO content as well as excellent solvent and weather resistance; furthermore, it does not turn yellow.

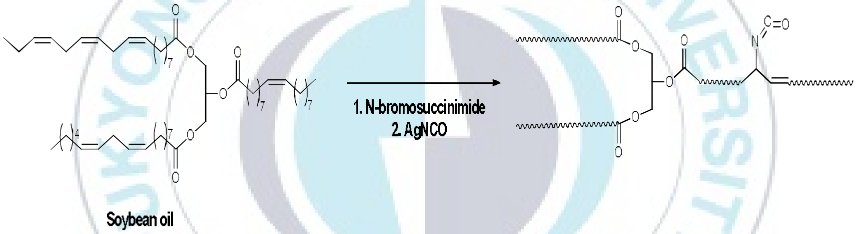


Figure 3. Preparation of linear diisocyanates from vegetable oil using AgNCO.

3. Experimental

3.1. Materials

Bio-based isosorbide carbonate diol (ICD-44220, Mw = 2372.09 g/mol, Samyang, Korea) and poly(tetramethylene adipate)glycol (DT-2040, Mw = 2000 g/mol, Dewon, Korea) were dried at 85 ℃ under 0.1 mmHg for several hours until no bubbling was observed. Bio-based 1,5-pentamethylene diisocyanate (STABiO^{TM}PDI, Mitsui Chemical, Japan) was used as isocyanate. Dimethylol propionic acid (DMPA, Aldrich Chemical, USA) was dried in vacuum oven at 100 ℃ for 4 h. 1,6-hexanediol (1,6-HD, TCI, Japan), ethylene diamine (EDA, Aldrich Chemical, USA) were used as chain extender. Dibutyltin dilaurate (DBTDL, Aldrich Chemical, USA) was used as catalyst. Triethylamine (TEA, Aldrich Chemical, USA) was used as neutralizer. Methyl ethyl ketone (MEK, Samchun Chemical, Korea), acetone (Samchun Chemical, Korea), n-n-dimethylacetamide (DMAc, Aldrich Chemical, USA) were used as solvents without purification.

3.2. Synthesis of waterborne polyurethane using bio-based isosorbide carbonate diol and 1,5-pentamethylen diisocyanate (WPIP)

Isosorbide carbonate diol or poly(tetramethylene adipate)glycol and dimethylol propionic acid (DMPA) were placed in a 500 ml four-neck and round-bottom flask equipped with a nitrogen inlet, a mechanical stirrer, a dropping funnel and reflux condenser, and then uniformly mixed at 80 ℃ for 1 h using an oil bath. Thereafter, dimethylol propionic acid (DMAc), which is a polar solvent, was added and stirred for about 30 min to lower the initial high viscosity of the mixture so that DMPA was uniformly dispersed in the mixture. After, dibutyltin dilaurate (DBTDL) was added under a nitrogen atmosphere, and then dropping PDI for 1 h, the reaction was continued for about 3 h. The NCO content of the reaction mixture was continuously confirmed FT-IR, the viscosity of the reaction product was adjusted methyl ethyl ketone (MEK) while the reaction proceeded, and finally NCO-terminated prepolymer was synthesized. And, triethylamine (TEA) diluted with acetone was added to the produced prepolymer, and a neutralization reaction was performed at 35 ℃ for about 1 h. At the room temperature, distilled water (about 90 wt%) was added into the mixture with stirring (over 600 rpm). Finally, ethylene diamine (EDA) was diluted with distilled water and dropped to perform chain extension reaction. Table 5 lists the sample designation and composition of WPIP. And, Figure 4 shows synthesis mechanism of WPIP.

Table 5. Sample designations and compositions for synthesis of waterborne polyurethane using bio-based isosorbide carbonate diol and 1,5-pentamethylene diisocyanate (WPIP)

Sample	Compositions of raw materials								Ratio of NCO/OH	Soft segment (%)
	Isosorbide carbonate diol	Poly(tetramethylene adipate)glycol	TMP	1,6-HD	PDI	DMPA	TEA	EDA		
	(mole ratio)									
I-P1	0.350	-	-	-	1.100	0.650	0.650	0.100	1.1	71.65
I-P2	0.350	-	-	-	1.200	0.650	0.650	0.200	1.2	70.35
I-P3	0.350	-	-	-	1.300	0.650	0.650	0.300	1.3	69.10
I-P4	0.350	-	-	-	1.400	0.650	0.650	0.400	1.4	67.89
I-PT1	0.280	-	0.070	-	1.300	0.650	0.650	0.300	1.3	63.76
I-PT2	0.300	-	0.200	-	1.300	0.500	0.500	0.300	1.3	66.78
D-P1	-	0.369	-	0.461	1.100	0.170	0.170	0.100	1.1	73.20
D-P2	-	0.369	-	0.461	1.200	0.170	0.170	0.200	1.2	71.70
D-P3	-	0.369	-	0.461	1.300	0.170	0.170	0.300	1.3	70.30
D-P4	-	0.369	-	0.461	1.400	0.170	0.170	0.400	1.4	68.90

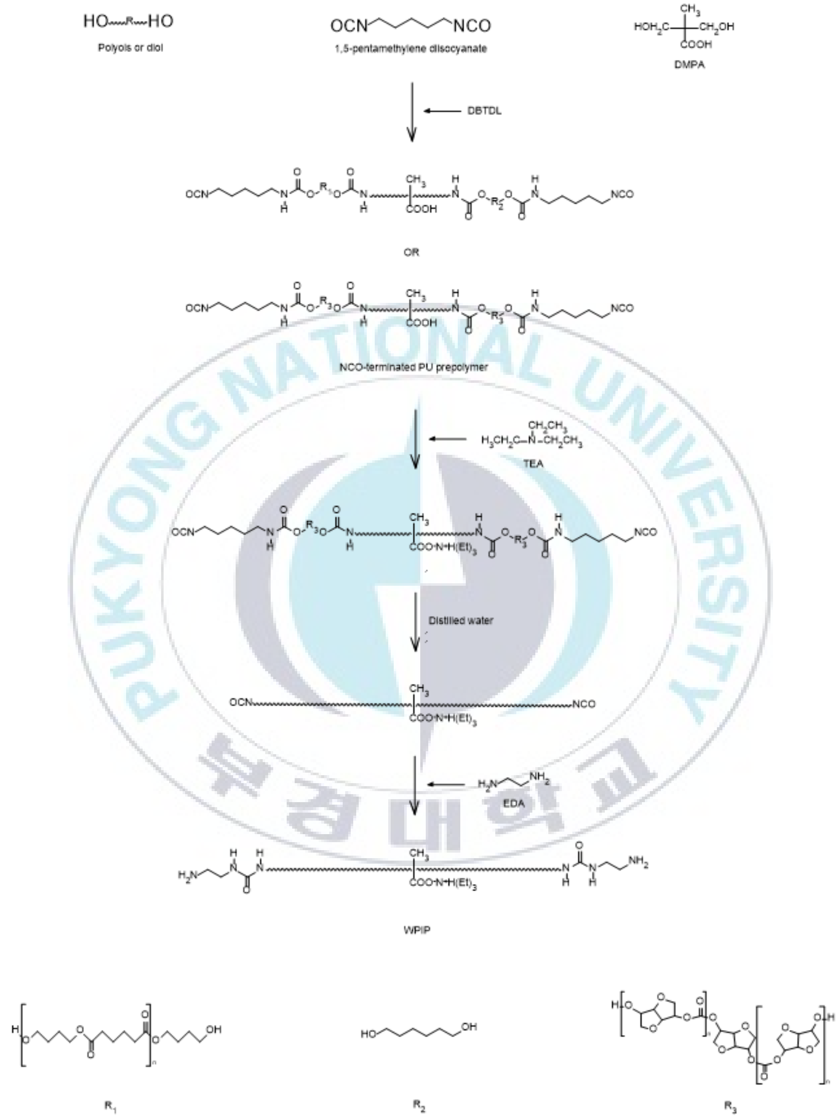


Figure 4. Synthetic process of WPIP.

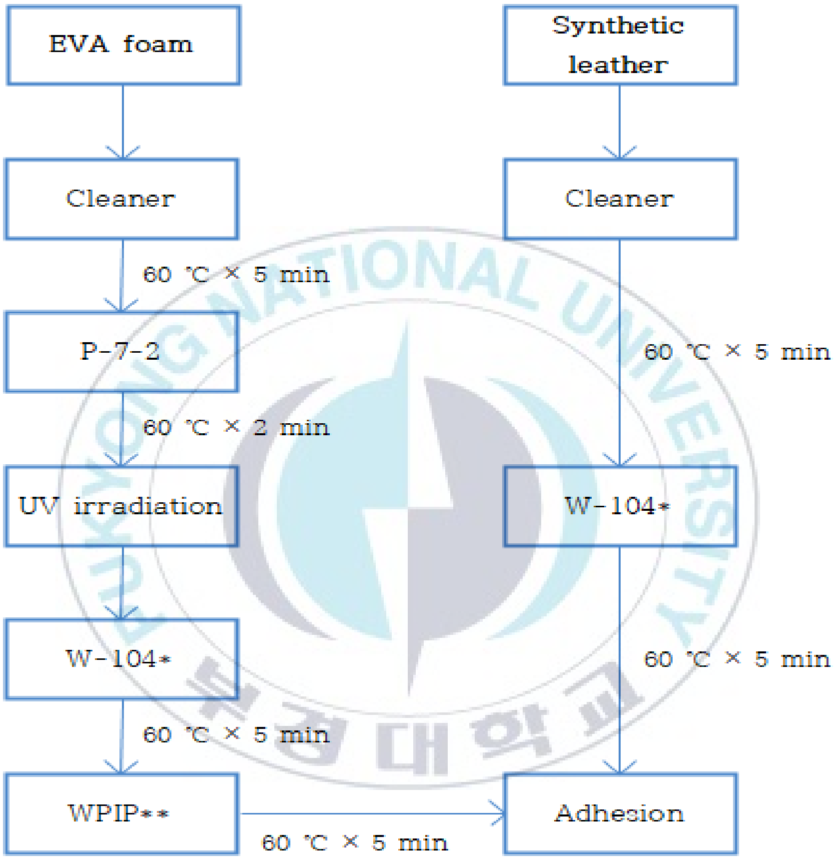
3.3. Formulation of adhesives for footwear

Footwear adhesives were formulated from WPIP emulsions, a hardener and a thickener. An appropriate amount of WPIP emulsion was mixed with the hardener (ARF-40, 5.0 wt% of WPIP) and the thickener (UH-420, 1 wt% of WPIP) to obtain a homogeneous mixture at room temperature.

3.4. Process of adhesion between midsole (EVA) and upper (synthetic leather)

The steps required to bond the upper (synthetic leather) to the midsole (EVA) follows : MEK was used as cleaner onto EVA and synthetic leather, and then dried at 60 ℃ for 5 min. UV primer (P-7-2) was coated onto EVA, and then dried at 60 ℃ for 2 min followed by UV-cured. Mixture of hardener (ARF-40, 5.0 wt% of W-104)/primer (W-104) was coated onto both the UV primer treated EVA and synthetic leather, and then dried at 60 ℃ for 5 min. Formulated adhesive was brushed onto EVA and synthetic leather surface by hand, and allowed to dry at 60 ℃ for 5 min.

Two surfaces (midsole and upper surfaces) were brought into contact, and pressed 2 times using roller, and then finally dried at room temperature for 30 min and 24 h.



*hardener (ARF-40) 5 wt%
**hardener (ARF-40) 5 wt%, thickener (UH-420) 1 wt%

Figure 5. Schematic diagram of the adhesion process.

3.5. Characterization

3.5.1. Structural analysis

3.5.1.1. Fourier transform infrared (FT-IR) spectroscopy

In order to characterize the synthesized WPIP, fourier transform infrared spectroscopy (FT-IR) analysis was performed using NICOLET iS10 spectrometer in the range between 4000 and 400 cm^{-1} at ambient temperature.

3.5.1.2. Nuclear magnetic resonance (^1H-NMR) spectroscopy

In order to characterized the synthesized WPIP, nuclear magnetic resonance spectra (^1H-NMR) were recorded on a 600 MHz Agilent superconducting FT-NMR spectrometer system using deuterated chloroform ($CDCl_3$) as solvent.

3.5.2. Molecular weight

In order to measure molecular weight and polydispersity of the synthesized WPIP, gel permeation chromatography (GPC) was performed using Alliance e2695 (Waters). As analysis conditions, tetrahydrofuran (THF) was used as a solvent, and Waters Styragel HR3, Waters Styragel HR4 and Waters Styragel HR5E were used for the column, and analysis was performed at 35 ℃ at a flow rate of 1 ml/min.

3.5.3. Mechanical properties

The test pieces were manufactured based on ASTM D638 to measure the physical properties of the synthesized polyurethane, the tensile strength and elongation were measured by using Universial testing machine (UTM, model : DTU-900, PED Korea). The test pieces were dried in an oven at 60 ℃ for 4 h after film production, and then aged at room temperature for 24 h. Thereafter, it was cut into a dumbbell shape (length/width: 2.0/0.5 cm), which is the standard for tensile strength test pieces, and measured at room temperature as a condition of a cross-head speed of 500 mm/min.

3.5.4. Thermal properties

3.5.4.1. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) measurement of the WPIP film was performed using Q-100 (TA instrument). Samples of 10 mg were cut from the films and used for analysis. The samples were heated from -90 ℃ to 100 ℃ at a heating rate of 10 ℃/min. The glass transition temperature (Tg) of the samples was determined from the midpoint temperature in the heat capacity change of the DSC curve.

3.5.4.2. Thermogravimetric analysis (TGA)

In order to observe the thermogravimetric change of the synthesized WPIP, it was measured using TGA Q-500 (TA instrument). Film samples of 10 mg were in aluminium pan and heated from room temperature to 600 ℃, at a heating rate of 10 ℃/min, under N_2 . During the heating period, the temperature difference and weight loss were recorded as a function of temperature.

3.5.5. Adhesive property

The adhesive strength of dry-samples (width/length: 2/10 cm) dried for 30 min and 24 h at room temperature and wet-samples (24 h dried samples soaked in water for 48 h at room temperature) were measured by using Universial testing machine (UTM, model : LT2100C, Labtron co.) operated at a crosshead speed of 150 mm/min according to T-peel test. The quoted are the average of three measurements.

4. Results and Discussion

4.1. Structural analysis

4.1.1. Fourier transform infrared (FT-IR) spectroscopy

The results of Fourier transform infrared (FT-IR) spectroscopy confirming the structure of the two types of polyols used in the synthesis, the structure obtained in each step of the synthesis, and the final WPIP are shown in Figures 6-8.

In Figure 6, (a) and (b) show the FT-IR spectra of the WPIP produced using poly(tetramethylene adipate)glycol (DT-2040) and isosorbide carbonate diol (ICD), respectively. In general, a broad OH peak at around 3500 cm^{-1} and a C=O peak of 1740 cm^{-1} can be observed. The difference is that, in the case of ICD, the two peaks at around 2800-2900 cm^{-1} are broader than those of DT-2040.

Figure 7 shows a step FT-IR spectrum of the WPIP synthesized using ICD as the polyol. (a) represents the step in which ICD and DMPA were stirred, (b) represents the step immediately after isocyanate and DBTDL are added, (c) represents the a step in which the final prepolymer was synthesized, and (d) represents the step after the addition of EDA as a chain extender. It was confirmed that a urethane group was formed by the COO peak at 1700 cm^{-1}, a decrease in the NCO peak at 2275 cm^{-1}, a decrease in the OH peak at around 3500 cm^{-1}, and N-H stretching vibration peaks close to 3200 cm^{-1} and 1500 cm^{-1}[31].

Figure 8 shows the FT-IR spectrum of the final WPIP product synthesized on DT-2040 and ICD. The spectrum demonstrates that the WPIP synthesized contained urethane bonds, as NCO peaks at 2275 cm^{-1} disappeared completely after the chain extension reaction.

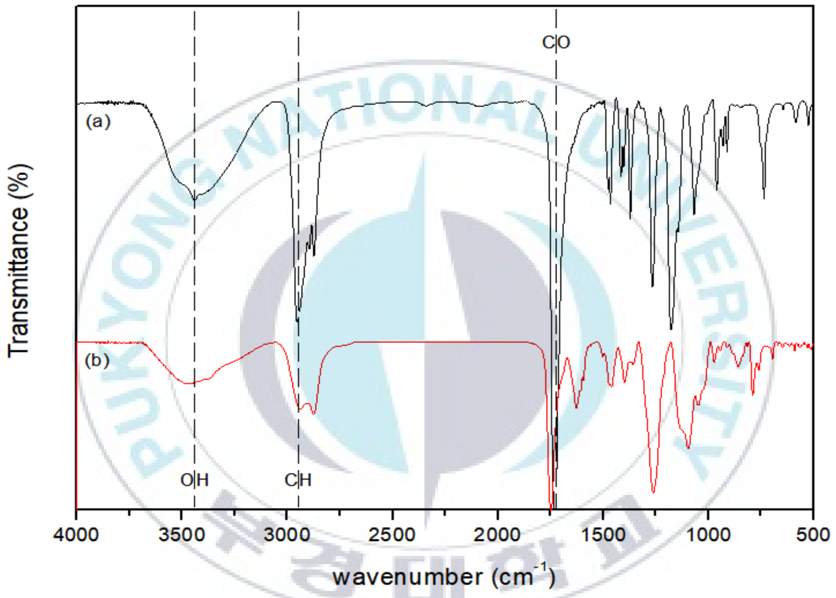


Figure 6. FT-IR spectra of WPIP.

(a) WPIP using poly(tetramethylene adipate)glycol

(b) WPIP using isosorbide carbonate diol

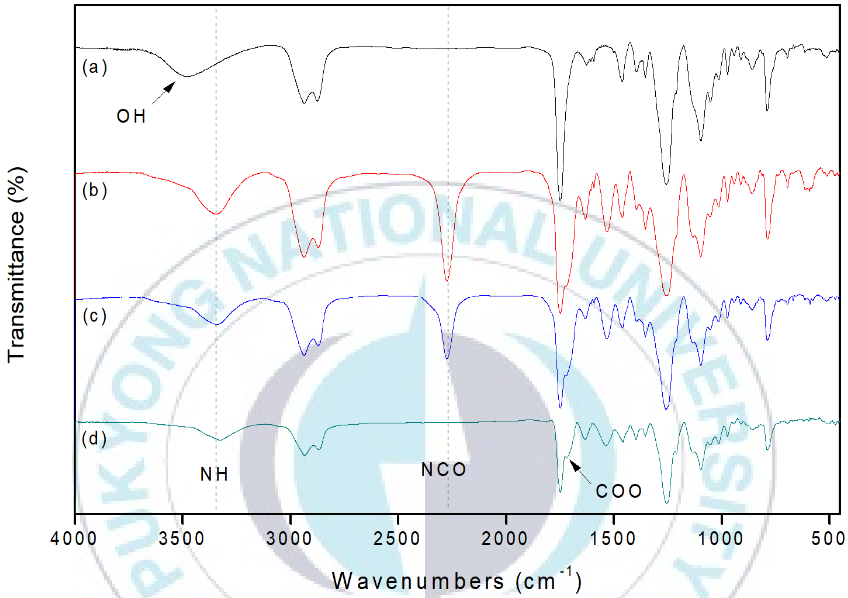


Figure 7. FT-IR spectrum of WPIP using isosorbide carbonate diol.

(a) Polyol + DMPA

(b) (a) + Isocyanate

(c) Prepolymer

(d) Synthesised polyurethane compound after adding EDA

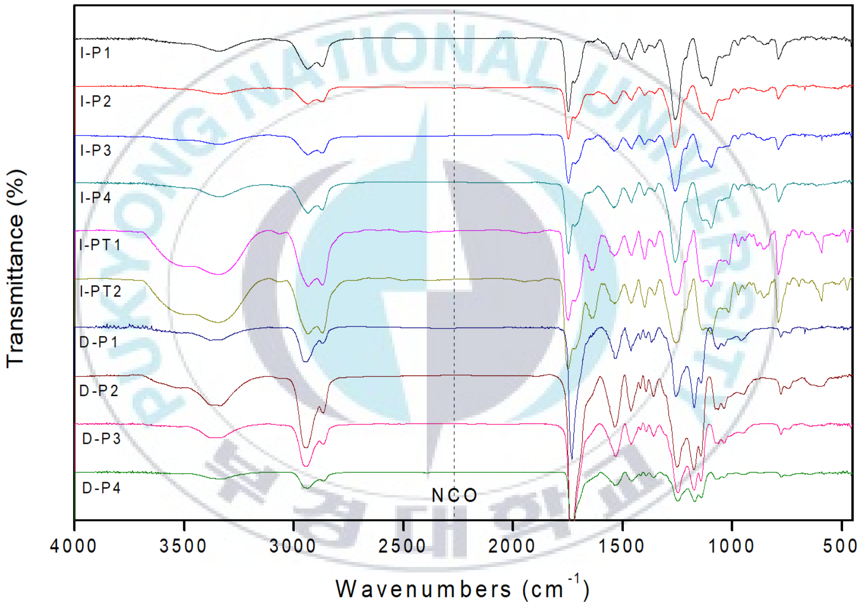


Figure 8. FT-IR spectra of final step of the WPIP.

4.1.2. Nuclear magnetic resonance (^{1}H-NMR) spectroscopy

The results of ^{1}H-nuclear magnetic resonance (^{1}H-NMR) are shown in Figures 9 and 10 to confirm the chemical structure of WPIP. Figure 9 is ^{1}H-NMR spectra of WPIP using isosorbide carbonate diol. In the case, 3.5-4.75 (protons of isosorbide), 3.04 ($CONHCH_2$ -), 2.94 ($CONHCH_2$ CH_2 CH_2 CH_2 CH_2 -), 1.32 ($CONHCH_2$ CH_2 -), 1.14 ($CONHCH_2$ CH_2 CH_2 -) were confirmed[32,33]. Figure 10 is ^{1}H-NMR spectra of WPIP using poly(tetramethylene adipate)glycol. In the case, 4.13 ($OHCH_2$ CH_2 CH_2 CH_2 -), 3.2 ($OCONHCH_2$ -), 2.32 ($OCOCH_2$ -), 1.62 ($OHCH_2$ CH_2 CH_2 -, $OCOCH_2$ CH_2 -), 1.52 ($OCONHCH_2$ CH_2 -), 1.3 ($OCONHCH_2$ CH_2 CH_2 -) were confirmed[34,35].

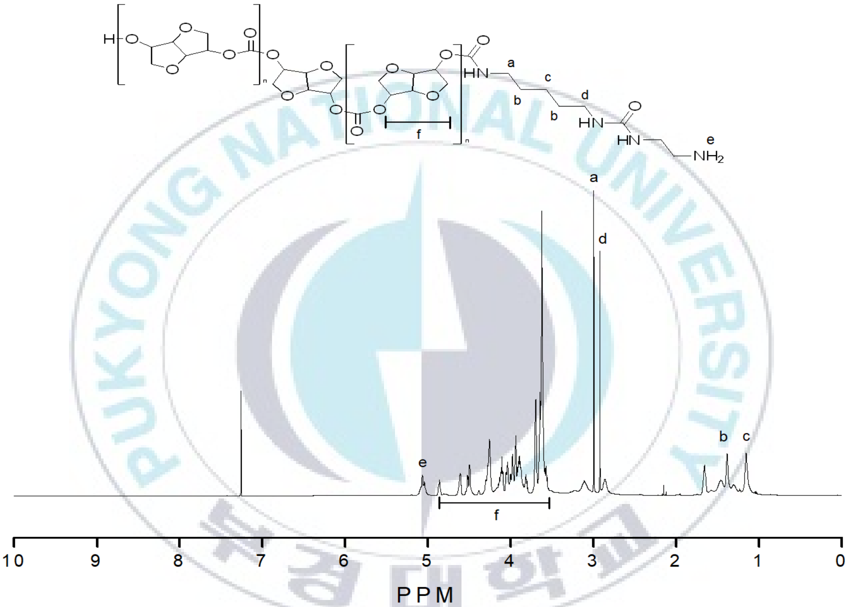


Figure 9. ^{1}H-NMR spectrum of WPIP using isosorbide carbonate diol.

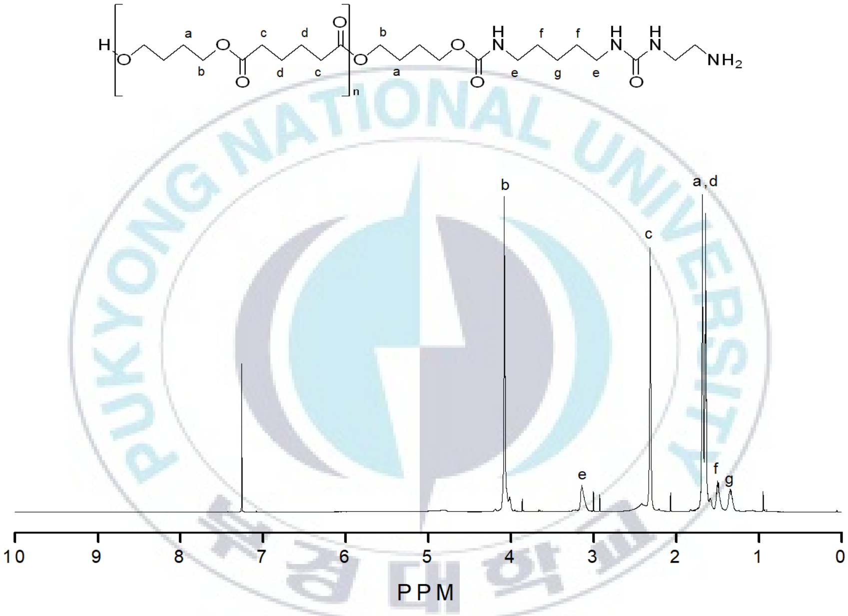


Figure 10. ¹H-NMR spectrum of WPIP using poly(tetramethylene adipate)glycol.

4.2. Molecular weight

Table 6 shows the number average molecular weight (Mn), weight average molecular weight (Mw) and polydispersity of the WPIP. In the case of I-P1~PT2, isosorbide carbonate diol (ICD) was used as the polyol, and in the case of D-P1 to D-P4, poly(tetramethylene adipate)glycol (DT-2040) was used as the polyol. It can be seen in Table 6 that the Mn and Mw decreased as I-P1 and D-P1 transformed into I-P4 and D-P4, respectively, i.e., as the content of chain extender increased, and the polydispersity also decreased. The reason for this is that the lower the content of the chain extender is, the longer is the NCO-terminated prepolymer formed, and thus the longer are the extended chains. It can also be seen that the WPIP synthesized using DT-2040 as the polyol had a much higher molecular weight than that of the other ones. Thus, it was established that the reaction between the biopolyol and the bioisocyanate was not better than that achieved for existing petroleum-based polyols.

Table 6. Molecular weights of WPIP

Sample	Mn	Mw	Polydispersity
Reference	64936	99070	1.52
I-P1	5262	8643	1.64
I-P2	4983	8088	1.62
I-P3	4664	7550	1.61
I-P4	4348	6996	1.60
I-PT1	3950	6033	1.52
I-PT2	4481	6712	1.49
D-P1	33096	72239	2.18
D-P2	24102	51583	2.14
D-P3	22669	42228	1.86
D-P4	12667	21623	1.70

4.3. Mechanical properties

Figure 11 shows the tensile strength and elongation of the synthesized WPIP films. In the case of the WPIP synthesized using isosorbide carbonate diol (ICD), the film formation failed because of the low molecular weight and poor physical properties of the material. However, in the case of the WPIP synthesized using poly(tetramethylene adipate)glycol (DT-2040), it was possible to produce a film. It was also confirmed that the tensile strength increased and the elongation decreased as the content of the chain extender increased. The reason is that the hard segment content in polyurethane increased as the chain extender content increased, and increasing the hard segment content increased the physical crosslinking density formed by hydrogen bonding between hydrogen in the water-dispersed polyurethane and oxygen in the carbonyl group. Thus, increasing the crosslink density increased the physical strength, affected the fluidity of the molecule, and decreased the elongation[36-39]. However, further increase in $R_{NCO/OH}$ beyond a critical ratio (r=1.3) led to very hard and fragile films for which the mechanical properties could not be determined.

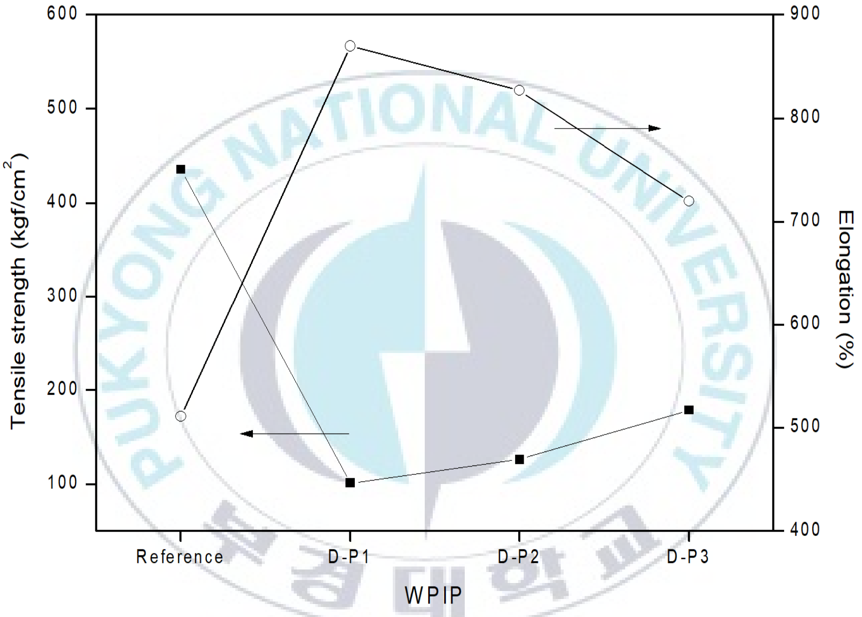


Figure 11. Tensile strength and elongation of WPIP films.

Table 7. Tensile strength and elongation of WPIP films

Sample	Mechanical property	
	Tensile strength (kgf/cm²)	Elongation (%)
Reference	435.5	511.2
I-P1	-	-
I-P2	-	-
I-P3	-	-
I-P4	-	-
I-PT1	-	-
I-PT2	-	-
D-P1	100.93	869.67
D-P2	126.13	826.57
D-P3	178.72	719.65
D-P4	-	-

4.4. Thermal properties

4.4.1. Differential scanning calorimetry (DSC)

The glass transition temperature (Tg) is the temperature at which a polymer compound begins to move with heat, and the higher Tg of the polymer is, the larger are its crystals. Factors affecting the Tg of polyurethane containing aliphatic isocyanate include the crystallization temperature of the soft segment and the hard segment, steric hindrance posed by hydrogen bonding in the hard segment, and the solubility of the material[40].

Figures 12 and 13 show Tg and the values are summarized in Table 8. Figure 12 shows DSC curves of the WPIP synthesized using isosorbide carbonate diol (ICD) as a polyol, and the Tg values observed were in the range of -30 °C to −10 °C. Figure 13 shows results for the WPIP synthesized using poly(tetramethylene adipate)glycol (DT-2040) as a polyol, and the Tg was observed at around −45 °C. Moreover, it could be confirmed that the Tg increased as the content of chain extender increased, as in the case of WPIP synthesized using ICD. The reason is that as the length of the soft segment was smaller, phase mixing occurred in a state where the domain of the soft segment was not greatly developed, and the behavior of the soft segment was greatly disturbed by the surrounding hard segments[41-43].

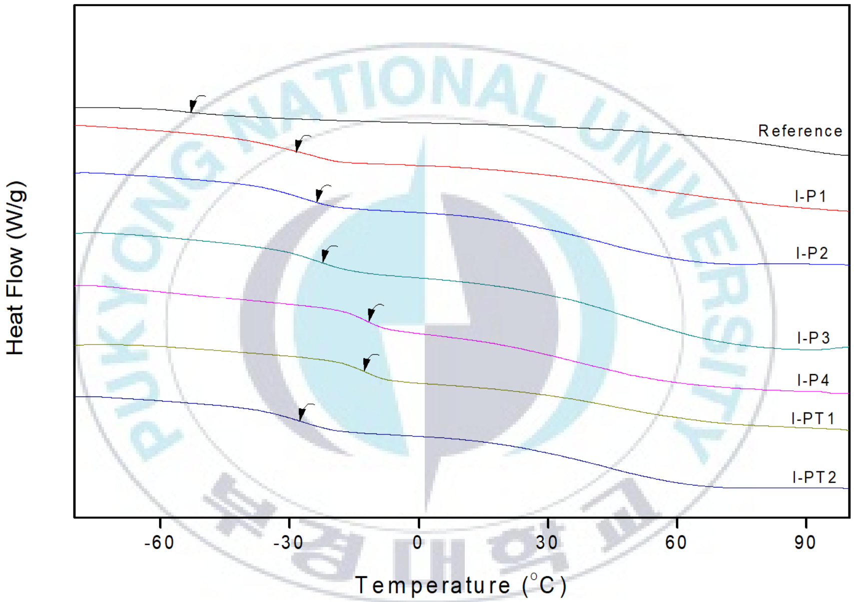


Figure 12. DSC thermograms of WPIP using isosorbide carbonate diol : The arrows indicate Tg of samples.

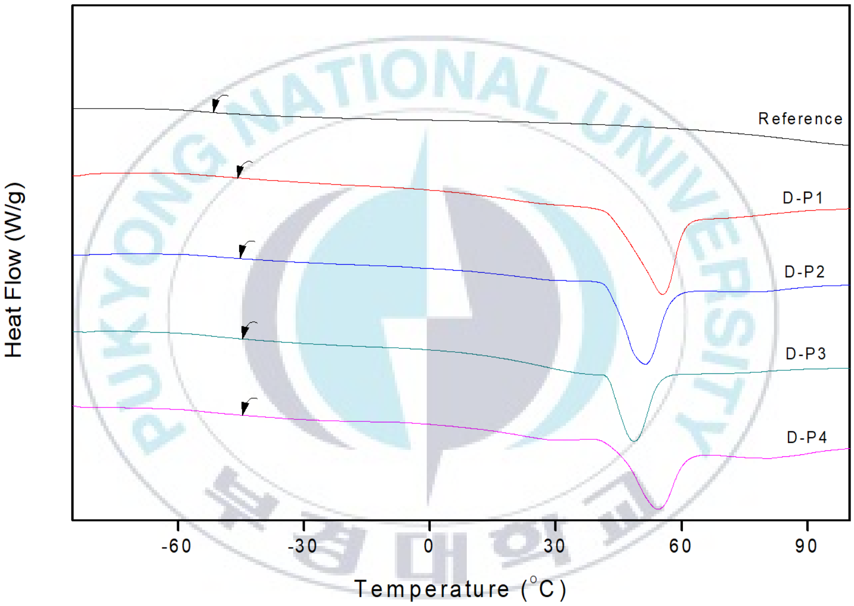


Figure 13. DSC thermograms of WPIP using poly(tetramethylene adipate)glycol : The arrows indicate Tg of samples.

Table 8. Thermal properties of WPIP films

Sample	Tg(℃)
Reference	-52.14
I-P1	-28.97
I-P2	-23.57
I-P3	-23.03
I-P4	-12.49
I-PT1	-12.97
I-PT2	-28.71
D-P1	-46.55
D-P2	-46.40
D-P3	-45.96
D-P4	-45.42

4.4.2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is a method that can determine the composition, thermal stability, etc., of a copolymer, especially the thermal decomposition behavior of polymeric substances and inorganic and organic matter. It is an extremely useful analytical technique for studying the thermal decomposition of samples that undergo liquid evaporation and solid sublimation and measuring the moisture and volatile components in samples and their the evaporation or sublimation rate, as well as investigating the dehydration and absorption behavior of materials and reaction rates.

Figures 14 and 15 show TGA thermograms obtained for the WPIP using isosorbide carbonate diol (ICD) and poly(tetramethylene adipate)glycol (DT-2040), respectively. The temperature at which the polyurethane using ICD began to decompose was about 190 - 200 ℃, and the temperature at which the polyurethane using DT-2040 began to decompose was about 270 - 290 ℃. It was thus confirmed that the thermal decomposition temperature of isosorbide was 190 ℃ and that, as the chain extender content increased, the thermal decomposition temperature increased[32]. This is presumably because the higher the chain extender is, the higher is the crosslinking density of the polyurethane and the better is the thermal stability[41].

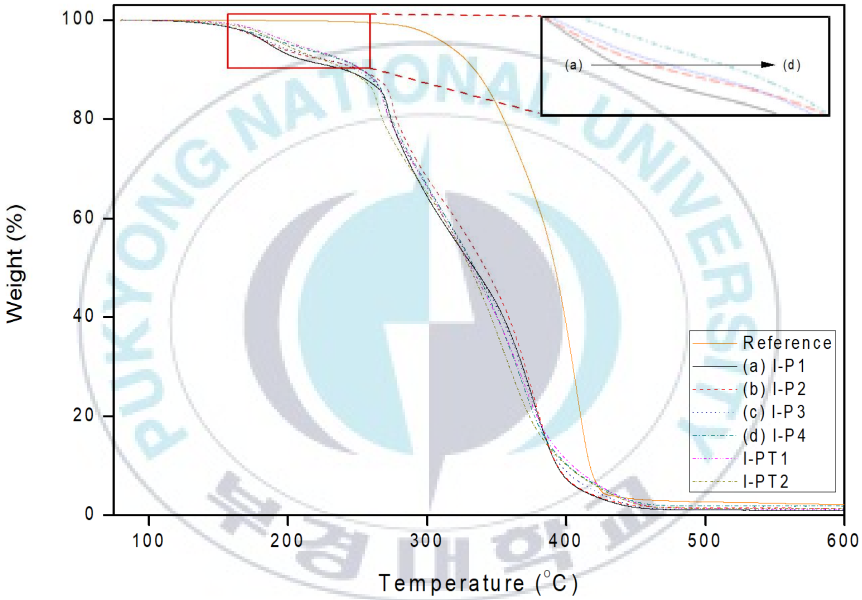


Figure 14. TGA thermograms of WPIP using isosorbide carbonate diol.

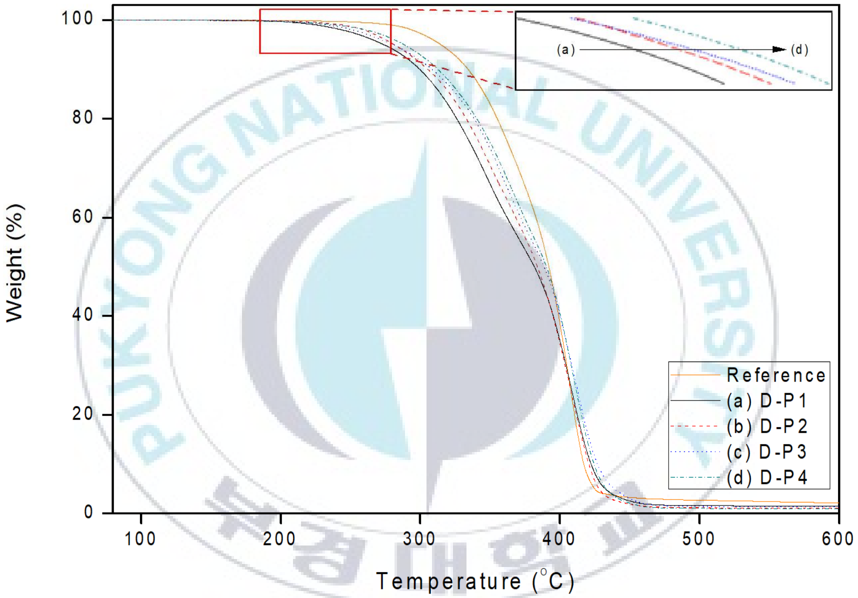


Figure 15. TGA thermograms of WPIP using poly(tetramethylene adipate)glycol.

Table 9. Decomposition temperature of WPIP films

Sample	Td$^{95\%}$(℃)
Reference	314.58
I-P1	187.12
I-P2	188.93
I-P3	191.52
I-P4	201.92
I-PT1	206.15
I-PT2	198.03
D-P1	273.77
D-P2	280.50
D-P3	281.14
D-P4	288.27

4.5. Adhesive property

Figures 16-17 show the adhesive strength and water resistance of the synthesized WPIP adhesive, and the values are summarized in Table 10. Figures 16-17 and Table 10 show that the higher the increase in the content of the chain extender in the synthesized WPIP was, the greater was the increase in the initial (for 30 min) and the state (for 24 h) adhesive strength and water resistance. The values of these parameters, however, showed a decreasing trend beyond a critical chain extender content. For example, in the case of WPIP using poly(tetramethylene adipate)glycol (DT-2040), when $R_{NCO/OH}$ was 1.3, the initial and the state adhesive strengths and water resistance were the highest at 3.1 kgf/cm and 3.4 kgf/cm and 3.0 kgf/cm, respectively, and then decreased again. This might be because, with increasing chain extender content, a higher crosslinking density was achieved for the WPIP adhesive, leading to an increased adhesive strength and enhanced rigidity[44]. However, if the critical ratio (r = 1.3) was exceeded, the crosslinking was too high, the cohesive strength of the adhesive was very strong, and the wettability with the adherend was reduced, indicating low adhesive strength. Further increase in the value of $R_{NCO/OH}$ beyond the critical point (r=1.3) likely caused more complex side reactions, as well, such as the reaction of isocyanate with water to form ureas and the reaction of ureas with isocyanate again to form biuret, which increases the stiffness of WPIP adhesives and leads to decreased adhesive strength[45,46].

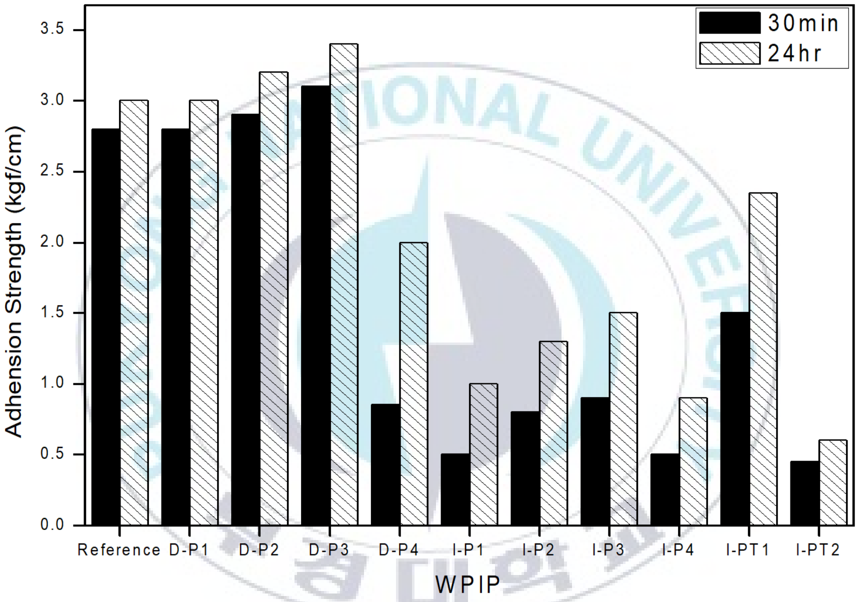


Figure 16. Adhesive strength of WPIP adhesives.

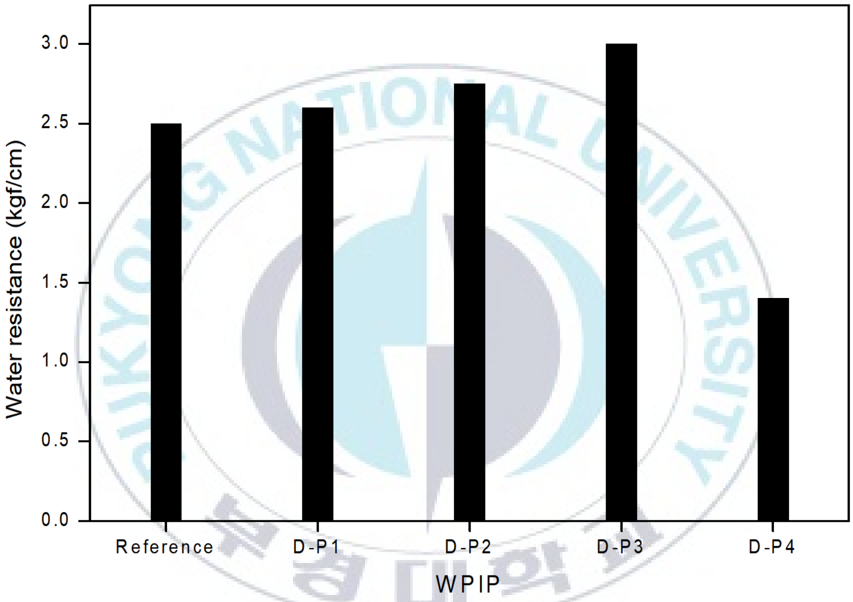


Figure 17. Water resistance of WPIP adhesives.

Table 10. Adhesive strength of WPIP adhesives

Sample	adhesive strength (kgf/cm)		
	30min	24hr	Water resistance
Reference	2.8	3.0	2.5
D-P1	2.8	3.0	2.6
D-P2	2.9	3.2	2.75
D-P3	3.1	3.4	3.0
D-P4	0.85	2.0	1.4
I-P1	0.5	1.0	-
I-P2	0.8	1.3	-
I-P3	0.9	1.5	-
I-P4	0.5	0.9	-
I-PT1	1.5	2.35	-
I-PT2	0.45	0.6	-

5. Conclusion

In this study, bio-based isosorbide carbonate diol and 1,5-pentamethylene diisocyanate were used together or only bio-based 1,5-pentamethylene diisocyanate was used to synthesize a new eco-friendly biopolyurethane adhesive (WPIP) with varied monomer contents, and compared according to their structures, molecular weights, and thermal, mechanical and adhesive properties.

1. FT-IR and ^{1}H-NMR analysis of the synthesized WPIP showed that a bio-based waterborne polyurethane had been synthesized.
2. GPC analysis confirmed that the lower the chain extender contents is, the higher is the molecular weight.
3. The synthesized WPIP improved in terms of the tensile strength and showed decreased elongation as the chain extender content increased.
4. DSC and TGA measurements of the synthesized WPIP showed that the Tg and Td increased as the chain extender content increased.
5. It was observed that the higher the increase in the chain extender content in the synthesized WPIP, the higher was the

increase in the adhesive strength and water resistance but they decreased again when the content was higher than a certain value (r=1.3).

In most cases, as the chain extender content increased, i.e., as the hard segment content increased, the crosslinking density of the polyurethane increased and the mechanical, thermal, and adhesive properties improved. In addition, a critical ratio (r=1.3) was noted for the mechanical and adhesive properties. In the case of the polyurethane synthesized using bio-based polyol and isocyanate, some properties were not as good as those of the polyurethane synthesized using only bio-based isocyanate. Therefore, more research is necessary to improve the properites of the said materials.

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