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EFFECTS OF HYDROPHILIC CONTENT ON PROPERTIES OF WATERBORNE POLYURETHANE

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ได้สังเคราะห์พอลิยูรีเทนสูตรน้ำที่มีหมู่ไอออนิกอยู่ในส่วนอ่อนนุ่ม (พียู-เอ็ม)โดยการดัดแปรวิธีการสังเคราะห์แบบเดิม ได้แปรปริมาณหมู่ไอออนิกโดยการเปลี่ยนแปลงปริมาณของอิมัลซิไฟเออร์ภายใน-ไดเมทิลอลโพรพิโอนิกแอซิด (ดีเอ็มพีเอ) จาก 3 ถึง 7 เปอร์เซ็นต์โดยน้ำหนัก พอลิเททราเมทิลีนอีเทอร์ไกลคอลและดีเอ็มพีเอ ทำปฏิกิริยากับส่วนแรกของปริมาณไอโซโฟโรนไดไอโซไซยาเนต (ไอพีดีไอ) ทั้งหมด จากนั้นจึงเติม 1,4-บิวเทนไดออลและส่วนที่เหลือของไอพีดีไอ สุดท้ายจึงทำให้พรีพอลิเมอร์ที่ได้เป็นกลาง และทำให้กระจายตัวด้วยน้ำ ได้สังเคราะห์พอลิยูรีเทนสูตรน้ำแบบเดิมที่มีปริมาณไอออนิกเท่ากัน (พียู-ซี) เพื่อการเปรียบเทียบ ได้พิสูจน์เอกลักษณ์ของพอลิยูรีเทนสูตรน้ำทั้งหมดด้วยเครื่องเอฟทีไออาร์และโปรตอนเอ็นเอ็มอาร์ เครื่องวัดการกระจายขนาดอนุภาคด้วยเลเซอร์ ดิฟเฟอเรนเชียลสแกนนิงแคลอริมิเตอร์ เครื่องวิเคราะห์เทอร์โมกราวิเมทริก และเครื่องทดสอบความแข็งแบบดินสอ ที่ปริมาณหมู่ไอออนิกเท่ากัน พียู-เอ็ม มีขนาดอนุภาคเล็กกว่าและมุมสัมผัสกับน้ำกว้างกว่าพียู-ซี มีอุณหภูมิเปลี่ยนสภาพแก้วสูงกว่าและความแข็งมากกว่าพียู-ซี การเพิ่มปริมาณหมู่ไอออนิกทำให้ได้ขนาดอนุภาคเล็กลง อุณหภูมิเปลี่ยนสภาพแก้วสูงขึ้นและความแข็งมากขึ้นสำหรับทั้งพียู-เอ็มและพียู-ซี

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Polyurethane dispersion containing ionic soft segments (PU-M) was synthesized by modification of the conventional method. The ionic group content was varied by changing the amount of the internal emulsifier—dimethylolpropionic acid (DMPA) from 3 to 7 wt%. Polytetramethylene ether glycol and DMPA were reacted with the first portion of the total isophorone diisocyanate (IPDI) content. Then 1,4-butane diol and the rest of IPDI were added. Finally, the resulting prepolymer was neutralized and dispersed with water. The conventional PU dispersion containing the same ionic content was also synthesized for comparison. All PU dispersions were characterized by FTIR and ^{1}H NMR spectrometer, laser particle size distribution analyzer, differential scanning calorimeter, thermogravimetric analyzer and pencil hardness tester. At the same content of ionic groups, PU-M had smaller particle size and larger contact angle with water. It also had higher T_g and hardness than PU-C. The increase in the ionic group content also gave smaller particle size, higher T_g and higher hardness for both PU-M and PU-C.

Field of Student: Petrochemistry and Polymer Science Student‘s Signature............................
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LIST OF ABBREVIATIONS AND SIGNS

VOC	volatile organic content
PUD	polyurethane dispersion
SS	soft segment
HS	hard segment
OHv	hydroxyl value
Av	acid value
T_g	glass transition temperature
T_m	melting temperature
equiv.	equivalent
g	gram
M	molarity
N	normal
wt%	weight percentage
mL	millilitre
µm	micrometer
mm	millimeter
in	inch
nm	nanometer
°C	degree Celsius
cm^{-1}	wavenumber
min	minute
h	hour
rpm	revolutions per minute
mV	millivolt

CHAPTER I

INTRODUCTION

1.1 Introduction

Polyurethane (PU) dispersions have become commercially available since the 1960s. The increase interest in waterborne coatings is due to its low VOC content. The PU dispersion is a binary colloidal system in which the particles of PU are dispersed in continuous water phase. The particles have a high surface energy. This results in a strong driving force for film formation after water evaporation. PU dispersions are of three types; non-ionic, cationic and anionic depending upon the type of hydrophilic segments present in the PU backbone. Generally, PU dispersions can be prepared by incorporating hydrophilic groups into the polymer backbone or by adding a surfactant. The former material known as a PU ionomer in which the ionic groups act as internal emulsifiers. Therefore, PU ionomers consist of PU backbones with a minority of pendant acid or tertiary nitrogen groups, which are completely or partially neutralized, to form salts. Various processes have been developed for the preparation of PU dispersions. In all of these processes, a medium molecular weight polymer (the prepolymer) is formed by the reaction of suitable diols or polyols (usually macrodiols such as polyethers or polyesters) with a molar excess of diisocyanates or polyisocyanates in the presence of an internal emulsifier as first step. The emulsifier is a diol with an ionic group (carboxylate, sulfonate, or quaternary ammonium salt) or a non-ionic group [poly(ethylene oxide)] is usually added to allow the dispersion of the polymer in water. The most important processes are the acetone process, prepolymer mixing process, melts dispersion process and ketimine process. Usually, PU polymers are not soluble in water and the degree of hydrophilicity is one of the key factors determining the particle size distributions in the PU dispersion. The shelf life colloidal stability of PU dispersions is influenced by their particle size distribution. Therefore, a special treatment or structural modification is necessary for the polymer to be dispersible in water [1,2,3,4].

Conventional PU dispersions were prepared by dispersing an isocyanate terminated PU prepolymer, which contains stabilizing groups, in water. However, in previous instances the ionic groups were located in the hard segment. These ions increase the polarity of the hard segment and hence decrease the compatibility of the hard and soft segments [5,6].

In this study, PU dispersions containing ionic groups in soft segments are prepared and structurally modified and then compared them with the conventional PU dispersions. The ionic groups content in the PU ionomer structure is varied by changing the amount (3, 5 and 7 wt% (with respect to the prepolymer weight) of the internal emulsifier—dimethylolpropionic acid (DMPA). The influence of molecular structure and content of ionic groups on the size of particle, viscosity, contact angle, morphological, thermal and mechanical properties of PU dispersions are discussed.

1.2 Objectives of Research

The objectives of this research work are:

1. To synthesize the environmental friendly coatings.
2. To synthesize modified PU dispersions (PU-M) containing ionic groups in soft segments.
3. To synthesize conventional PU dispersions (PU-C) by pre-polymer mixing process.
4. To investigate and compare the influence of molecular structure and content of ionic groups on chemical and physical properties of both types of PU dispersions.

1.3 Scope of Research

The stepwise investigation was gone through as follows:

1. Literature survey for related research work

2. To synthesize conventional PU dispersions (PU-C) by pre-polymer mixing process. The ionic groups content was varied by changing the amount (3, 5 and 7 wt% (with respect to the prepolymer weight) of the internal emulsifier—dimethylolpropionic acid (DMPA). The polymer concentrations were maintained at 37 wt% and chain extension at 90% and the neutralizing amine (TEA) content was adjusted to keep a 1:1 ratio of COOH to $N(C_2H_5)_3$ (100% neutralization).
3. To synthesize modified PU dispersions (PU-M) which the ionic centers were located in soft segments. The ionic groups content was varied by changing the amount (3, 5 and 7 wt% (with respect to the prepolymer weight) of the internal emulsifier—dimethylolpropionic acid (DMPA). The polymer concentrations were maintained at 37 wt% and chain extension at 90% and the neutralizing amine (TEA) content was adjusted to keep a 1:1 ratio of COOH to $N(C_2H_5)_3$ (100% neutralization).
4. To investigate the influence of molecular structure and content of ionic groups on the size of particle, viscosity, contact angle, morphological, thermal and mechanical properties of both types of PU dispersions.

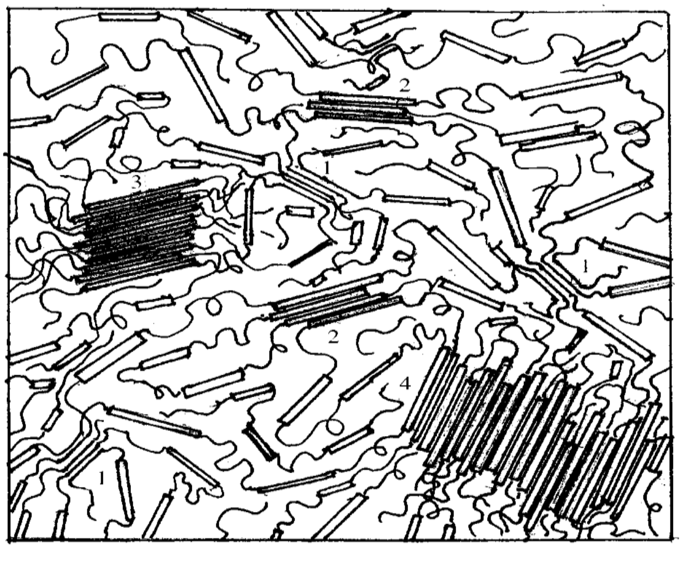
CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Theory

2.1.1 Thermoplastic Polyurethane Coatings

Thermoplastic PU may be described as the linear structural block copolymer of $(SH)_n$ type, where S is soft and H is hard segment (HS) [7]. The isocyanate and chain extender react to form a rigid or _hard‘ sequence that is are linked through the polyol soft blocks to form the final polymer structures that can be described as a segmented block copolymer with the general structure $(SH)_n$, shown in Scheme 2.1, having alternating hard and soft segments. These alternating hard and soft segments are the key feature that these materials have such a good mechanical properties over a wide temperature range [8].



Scheme 2.1 Morphology of polyurethane: (∿) soft segment, (=) hard segments, (1) soft segment ordering domain, (2) short range ordering hard segment domain, (3) long range ordering hard segment domain, and (4) microcrystalline structure of hard segments

Due to the wide variety of properties between soft and hard segment, phase separation may be observed in the final material. Phase separation occurs due to the intrinsic incompatibility or thermodynamic immiscibility between the hard and soft segments (SSs). The hard segments (HSs), composed of polar materials, can form carbonyl to amino hydrogen bonds and thus tend to cluster or aggregate into ordered hard domains [7], whereas SSs form amorphous domains. The HS acts as filler particle as well as crosslinker to restrain the motion of SS chains. Such a structure was first proposed by Cooper and Tobolsky in 1966 [9]. The early work of Schollenberger [10] as well as Cooper and Tobolsky [9] established that segmented PUs consist of high glass transition temperature (T_g) or high melting temperature (T_m) HS microphase separated from relatively low T_g SS. The degree of phase separation plays a vital role in determining the solid-state properties of these multi-block coatings.

Properties of thermoplastic PU coatings depend on several factors such as the composition of soft and hard segments, lengths of soft and hard segments and the sequence of length distribution, chemical nature of the units composing the polymer, anomalous linkages (branching, crosslinking), molecular weight and the morphology in the solid state. At room temperature, soft macroglycol segments are above their T_g and have easy segmental rotations, which therefore impart the material its rubber-like behavior or elastomeric properties. On the other hand, hard domains are below their glassy or melt transition temperature and are thought to govern the hysteresis, permanent deformation, high modulus, and tensile strength and provide dimensional stability [11]. Compositional variables and processing conditions such as structure of soft and hard segments [12,13], symmetry of diisocyanate, type of chain extender (diol or diamine) [14], number of carbons in linear low molecular weight chain extender [15], the type (polyester or polyether) and chain lengths of soft segments [15,16], crystallizability of either segment [17], thermal history of the PUs [18,19] and the method of synthesis [12] are known to affect the degree of phase segregation, phase mixing, HS domain organization, and subsequent PU coating properties.

2.1.1.1 Effects of SS

The chemical composition and molecular weight distribution (MWD) of the incorporated soft block influence the macroscopic properties of the resulting coatings. For example, Van Bogart et al. [20] and Hartmann et al. [21] revealed that increasing the SS molar mass at a fixed HS length gave rise to an increased tendency for the HS domains to be isolated in the SS matrix. A similar conclusion was reached in PU based on MDI and polycaprolactone using various instrumental techniques [22]. This phenomenon resulted in a higher degree of phase separation between hard and soft blocks, which produced a lower T_g value. In addition, increasing SS prepolymer molar mass at constant functionality (i.e., increasing the molar mass per functional group or equivalent weight, E_n) result [23,24] in a higher degree of phase separation again, owing to increased thermodynamic incompatibility between the two copolymer segments, resulting from the higher Flory–Huggins interaction parameter (χ) [25] and/or the higher crystallizability [26]. Stanford et al. [23] showed that increasing SS functionality significantly increases the strength of PU and reduces the overall degree of phase separation developed in these materials due to increased domain boundary mixing.

2.1.1.2 Effects of HS

HS structure, length and distribution are very important parameters and largely affect morphology, thermal behavior as well as performance of segmented PU coatings [27]. Wang and Cooper [26] observed that the mechanical properties of polyether PUs depend primarily on the HS content. The presence of three-dimensional hydrogen bonding within hard domains leads to usually strong hard domain cohesion. On increasing the HS content, a morphological change occurs from interconnecting to isolated hard domains. The effect of HS content on the phase separation in PU based on MDI was studied by measuring the T_g of the SS [28]. The SS T_g was influenced by the restricted movement imposed at the HS junctions and at phase boundaries, where the hard domain acts as a filler particle [29]. Bengston et al. [30] explained the variation in mechanical properties with increasing the HS content as due to morphology change. Models containing MDI/BDO repeating units have been described and investigated; and these studies pointed out that the melting of model compounds increases with the number of MDI units, and an extrapolated value for homopolymer, accounting for the chain end defects, was also achieved [12,31]. Tonelli et al. [32] used the model compounds R-(MDI–HQE)$_{p-1}$–MDI–R‘ [where p = 1, 2, 3; R, R‘ is ethanol and/or 2-phenoxyethanol; and HQE is bis(2-hydroxyethyl) ether] and shown that the melting point increases with increasing the oligomer length and quickly reaches an asymptotic values. They also calculated the limiting value of melting points for infinite molecular weight calculated by group contribution [33].

2.1.1.3 Hydrogen Bonding Effect

Hydrogen bonding in PUs plays a vital role in determining their macroscopic properties. The high electronegativity of nitrogen atom in the urethane or urea moiety withdraws N–H bonded electrons and develops partial positive charge on the hydrogen, which thereby forms hydrogen bonding with the neighboring oxygen atom. In all cases, the hydrogen atom of the N–H group in the urethane or urea linkages is the donor proton, while the acceptor group can be the carbonyl of the imide groups, urethane‘s C=O, urea‘s C=O or the oxygen atom of the ester or ether linkage when polyester or a polyether are present as the SS. The hydrogen bonding interaction produces physical crosslinks, and thereby reinforces the PU matrix; increase strength and stiffness [34,35]. Fourier transform infrared spectroscopy (FT-IR) is well established as an analytical technique for functional group analysis and to study the hydrogen bonding and phase separation behavior in PUs. Pimentel and Sederholm [36] suggested a linear relationship between the length of the hydrogen bond (R) and the frequency shift ($\Delta\nu$) of the N–H absorption band caused by hydrogen bonding, as expressed in

$$R = 3.21 - \frac{\Delta\nu}{0.548\times10^{3}}$$

The shorter the hydrogen bonding, the stronger the bonding.

In most cases, the degree of PU microphase separation as observed from FTIR study has been found to be incomplete. That is, the microphase is not pure due to the intersegmental mixing. Mixing within the soft microphase is reflected by an elevation in its T_g compared to the pure component value. The more SS domains are contaminated with the dissolved HS of high glass transition temperature, the higher the SS T_g. The degree of HS–SS mixing depends on HS length, SS length, overall HS content and the affinity of one segment toward the other [37].

2.1.1.4 Effect of CE

The effect of different CEs on morphology and properties of PUs were reported by various authors [38]. The chain length, molecular volume, functionality of the CE and its conformation can influence HS packing and crystallinity in the hard domains [39]. Blackwell and Nagarajan [40] and Blackwell et al. [38] suggested that for chain extended PUs, CEs containing an even number of carbons produced polymers with a more phase separated structure than those containing an odd numbers of carbons. Auten and Petrovic [41] reported the effect of unsaturation in the CE on the structure and properties of derived PUs. They utilized CEs of the BDO series with increasing bond order at the 2,3 carbons such as BDO, cis-2-butene-1,4-diol (BED) and 2-butyne-1,4-diol (BYD) and showed that increasing bond order progressively limit backbone chain flexibility. Consequently, HS size may increase, but hydrogen bonding groups may be forced into positions that do not allow effective interchain bonding, resulting in poor physicochemical properties. In addition, the relative acidity of the terminal alcoholic protons is expected to increase with increasing CE bond order because electron density at the oxygen atoms would be progressively shifted toward the p bonds. As the acidity of the CE O–H group increases, the reaction rates during polymer synthesis, polymer molecular weight, and thermal stability of the urethane groups formed could all be adversely affected.

2.1.2 Reactions of Isocyanate

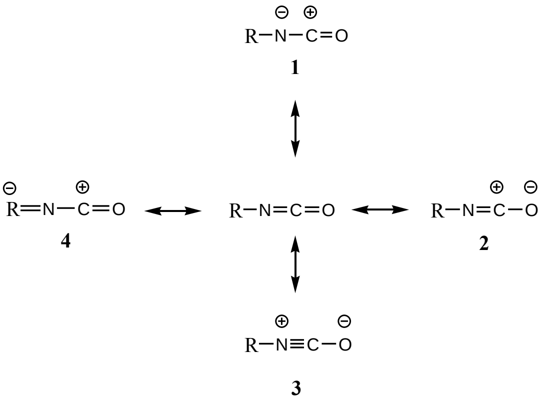
Isocyanates are highly reactive chemicals. The electronegativity of the oxygen and nitrogen imparts a large electrophilic character on carbon, thereby the charge density on carbon is least and the resonance forms are shown in Scheme 2.2 [8].

Structure one is more important than structure two whilst the contribution of structure three is small. The reactivity of isocyanates towards nucleophilic attack can be demonstrated the electron deficiency on the carbon. The reactions occur across the C=N bond mostly as structure one contributes more than structure two. Structure four becomes essential if R is aromatic. Since the negative charge on the nitrogen is distributed through the benzene ring, the electron charge on the center of isocyanate is decreased. Consequently, aromatic isocyanates such as MDI and TDI are more reactive than aliphatic isocyanates like HDI and IPDI.

As a principle, if R is connected with any electron-withdrawing group, increasing the positive charge on carbon, thus isocyanate group will be attack easily by a nucleophile.

On the other hand, electron-donating groups will decrease the reactivity of isocyanate groups. Consequently, TDI is more reactive than MDI because the second isocyanate in the TDI molecule will activate the other isocyanate.

It is realized that isocyanates are highly reactive chemicals thus the polyurethane chemistry is focused on the reactions of isocyanates with –OH and –NH functional substances, containing active hydrogen groups such as hydroxyl, water, amines, urea and urethane.

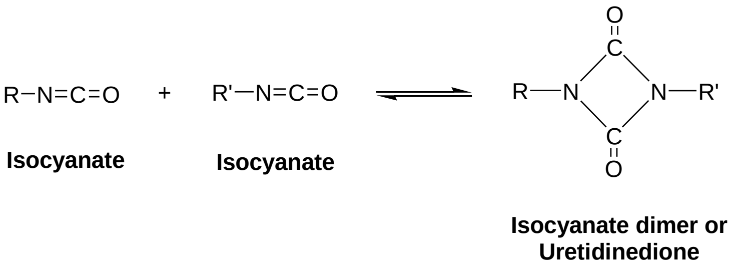


Scheme 2.2 Resonance forms of isocyanates

2.1.2.1 Isocyanate Reactions with Isocyanates

Dimerisation

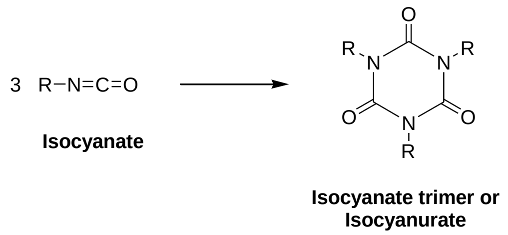
Isocyanates undergo a mildly exothermic cyclo-addition reaction across two C=N bonds resulting in a four-membered ring call a dimer or uretidinedione, Scheme 2.3.



Scheme 2.3 Dimer formation

Trimerisation

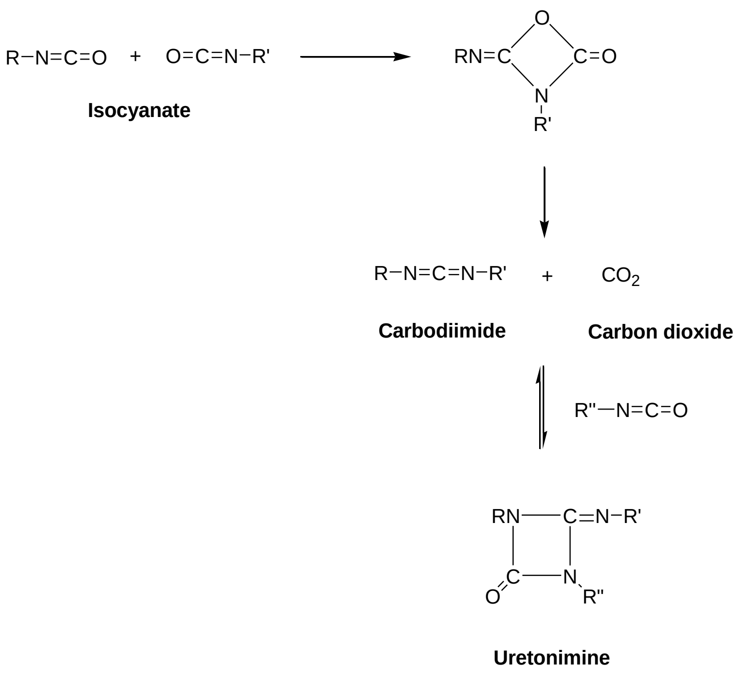
Three isocyanates can undergo a highly exothermic cyclisation reaction across the C=N bond resulting in a six-membered ring call a trimer or isocyanurate, Scheme 2.4. Trimerisation carries on until all NCO groups have reacted.



Scheme 2.4 Trimer formation

Carbodiimides and Uretonimines

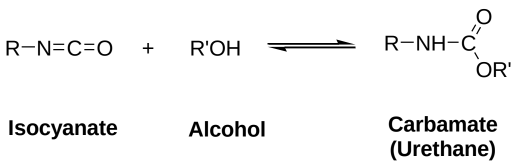
The formation of carbodiimides describes as a cyclo-addition reaction across the C=N bond and the C=O bond of two isocyanate groups with elimination of carbon dioxide. Because of the loss of carbon dioxide, the reaction is irreversible. Carbodiimide can then react with another isocyanate across the C=N bond forming uretonimine, Scheme 2.5.



Scheme 2.5 Carbodiimides and uretonimines

2.1.2.2 Isocyanate Reactions with Hydroxyl

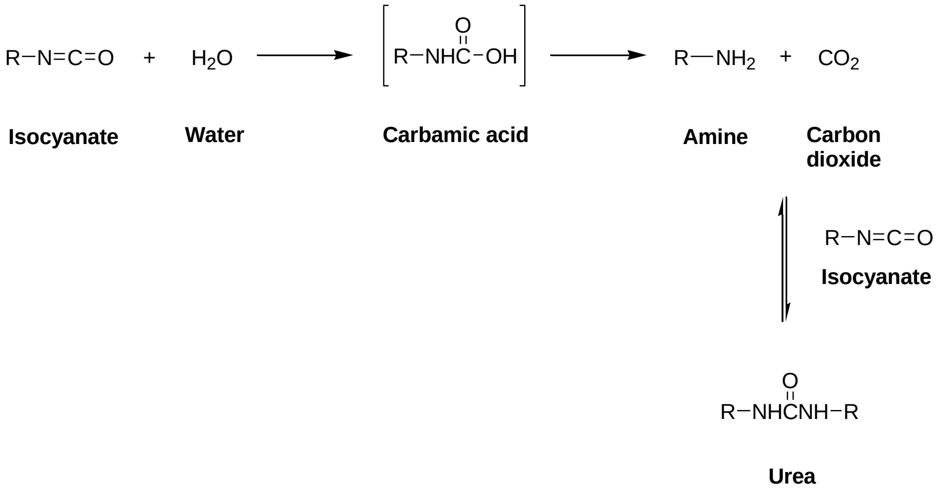
The reaction between isocyanates and hydroxyl groups is the most important method in the manufacture of polyurethanes, Scheme 2.6. The reaction product is cabamate, which is called a urethane when high molecular weight polymers are received. The reaction is exothermic and reversible.



Scheme 2.6 Urethane reaction

2.1.2.3 Isocyanate Reactions with Water

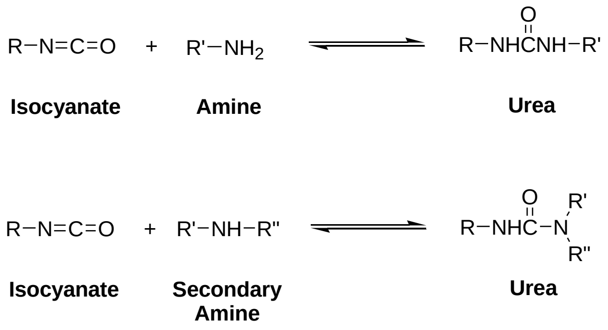
Water reacts with isocyanates and initially forms of an unstable carbamic acid, which breaks down into carbon dioxide and primary amine, Scheme 2.7. The amine will react with another isocyanate to produce a symmetric urea. This reaction is highly exothermic. The water reaction is often used as a blowing agent owing to the formation of carbon dioxide.



Scheme 2.7 Water reaction

2.1.2.4 Isocyanate Reactions with Amines

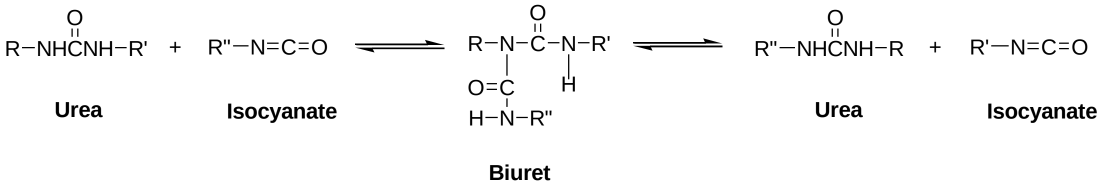
Isocyanates react with primary and secondary amines to give di- and tri-substituted ureas respectively, Scheme 2.8. These conversions are exothermic and diamines are used as chain extending and curing agents in polyurethane production. The resulting polyurea segments increase the potential for cross-linking.



Scheme 2.8 Urea formation

2.1.2.5 Isocyanate Reactions with Urea

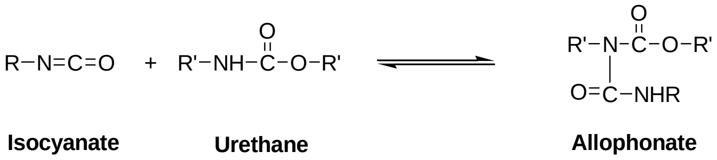
A lone pair of electrons available on the nitrogen atom of urea group makes them nucleophilic centers. It collides with one molecule of isocyanate to produce biuret as shown in Scheme 2.9. In polyurethane system this reaction, is reversible upon heating, is often a source for additional cross-linking.



Scheme 2.9 Biuret formation and equilibria

2.1.2.6 Isocyanate Reactions with Urethanes

An isocyanate reacts with the active hydrogen on a urethane group to produce an allophanate group, Scheme 2.10. This reaction is exothermic and reversible at temperature above 150 ˚C.



Scheme 2.10 Allophonate formation

2.1.3 Isocyanates

Methylene diphenyl diisocyanate (MDI), with a 61.3 per cent share and toluene diisocyanate (TDI) at 34.1 per cent dominated the global isocyanate market of 4.4 million tons in 2000, Figure 2.1. In comparison to these aromatic diisocyanates, the two major aliphatic diisocyanates, hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) had a 3.4 per cent share whilst all other commercial isocyanates such as 4,4‘-diisocyanatodicyclohexylmethane (H_{12}MDI), 1,5-naphthalene diisocyanate (NDI), tetramethylxylene diisocyanate (TMXDI), *p*-phenylene diisocyanate (PPDI), 1,4-cyclohexane diisocyanate (CDI) and tolidine diisocyanate (TODI) together only amounted to 1.2 per cent.

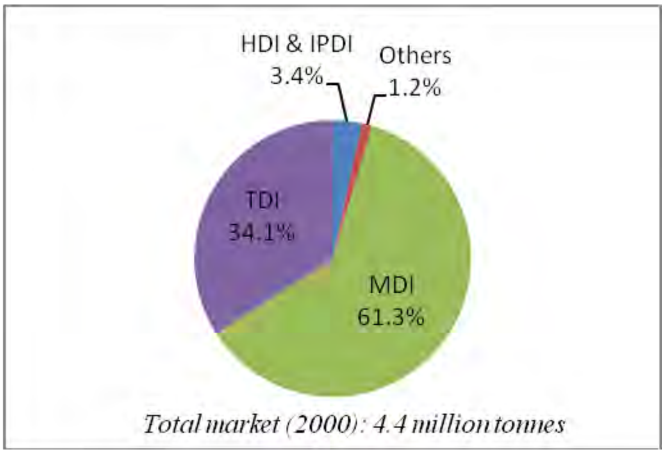


Figure 2.1 Global split of isocyanate market in 2000

The polyfunctional isocyanate used to prepare PU coatings can be aromatic, aliphatic, cycloaliphatic or polycyclic in structure. Aromatic isocyanates have high reactivity than aliphatic or cycloaliphatic diisocyanates. Different diisocyanates contribute to the PU properties in different ways. For example, aromatic diisocyanates give more rigid PUs than do aliphatic ones, but their oxidative and ultraviolet stabilities are lower [42].

2.1.3.1 Methylene Diphenyl Diisocyanate (MDI)

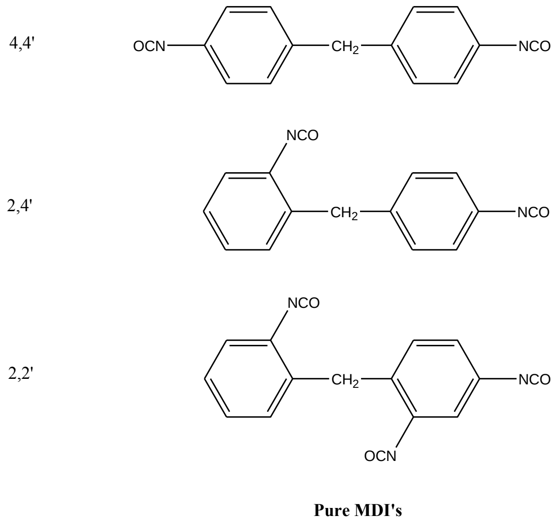


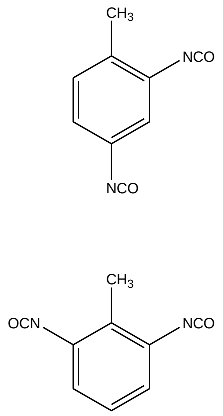
Figure 2.2 Chemical structure of MDI

Pure 4,4‘-MDI is a symmetrical molecule with two aromatic isocyanate groups of equal reactivity. Commercial products normally contain one to two per cent of the 2,4‘ isomer and have hydrolysable chlorine levels below five ppm.

2,4‘-MDI is an asymmetrical molecule with two aromatic isocyanates of different reactivity. The 4-position is approximately four times more reactive than the

2-position and is of similar reactivity to the two groups in 4,4‘ isomer (2,4‘/4,4‘, 55/45). Normally hydrolysable chlorine levels are less than 50 ppm [8].

2.1.3.2 Toluene Diisocyanate (TDI)



2,4-TDI

2,6-TDI

Figure 2.3 Chemical structure of TDI

The isocyanate groups on 2,4-TDI have different reactivities with the 4-position approximately four times the reactivity of the 2-position and about 50 per cent more reactive than the 4-position group in MDI, whilst for the 2,6 isomer the groups have equal reactivity that is approximately the same as that of the 2-position in 2,4-TDI.

Since the two isocyanate groups in each TDI molecule are on the same aromatic ring, the reaction of one of the groups tends to cause a change to the reactivity of the second group.

TDI is typically available as pure 2,4, as an 80/20 (2,4/2,6) mixture or as a 65/35 (2,4/2,6) mixture.

2.1.3.3 Hexamethylene Diisocyanate (HDI)

HDI is a flexible, linear, symmetrical molecule with two primary aliphatic isocyanate groups of equal reactivity. Their reactivity is at least two orders of magnitude lower than that in the 4-positon of MDI. Of all the commercially available polyisocyanates, it has the highest isocyanate content. Because it is totally aliphatic, it gives rise to light-stable polyurethanes.

2.1.3.4 Isophorone Diisocyanate (IPDI)

Isophorone diisocyanate (IPDI) is a bulky and very asymmetric molecule. In fact, of all the commercially available polyisocyanates, it is the only one with no degree of symmetry. It is totally aliphatic, therefore giving rise to light-stable polyurethanes. It is available as a mixture of two isomeric forms (25/75 *cis/trans*).

Because of this, it has effectively four different isocyanate groups. Two are secondary aliphatic groups with similar reactivity, about half that in HDI. The other two are primary groups, but both are sterically hindered, rendering them even slower, by a factor of about five than MDI. Thus, IPDI has the slowest reactivity of all the commercially available polyisocyanates.

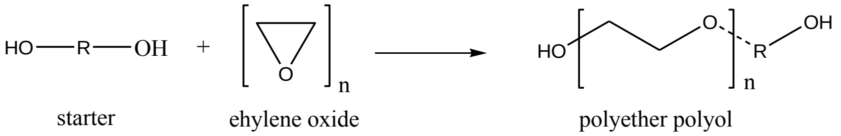
2.1.4 Diols/Polyols

The other component of polyurethane is a polyol. The term “polyol” explains compounds contain two to eight reactive hydroxyl groups that react with isocyanates to produce polyurethane polymers. The average molecular weights of polyols range from 200 to 8,000. The two main classes of polyols are polyether polyols (e.g., polyethylene glycol, polypropylene glycol, PTMG or polycaprolactone diol) and polyester polyols.

In the late 1950s, polyesters were prevalent polyols as they displayed outstanding resistance to light and aging.

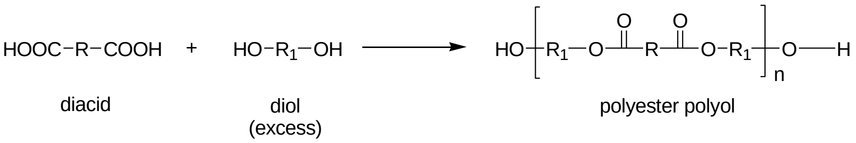
It was known that polyethers were more desirable polyols for production of slabstock foam. Even if they were sensitive to light and oxygen, they improved water dispersion and impart chain flexibility. Consequently, they became the predominant class of polyol, and had a 80 per cent of total consumption nowadays.

Polyether polyols are produced by the addition of either ethylene oxide or propylene oxide to a polyhydroxy ‗starter' molecule in the presence of a catalyst (Scheme 2.11). Typical starter molecules include glycerol, ethylene glycol, propylene glycol and trimethylolpropane.



Scheme 2.11 Synthetic method of polyether polyol

Polyester polyols are produced by the condensation reaction of polyfunctional carboxylic acids or anhydrides with polyfunctional alcohols (Scheme 2.12).



Scheme 2.12 Synthetic method of polyester polyol

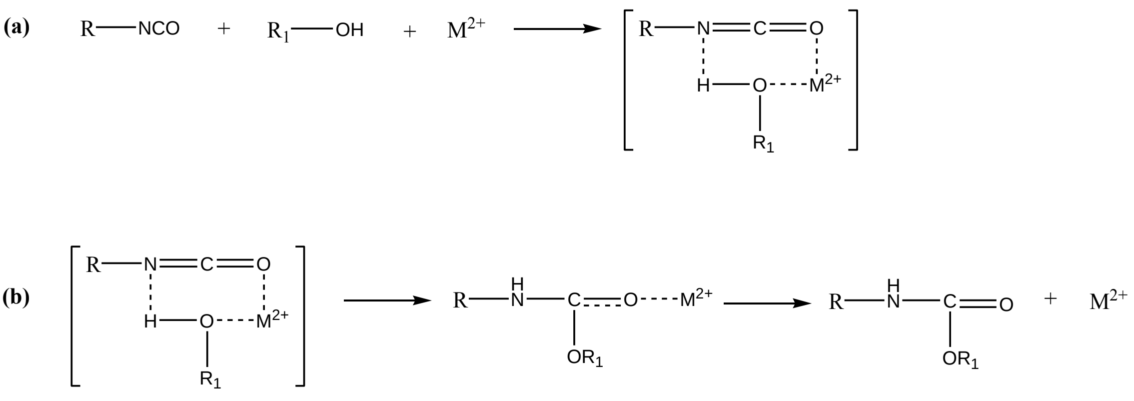
The molecular weight and functionality of the polyols are very important parameters and determine the properties of the final polyurethane polymer. The simplest polyols are glycols, such as ethylene glycol, 1,4-butane diol and 1,6-hexane diol. The low molecular weight reactants result in hard and stiff polymers because of a high concentration of urethane groups. On the other side, the high molecular weight polyols produce polymer chains with fewer urethane groups and more flexible alkyl chains. Long-chain polyols with low functionality (1.8–3.0) give soft, elastomeric polyurethane while short chain polyols of high functionality (greater than 3) give more rigid, crosslinked product.

2.1.5 Catalysts

The reaction of isocyanates with water (blowing) and polyols (polymer gelation) was catalysed using Tertiary amines, carboxylic acid salts and organometallics (principally tin compounds). The catalyst is added to control the relative reaction rates of isocyanates with polyols and water, and to allow the reaction to take place at lower temperatures also.

Typically, Amine catalysts are used as blowing catalysts because they incline to catalyse the isocyanate-water reaction better than the isocyanate-polyol reaction. Nonetheless, the relative rates of both reactions are relied upon the specific amine catalyst used. Potassium and sodium carboxylic acid salts and quaternary ammonium carboxylic acid salts are used mainly in isocyanurate foams because they are used to catalyse the trimerisation reaction. Organometallic catalysts are mainly used as gelation catalysts for the isocyanate-polyol reaction. Organotins are the most widely used. The mercury catalysts are used in elastomers. The lead catalysts are often used in rigid spray foams. However, both mercury and lead catalysts are toxic.

Dibutyltin dilaurate (DBTDL), stannous octoate and THORCAT are organotin compounds. Tetravalent tin compounds of the type $R_nS_nX_{(4-n)}$ with R being a hydrocarbon group (alkyl, aryl, cycloalkyl, etc.) and X being a halogen atom or a carboxylate group (acetate, laurate, etc.) have shown catalytic effect in urethane reaction. The catalytic effect of organometallic compounds is due to their complex forming ability with both isocyanate and hydroxyl groups. The mechanism suggested by Britain and Gemeinhardt is shown in Scheme 2.13. The interaction of metal cation with isocyanate, alcohol molecule results an intermediate complex (Scheme 2.13a), which may then immediately rearrange to yield the urethane product (Scheme 2.13b).



Scheme 2.13 Reaction mechanism for the isocyanate-polyol reaction due to: (a) and (b) organometallic catalysis

2.1.6 Polyurethane Coatings

Polyurethane technology used in the coating industry can be broadly divided into four types. The first three of systems are reactive whilst the fourth class covering all systems with no isocyanate reaction during final application:

- **Two-component systems** composing of a polyisocyanate and a polyol or polyamine that are mixed just prior to use with cure generally occurring at ambient temperature (53 per cent).
- **Oven-curing polyurethanes** use same substances to the first category except that a blocked isocyanate is applied to provide a storage stable one-pack mix with the polyol or polyamine. The isocyanate is de-blocked at the stoving temperature and reacts (10 per cent).
- **Moisture-curing polyurethanes** are one-component, high molecular weight, low free-isocyanate content prepolymers. They react with moisture from environment to form urea linkages (4 per cent).
- **Non-isocyanate reactive systems**, such as thermoplastic polyurethane-based lacquers, aqueous polyurethane dispersion, urethane oils and alkyds, and radiation-cured polyurethanes already containing urethane or urea

linkages and where there are no further isocyanate reactions during application (33 per cent).

2.1.6.1 Materials Selection for Polyurethane Coatings

Isocyanates

There are five types of isocyanates regularly used in coating formulations:

- MDI – 46 per cent.
- Aliphatics – 37 per cent (H_{12}MDI, HDI, IPDI).
- TDI – 17 per cent.

Aliphatic isocyanates have a lower rate of reaction and form softer coating than aromatic isocyanates when used in comparable formulations. Moreover, they are generally used where UV or light stability is required, for instance in top-coats, and in water-borne systems. HDI and HDI adducts are the most widely used whilst H_{12}MDI is generally used in waterborne systems.

Aromatic isoyanates are used as primers, and heavily pigmented maintenance coating, which are not light sensitive applications.

Polyols

There are three types of polyols regularly used in coating formulations, with hydroxyl values (OHv) range from 30 to 500:

- Acrylics.
- Polyethers.
- Polyesters.

Acrylics and polyesters are generally used for harder coating with better weatherability.

Table 2.1 Coatings performance versus polyol type

	Acrylic	**Polyester**	**Polyether**
Application condition	Equal	Equal	Equal
Viscosity	Medium	High	Low
Appearance	Excellent	Very good	Good
Hardness	Hard	Medium	Soft
Brittleness	Fair	Excellent	Excellent
Gloss retention	Excellent	Fair	Poor
Solvent resistance	Excellent	Fair	Fair
Salt water spray resistance	Excellent	Very good	Good

Solvents

Solvents are added to reduce the viscosity of components, in order to improve processing. They should not react with isocyanates and have a water content of less than 500 ppm.

Solvents such as esters, ketones, ether-ester and polar aromatic and aliphatic solvents are divided into three groups:

- Fast-boiling point under 100 ˚C.
- Medium-boiling point 100 to 150 ˚C.
- Heavy-boiling point greater than 150 ˚C.

Environmental concerns and economic competitiveness have driven to reduce the volatile organic components (VOCs) of all formulations in every application. Because of this regulative pressure, low viscosity polyol and isocyanate components leading to lower solvent usage (and also waterborne systems) were developed. Systems that containing more than 60 wt-% or 70 vol-% non-volatiles are termed –high solids” coatings.

2.1.7 Aqueous Polyurethane Dispersions

Aqueous polyurethane dispersions (PUDs) are fully-reacted polyurethane systems produced as small discrete particles and dispersed in continuous water phase to give a chemically and colloidally stable product. The polyurethane particles have a high surface energy resulting in a strong driving force for film formation after water evaporation. Since low amounts of solvents are required in these systems, the volatile organic compounds (VOCs) are emitted very little.

Typically, PU polymers are not soluble in water. The degree of hydrophilicity is one of the main parameters determining the particle size distributions that affecting the shelf life colloidal stability of PUDs directly. Thus, a special treatment or structural modification is essential for the polymer to be dispersible in water.

Aqueous PUDs are generally depended on incorporating hydrophilic groups into the polymer backbone. The former material known as a PU ionomer in which the ionic groups act as internal emulsifiers. Therefore, waterborne PU ionomers consist of PU backbones with a minority of pendant acid or tertiary nitrogen groups, which are completely or partially neutralized to form salts.

Aqueous PUDs can be prepared by various processes such as acetone process, pre-polymer mixing process, melts dispersion process and ketimine process. A medium molecular weight polymer (the prepolymer) is formed by the reaction of suitable diols or polyols (usually macrodiols such as polyethers or polyesters) with a molar excess of diisocyanates or polyisocyanates in the presence of an internal emulsifier as first step. The emulsifier is a diol with an ionic group (carboxylate, sulfonate, or quaternary ammonium salt) or a non-ionic group [poly(ethylene oxide)] is usually added to allow the dispersion of the polymer in water.

Aqueous PUDs can be divided into three types; non-ionic, cationic and anionic depending on the type of hydrophilic segments present in the PU backbone. Depending on the type of ionic species, a minimum ionic content is required for the formation of a colloidally stable PU ionomer. The interaction between ions and their counter ions is responsible for the formation of stable dispersion. The ion-dipole interaction between the ionomer and dispersing media (e.g., water) results in the formation of a salvation sheath, where the ionomer properties bases on the degree of neutralization and content of ionic component.

2.1.7.1 Cationic PU

According to Lorenz and Hick [43], the formation of an electric double layer can stabilize cationic PU ionomers in water. The soft segment (SS) of cationic PU is hydrophobic and the hard segment (HS) with NHR_2^+ is hydrophilic. Consequently, the molecular chains of cationic PU can self-organize to form micelles when dispersed in water, with positively charged hydrophilic groups at the surface and hydrophobic groups concentrated in the micelle interior. An electric double layer forms around the micelles, which undergo Brownian motion, stabilized against intermicelle aggregation by electrostatic forces. At the same time, there are hydrogen bonds between the hydrophilic groups and water molecules, and then the particles are surrounded by a layer of water molecules making a solvation sheath. These phenomena restrain the aggregation of particles [44]. For the preparation of a cationic PUD, 3-dimethylamino-1,2-propanediol can be used to disperse the medium after neutralizing with a weak protonic acid in water.

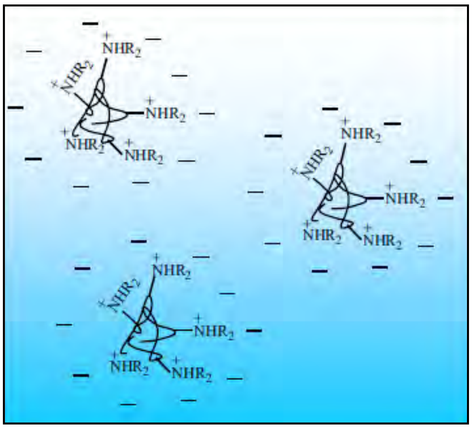


Figure 2.4 Schematic diagram of micelles formed by cationic polyurethane ionomers in water [45]

2.1.7.2 Anionic PU

Dimethylol propionic acid (DMPA) is commonly incorporated into PU backbones because it is very effective for water dispersion in the subsequent neutralization reaction with triethylamine (TEA) [45,46]. The carboxylic ion of DMPA in the polymer is hydrophilic and serves as an anionic center as well as internal emulsifier. Carboxylic ions do not only stabilize aqueous PUDs, but may also become the curing site. The carboxyl groups in PUDs provide charges to the surfaces of PU micelles (particles), thereby causing repulsion between PU particles resulting in uniform PU particle size distribution in the water phase. Schematic diagrams of micelles formed by (a) cationic and (b) anionic PU ionomers in water are shown in Fig. 1. Because of the hydrophilic properties of the carboxyl group, these PUs become a self-emulsified (or water-reducible) in the water phase. Such conventional aqueous-based PUs have a disadvantage similar to that of a polymer surfactant, in that they exhibit high hydrophilicity after drying into a film. Therefore, the weight percent of DMPA used in the prepolymer not only influences the particle size and stability of the dispersion, but also the hydrophobicity of the coatings. For example, the use of higher amount of DMPA results in a smaller average particle size and high hydrophilicity in the film, which reduces the water resistance of the coating. Therefore an optimum amount of DMPA should be used for making a high performance coating.

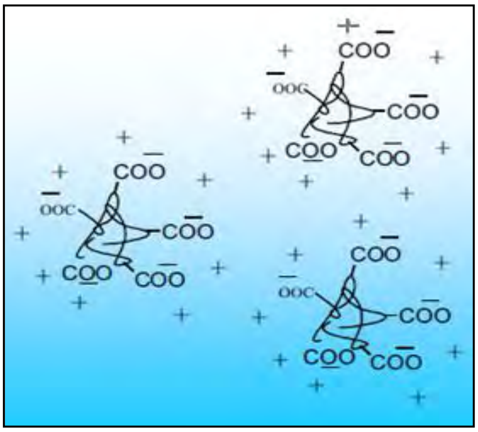


Figure 2.5 Schematic diagram of micelles formed by anionic polyurethane ionomers in water [45]

2.1.7.3 PU Non-Aqueous Dispersion

Polymerization in a non-aqueous dispersion was found to be an effective alternative route for the preparation of uniform polymeric particles in the 1–10 mm size range [47]. Typically, polymerization in a dispersed medium starts with the monomers partially or totally soluble in the organic phase, and results in the formation of an insoluble polymer in the form of stable colloidal dispersion. Polymer microspheres with very narrow size distribution can be prepared in appropriate conditions. The role of the steric stabilizer is crucial in this procedure as it not only provides stability to the resultant particles, but also affects the final particle size and size distribution as well as the polymer molar mass. Usually, amphipathic polymers—block or graft copolymers—are effective stabilizers [48]. These stabilizers strongly adsorb onto the forming particle surface by virtue of the insolubility of one of their block units (also called the anchor part), and stabilizer desorption from the final material may cause irreversible changes, such as the loss of the stabilization of the particles. One possibility to avoid this major drawback is to use reactive stabilizers or macromonomers that remain attached to the final particle. PU particles formed by suspension polymerization in a non-aqueous medium have been reported by Yabuuchi et al. [49]. According to their work, PU microspheres in the 5–50 mm size range were obtained by condensing oligomeric glycols with diisocyanates or isocyanateterminated prepolymer in an organic medium, using poly(ethylene oxide)-b-poly(dimethylsiloxane) block copolymer as the steric stabilizer.

2.2 Literature Reviews

In 1998, Son *et al.* [50], prepared aqueous polyurethane (PU) dispersion by pre-polymer mixing and neutralization emulsification method. The particle sizes were sensitive to the molecular weights of PU pre-polymer, the degree of neutralization, and the dielectric constant of the dispersion medium. The lower the concentration of carboxyl groups per unit chain length, the larger the particle size of the PU dispersion.

The PU particle sizes decreased as the degree of neutralization increased were shown in Figure 2.6, because the dissociated carboxyl groups were capable of stabilization.

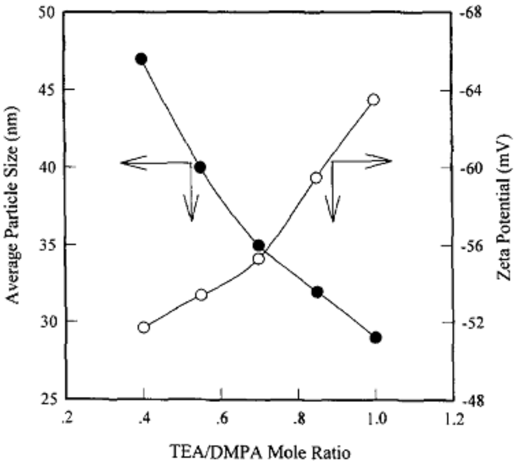


Figure 2.6 The effect of TEA/DMPA mole ratio on zeta potentials and average particle sizes of PU dispersion (polyol Mw = 2000)

In 2003, Kim *et al.* [51], prepared polyurethane ionomer dispersions with ionic groups in soft segments (called ionic soft segments) as well as in hard segments (ionic hard segments). Ionic soft segments gave significantly lower solution viscosity, smaller particle size and greater dispersion viscosity, larger contact angle with water and greater water compared with ionic hard segments. These properties were interpreted in terms of delocalization of hydrophilic groups among soft segments and hard segments leading to increased soft segment–hard segment phase mixing, evidenced from IR, thermal and dynamic mechanical measurements which proved a higher glass-transition temperature, T_g, and greater phase mixing with ionic soft segments. The increase in the hard segment length as well as the crosslinking density also gave a higher T_g, modulus, and yield strength for the ionic soft segments.

In 2004, Lee *et al.* [52], designed and synthesized two types of shape memory polyurethanes (PUs) with various hard segment contents based on the position of crosslinks, either in the soft segment or in the hard segment, and tested for tensile cyclic loading behavior as well as mechanical and dynamic mechanical properties. It was found that hard segment crosslinks gave much smaller shape fixability and much higher shape recoverability as compared with soft segment crosslinks at the same hsc. For soft segment crosslinks, shape recovery increased as the hsc decreased.

In 2005, Limiñana *et al.* [53], prepared different aqueous polyurethane dispersions by using the prepolymer mixing process. The ionic groups‘ content in the polyurethane ionomer structure was varied by changing the amount of the internal emulsifier- dimethylolpropionic acid (DMPA). The decrease in the DMPA content slightly increased the particle size in number due to the decrease in both the hydrophilicity and the electrolytic stability of the aqueous polyurethane dispersion. Moreover, the lower the DMPA amount, the lower the hard segment content in the ionomer and the higher the resistance to thermal degradation of the polyurethane ionomer. Finally, high initial adhesive strength was obtained and the adhesion to PVC increased as the DMPA content in the polyurethane ionomer decreased.

In 2005, Nanda *et al.* [54], focused on the effect of the degree of DMPA content, solid content, pre/postneutralization and degree of chain extension on particle size, viscosity, pH, molecular weights, glass transition temperature, and degradation temperature of a given formulation prepared by prepolymer method. Both the particle size and viscosity increased with increase in the solid content. The order of neutralizing amine addition was found to be critical. Lower particle size was obtained with increase in the degree preneutralization of the PU prepolymer; however, a significant increase in the particle size and viscosity of PU dispersion was seen by the postneutralization. The PU films showed the presence of two T_g at lower and higher temperatures corresponded to soft and hard segments, respectively. TGA studies showed the degradation of PU films at 260 ˚C.

In 2006, Nanda *et al.* [55], evaluated the impact of the chemical variables on PU dispersions prepared by the acetone process. Changes in carboxylic acid concentration, degree of pre/post-neutralization and chain extension were found to have the expected impacts on dispersion solution properties. Increased ionic concentration, and degree of pre-neutralization led to lower particle size and higher viscosity, increased degree of chain extension led to larger particle size and lower viscosity, increased post-neutralization increased both particle size and viscosity, and increased concentration of the polymer led to a viscosity increase without any change in particle size.

In 2009, Temnil *et al.* [56], synthesized a series of new polypyrrole (PPy)/polyurethane (PU)/ poly (methyl methacrylate) (PMMA) latex. Firstly, aqueous PU dispersion was synthesized by prepolymer mixing process. The most critical parameters on its particle size were due to the molar ratios of NCO/OH in prepolymer mixing process and TEA/DMPA in aqueous PU dispersion. PU/PMMA latex was then obtained by soap free emulsion polymerization. When PU/PMMA weight ratio was greater than 1:1, the average particle size of PU/PMMA latex became larger than PU particle. Finally, the oxidative polymerization of pyrrole in PU/PMMA latex was used for PPy/PU/PMMA synthesis. The addition of pyrrole in the reaction was limited at 1.5% of the solid content of PU/PMMA latex. This PPy/PU/PMMMA latex had good film forming and could retard corrosion compared with PU/PMMA, PU and no coating, in a sequence.

CHAPTER III

EXPERIMENTAL

3.1 Materials

Chemicals	Suppliers
Polytetramethylene Ether Glycol (PTMG-1000) OHv#107, Av#0.05	Siam Chemical Industry
1,4-Butane Diol (1,4-BD)	Siam Chemical Industry
Dimethylol Propionic Acid (DMPA)	Siam Chemical Industry
Isophorone Diisocyanate (IPDI)	Siam Chemical Industry
Dibutyltin Dilaurate (DBTDL)	Siam Chemical Industry
Triethylamine (TEA)	Carlo Erba
1-Methyl-2-Pyrrolidinone (NMP)	Acros
Methyl methacrylate (MMA)	FLUKA
Tertiary butyl hydroperoxide (TBHP)	FLUKA
Potassium Phthalate Acid	Carlo Erba
Potassium Hydroxide (KOH)	Fluka
Pyridine	Acros
Acetic Anhydride	Acros
Hydrochloric Acid 37%	Carlo Erba
Phenolphthalein	Fluka
Toluene	Fluka
n-Butanol	Fluka
Ethyl Alcohol Absolute	Carlo Erba
Chlorobenzene	Acros
Di-*n*-Butylamine	Fluka
Methanol	J.T. Baker
Bromophenol Blue	Carlo Erba

3.2 Glasswares and Equipments

1. 1000 ml five-necked, round-bottom flask
2. 500 ml five-necked, round-bottom flask
3. Mechanical stirrer
4. Thermometer
5. Condenser with drying tube
6. Ultra turrax dispersion (UTD)
7. Heating mantle
8. Silicone oil bath
9. Dropping funnel
10. Burette
11. Pipette

3.3 Purification and Preparation of Materials

3.3.1 Polytetramethylene ether glycols and 1,4-butane diol were dried and degassed at 80 °C under a vacuum for 2 h before used.

3.3.2 Dimethylol propionic acid was dried at 50 °C for 48 h in a vacuum oven.

3.3.3 Triethylamine was dried over 4 $\overset{\circ}{A}$ molecular sieves before use.

3.3.4 1-Methyl-2-Pyrrolidinone was refluxed with calcium hydride (CaH_2) for 2 h and then distilling off.

3.4 Instruments

3.4.1 Fourier-Transform Infrared Spectrometer (FT-IR)

The chemical structure of the polyurethane ionomers was analyzed in a Perkin-Elmer (Spectrum One) infrared spectrophotometer, provided with Fourier transform analysis (FT-IR).

3.4.2 Nuclear Magnetic Resonance (NMR) Spectrometer

^{1}H NMR spectra of polyurethane ionomers were recorded using a Varian, model Mercury-400 nuclear magnetic resonance spectrometer (USA) operating at 400 MHz. Polyurethane ionomer was dissolved in solution of $CDCl_3$.

3.4.3 Laser Particle Size Distribution Analyzer

The particle size and its distribution were measured in aqueous suspension, using dynamic light scattering (NanoZs, MALVERN). The samples were diluted to the required concentration with distilled water before measurement. The analysis was carried out with estimated solution parameters as follows: refractive index of 1.81 and particle density at 1 gm/cm^3.

3.4.4 Zeta Potential Measurement

The potential of the dispersions was measured using a dynamic light scattering technique (NanoZs, MALVERN). The original dispersions were diluted by around 10,000 times with deionized water.

3.4.5 Brookfield Viscosity

The viscosities of PU dispersions were measured in a Brookfield viscosimeter DV-III. Measurements were carried out at 25 °C, using the spindle no. 64 at 250 rpm.

3.4.6 Contact Angle Measurements

The contact angles of the dispersion cast films with deionized water were measured with a standard goniometer (200-F1, Ramé-hart). The tests were performed at ambient temperature and the results reported are the average values of at least three runs.

3.4.7 Differential Scanning Calorimetry (DSC)

The thermal properties of the films were determined using Differential Scanning Calorimetry (Netzsch, 204 F1 Phoenix). 2–20 mg polyurethane ionomer films were placed in an aluminium pan and the experiments were carried out under nitrogen atmosphere by using a heating rate of 10 °C/min. To remove the thermal history of the polyurethane ionomers, two consecutive runs were carried out: (i) Heating from –100 to 110 °C followed by an isothermal cycle at 110 °C for 3 min. (ii) Heating from –100 to 300 °C.

3.4.8 Thermogravimetric Analysis (TGA)

Thermal gravimetric (TG) experiments were performed in a Simultaneous thermal analyzer (Netzsch, STA409C). 20–150 mg polyurethane ionomers films were placed in an aluminium pan and heated from 30 to 500 °C under nitrogen atmosphere, at a heating rate of 10 °C /min.

3.4.9 Pencil Hardness Test

Film hardness was determined by pencil test. The samples were applied onto glass panels using a make bar coater. Coated panels were then allowed to air dry at room temperature in fully ventilated atmosphere and were subjected to testing only after 7 days to ensure the full maturation of coated films. Pencil hardness was determined by ASTM 3363.

3.5 ASTM Standardized Methods

3.5.1 Determination of Isocyanate Groups (NCO) Content: ASTM 2572-97

This test method covers the determination of the isocyanate group (NCO) content of prepolymer.

Reagents:

1. Di-*n*-Butylamine in chlorobenzene 1.0 N
2. Hydrochloric acid (HCl) 1.0 N
3. Bromophenol blue 1% in ethanol
4. Methanol

Procedure:

Weight 1.00 g of prepolymer in a 250 mL Erlenmeyer flask. Add 10 mL of chlorobenzene. Add 20.00 mL of 1.0 N dibutylamine in chlorobenzene solution. Leave the solution stand for 1-1.5 h in the flask with the stopper. Add 40 mL of methanol. Add 4-6 drops of indicator solution. Titrate with 1.0 N HCl until reaching a yellow end point. A blank titration is done using all reagents without the addition of the sample.

$$\%\ \text{free} - \text{NCO} = \frac{(\text{V1} - \text{V2}) \times \text{M} \times 4.2}{\text{W}}$$

Where;

V1 = the volume of 1.0 N HCl used in the blank titration

V2 = the volume of 1.0 N HCl used in the sample titration

M = Molarity of HCl

W = Weight of sample (g)

3.5.2 Determination of Hydroxyl Value (OHv) Content: ASTM D 4274-05

The hydroxyl value (OHv) of a polyol is determined by acetylating the polyol with pyridine and acetic anhydride with standard KOH solution, measuring the difference between a blank solution and one containing polyol.

$$ROH + (CH_3CO)_2 \longrightarrow RO{-}COCH_3 + CH_3COOH$$

Reagents:

1. Methanolic potassium hydroxide, 1 M KOH
2. Pyridine/acetic anhydride solution
3. 1% Phenolphthalein indicator solution

Procedure:

Weight approximately 5 g of the polyol into a 250 mL Erlenmeyer flask. Pipette 20 mL of the pyridine/acetic anhydride solution. Then fit a condenser to the flask and place on a temperature oil bath at 90 ± 2 °C for 2 h, swirling regularly. After that, cool the flask with ice water and rinse the condenser with 20 mL of deionized water. Add 4-6 drops of phenolphthalein indicator solution and titrate with 1 M methanolic potassium hydroxide rapidly until reaching the first faint pink end point. A blank titration is undergone using all reagents without the addition of the sample. It is important that the blank and the sample be titrated at the same temperature.

3.5.3 Standard Test Method for Film Hardness by Pencil Test: ASTM D3363

This test method covers a procedure for rapid, inexpensive determination of the film hardness of an organic coating on a substrate in terms of drawing leads or pencil leads of known hardness.

Apparatus:

1. A set of calibrated drawing leads (preferred) or equivalent calibrated wood pencils meeting the following scale of hardness: The difference between two adjacent leads shall be considered one unit of hardness.

$5B - 4B - 3B - 2B - B - HB - F - H - 2H - 3H - 4H - 5H$

Softer **Harder**

Procedure:

A coated panel is placed on a firm horizontal surface. The pencil is held firmly against the film at a 45° angle. The process is started with the hardest pencil and continued down the scale of hardness to either of two end points: one, the pencil that will not cut into or gouge the film (pencil hardness).

3.6 Synthesis of PU Dispersions

3.6.1 Synthesis of Conventional PU Dispersions (PU-C)

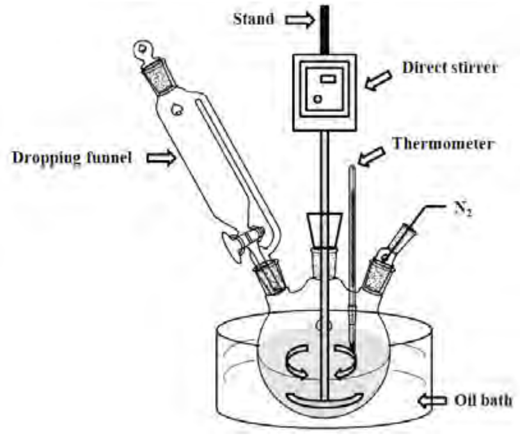


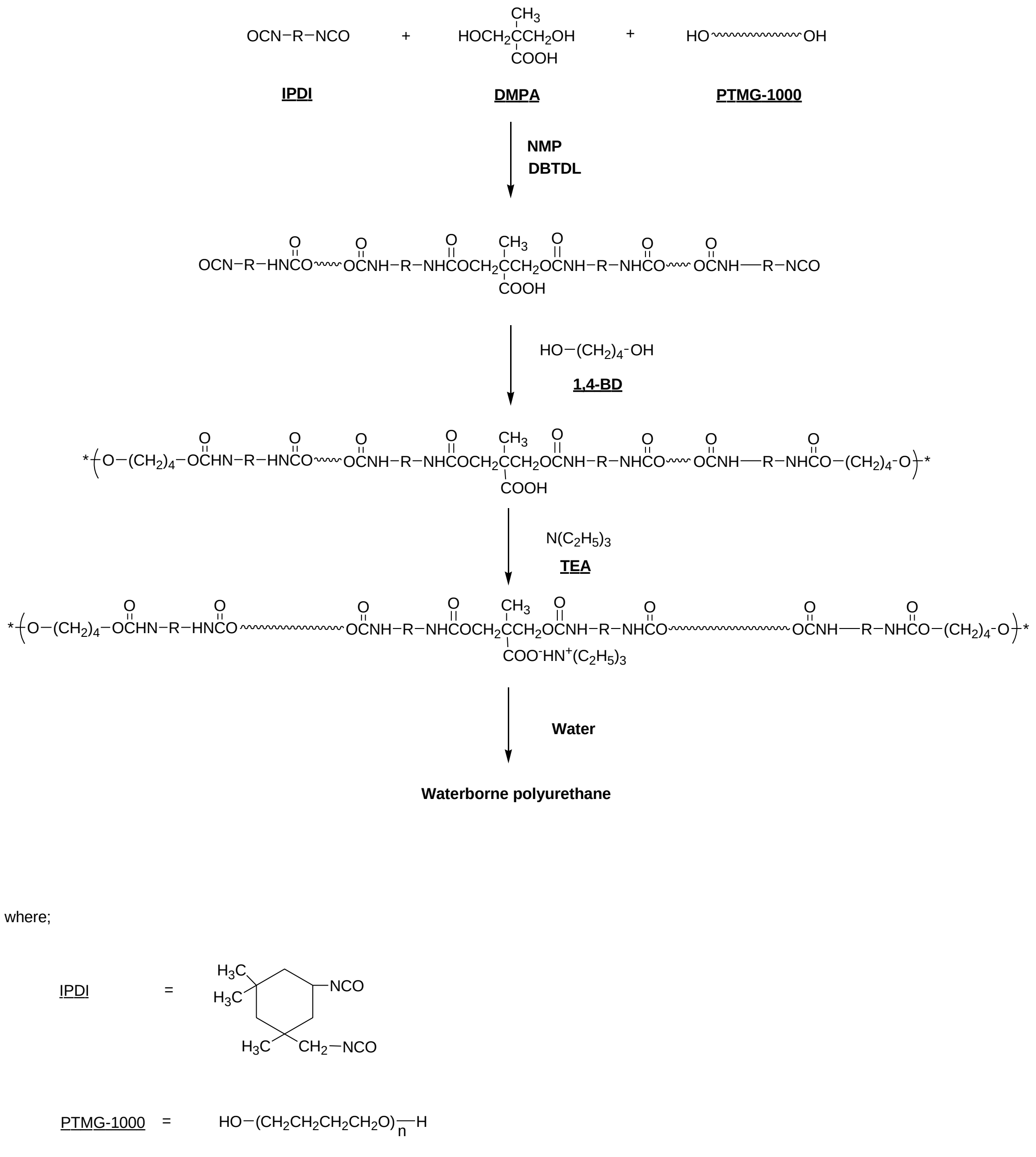
Figure 3.1 The apparatus for the synthesis of PU dispersion

A 1000-ml five-necked, round-bottom flask was equipped with a heating mantle/temperature controller, mechanical stirrer, thermometer and nitrogen inlet tube. The polymerization was maintained using a constant temperature oil bath. Figure 3.1 shows the apparatus for the synthesis of PU dispersion.

Table 3.1 Recipe for the variation in carboxylic acid content of conventional PU dispersions– g (equiv.)

Reagent	**PU3-C**	**PU5-C**	**PU7-C**
DMPA	3.0 (0.045)	5.0 (0.075)	7.0 (0.104)
PTMG-1000	57.6 (0.110)	51.5 (0.098)	45.2 (0.086)
IPDI	31.7 (0.286)	34.1 (0.307)	36.7 (0.331)
1,4-BD	5.4 (0.120)	5.6 (0.124)	5.8 (0.129)
TEA	2.3 (0.022)	3.8 (0.037)	5.3 (0.052)
NMP	20	20	20
Water	150	150	150
Polymer Concentration (%)	$\left[\frac{100}{100+20+150}\right] \times 100 = 37$	37	37

Polytetramethylene ether glycol (PTMG-1000) and dimethylol propionic acid (DMPA) were charged into the dried flask. While stirring, 1-methyl-2-pyrrolidinone (NMP) (20 wt %) was added at 70 °C, and stirring was continued until homogenized mixture was obtained. Isophorone diisocyanate (IPDI) and dibutyltin dilaurate (DBTDL) were added dropwise, and stirring was continued for 30 min at this temperature. The mixture was heated to 80 °C for about 3 h to afford NCO-terminated prepolymers. The change of the NCO content during the reaction was determined using a standard dibutylamine back titration method. Upon reaching the theoretical NCO value, the prepolymer was chain extended by the addition of 1,4-butane diol (1,4-BD), and allowed to react for 1 h at 80 °C to make the PU polymer. The reactions were cooled to 60 °C, and the neutralizing solution triethylamine (TEA) was added, and stirred for 30 min while maintaining the temperature at 60 °C. Dispersion was accomplished by slowly adding water to the neutralized PU solution at 45–50 °C over 30 min with agitation speed of 700 rpm. The basic formulation and preparation procedure are shown in Table 3.1 and Scheme 3.1, respectively.



Scheme 3.1 Synthesis procedure of conventional PU dispersion

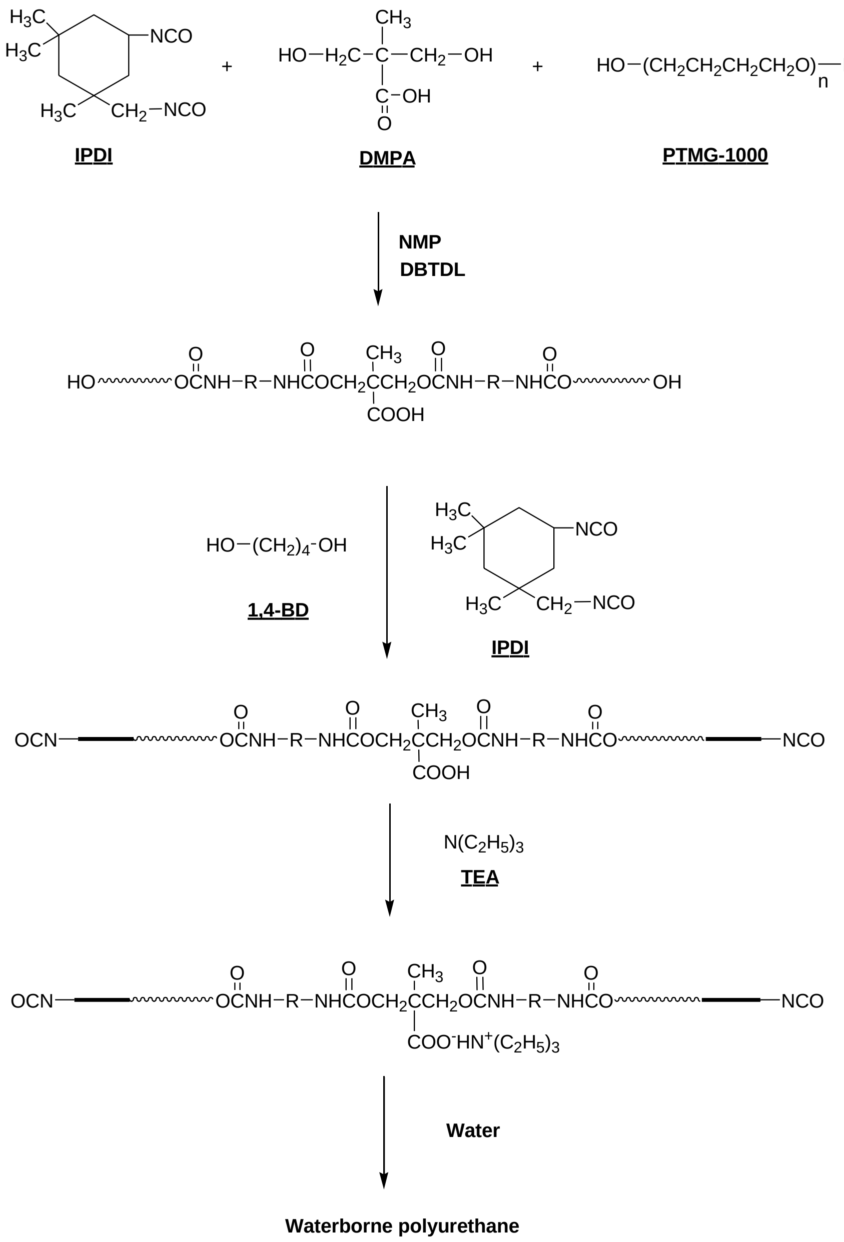
3.6.2 Synthesis of Modified PU Dispersions (PU-M)

Table 3.2 Recipe for the variation in carboxylic acid content of modified PU dispersions– g (equiv.)

	Reagent	PU3-M	PU5-M	PU7-M
First portion	**DMPA**	3.0 (0.045)	5.0 (0.075)	7.0 (0.104)
	PTMG-1000	57.6 (0.110)	51.5 (0.098)	45.2 (0.086)
	IPDI	16.1 (0.145)	18.1 (0.163)	20.1 (0.181)
Second portion	**IPDI**	15.6 (0.141)	16.0 (0.144)	16.6 (0.150)
	1,4-BD	5.4 (0.120)	5.6 (0.124)	5.8 (0.129)
Others	**TEA**	2.3 (0.022)	3.8 (0.037)	5.3 (0.052)
	NMP	20	20	20
	Water	150	150	150

A 1000-ml five-necked, round-bottom flask was equipped with a heating mantle/temperature controller, mechanical stirrer, thermometer and nitrogen inlet tube. The reaction was carried out in a constant temperature oil bath. Polytetramethylene ether glycol (PTMG-1000) and dimethylol propionic acid (DMPA) were charged into the dried flask. While stirring, 1-methyl-2-pyrrolidinone (NMP) (20 wt %) was added at 70 °C, and stirring was continued until homogenized mixture was obtained. The first portion of isophorone diisocyanate (IPDI) and dibutyltin dilaurate (DBTDL) were added dropwise, and stirring was continued for 30 min at this temperature. The mixture was heated to 80 °C for about 3 h to afford OH-terminated prepolymers. The change of the NCO content during the reaction was determined using a standard dibutylamine back titration method. Upon reaching the theoretical NCO value, the prepolymers was reacted with the rest of IPDI and chain extender (1,4-BD) to build up the hard segments, and allowed to react for 1 h at 80 °C. The reactions were cooled to 60 °C, and the neutralizing solution triethylamine

(TEA) was added, and stirred for 30 min while maintaining the temperature at 60 °C. Dispersion was accomplished by slowly adding water to the neutralized PU solution at 45–50 °C over 30 min with agitation speed of 700 rpm. The basic formulation and preparation procedure are shown in Table 3.2 and Scheme 3.2, respectively.



Scheme 3.2 Synthesis procedure of modified PU dispersion

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of Polyurethane Dispersions

The ionic groups content in the polyurethane ionomer structure was varied by varying the amount (3, 5 and 7 wt% (with respect to the prepolymer weight) of the internal emulsifier—dimethylolpropionic acid (DMPA).

In this study, the synthesis of polyurethane dispersion was carrying out as the conventional way, which often prepared by incorporating hydrophilic groups into the polymer backbone, which the hydrophilic groups acted as internal emulsifiers. Then they were chain extended, neutralized to form salts and dispersed the isocyanate terminated PU prepolymer, which contained stabilizing groups, into water. The formation of polyurethane particle in the water phase was shown in Figure 4.1. The polyurethane particles were dispersed in the water by self anionic emulsifier, $–COO^- HN^+(C_2H_5)_3$.

However, the synthetic method was modified so that the obtained PU dispersion would have the ionic groups in soft segments. In this case, polyol and ionic diol (internal emulsifier) were reacted with the first portion of isocyanate to obtain OH-terminated prepolymer. Then, the OH-terminated prepolymer was reacted with the rest of isocyanate and chain extender to build up hard segments. Finally, the resulting prepolymer was neutralized and dispersed with water.

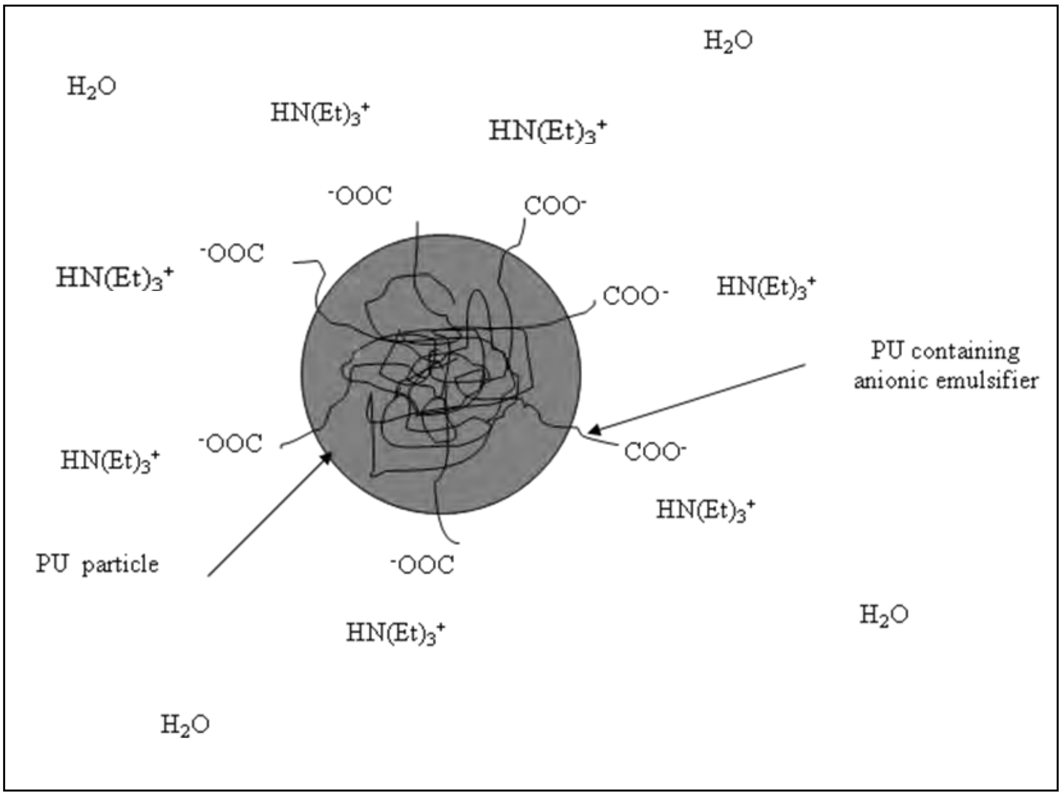


Figure 4.1 Diagrammatic formation of PU dispersion [56]

4.1.1. Fourier Transform Infrared (FTIR) Analysis

H-bondings in PUs have been extensively studied [57] using infrared spectroscopy, which has been well-confirmed as a particularly useful tool in characterizing the hydrogen-bonding characteristics in the domain. The typical examples of the IR spectra for both PUs containing 5 wt% DMPA are shown in Figure 4.2 and 4.3, respectively. One is conventional PU dispersion whiles another is modified PU dispersion that containing the ionic groups only in the soft segment. The assignments of the most useful characteristic IR bands are given in Table 4.1[53,57].

Table 4.1 Characteristic IR bands of the PU ionomers

Wavelength (cm^{-1})	Assignments
3480	ν(NH), free
3330	ν(NH), hydrogen-bonded
3000-2840	ν(C-H)
1729-1739	ν(C=O), free urethane carbonyl
1706-1716	ν(C=O), hydrogen-bonded urethane carbonyl
1540	δ(N-H) + ν(C-N), amide II
1240	δ(N-H) + ν(C-N), amide III
1110	ν(C-O-C), ether group

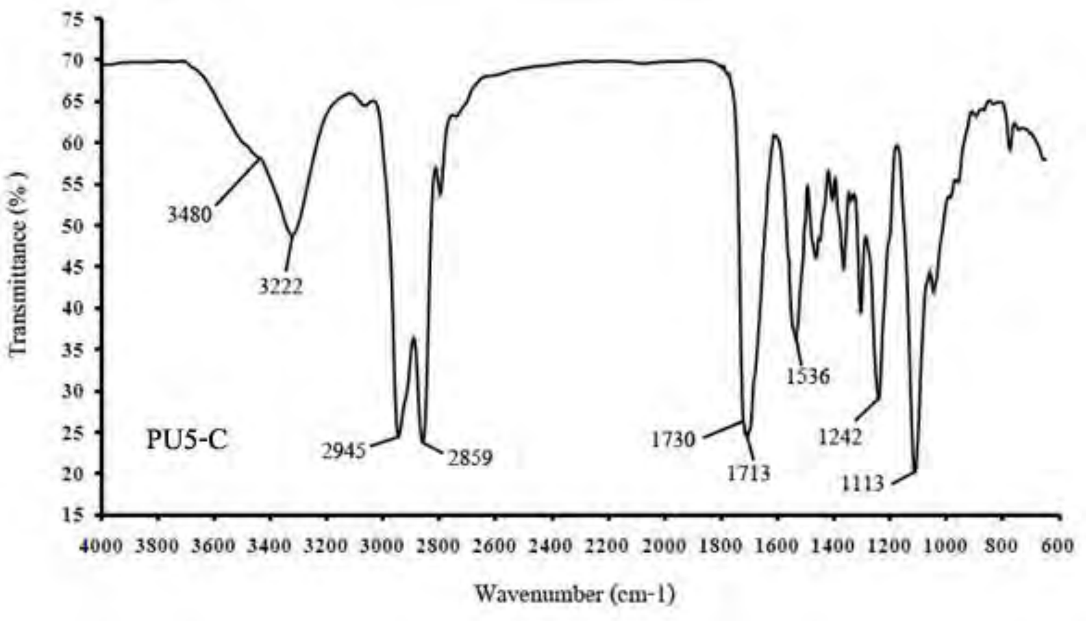


Figure 4.2 IR spectra of conventional PU dispersion containing 5 wt% DMPA

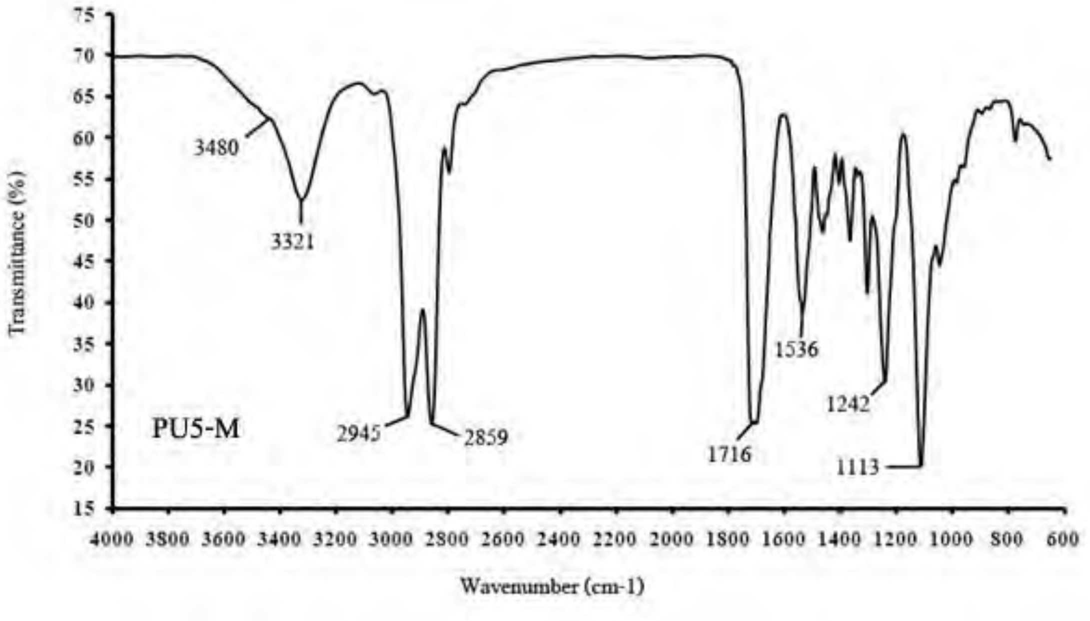


Figure 4.3 IR spectra of modified PU dispersion containing 5 wt% DMPA

Figure 4.2 and 4.3 show typical examples of the IR spectra and the characteristic functional groups of both types of PUs containing 5 wt% DMPA. In the present case, the –NH stretching vibration bands are composed of hydrogen-bonded –NH (3322 cm^{-1}) and free –NH (3480 cm^{-1}), while –C=O bands consist of hydrogen bonded –C=O (1713 cm^{-1}) and free –C=O (1730 cm^{-1}) [57]. The –CH stretching absorption band is observed at 2859-2945 cm^{-1}. The band at 1536 cm^{-1} can be assigned to amide II (δNH+ νCN) and the band at 1242 cm^{-1} is amide III (another type of δNH+ νCN) band, which also testify that –NH is in the hydrogen-bonded state [58]. The absorption band of the macroglycol appears at 1113 cm^{-1} due to C–O–C stretching [53]. So it can be concluding from the IR spectra that the formation of urethane group –NHCOO- is confirmed, which supported the polyurethane dispersion structure.

4.1.2 Nuclear Magnetic Resonance (NMR) Analysis

Figure 4.4 shows as a typical ^{1}H-NMR spectrum of conventional PU dispersion containing 5 wt% DMPA.

The signal at 0.9 ppm can be ascribed to linear unit of $–CH_3$ (CH_3-C-). The signal at 1.2 ppm corresponds to the cyclic unit of $–CH_2$ (-C-CH_2-C-). The signal at 1.6 ppm relates to the acyclic unit of $–CH_2$ (-C-CH_2-C-O-). The signal at 2.8 ppm should be attributed to -C-CH_2-NH-. The signal at 3.4 ppm can be described to $–CH_2$ (-CH_2-O-CO-). Thus, the signal at 1.6 and 3.4 ppm can be ascribed to only the polytetramethylene ether glycol, i.e. the soft segments in the polyurethane, whereas the signal at 0.9, 1.2 and 2.8 ppm only corresponds to the isophorone diisocyanate, i.e. the hard segments in the polyurethane. This interpretation is similar to the work done by Angeles Pérez-Limiñana, M. *et al.* [53]. Accordingly, the ^{1}H-NMR spectrum clearly confirmed the structure of the PU dispersion. Figure 4.5 also expresses the ^{1}H-NMR spectrum of modified PU dispersion containing 5 wt% DMPA, which presenting the similar spectrum.

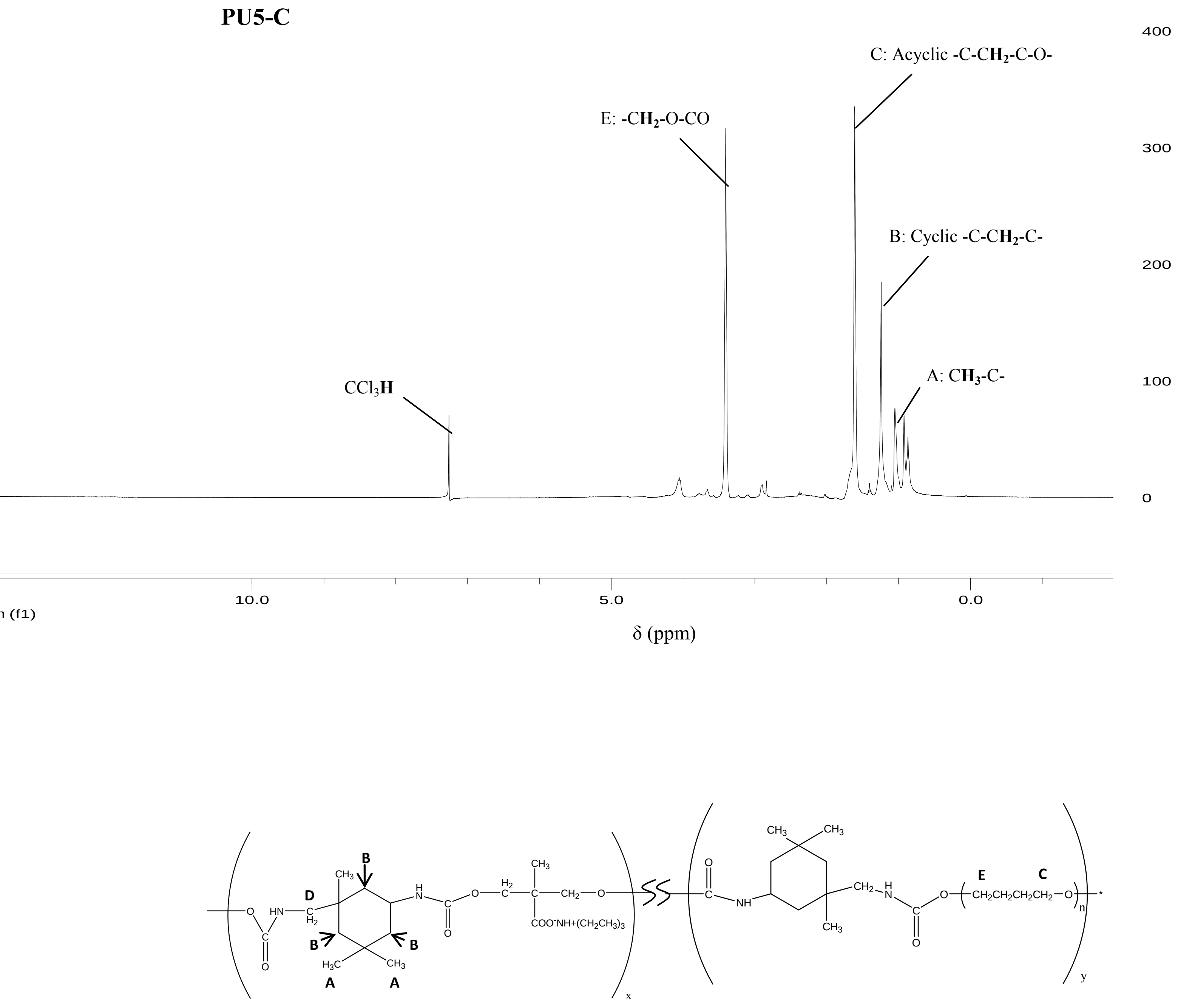


Figure 4.4 ^{1}H-NMR spectrum of conventional PU dispersion containing 5 wt% DMPA

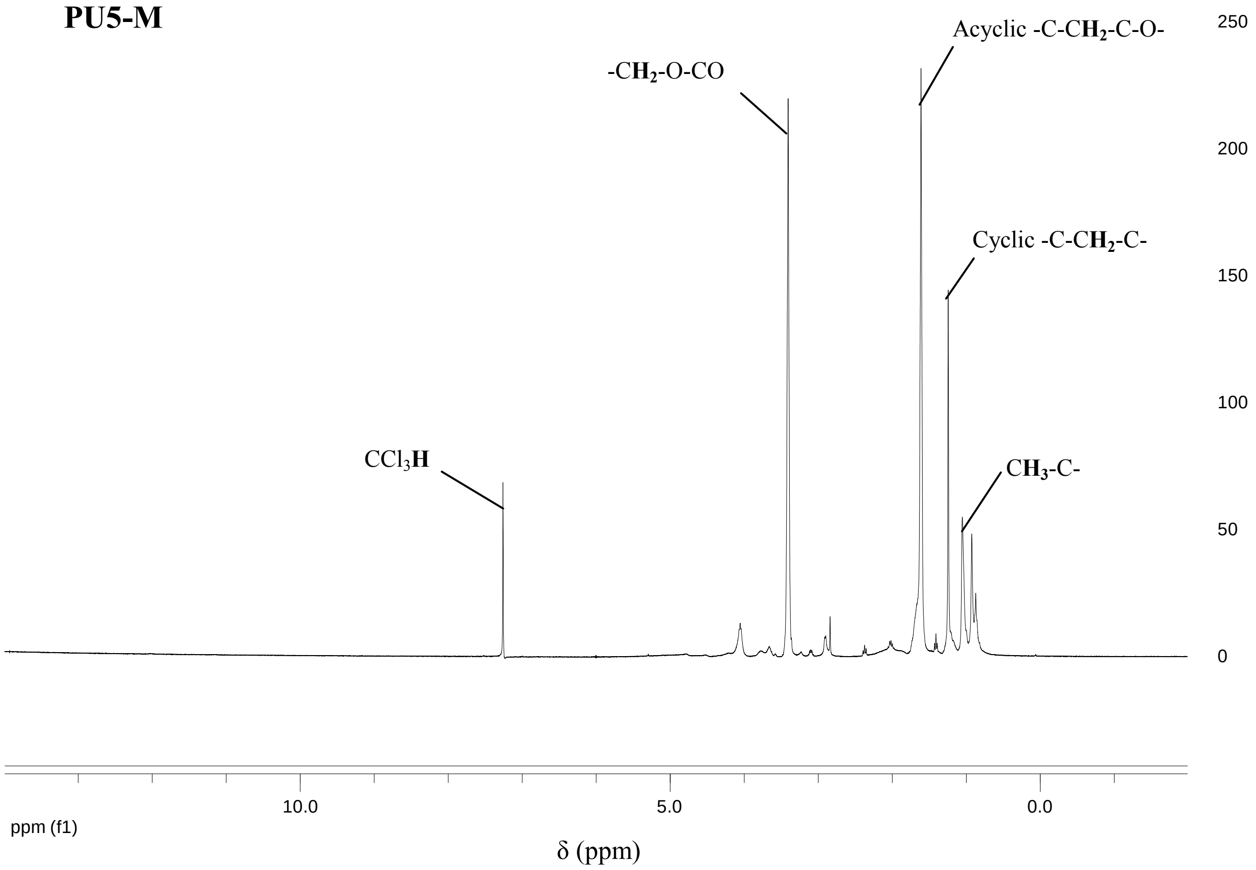


Figure 4.5 ^{1}H-NMR spectrum of modified PU dispersion containing 5 wt% DMPA

4.1.3 Dispersion Size Analysis

The average particle size of anionic polyurethane dispersion is an important factor of coatings that affecting the adhesion to the surface. The average particle size is mainly depends upon both functional monomers incorporated and the concentration of dispersing groups. In the present PU systems, ammonium carboxylate anions [$–COO^-HN^+(C_2H_5)_3$] are used as ionic salts.

The mean particle size for modified PU dispersions (PU-M) and conventional PU dispersions (PU-C) containing 3, 5 and 7 wt% DMPA are summarized in Table 4.3. Where –d” stands for diameter and –PI” is a shorten word for polydispersity index. Three replicate measurements are taken for all samples. The influence of ionic group‘s position and content of ionic groups on the size of particle and its distribution are investigated in this study.

Angeles Pérez-Limiñana, M. *et al.* [53] synthesized PU dispersion adhesives and measured particle size and its distribution by laser particle size analyzer. They found some scatters between the two measurements and suggested that elongated shaped particles were produced, which were responsible of the different measurements taken by the laser beam detector in the particle size analyzer. In contrast with the present study, all PU dispersions show a narrow particle size distribution (by intensity) indicating that most particles have the same size. In addition, the scattering between three measurements are not found in all cases. This indicates that spherical shaped particles are produced, which are responsible of the same measurements taken by the laser beam detector in the laser particle size analyzer as shown in Table 4.2.

Table 4.2 Three replicate measurements of particle size and particle size distribution of PU dispersions

Measurement **Series**	**Mean particle size (nm)**		
	1	**2**	**3**
PU3-C	82	83	83
PU3-M	61	61	62
PU5-C	49	49	48
PU5-M	36	36	36
PU7-C	26	26	25
PU7-M	20	21	20

At the same DMPA content, modified PU dispersions (PU-M) provide smaller particle size than conventional PU dispersions (PU-C). PU-M also gives a narrower particle size distribution (by intensity) as compared to PU-C. The polydispersity index

(PI) confirms this conclusion. The polydispersity index (PI), in this case, is a measure of the distribution of particle size, not the distribution of molecular mass [56], in a given polymer sample. The polydispersity index (PI) has a value equal to or greater than zero, but as the particles approach uniform size, the ‗PI‘ approaches zero (0). The ‗PI‘ value of PU-M is smaller and approached to zero (0) than PU-C. Thus most of particles in PU-M are smaller than PU-C. Whereas, PU-C provides a wider particle size distribution, indicating that there are largely differences in size of the particles. The greater particle size in PU-C could be due to excessive viscosity of the prepolymer during the dispersion step, leading to the difficult breakup during dispersion. These results are also summarized in Table 4.3.

Table 4.3 The solution and dispersion characteristic of the PU dispersions

Series	**DMPA (wt%)**	**Mean particle size (nm)**	**PI**	**Brookfield Viscosity* (cP)**	**Contact Angle (˚)**	**Z-potential (mV)**
PU3-C	3	83	0.080	214	112±1	-49
PU3-M	3	61	0.027	45	121±2	-42
PU5-C	5	49	0.175	367	97±2	-42
PU5-M	5	36	0.104	110	104±2	-42
PU7-C	7	26	0.220	684	64±1	-36
PU7-M	7	20	0.203	245	73±3	-39

* Brookfield viscometer: Spindle no. 64, speed = 250 rpm, T = 25 ˚C.

Because the chemical compositions of the two types of PUs are the same, the total hydrophilicity should be the same. Therefore, the difference in particle size distribution is presumably due to the chain flexibility adjacent to ionic groups.

The flexibility of the chains adjacent to dispersing groups is mainly influenced the mobility of dispersing groups. The hard segments provide rigid chains whereas the soft segments provide flexible chains. Because of more chain flexibility, PU-M requires the lower energy for the conformation change compared with PU-C. Thus ionic groups incorporated into soft segments can be more easily exposed to the surface and then provide the higher concentration of ionic groups at the surface also [51,59]. The ionic groups are electrical charges. The identical charges have a mutual repulsion. This repulsive force between identical particles provides colloidal particles separate, leading to the easier breakup of the dispersed phase during phase inversion with water addition. This will provide a decrease of the particle size and resist settling out under the influence of gravity. The viscosity of emulsion bases on many factors such as particle size, particle size distribution, particle concentration, and particle-particle interactions etc.

In Table 4.3, PU-M provides significantly lower solution viscosity than PU-C at the same DMPA content. This may be due to easier breakup of the dispersed phase during dispersion. In contrast, the larger particle size of PU-C is mainly due to the higher solution viscosity leading to the difficult breakup during dispersion. This observation is consistent with the explanation by Kim, B.K. *et al.* [51], which can be explained by Equation 4.1

Assuming that interfaces have stress continuity, the lower dispersed phase viscosity leads to higher shear rate (higher dispersed phase deformation) according to Equation 4.1 [51].

$$\dot{\gamma}_d = \frac{\mu_c}{\mu_d} \times \dot{\gamma}_c \qquad \text{Equation 4.1}$$

Where γ and μ are the shear rate and the viscosity, and the subscripts c and d designate continuous and dispersed phases, respectively. Thus, the lower dispersed phase viscosity of PU-M makes it easily breakup during water addition, resulting in a decrease in solution viscosity.

The influence of dispersing group concentration on dispersion solution properties is shown in Table 4.3. The particle size decreases with increasing DMPA content owing to the higher hydrophilicity of the particles. In addition, with the particle size decreases, there is an increase in the number of particles. Hence, the effective hydrodynamic volume (the volume of a polymer coil when it is in solution) of the dispersed phase increases and the force of friction among particles increases, resulting in an increase of viscosity [6,53].

4.1.4 Contact Angle Measurements

Contact angle, Θ, is a quantitative measure of the wetting of a solid by a liquid. Low values of Θ indicate that the liquid spreads over the substrate, or wets well, while high values indicate poor wetting. If Θ is greater than 90° the liquid tends to form droplets on the surface. If Θ is less than 90° the liquid tends to spread out over the surface and when Θ tends to zero, it presents the liquid forms a thin film or complete wetting.

In this study, contact angle measurements using water are carried out to compare the film properties of both types of PUs containing various DMPA content. The results are summarized in Table 4.3**.** The influence of ionic group‘s position and dispersing group concentration on the film properties are discussed respectively.

At the same DMPA content, modified PU dispersions (PU-M) have higher contact angles for water than conventional PU dispersions (PU-C). These data indicate that PU-M can increase the hydrophobicity of PU coatings relative to conventional PU-C. These may be due to conformational rearrangements. It is well-recognized that hydrophilic groups are preferentially positioned on the surface of the particle and form the film surface upon casting and drying. These conformational rearrangements can occur instantly for PU-C because most of the urethane groups which are hydrophilic as well as ionic groups are located in hard segments. Both of hydrophilic group and hydrophilic urethane augment the hydrophilicity of the hard segment. As a result, the greater the hydrophilicity, the lower the water contact angle, and thus the worse the water resistance are obtained. PU-M, in contrast, most of the urethane groups are located in the core of the particles even if the ionic groups are positioned on the surface. Thus the surface of the particle of PU-M exhibits lower hydrophilicity than PU-C. As a result, the lower the hydrophilicity, the higher the water contact angle, and thus the better the water resistance is obtained [51,59].

An increase in the DMPA content from 3 to 7 wt% provides lower water contact angle in both types of PUs as shown in Table 4.3. This is due to an increase in ionic groups on the surface of the PU film. The higher the ionic group is, the more excellent the hydrophilicity of the film surface is, the lower the water contact angle is, and thus the worse the water resistance is.

4.1.5 Colloidal Stability

The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system, which determines their storage period. [59]. Particles with zeta potentials more positive than +30 mV or more negative than -30 mV are normally considered stable. In this study, all the samples have a large negative zeta potential which their zeta potentials are more negative than -30 mV as shown in Table 4.3. Thus, they will tend to repel each other, prevent the particles coming together and flocculating. The results reveal that all the samples are stable and show very good performance in terms of shelf-life.

4.1.6 Differential Scanning Calorimetry (DSC) Analysis

Differential scanning calorimetry is a well-recognized method to study the morphology of segmented polyurethanes. The thermal transitions of synthesized PU dispersions are therefore determined by DSC analysis. DSC thermograms of both types of PUs containing 3, 5 and 7 wt% DMPA are shown in Figure 4.6. In this study, the tests were done under nitrogen atmosphere.

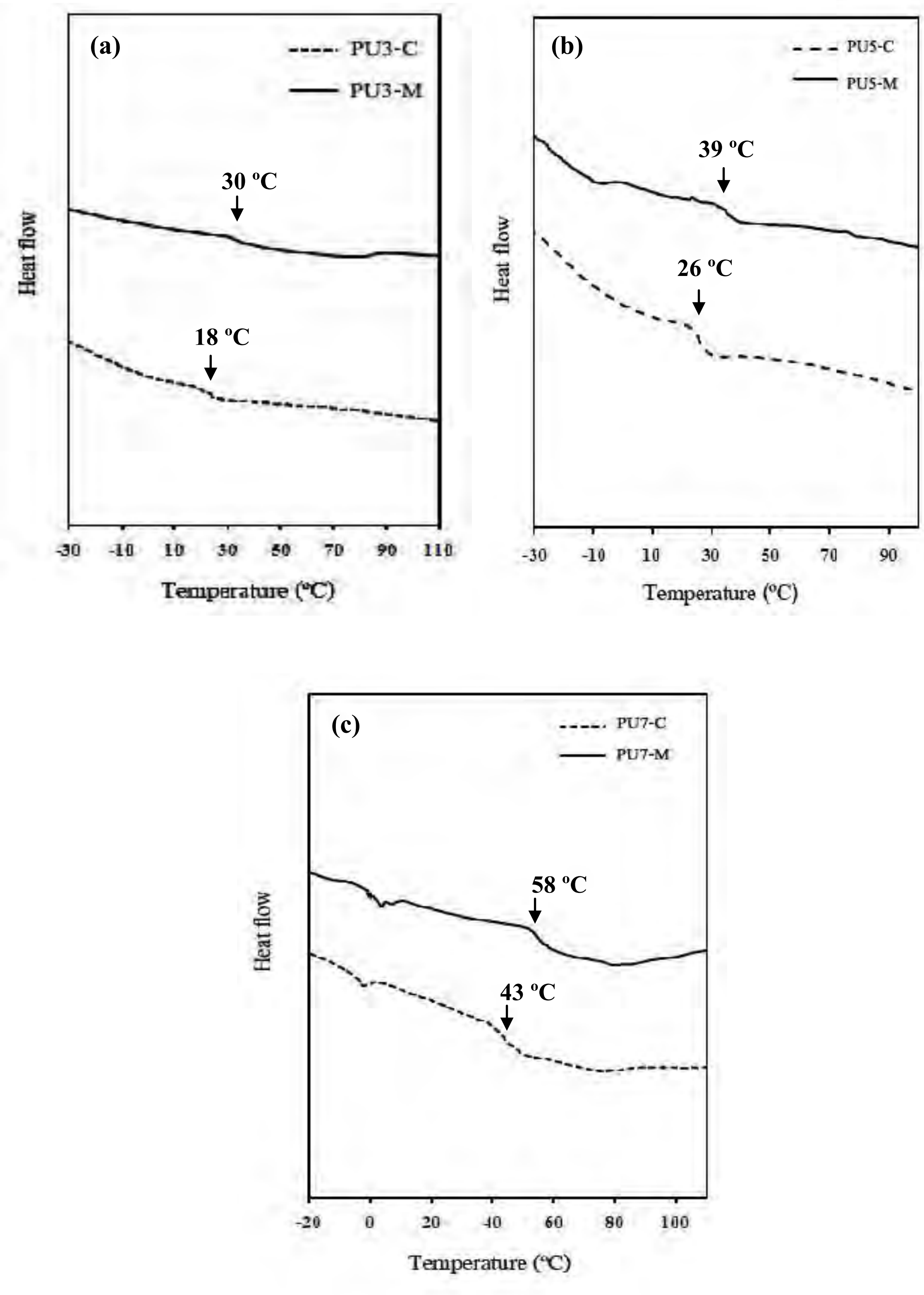


Figure 4.6 DSC thermograms of the two types of PUs containing (a) 3, (b) 5 and (c) 7 wt% DMPA

Table 4.4 DSC results of both types of PU films

Series	**DMPA (wt%)**	**T_g (ºC)**
PU3-C	3	18
PU3-M	3	30
PU5-C	5	26
PU5-M	5	39
PU7-C	7	43
PU7-M	7	58

The glass transition temperature (T_g) varied between 18 ºC and 52 ºC. All the samples show a single T_g [60]. The increase in the T_g indicates the presence of hard segments dispersed in the soft segment microdomains. Polyurethanes consist of two phases, the nearly pure hard microdomains with high T_g and the soft microdomains with low T_g. In fact, both PU-M and PU-C were synthsised in different processes. The different methods may be the important factor that affecting the properties of PU films. For the synthesis of PU-M, PTMG and DMPA were reacted with the first portion of the total IPDI content. Then 1,4-BD and the rest of IPDI were added. In case of PU-C, the synthesis was carried out by the conventional pre-polymer mixing process. Owing to the synthesized process of PU-SS, partial soft segments of PU-SS are extended conformation together with some trapped hard segments. The chain mobility of the soft segments is restricted by the trapped hard segments resulting in an increase in the T_g of the soft microdomain [61,62].

There is an elevation in T_g which increasing DMPA content. PUs containing 7 wt% DMPA has the highest T_g among all the samples due to the largest fraction of hard segments. So the increase in the DMPA content provides an increase in the hard segment content of the polyurethane ionomer. The higher hard segment content, the higher restriction to the chain mobility of the soft segments is, resulting in the elevation in the T_g [53].

4.1.7 Thermogravimetric (TG) Analysis

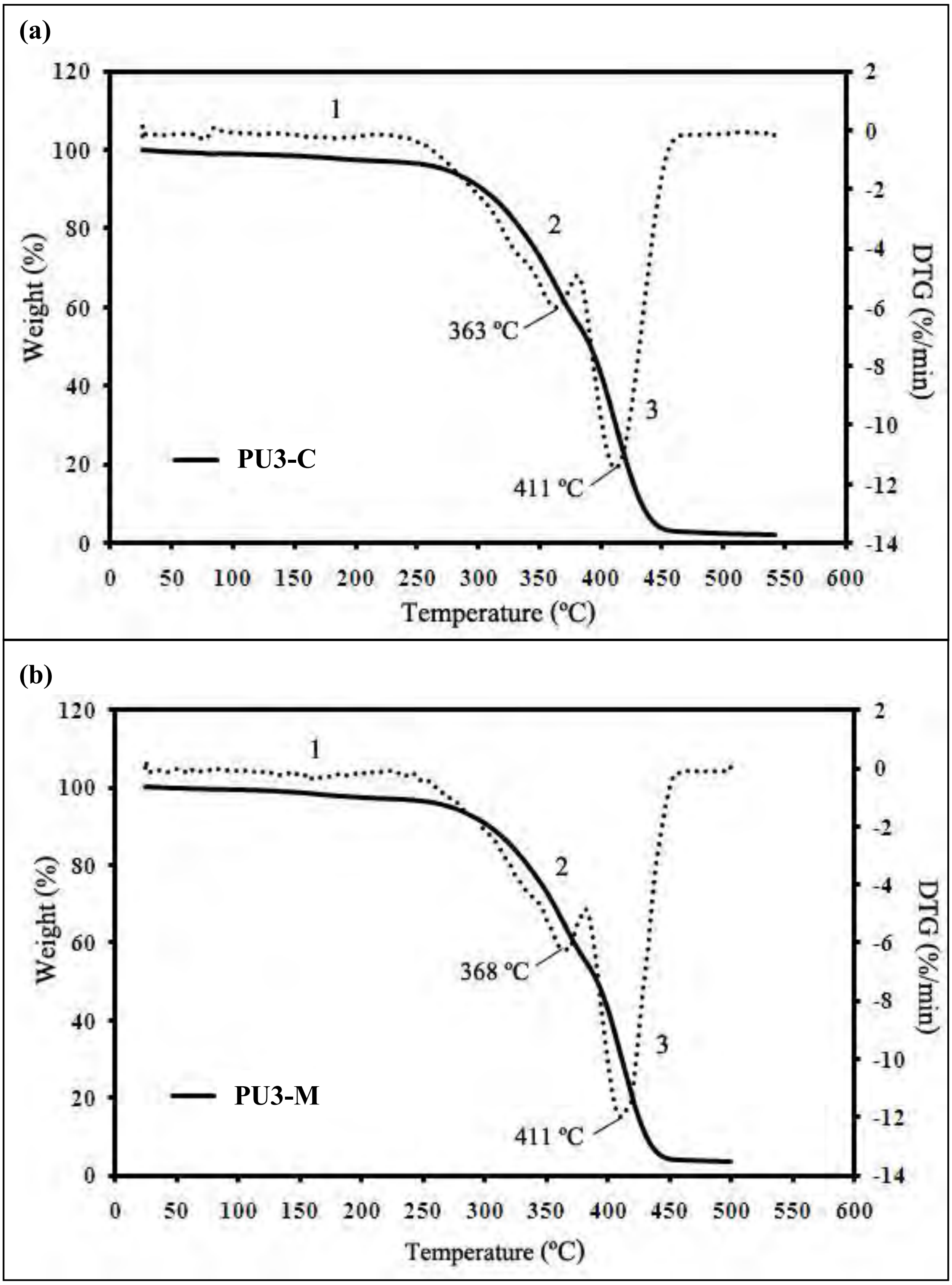


Figure 4.7 TG/DTG curves: (a) PU3-C and (b) PU3-M

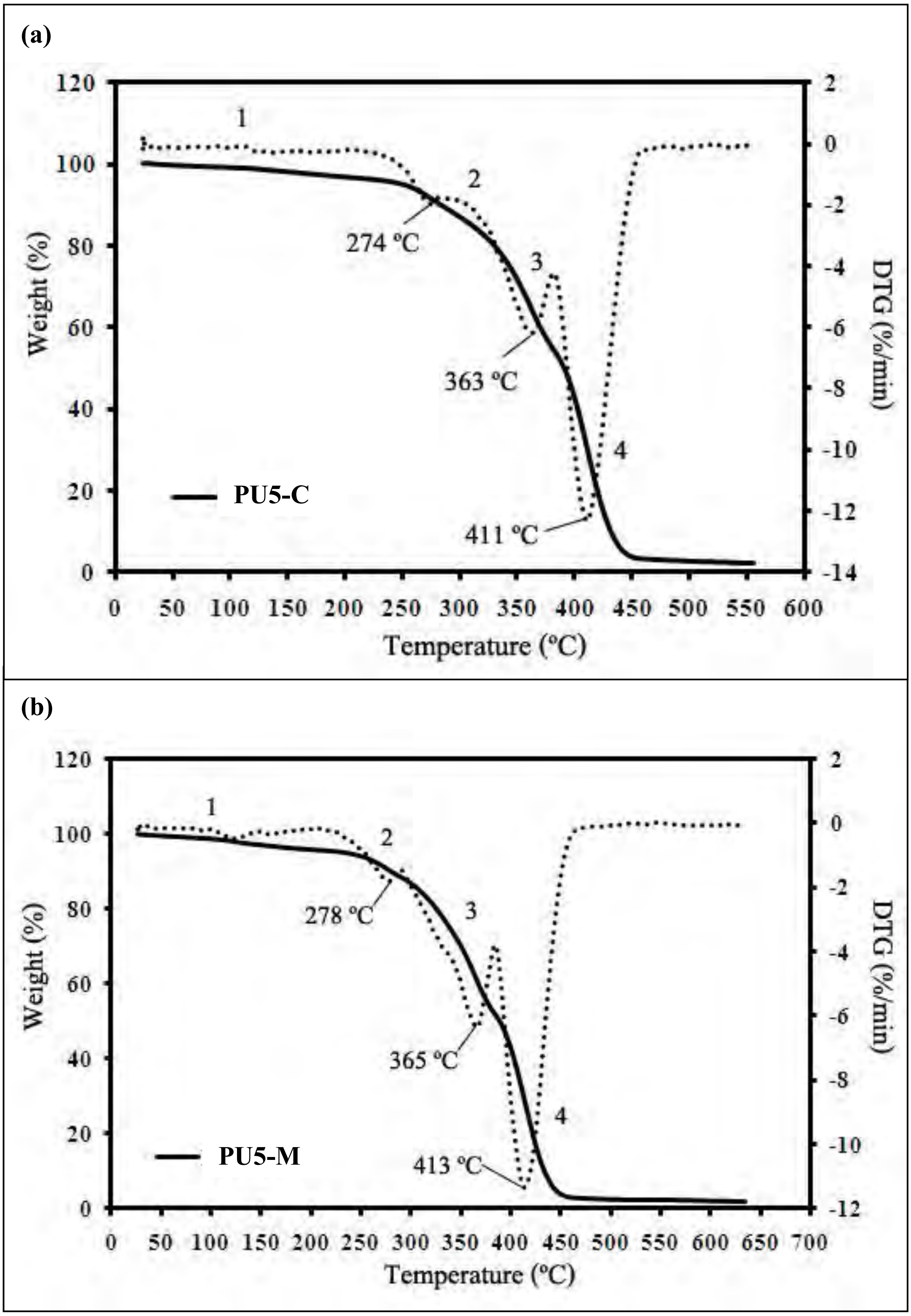


Figure 4.8 TG/DTG curves: (a) PU5-C and (b) PU5-M

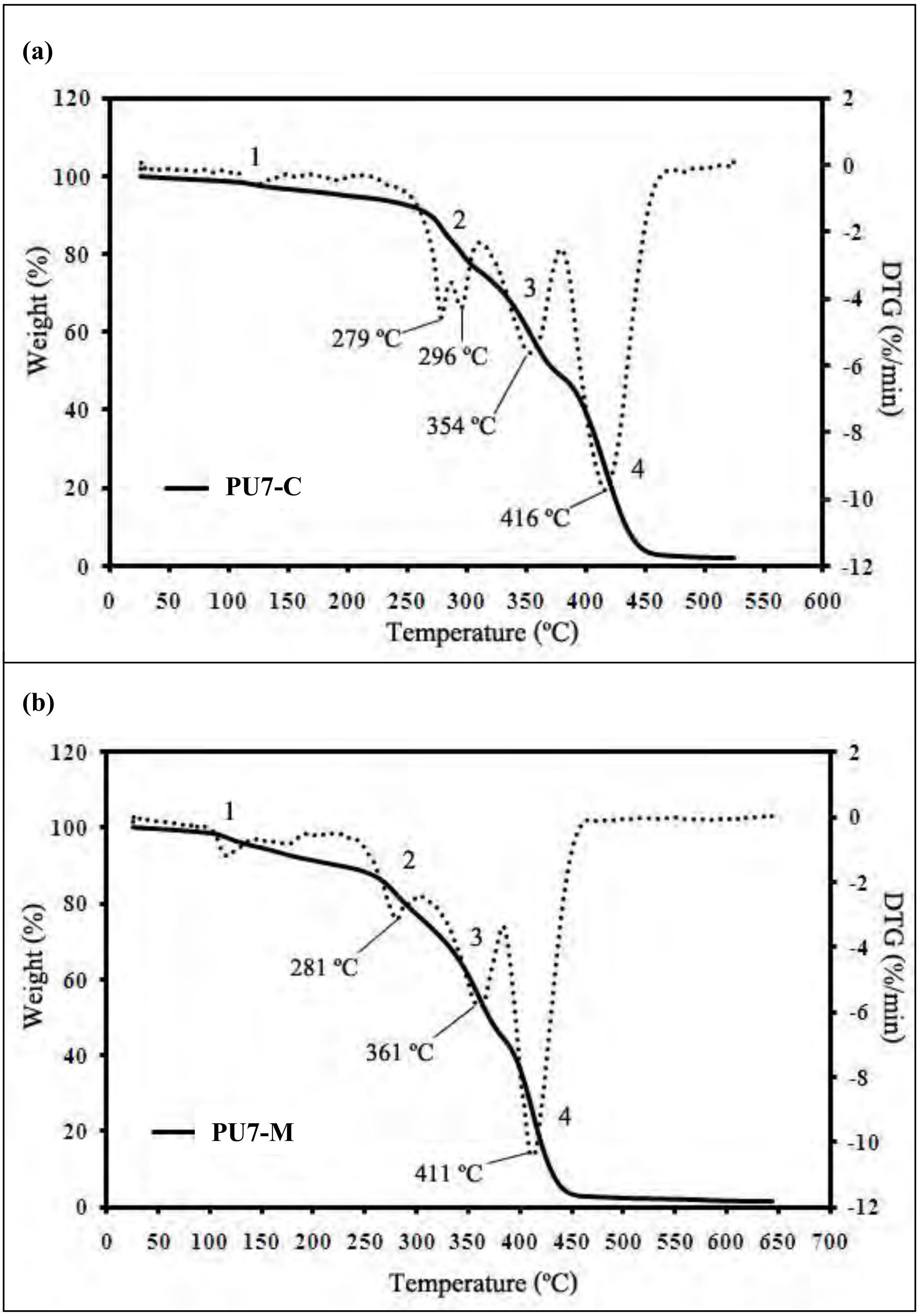


Figure 4.9 TG/DTG curves: (a) PU7-C and (b) PU7-M

Thermogravimetric analysis is used to analyze the decomposition behavior and thermal resistance of PU films. TG/DTG curves of both types of PUs containing 3, 5 and 7 wt% DMPA are shown in Figure 4.7, 4.8 and 4.9, respectively. Four decomposition steps can be seen, except in samples from both types of PU dispersions containing 3 wt% DMPA (*PU3-C and PU3-M*) that had three decomposition steps.

Three degradation steps are found in both types of PU dispersions containing 3 wt% DMPA as shown in Figure 4.7. The thermal decomposition temperature in the first step is occurred at about 280 ºC with a weight loss less than 5%, as a result of evaporation of residual moisture. By increasing the temperature, two additional decomposition processes occur at about 300 and 410 ºC. The thermal decomposition temperature in the second step starts at approximately 300 ºC and continues up to 360~370 ºC [6]. Since PTMG (a polyol) and 1,4-butane diol (a chain extender) were used in this synthesis, only one kind of hard segments (urethane) is produced in the polyurethane ionomers. Moreover, It is well-known that the isocyanate-based polymers provide their thermostability in the following order [6]: isocyanurate > urea > urethane > biuret > allophanate. As a result, the second degradation step relates to a reaction of polymerization. This depolymerization corresponds to the urethane bond dissociating into its starting materials, i.e., alcohol and isocyanate and then the monomers slowly volatilize. Figure 4.7, the thermogram of the macroglycol was obtained (which constitutes the soft segments) and only one decomposition stage was found at 411 ºC. Therefore, the third degradation step corresponds to the soft segments in the polyurethane ionomers.

Both types of PU dispersions containing 5 and 7 wt% DMPA exhibit four degradation steps as expressed in Figure 4.8 and Figure 4.9, respectively. The first decomposition step is due to evaporation of trapped moisture, is occurred before 260 ºC with a weight loss less than 5%. The second step of degradation at approximately 270-300 ºC is related to unreacted IPDI monomers in the reaction product [63,64]. This interpretation is similar to the work done by Zhang, Y. *et al.* [63]. It is well-known that the condensation polymerization reaction is completed hardly. In addition, IPDI is an aliphatic isocyanate which has the slowest reactivity of all the commercially available polyisocyanates. So it is possible to observe some unreacted monomers left in the reaction product. The third decomposition step starts at approximately 300 ºC and continues up to 350~360 ºC [6]. This corresponds to the degradation of hard segments. The last weight loss step is about 410 ºC, corresponds to the soft segments in the polyurethane ionomers.

From the above results, it can be concluded that:

- PU3-C and PU3-M have similar TG/DTA profiles as shown in Figure 4.7.
- PU5-C and PU5-M have similar TG/DTA profiles as shown in Figure 4.8.
- PU7-C and PU7-M have similar TG/DTA profiles as shown in Figure 4.9.

So both types of PUs with the same DMPA content have similar thermal stability.

To investigate the effect of hydrophilic group content on thermal properties of PU films, the DMPA content was varied (3, 5 and 7 wt% with respect to the prepolymer weight). While the others parameters are kept constant. TG/DTG curves of both types of PUs with various DMPA content are shown in Figure 4.10 and 4.11, respectively.

The decrease in the DMPA content provides a slight increase in the decomposition temperature. As can be seen from Figure 4.10 and 4.11, their TG profiles in the temperature range of 200–400 ºC are shift to the right. The decomposition temperature of the soft segments is produced around 410–420 ºC. The effect of the decrease in the ionic group content on the thermal behavior of PUs can be ascribed to a decrease in the amount of hard segments. The presence of a lower amount of hard segments in polyether backbone makes the PU insensitive to chain scission and exacerbates the structural crowding, resulting in higher stability and lower degradation. It can be concluding that: when the ionic group‘s position is the same, the lower the amount of DMPA, the higher stability and lower degradation are obtained.

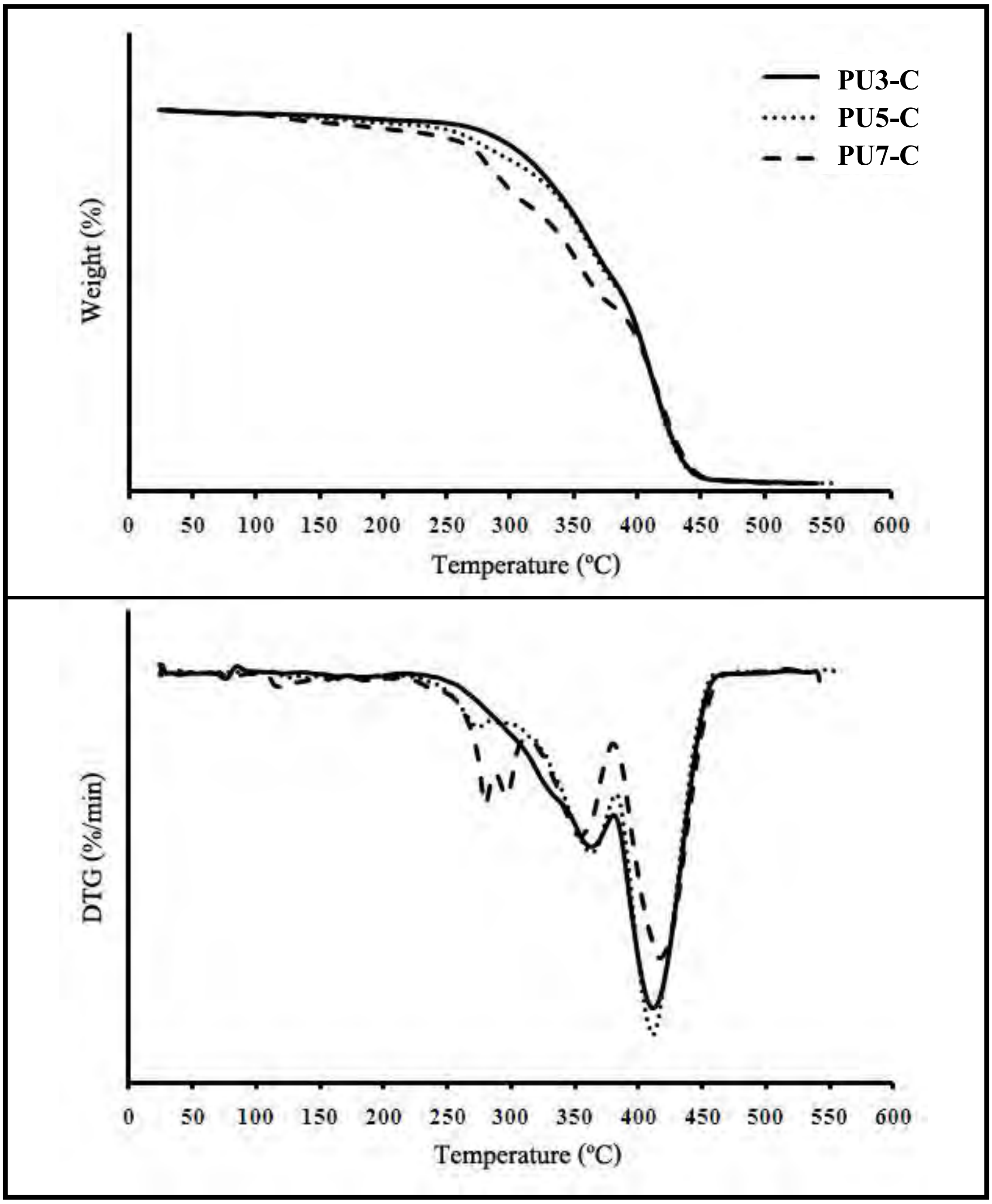


Figure 4.10 TG/DTG curves of PU-C with various DMPA content

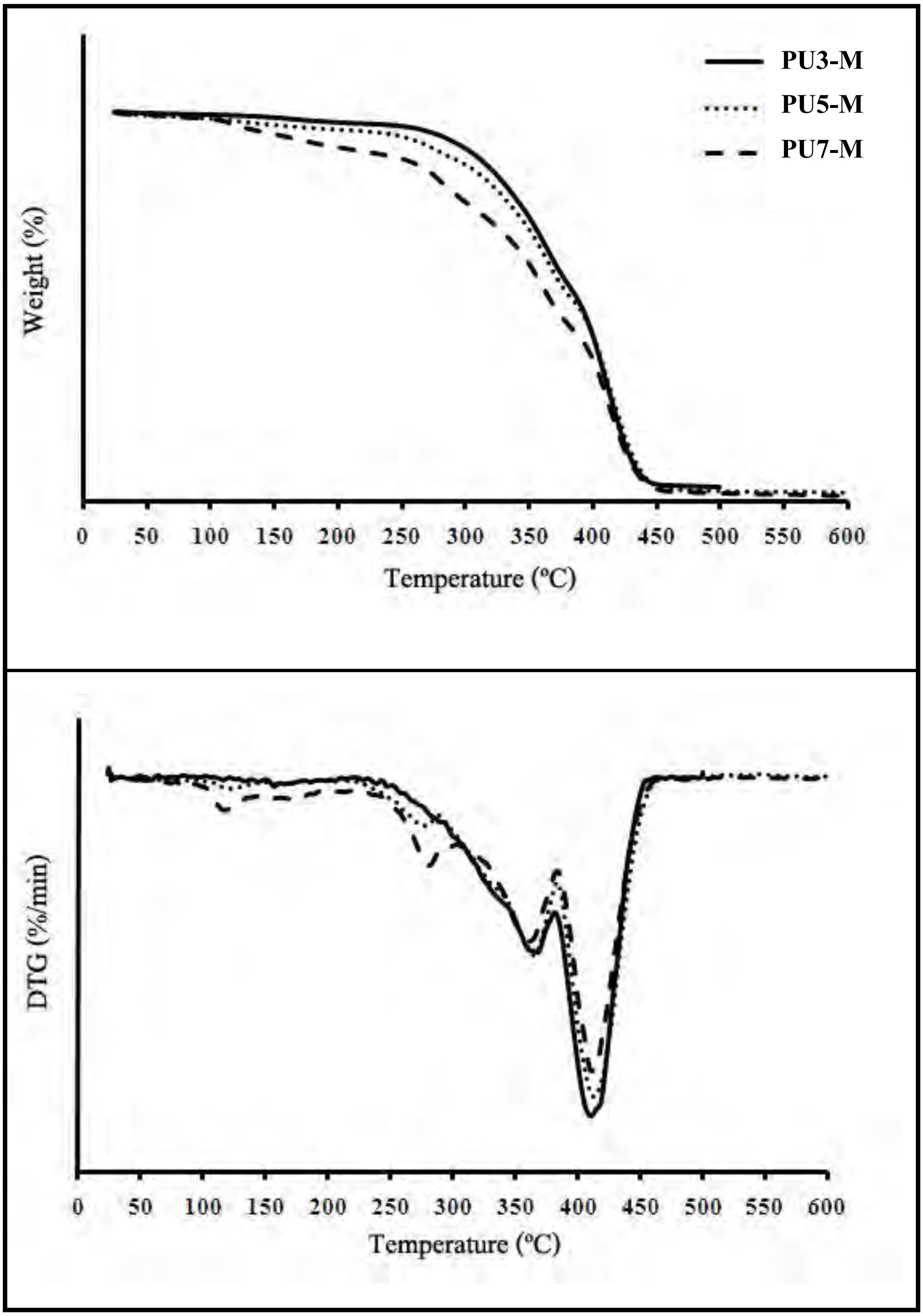


Figure 4.11 TG/DTG curves of PU-M with various DMPA content

4.1.8 Mechanical Properties

Hardness is one of the most important properties of a coating surface. The pencil hardness test is typically used in industry. Pencil hardness is a measure of the resistance of the surface of a film to marking. The calibrated pencil is used to move over sample at fixed degree and pressure. Total 12 pencils (5H-5B) as shown below are used in this test method. Set of calibrated pencils, of the following hardness.

5B – 4B – 3B – 2B – B – HB – F– H – 2H – 3H – 4H – 5H

Softer **Harder**

Table 4.5 shows the pencil hardness of both types of PUs film which was coated on a glass plate at various DMPA content. The pencil hardness of these PU films measured between 4B and 2H. The influence of ionic group‘s position and hydrophilic content on mechanical properties of PU dispersions was discussed.

Table 4.5 Mechanical properties of PU dispersions

Series	DMPA (wt%)	Pencil hardness
PU3-C	3	4B
PU3-M	3	2B
PU5-C	5	B
PU5-M	5	HB
PU7-C	7	F
PU7-M	7	2H

It can be observed from Table 4.5 that all PU-M exhibit better hardness properties than PU-C. At fixed DMPA content, the higher hardness in case of PU-M can be attributed to their higher T_g values as compared to PU-C. It is well-known that T_g constitutes the most important mechanical property for all polymers. The glass transition temperature (T_g), is the temperature at which the amorphous phase of the polymer is converted between rubbery and glassy states. Thus, the higher the glass transition temperature (T_g), the greater percentage of these polymers exist in hard and glassy state and hence exhibit enhanced hardness properties [30].

Moreover, an increase in the DMPA content provides better hardness properties as can be seen from Table 4.5. The effect of the increase in the ionic group content (from 3 to 7 wt% DMPA) on the mechanical properties of PUs can be ascribed to an increase in the amount of hard segments. The presence of a higher amount of hard segments in polyether backbone restricts segmental mobility of the macromolecular chains, resulting in an increase in the glass transition temperature (T_g) and hence exhibit better hardness properties of PUs.

CHAPTER V

CONCLUSIONS AND SUGGESTIONS

Two types of PU dispersions with 37 wt% solid content were prepared. It was found that modified PU dispersions containing ionic soft segment (PU-M) had smaller particle size compared with conventional PU dispersions (PU-C) of the same DMPA content. In addition, PU-M exhibited better properties than PU-C in water resistance and hardness, while its thermal property was similar to PU-C. When DMPA content increased, the particle size and particle size distribution of both PU-C and PU-M decreased. It was also found that DMPA content would affect PU properties. At higher DMPA content, both PU-C and PU-M films showed lower water resistance and thermal stability, but higher hardness.

5.1 Further works

Synthesis of PU dispersion with an ionic group in the soft segment using different isocyanates and polyols should be studied and compared with this work.

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APPENDICES

APPENDIX A

APPENDIX A

Calculations

The amount of isocyanate required to react with the polyol and any other reactive additives is calculated in order to obtain the chemically stoichiometric equivalents. This theoretical stoichiometric amount of isocyanate may then be adjustd upwards or downwards by varying the isocyanate index, dependent on the polyurethane system, the properties required of the polymeric product and known effects such as the scale of manufacture and the ambient conditions.

Hydroxyl value

The hydroxyl value (OHv) of a polyol, sometimes called the hydroxyl number, is determined by acetylating the polyol with pyridine and acetic anhydride with standard KOH solution, measuring the difference between a blank solution and one containing polyol.

The OHv can then be defined as the weight of KOH in milligrams that will neutralize the acetic anhydride capable of reacting by acetylation with one gramme of polyol. The molecular weight of KOH is 56.1.

Percent hydroxyl

An alternative way of expressing the hydroxyl content of a polyol is as the percent hydroxyl groups present in the structure and this value is obtained from the following formula:

$$\text{Percent hydroxyl (\%OH)} = \frac{\text{OHV} \times (\text{MWt OH}) \times 100}{56.1 \times 1{,}000} = \frac{\text{OHv} \times 17 \times 100}{56.1 \times 1{,}000}$$

$$= \frac{\text{OHv}}{33}$$

Acid value

The acid value (Av) of a polyol, sometimes called the acid number, is determined by measuring the difference between titrating, with a standard KOH solution, a blank solution and one containing polyol.

Molecular weight of a polyol

The molecular weight of a polyol is determined from the OHv and the Av as follows:

$$\text{Molecular weight polyol} = \frac{\text{Functionality} \times 56.1 \times 1{,}000}{(\text{OHv} + \text{Av})}$$

Equivalent weight of a polyol

The equivalent weight of a polyol is defined as the portion of the molecular weight that contains one hydroxyl group and is defined as:

$$\text{Equivalent weight} = \frac{\text{Molecular weight}}{\text{Functionality}} = \frac{56.1 \times 1{,}000}{(\text{OHv} + \text{Av})}$$

Equivalent weight of chain extenders
(hydroxyl- and amine-terminated)

The molecular and equivalent weights of a range of common hydroxyl- and amine-terminated chain extenders are given in Table A-1.

Table A-1 Functionality, OHv and molecular/equivalent weights for a range of chain extenders

Chain extender	Molecular weight	OHv (mg KOH/g)	Functionality	Equivalent weight
Ethylene glycol	62.07	1,808	2	31.04
Diethylene glycol	106.12	1,057	2	53.06
Propylene glycol	76.09	1,474	2	38.05
Dipropylene glycol	134.17	836	2	67.09
1,4-Butane diol	90.12	1,245	2	45.06
1,6-Hexane diol	118.17	949	2	59.09
1,4-Cyclohexandimethanol	144.21	778	2	72.11
Hydroquinone dihydroxyethyl ether	198.21	566	2	99.11
1,2,4-Butanetriol	106.12	1,586	3	35.37
Trimethylol propane	106.12	1,586	3	35.37
Glycerol	92.09	1,827	3	30.70
Water	18.02	6,230	2	9.01
Ethanolamine	77.09	1,456	2	38.55
Diethanolamine	105.14	1,601	3	35.05
Triethanolamine	149.19	1,128	3	49.73
m-Phenylene diamine	108.14	1,038	2	54.07
Diethyl toluene diamine	178.27	629	2	89.14
Dimethylthiotoluene diamine	214.34	523	2	107.17

Isocyanate value

The isocyanate value is the weight percentage of reactive isocyanate (NCO) groups in an isocyanate, modified isocyanate or prepolymer and is determined using the following equation, where the molecular weight of the NCO group is 42:

$$\text{Isocyanate value} = \%\text{NCO groups} = \frac{42 \times \text{Functionality}}{\text{Molecular weight}} \times 100$$

$$= \frac{4{,}200}{\text{Equivalent weight}}$$

The isocyanate values and molecular and equivalent weights of a range of isocyanates are given in Table A-2.

Table A-2 Isocyanate values and molecular/equivalent weights for a range of isocyanates

Isocyanate	**Molecular weight**	**Isocyanate value (%)**	**Functionality**	**Equivalent weight**
TDI	174.16	48.2	2	87.07
MDI	250.26	33.6	2	125.13
NDI	210.19	40.0	2	105.10
IPDI	222.30	37.8	2	111.15
H_{12}MDI	262.35	32.0	2	131.18
HDI	168.20	49.9	2	84.10
PPDI	160.13	52.5	2	80.07
CHDI	166.18	50.5	2	83.09
TMXDI	244.30	34.4	2	122.15
HDI trimer	504.60	25.0	3	168.20
MDI trimer	750.78	16.8	3	250.26
IPDI trimer	666.90	18.9	3	222.30
TDI-TMP adduct	628.60	20.0	3	209.53

Isocyanate index

The isocyanate index for a formulation is a measure of the excess isocyanate used relative to the theoretical equivalent amount required and is defined as:

$$\text{Isocyanate index} = \frac{\text{Actual amount of isocyanate used}}{\text{Theoretical amount of isocyanate required}} \times 100$$

An isocyanate index of 105, sometimes written as 1.05, indicates that there is a five percent excess of isocyanate.

Prepolymer formular

Table A-3 Synthesis of conventional PU dispersion containing 3 wt% DMPA: ***PU3-C***

Components	Wt.	Eq.Wt.	Eq.
Dimethylol Propionic Acid (DMPA) Mw 134/2	3.0	67	0.045
Polytetramethylene Ether Glycol (PTMG-1000) OHv#107, Av#0.05	57.6	$\frac{56100}{107.05} = 524$	0.110
Isophorone Diisocyanate (IPDI) Mw 222/2	31.7	111	0.286
1,4-Butane Diol (1,4-BD) Mw 90/2	5.4	45	0.120
Triethylamine (TEA) Mw 101/2	2.3	-	0.022
1-Methyl-2-pyrrolidinone (NMP)	20	-	-
Water	150	-	-

Theoretical %NCO = 5.50 Actual %NCO Titrated = 5.05

Theoretical %NCO

$$\boxed{\text{Theoretical \%NCO} = \frac{(\text{NCO Eq.} - \text{Total OH Eq.}) \times 42 \times 100}{\text{Formulation Wt.}}}$$

Example:

$$\text{Theoretical \%NCO} = \frac{(0.286 - 0.110 - 0.045) \times 42 \times 100}{100} = 5.50$$

Chain extension

Calculating the NCO equivalent of the prepolymer and adding stoichiometric amount of 1,4-Butane Diol. Exact %NCO is determined from titration methods.

Example:

%NCO		NCO Mw	1,4-Butane Diol Mw = 90/2
5.05	÷	42	

$$= 0.120 \times 45\ \text{Eq.Wt.} = {}^{5.41\ \text{g}}\!/_{100\ \text{g Preplymer}}$$

Neutralization

Amount added is determined by calculating the carboxyl equivalent of the prepolymer.

Example:

Prepolymer	DMPA Wt.		Mw DMPA		Eq.
100 g	3.0 g	÷	134	=	0.0224

Carboxyl Eq.		Mw TEA		TEA added
0.0224	×	101	=	2.2624 g

Table A-4 Synthesis of modified PU dispersion containing 3 wt% DMPA: ***PU3-M***

PUD	Components	Wt.	Eq.Wt.	Eq.
Soft segment	Dimethylol Propionic Acid (DMPA) Mw 134/2	3.0	67	0.045
	Polytetramethylene Ether Glycol (PTMG-1000) OHv#107, Av#0.05	57.6	$\frac{56100}{107.05} = 524$	0.110
	Isophorone Diisocyanate (IPDI) Mw 222/2	16.1	111	0.145
Hard segment	Isophorone Diisocyanate (IPDI) Mw 222/2	15.6	111	0.141
	1,4-Butane Diol (1,4-BD) Mw 90/2	5.4	45	0.120
	Triethylamine (TEA) Mw 101/2	2.3	-	0.022
	1-Methyl-2-Pyrrolidinone (NMP)	20	-	-
	Water	150	-	-

Table A-5 Synthesis of conventional PU dispersion containing 5 wt% DMPA: ***PU5-C***

Components	**Wt.**	**Eq.Wt.**	**Eq.**
Dimethylol Propionic Acid (DMPA) Mw 134/2	5.0	67	0.075
Polytetramethylene Ether Glycol (PTMG-1000) OHv#107, Av#0.05	51.5	$\frac{56100}{107.05} = 524$	0.098
Isophorone Diisocyanate (IPDI) Mw 222/2	34.1	111	0.307
1,4-Butane Diol (1,4-BD) Mw 90/2	5.6	45	0.124
Triethylamine (TEA) Mw 101/2	3.8	-	0.037
1-Methyl-2-pyrrolidinone (NMP)	20	-	-
Water	150	-	-

Theoretical %NCO = 5.63 Actual %NCO Titrated = 5.24

Theoretical %NCO

$$\boxed{\text{Theoretical \%NCO} = \frac{(\text{NCO Eq.} - \text{Total OH Eq.}) \times 42 \times 100}{\text{Formulation Wt.}}}$$

Example:

$$\text{Theoretical \%NCO} = \frac{(0.307 - 0.098 - 0.075) \times 42 \times 100}{100} = 5.63$$

Chain extension

Calculating the NCO equivalent of the prepolymer and adding stoichiometric amount of 1,4-Butane Diol. Exact %NCO is determined from titration methods.

Example:

%NCO		NCO Mw	1,4-Butane Diol Mw = 90/2
5.24	÷	42	

$$= 0.125 \times 45 \text{ Eq.Wt.} = {}^{5.61\ \text{g}}/_{100\ \text{g Preplymer}}$$

Neutralization

Amount added is determined by calculating the carboxyl equivalent of the prepolymer.

Example:

Prepolymer	DMPA Wt.		Mw DMPA		Eq.
100 g	5.0 g	÷	134	=	0.0373

Carboxyl Eq.		Mw TEA		TEA added
0.0373	×	101	=	3.7687 g

Table A-6 Synthesis of modified PU dispersion containing 5 wt% DMPA: ***PU5-M***

PUD	Components	Wt.	Eq.Wt.	Eq.
Soft segment	Dimethylol Propionic Acid (DMPA) Mw 134/2	5.0	67	0.075
	Polytetramethylene Ether Glycol (PTMG-1000) OHv#107, Av#0.05	51.5	$\frac{56100}{107.05} = 524$	0.098
	Isophorone Diisocyanate (IPDI) Mw 222/2	18.1	111	0.163
Hard segment	Isophorone Diisocyanate (IPDI) Mw 222/2	16.0	111	0.144
	1,4-Butane Diol (1,4-BD) Mw 90/2	5.6	45	0.124
	Triethylamine (TEA) Mw 101/2	3.8	-	0.037
	1-Methyl-2-Pyrrolidinone (NMP)	20	-	-
	Water	150	-	-

Table A-7 Synthesis of conventional PU dispersion containing 7 wt% DMPA: ***PU7-C***

Components	**Wt.**	**Eq.Wt.**	**Eq.**
Dimethylol Propionic Acid (DMPA) Mw 134/2	7.0	67	0.104
Polytetramethylene Ether Glycol (PTMG-1000) OHv#107, Av#0.05	45.2	$\frac{56100}{107.05} = 524$	0.086
Isophorone Diisocyanate (IPDI) Mw 222/2	36.7	111	0.331
1,4-Butane Diol (1,4-BD) Mw 90/2	5.8	45	0.128
Triethylamine (TEA) Mw 101/2	5.3	-	0.052
1-Methyl-2-pyrrolidinone (NMP)	20	-	-
Water	150	-	-

Theoretical %NCO = 5.92 Actual %NCO Titrated = 5.10

Theoretical %NCO

$$\boxed{\text{Theoretical \%NCO} = \frac{(\text{NCO Eq.} - \text{Total OH Eq.}) \times 42 \times 100}{\text{Formulation Wt.}}}$$

Example:

$$\text{Theoretical \%NCO} = \frac{(0.331 - 0.104 - 0.086) \times 42 \times 100}{100} = 5.92$$

Chain extension

Calculating the NCO equivalent of the prepolymer and adding stoichiometric amount of 1,4-Butane Diol. Exact %NCO is determined from titration methods.

Example:

%NCO		NCO Mw	1,4-Butane Diol Mw = 90/2
5.40	÷	42	

$$= 0.129 \times 45\ \text{Eq.Wt.} = {}^{5.81\ \text{g}}/_{100\ \text{g Preplymer}}$$

Neutralization

Amount added is determined by calculating the carboxyl equivalent of the prepolymer.

Example:

Prepolymer	DMPA Wt.		Mw DMPA		Eq.
100 g	7.0 g	÷	134	=	0.0522

Carboxyl Eq.		Mw TEA		TEA added
0.0522	×	101	=	5.2761 g

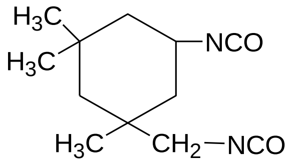
Table A-8 Synthesis of modified PU dispersion containing 7 wt% DMPA: ***PU7-M***

PUD	Components	Wt.	Eq.Wt.	Eq.
Soft segment	Dimethylol Propionic Acid (DMPA) Mw 134/2	7.0	67	0.104
	Polytetramethylene Ether Glycol (PTMG-1000) OHv#107, Av#0.05	45.2	$\frac{56100}{107.05} = 524$	0.086
	Isophorone Diisocyanate (IPDI) Mw 222/2	20.1	111	0.181
Hard segment	Isophorone Diisocyanate (IPDI) Mw 222/2	16.6	111	0.150
	1,4-Butane Diol (1,4-BD) Mw 90/2	5.8	45	0.128
	Triethylamine (TEA) Mw 101/2	5.3	-	0.052
	1-Methyl-2-Pyrrolidinone (NMP)	20	-	-
	Water	150	-	-

APPENDIX B

APPENDIX B

Physical Properties of Isophorone Diisocyanate (IPDI)



Isophorone diisocyanate (IPDI) is a cycloaliphatic diisocyanate. It is colorless or light yellow with low viscosity. IPDI is nearly odorless.

Table B-1 General properties of IPDI

	IPDI
Molecular weight	222.3 g/mol
Density at 20 ˚C	1.061 g/cm^3
Boiling point (˚C)	216 ˚C
Vapor pressure at 20 ˚C	10^{-4} hPa
Viscosity at 20 ˚C	15 mPa·s
Flash point (closed up)	155 ˚C

Table B-2 Grades and specifications of IPDI

Specifications	**IPDI**
Assay	>99% (GC, area-%)
NCO-content	37.5 – 37.8% by weight
Color	< 30 Hazen

Uses of IPDI

Isophorone diisocyanate is frequently used for light-stable PUR systems. Most important are IPDI prepolymers, which are obtained by reactions of IPDI with polyols. However, trimeric isophorone diisocyanate and block polyisocyanates are preferred for coating applications. The resulting polyurethanes show good mechanical properties, excellent thermal stability and chemical resistance. Main applications are in light-stable coatings, adhesives and artificial leather.

Physical Properties of Polytetramethylene Ether Glycol (PTMG)

$$HO-(CH_2CH_2CH_2CH_2O)_n-H$$

Polytetramethylene ether glycol (PTMG) is a linear glycol which has primary hydroxyl groups at both ends. It easily reacts with polyisocyanates (ex. MDI, TDI) as well as polycarbonic acids (ex. TPA) to form polymers with following excellent qualities.

Table B-3 General properties of PTMG

	PTMG-1000
Appearance	Transparent liquid or white waxy solid at low temperature
Average molecular weight	1,000
Boiling point (˚C)	Higher than 204
Flash point (˚C)	Higher than 260
Specific gravity (40/4˚C)	0.976
Viscosity (cps)	290(40˚C)
Specific heat (kcal/kg·˚C)	0.523

Table B-4 Grades and specifications of PTMG

Specifications	PTMG-1000
Molecular weight	1,000 ± 50
Hydroxyl number (mg KOH/g)	107 - 118
Acid number (mg KOH/g)	0.05MAX.
Moisture (%wt)	0.03MAX.
Volatiles (%wt)	0.1MAX.
Color (APHA)	90MAX.

Uses of PTMG

PTMG is raw material for high performance polyurethane and polyester which are used in widespread fields ranging from general consumer goods such as clothing and wrapping materials for foodstuffs to industrial goods such as machinery parts. Expansion of uses and consumption is expected even further in the future.

- Polyurethanes
  Elastic polyurethane fibers
  Thermosetting elastomers
  Thermoplastic elastomers
  Paints and coatings
  Adhesives
  Sealants
  Synthetic and artificial leather
- Polyesters
  Polyester resins

APPENDIX C

APPENDIX C

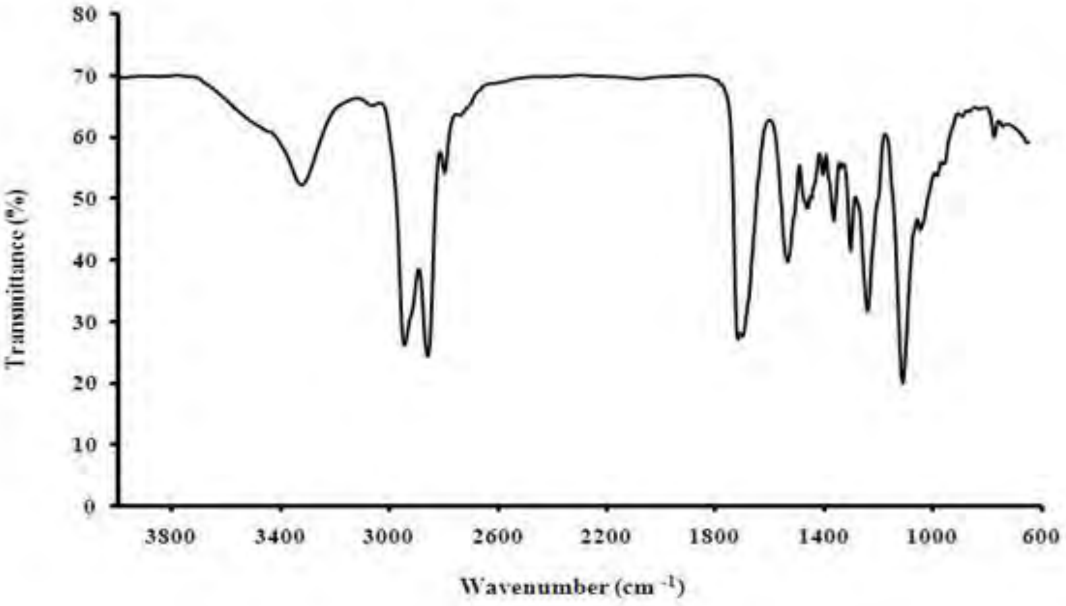


Figure C-1 FTIR spectrum of conventional PU dispersion containing 3 wt% DMPA *(PU3-C)*

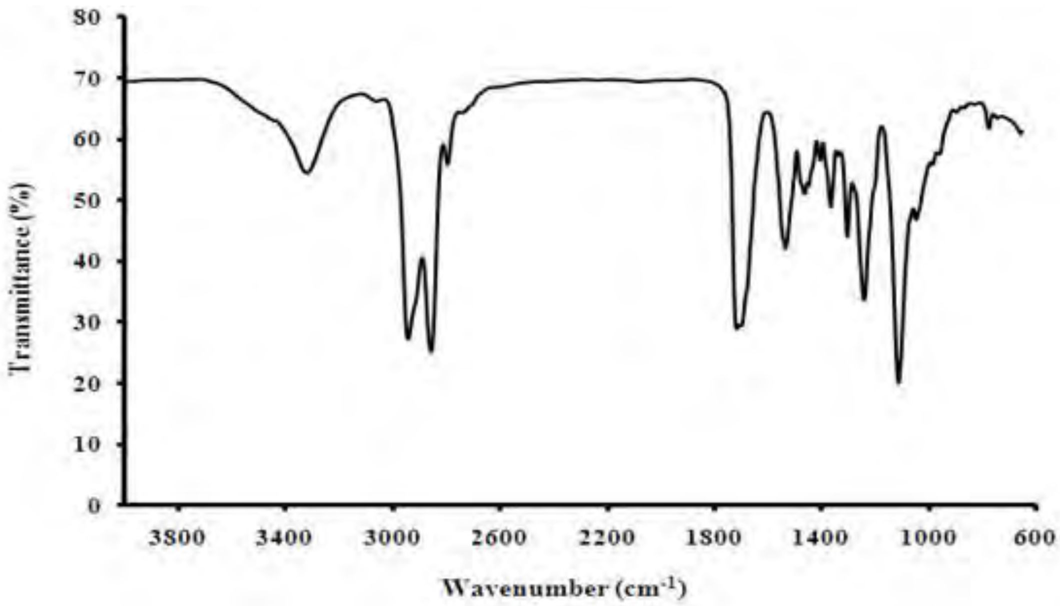


Figure C-2 FTIR spectrum of modified PU dispersion containing 3 wt% DMPA *(PU3-M)*

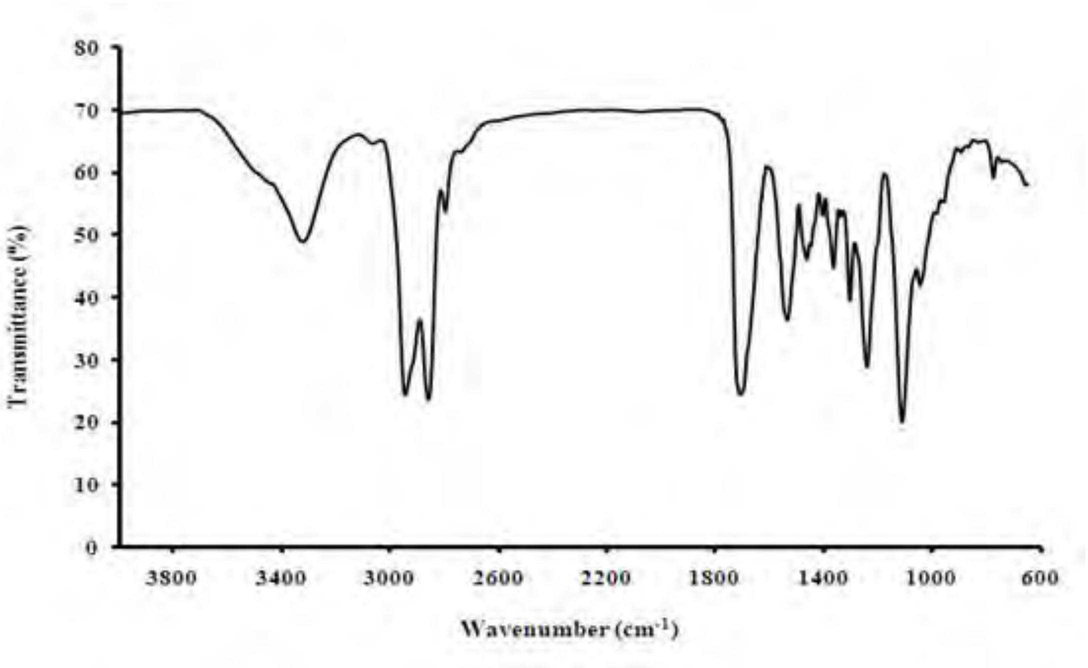


Figure C-3 FTIR spectrum of conventional PU dispersion containing 5 wt% DMPA *(PU5-C)*

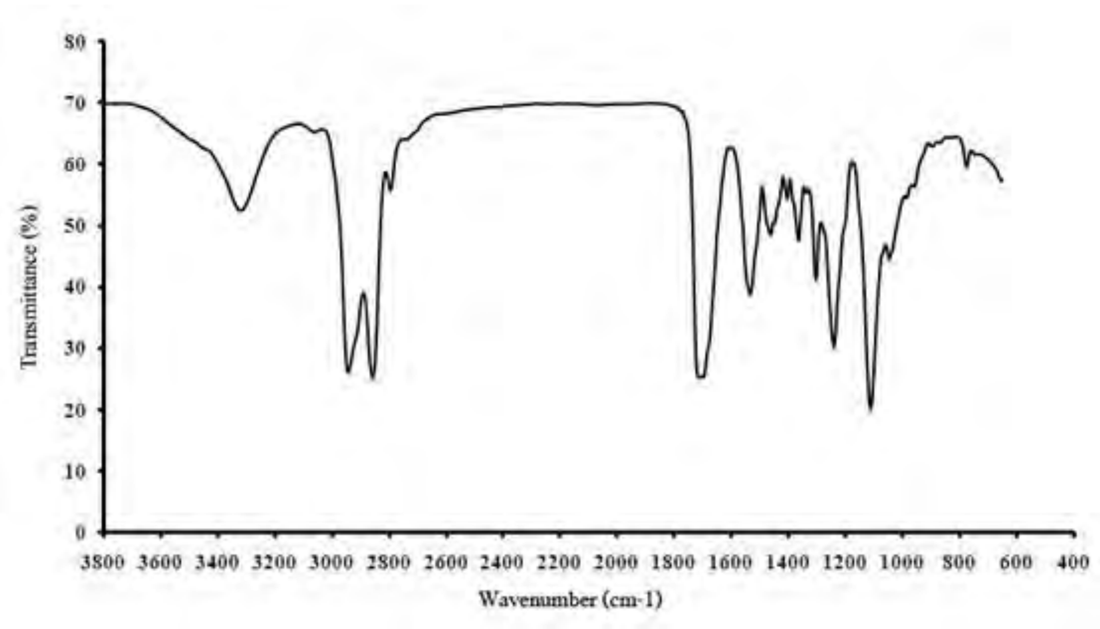


Figure C-4 FTIR spectrum of modified PU dispersion containing 5 wt% DMPA *(PU5-M)*

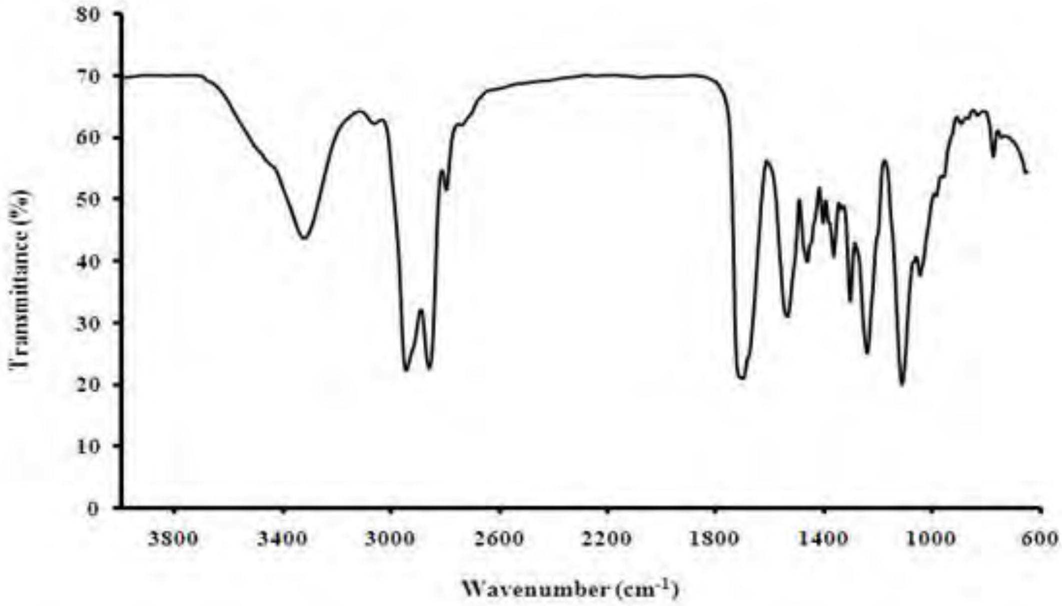


Figure C-5 FTIR spectrum of conventional PU dispersion containing 7 wt% DMPA *(PU7-C)*

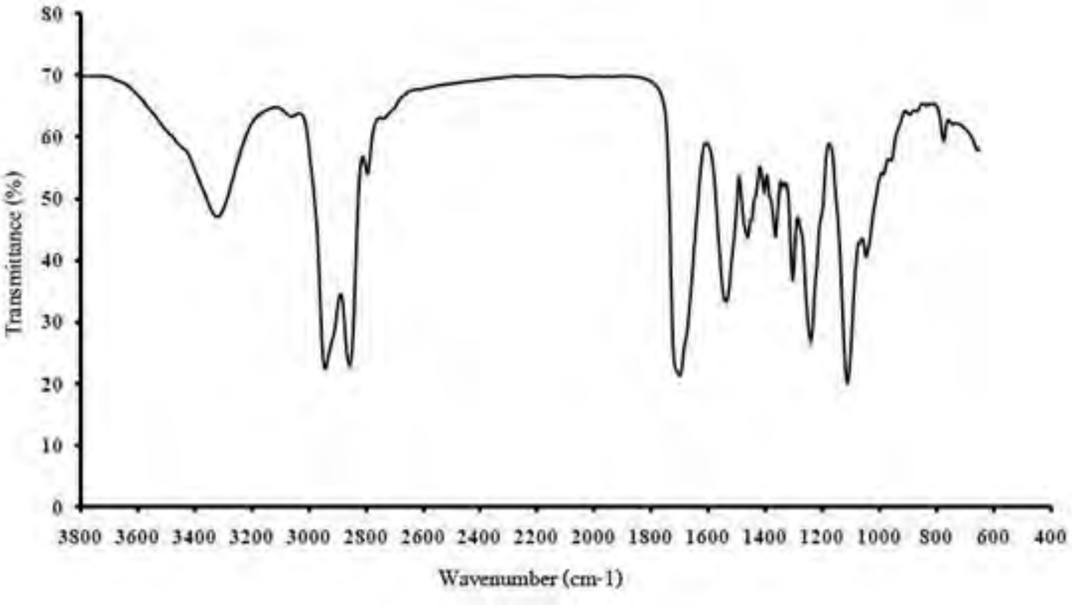


Figure C-6 FTIR spectrum of modified PU dispersion containing 7 wt% DMPA *(PU7-M)*

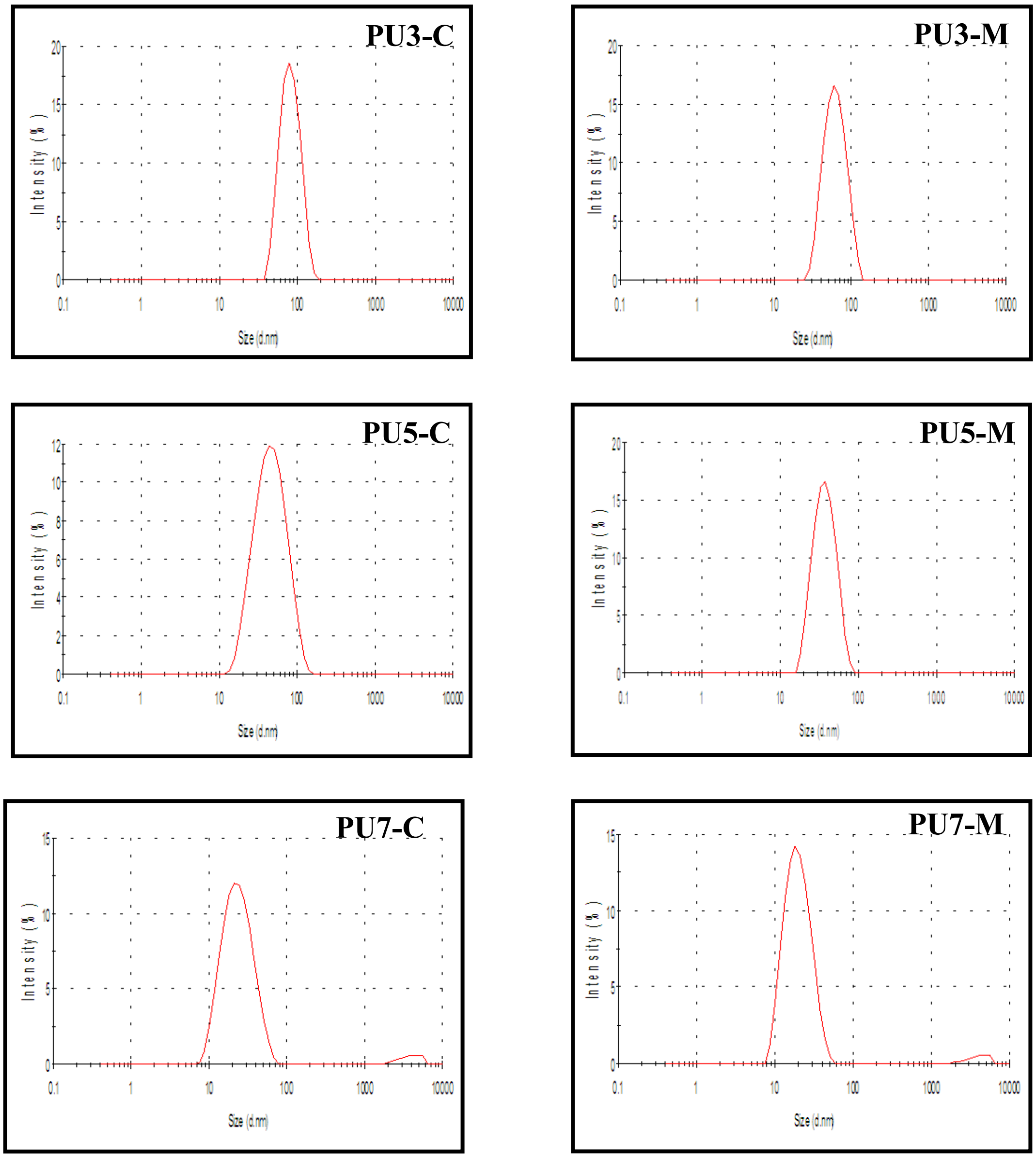


Figure C-7 Particle size distributions by intensity of both PUs containing with various DMPA content

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