

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**PREPARATION OF WATERBORNE POLYURETHANE-OMt
NANOCOMPOSITES**

Ph.D. THESIS

Engin AÇIKALIN

Department of Polymer Science and Technology

Polymer Science and Technology Programme

NOVEMBER 2011

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Thesis Advisor: Prof. Dr. Oya ATICI

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

SU BAZLI POLİÜRETAN-OMt NANOKOMPOZİTLERİNİN ELDESİ

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To my wife and family,

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ABBREVIATIONS

BD	: 1,4-Butanediol
¹³CNMR	: Carbon Magnetic Resonance
CE	: Chain Extender
CEC	: Cation Exchange Capacity
CHD	: Cyclohexane dimethanol
DABCO	: Diazobiscyclooctane
DBTDL	: Dibutyl Tin Dilaurate
DMA	: Dimethylolamine
DMPA	: Dimethyl Propionic Acid
DMSO	: Dimethyl Sulfoxide
DSC	: Differential Scanning Calorimetry
EDS	: Energy Dispersive X-Ray Spectroscopy
EG	: Ethylene Glycol
EVA	: Ethylene Vinyl Acetate
FTIR	: Fourier Transform Infrared
GPC	: Gel Permeation Chromatography
H₁₂MDI	: 4,4-Dicyclomethane diisocyanate
HD	: 1,6-hexanediol
HDI	: 1,6-Hexamethylene diisocyanate
HDPE	: High Density Polyethylene
HMTA	: Hexamethylene tetramine
¹HNMR	: Proton Magnetic Resonance
HQEE	: hydroquinone bis(2-hydroxyethyl) ether
IPDI	: Isophorone diisocyanate
MDI	: Methylene diphenyl diisocyanate
Mn	: Number average molecular weight
Mt	: Montmorillonite clay
Mw	: Weight average molecular weight
NaMt	: Sodium modified montmorillonite clay
NDI	: Naphtalene diisocyanate
NMP	: N-methyl pyrrolidone
OMt	: Organically modified montmorillonite clay
PEG	: Polyethylene glycol
PEG600	: Polyethylene glycol 600
PEG1500	: Polyethylene glycol 1500
PG	: Propylene Glycol
PLS	: Polymer Layered Silicates
PMMA	: Poly (Methyl Metacrylate)
PP	: Polypropylene
PPG1000	: Polypropylene glycol 1000
PS	: Poly Styrene
PTAA	: Poly(diethylene glycol/Trimethylolpropane-alt-adipic acid) polyol
PU	: Polyurethane

RIM	: Reaction Injection Molding
SEM	: Scanning Electron Microscopy
T_c	: Crystallization Temperature
T_d	: Decomposition Temperature
TDI	: Toluene diisocyanate
TEA	: Triethyl amine
TEM	: Transmission Electron Microscopy
T_g	: Glass Transition Temperature
TGA	: Thermogravimetric Analysis
THF	: Tetrahydrofurane
TPO	: Thermoplastic Polyolefins
UV	: Ultraviolet
VOC	: Volatile Organic Compounds
WPU	: Waterborne Polyurethane
XRD	: X-Ray Diffraction

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PREPARATION OF WATERBORNE POLYURETHANE-OMt NANOCOMPOSITES

SUMMARY

WPU which is a binary colloidal system of polyurethane polymers have gained importance especially in the area of surface coatings and adhesives due to having little or no cosolvent content. Unlike the conventional polyurethane polymers, WPUs have ability to be mixed with water through external or internal emulsifiers.

The properties of polymers can be tailored either by adjusting starting materials or making a composite material by using several filler material. In conventional composites, polymers are filled with synthetic or/and natural conventional fillers in micrometer scale to improve the physical properties and reduce the cost. On the contrary, in nanocomposites polymer matrix is filled with loadings of which at least one dimension with nanometer range. In the last two decades polymer-layered silicate nanocomposites have been captivated great interest both in industry and academia. Mt, which is a class of layered silicate mineral, have acquired importance due to its availability, easy processing and ability to provide unique properties with very small amount loadings into polymers.

In this study, it was aimed that synthesis of linear and crosslinked WPU polymers by two different processes including acetone and prepolymer mixing processes and to prepare their composites by using OMt to improve their properties and investigate their environmental degradation properties. The study is summarized in following sections including preparation and characterization of linear and crosslinked WPU polymers, preparation of OMt, preparation, characterization of WPU/OMt nanocomposites (NWPU) to determine the effect of Mt on the properties of WPU polymers. Finally, the effect of Mt on stability against solar radiation and ozone environments.

In order to prepare WPUs, PEG600 (for WPU1) and PTAA (for WPU4) were used for linear WPU polymers, whereas PEG1500 (for WPU2) and PPG1000 (for WPU3) were used for crosslinked WPU polymers. DMPA was used as internal emulsifier to give the polymers ability of dispersibility in water. TEA was used for the neutralization of carboxyl groups of DMPA to obtain water miscible polymer. HDI was preferred as isocyanate component in all experiments. BD was used as chain extender for linear WPU polymers and water was used as chain extender for crosslinked WPU polymers in the presence of HMTA as crosslinker. Acetone process was preferred for the preparation of linear WPU polymers and prepolymer mixing process was preferred for the preparation of crosslinked WPU polymers. Finally, dispersion in water by vigorous agitation was carried out. In the prepolymer preparation stage, NCO ended PU prepolymers were obtained. Then, they were chain extended through unreacted NCO of prepolymer. The appropriate mole ratio of polyol/DMPA/HDI was found as 1/1/3 for film preparation and the same ratio was used for all experiments. The neutralization ratio of [TEA]/[DMPA] was kept

constant as 1/1 for all experiments. The suitable reaction temperature for the prepolymer preparation stage was taken as 60°C for WPU1, WPU2 and WPU4 due to using acetone as processing solvent whereas, 80°C was for WPU3 which was prepared in NMP solvent due to low reactivity of PPG1000.

According to structural analysis, desired linear polymers were obtained (WPU1 and WPU4). WPU polymers with trans-cis isomerism indicated characteristic bands such as N-H stretching at 3323 cm^{-1} , urethane C=O at around 1690 cm^{-1} , C-N and N-H stretching at 1532 cm^{-1} and asymmetric and symmetric stretching N-CO-O and C-O-C at around 1247 and 1249 cm^{-1} respectively. ^1H NMR results showed characteristic shifts of trans and cis urethane at 7.1 and 6.8 δ ppm respectively. The particle size of WPU1 was higher than WPU4 due to higher DMPA content. Tensile strength and elongation values of WPU4 were greater than WPU1 owing to WPU4 having higher molecular weight compared to WPU1 and containing ester units on the main chain because of containing polyether/ester type soft segment.

In crosslinked WPU-urea polymers, prepolymer synthesis stage was similar with linear WPU polymers. However, crosslinking with various ratio of HMTA was performed during chain extension with water. In dispersion stage, urea was formed as a result of reaction of NCO and water. On the other hand, in the presence of water, HMTA was decomposed into two moles of DMA and one mole of formaldehyde. Besides, methylolurea was formed as a result of reaction of formaldehyde with urea. In chain extension stage dendritic structures were obtained as a result of reaction between NCO ended prepolymer and DMA. As a result of structural analysis, characteristic FTIR bands were observed such as N-H stretching between at 3320-3335 cm^{-1} , urethane C=O peaks were identified between at 1679-1713 cm^{-1} depending on trans-cis or cis-cis isomerism and -CO-N- units from bound urea could be seen between at 1632-1647 cm^{-1} . C-N and N-H bands were identified between at 1529-1535 cm^{-1} . According to ^1H NMR analysis, in WPU2 and WPU3 polymers was generated with methylene or/and ether bridges through methylolamine and with dendritic architecture through DMA. NCH_2OCON band at 4.4 δ ppm and 4.8- 4.5 δ ppm belong to methylene and/or ether bridges increased with increasing HMTA content as well as 125 δ ppm bands in ^{13}C NMR spectra became apparent with increasing HMTA content showing that WPU2 was more likely to be dendritic structure compared to WPU3 polymer. This result was also supported by DSC analysis and mechanical tests. On the other hand, elongation at break values dramatically decreased with increasing HMTA content which was confirmed that the crosslinked domains increased. Particle size analysis of the crosslinked WPU-urea polymers were depend on polyol type. According to TGA analysis thermal resistance of neat WPU polymers were inversely proportional to their hard segment content. In addition, WPU4 containing ester units and having higher molecular weight than WPU1, showed higher thermal stability. However, in crosslinked WPU-urea polymers, WPU2 was more thermally resistant due to having higher crosslinked structure compared to WPU3. According to DSC results, T_g of WPU1 was higher than WPU4 because the mobility of the soft segment was limited due to containing higher hard segment content. However, T_g of WPU2 polymer was lower than WPU3. In addition, crystallization behaviour was observed only in WPU2 which could be due to having more ordered structure compared to WPU3.

Nanocomposites were prepared by using certain amounts of Mt via in-situ method. In this manner, OMt was initially prepared by melt blending of NaMt into polyol component and polymerization procedure the same as that of neat polymers were

carried out. Finally, spectroscopic, thermal, mechanical and morphologic characterizations and environmental tests were performed.

FTIR analysis showed that similar structures were obtained in the presence of Mt. Interaction of Mt with WPU matrix was exhibited by change on structural O-H vibration of NaMt at around 3625 cm^{-1} . The change in the peak would be shifting of frequency or difference in the intensity. In addition, change on the C-O-C stretching vibration bands of the polymers with the effect of Si-O stretching vibration bands of NaMt were determined. XRD analysis denoted the increase of interlayer spacing depending on the type and structure of polymers. The increase of d-spacing was maximum for 1% Mt for all samples except NWPU2 series. XRD results were consolidated by SEM and TEM micrographs which were indicated that WPU nanocomposites were mostly intercalated and regionally exfoliated. TGA which was performed under oxygen and nitrogen atmosphere showed that thermal resistance of linear NWPU1 nanocomposites having 1% Mt content showed better thermal resistance in low degradation temperatures whereas 3% Mt was better in higher degradation temperatures. However, in NWPU4 series the sample with 5% Mt content had better resistance. In NWPU2 and NWPU3 series, thermal resistance increased to their highest value with 3% Mt content in NWPU2 whereas with 5% Mt for NWPU3 series. DSC measurements showed that T_g values decreased (NWPU1, NWPU3) or raised (NWPU2, NWPU4) which could be due to changing of molecular weight. Tensile tests indicated that in the presence of OMt both tensile strength and elongation at break values increased. Elongation at break value increased almost by 50% for NWPU1 and 100% for both NWPU2 and NWPU4 with 5% Mt content and did not change for NWPU3 series. However, tensile strength raised almost by 20% for NWPU1, 100% for both NWPU2 and NWPU4, 500% for NWPU3. The elastic moduli also increased with NaMt loading.

Finally, environmental weathering tests were executed including solar radiation and ozone tests. The photo and oxidative degradation behaviours were monitored using FTIR spectroscopy. In the case of solar radiation test, the photodegradation behaviour of neat WPU polymers was quite different from each other. Photodegradation were expected to have occurred through hard segment units. In linear WPU polymers, WPU1 having higher hard segment content and containing polyether polyol segment showed rapid degradation compared to WPU4 containing ether/ester segmented polyol and being in higher molecular weight. In crosslinked WPU-urea polymers, WPU2 having more dendritic structure was more degradable than WPU3. In the case of nanocomposites, the photodegradation was accelerated especially with 5% Mt content which also showed discoloration. The oxidative degradation of WPU2 polymer by ozone was more rapid due to WPU2 containing additional hydroxyls came from methylolamine groups. On the other hand, oxidative degradation was reduced in the presence of 5% content of Mt for all nanocomposites.

Consequently, WPU polymers indicated different properties depending on the polyol type and hard segment content. Besides, it was demonstrated that HMTA can be used as crosslinking agent in WPU polymers to prepare dendritic WPU polymers with different thermal and mechanical properties which can be utilized in industry. By the preparation of WPU nanocomposites using OMt, mechanical and thermal properties of WPU polymers can be improved and WPU polymers can be used as photodegradable polymers by the preparation of their nanocomposites with NaMt which can be used industrially. Oxidative resistance of WPU polymers can be gained by the preparation of their composites with OMt.

SU BAZLI POLİÜRETAN-OMt NANOKOMPOZİTLERİNİN ELDESİ

ÖZET

Poliüretan polimerlerin ikili kolloid sistemleri olan su bazlı poliüretan dispersiyonları (WPU), çok az yardımcı çözücü içermeleri ya da hiç yardımcı çözücü içermemelerinden dolayı özellikle yüzey kaplama ve yapıştırıcılar alanında önem kazanmıştır. Geleneksel poliüretan polimerlerinin aksine, WPU'lar harici veya dahili emülsifiye ajanları eşliğinde su ile karışabilirler.

Polimerlere istenilen özellikler; başlangıç malzemelerini değiştirme veya dolgu maddeleri kullanarak kompozit elde edilmesi olmak üzere iki yol ile kazandırılabilir. Geleneksel kompozitlerde, polimerlerin fiziksel özelliklerini iyileştirmek ve maliyeti düşürmek için polimerlere mikro boyutlarda sentetik ve/veya doğal dolgu maddeleri ektenir. Diğer yandan, nanokompozitlerde, polimer matrisine eklenen dolgu malzemelerinin en az bir boyutu nano ölçeğindedir. Son yirmi yıldır, polimer-tabakalı silikat nanokompozitler hem sanayinin hem de akademinin ilgisini çekmiştir. Tabakalı silikat mineralleri sınıfından olan montmorillonit, kolay bulunabilirliği, kolay işlenebilirliği ve çok küçük miktarlarda kullanıldığında dahi polimer-kil nanokompozitlerine eşsiz özellikler kazandırabilmesinden dolayı önem kazanmıştır.

Bu çalışmada, lineer ve çapraz bağlı WPU'ların aseton ve prepolimer karıştırma prosesleri gibi iki farklı yöntemle sentezi yanında polimerlerin organo modifiye sodyum montmorillonit (OMt) ile kompozitlerinin hazırlanması, polimer özelliklerini iyileştirmek ve çevresel bozunma özelliklerinin incelenmesi amaçlanmıştır. Çalışmamızda, NaMt'nin WPU üzerindeki etkisini belirlemek için; lineer ve çapraz bağlı WPU'nun hazırlanması ve karakterizasyonu, OMt'nin hazırlanması, WPU/OMt nanokompozitlerinin (NWPU) hazırlanması ve karakterizasyonu ve son olarak da solar radyasyon ve ozon çevrelerinin stabilizasyonunda Mt'nin etkisini incelemeyi içeren bölümler halinde özetlenmektedir.

Lineer ve çapraz bağlı WPU'nun hazırlanmasında bir çok poliol yumuşak blok olarak kullanılmıştır. Polietilen glikol 600 (PEG 600)(WPU1 için) ve poli (dietilen glikol/trimetilolpropan-alt-adipik asit) poliol (PTAA) (WPU4 için) lineer WPU'lar için kullanılırken, diğer yanda polietilen glikol 1500 (PEG1500) (WPU2 için) ve polipropilen glikol 1000 (PPG1000)(WPU3 için) çapraz bağlı WPU'ların elde edilmesinde kullanılmıştır. Dimetilol propiyonik asit (DMPA), polimerlerin suda çözünmesini sağlamak amacıyla dahili emülsiyeciler olarak kullanılmıştır. DMPA, sterik engelleme yeteneği ile karboksil grubu ile izosiyanat gruplarının istenmeyen reaksiyonunu önlediği için en sık kullanılan iyonik merkezdir. DMPA'nın karboksil gruplarını nötralize ederek suda çözünür hale getirmek amacıyla trietilamin (TEA) kullanılmıştır. İzosiyanat bileşeni olarak heksametilen diizosiyanat (HDI) ortalama bir reaktiviteye sahip olması nedeniyle tercih edilmiştir. Lineer WPU polimerlerinde zincir uzatıcı olarak 1,4-Bütandiol (BD) kullanılmıştır. Ancak, çapraz bağlı poliüretan polimerlerinde zincir uzatıcı olarak heksametilentetramin (HMTA) eşliğinde su kullanılmıştır.

Lineer WPU polimerlerinin hazırlanmasında aseton prosesinin tercih edilmesinin sebepleri; yeniden üretilebilirliğindeki kolaylık ve elde edilen polimerin organik çözücü içermemesidir. Fakat çapraz bağlı WPU polimerlerinin sentezinde, çapraz bağlanma reaksiyonlarının kontrolünün kolaylığı açısından prepolimer karıştırma prosesi tercih edilmiştir. Her iki proses de prepolimer hazırlanması, nötralizasyon ve zincir uzaması aşamalarından oluşur ve son olarak da suda dispersiyon yer alır. Aseton prosesinde nötralizasyon aşaması zincir uzaması aşamasından sonra gelirken, prepolimer karıştırma prosesinde nötralizasyon aşaması, zincir uzaması aşamasından önce gelir. Son olarak, şiddetli karıştırma ile suda dispersiyonu elde edilir. Prepolimer hazırlama aşamasında, NCO ile sonlanan poliüretan prepolimerleri elde edilmiştir. Daha sonra, prepolimer zincirleri reaksiyona girmemiş NCO'ları aracılığıyla uzarlar. Stabil WPU polimeri filmlerinin elde edilebilmesi için optimum WPU1 sentez koşullarını belirlemek amacıyla öncelikle bir çok deney yapılmıştır. Film hazırlanması için uygun poliol/DMPA/HDI mol oranı 1/1/3 olarak bulunmuş ve tüm deneyler için bu oran kullanılmıştır. [TEA]/[DMPA] nötralizasyon oranı tüm deneyler için 1/1 oranında sabit tutulmuştur. Prepolimer hazırlama aşamasında uygun reaksiyon sıcaklığı WPU1, WPU2 ve WPU4 için çözücü olarak aseton kullanılmasından dolayı 60°C alınırken, WPU3 hazırlanırken PPG1000'in düşük reaktivitesinden dolayı çözücü olarak N-metil pirolidon (NMP) kullanıldığından reaksiyon sıcaklığı 80°C alınmıştır.

İstenilen özelliklerde lineer polimerlerin (WPU1 ve WPU4) elde edildiği yapısal analiz sonuçlarıyla kanıtlanmıştır. Su bazlı poliüretan polimerlerinin trans-cis izomerleşmesi; 3323 cm^{-1} 'de N-H gerilmesi, 1690 cm^{-1} civarında üretan C=O gerilmesi, 1532 cm^{-1} 'de C-N ve N-H gerilmesi ve N-CO-O ve C-O-C asimetrik ve simetrik gerilmelerinin sırasıyla 1247 ve 1249 cm^{-1} 'de yer alması gibi karakteristik bantlarla ispatlanmıştır. $^1\text{HNMR}$ sonuçları, trans ve cis üretanın sırasıyla 7.1 ve 6.8 δ ppm'de karakter kaymaları yaptığını göstermiştir. WPU1'in parçacık büyüklüğü WPU4'e kıyasla daha yüksek bulunmuştur, bunun sebebi WPU1'in daha yüksek DMPA içermesidir. Bu yüzden, WPU4'ün yüzeye nüfus etmesinin WPU1'den daha iyi olması beklenir. WPU1 ve WPU4'ün molekül ağırlıkları GPC analizi ile ölçülmüştür. WPU4'ün WPU1'e kıyasla daha yüksek molekül ağırlığına sahip olması ve polieter/ester tipi yumuşak bloklarından dolayı ana zincirde ester içermesinin, gerilme mukavemeti ve uzama değerlerinin WPU1'e göre daha yüksek olmasına yol açmıştır.

Çapraz bağlı WPU-üre polimerlerinde prepolimer sentezi aşaması, lineer WPU polimerlerinininki ile aynıdır. Ancak, su ile zincir uzatma sırasında HMTA ile çapraz bağ oluşturulmuştur. Dispersiyon aşamasında, NCO ve suyun reaksiyonu sonucunda üre elde edilmiştir. Diğer yandan, suyun varlığında, HMTA, 2 mol dimetilolamin (DMA) ve bir mol formaldehid olarak bozunur. Bunun yanı sıra, formaldehit ve ürenin reaksiyonu sonucunda metilolüre oluşur. Zincir uzama aşamasında, NCO ile biten prepolimerin DMA ile reaksiyona girmesi sonucunda dendritik yapılar elde edilmiştir. Ayrıca, metilen ve/veya eter köprüleri de elde edilmiştir. HMTA oranı ve poliol reaktivitesine bağlı olarak farklı özelliklere sahip çapraz bağlı WPU-üre polimerleri elde edilmiştir. HMTA'nın çapraz bağlanma üzerindeki etkisini incelemek amacıyla WPU2 ve WPU3 polimerleri farklı HMTA oranları kullanarak hazırlanmıştır; NCO/HMTA için 1/0.00 (WPU2.2, WPU3.1), 1/0.25 (WPU2.3, WPU3.2) ve 1/0.50 (WPU2.4, WPU3.3).

Çapraz bağlanmış WPU-üre polimerlerinin yapısal analizi sonucunda 3320-3335 cm^{-1} aralığında N-H gerilmesi, 1679-1713 cm^{-1} aralığında trans-cis veya

cis-cis izomerlerine bağı olarak üre tan C=O pikleri, 1632-1647 cm⁻¹ aralığında bağlanmış üre üzerinde –CO-N- üniteleri gibi karakteristik FTIR bantları gözlenmiştir. 1529-1535 cm⁻¹ aralığında C–N ve N–H bantları, 1095-1103 cm⁻¹ aralığında C–O–C gerilme bantları görülmüştür. ¹H NMR analizine göre; HMTA katalisti kullanılarak elde edilen poliüretan-üre WPU2 ve WPU3 polimerleri metilolamin ve dendirik DMA yapısının metilen ve/veya eter köprüleri ile meydana gelmiştir. 4.4 δ ppm ve 4.8- 4.5 δ ppm'deki NCH₂OCON bantı ve ¹³C NMR analizine göre 125 δ ppm' deki bantların belirginleşmesi HMTA'nın artmasıyla artan metilen ve/veya eter köprülerini göstermektedir. Bu sonuç WPU2'nin WPU3'e kıyasla dendirik yapıya daha yakın olduğunu gösterir. Bu sonuç, DSC analizleri ve mekanik testlerle de desteklenmiştir.

Diğer yandan, kopma anındaki uzama değerlerinin artan HMTA içeriğiyle birlikte dramatik düşüş yapması çapraz bağı bölgelerin artışı doğrular (WPU 2 ve WPU3). Çapraz bağlanmış WPU-üre polimerlerinin parçacık büyüklükleri kullanılan poliol ile ilişkilidir. PPG1000 ile hazırlanan WPU3'ün parçacık büyüklüğünün PEG1500 ile hazırlanan WPU2'den daha büyük olması, WPU2'nin substrata nüfusunun daha iyi olduğunu göstergesidir.

Katkısız polimerlerin TGA ve DSC kullanılarak termal analizleri yapılmıştır. Azot ve oksijen ortamında yapılan TGA analizi sonuçlarına göre katkısız polimerlerin termal dayanımları sert blok içerikleri ile ters orantılıdır; WPU4>WPU2>WPU3>WPU1. Ayrıca, WPU4'ün WPU1'e kıyasla daha yüksek molekül ağırlığına sahip olması ve yapısındaki ester yapıları termal stabilitesinin daha yüksek olmasına yol açmıştır. Ancak, çapraz bağı WPU-üre polimerlerinde WPU2'nin daha fazla çapraz bağı yapısından dolayı WPU3'e göre termal stabilitesi daha yüksektir. Lineer WPU polimerlerinin DSC sonuçlarına göre, yumuşak bloklarının hareketinin kısıtlanmasından dolayı, daha fazla sert blok oranı olan WPU1'in camsı geçiş sıcaklığı (T_g) WPU4'e göre daha yüksektir. Fakat, çapraz bağı poliüretan-üre polimerlerinde daha fazla dendirik yapıya sahip olan WPU2 polimerinin camsı geçiş sıcaklığı (T_g) WPU3'den daha düşüktür. Ayrıca, sadece WPU2'de bariz olarak tespit edilen kristallenme sıcaklığı (T_c) ile kristallenme davranışları incelenmiştir. Bunun nedeni WPU3'e göre daha düzenli yapıya sahip olmasıyla açıklanabilir.

Nanokompozitler belirli miktarlarda OMt kullanılarak yerinde polimerleştirme metoduyla hazırlanmıştır. OMt ise öncelikle NaMt'nin poliol ile modifikasyonu ile elde edilmiştir. Ardından, saf polimerlere uygulanan polimerleştirme işlemleri uygulanmıştır. Nanokompozitler NWPU1, NWPU2, NWPU3 ve NWPU4 olarak adlandırılmıştır. Son olarak, spektroskopik, termal, mekanik ve morfolojik ve solar radyasyon ve ozon testleri içeren çevresel testler ile karakterize edilmiştir.

FTIR analizleri Mt varlığında da benzer yapılar elde edildiğini göstermiştir. Mt ve WPU matrisinin etkileşimi 3625 cm⁻¹ civarındaki yapısal O–H titreşimindeki değişimle gösterilebilir. Pikteki değişiklik, frekans ya da yoğunluk farkında kaymadır. Ayrıca, NaMt'nin Si–O gerilme titreşim bantlarının etkisinden dolayı C–O–C gerilme titreşim bantlarında değişim görülmüştür. XRD analizleri polimer tipi ve yapısına bağı olarak katmanlar arası mesafenin arttığını göstermiştir. NWPU2 hariç tüm numunelerde %1 Mt için d-mesafesi artışının maksimum olduğu gözlenmiştir. Artış; NWPU1 için 3.63-3.78Å, NWPU2 için 4.71-5.64Å, NWPU3 için 3.57-3.15Å, ve NWPU4 için 3.91-5.39Å olarak ölçülmüştür. Su bazlı poliüretan nanokompozitlerinin çoğunlukla tabakalanmış ve bölgesel olarak yapraklanmış

olduğu XRD sonuçlarının yanı sıra SEM ve TEM mikrograflarıyla da gözlemlenmiştir.

TGA sonuçlarına göre düşük bozunma derecelerinde %1 Mt içeren lineer NWPU1'in daha iyi termal dayanım gösterdiği, yüksek bozunma derecelerinde ise %3 Mt içeren NPWU1'in daha iyi termal dayanım göstermiştir. Ancak, NWPU4 serisinde %5 Mt içeren örneğin daha iyi dayanım gösterdiği görülmüştür. Benzer sonuçlar çapraz bağlı WPU' larda da gözlenmiştir. NWPU2 ve NWPU3 serilerinde hem düşük hem de yüksek bozunma sıcaklıklarında en yüksek termal dayanım değeri NWPU2 serisi için %3 Mt içerikli örnekte gözlenirken NWPU3 serisinde %5 Mt içerikli örnekte gözlenmiştir. DSC ölçümlerinden, camsı geçiş sıcaklığı değerlerinin molekül ağırlığındaki değişime bağlı olarak düşüş (NWPU1) ya da artış (NWPU4) gösterdiği gözlemlenmiştir. Ancak; çapraz bağlı NWPU2 serisinde Tg, Mt içeriği ile artış ile göstermiştir. Ayrıca, tüm nanokompozitlerdeki Tc ve Td değerlerindeki değişim, polimerin OMt ile etkileşim gösterdiği belirtir.

Çekme testleri, Mt varlığında hem çekme mukavemeti hem de kırılma noktasındaki uzama değerinde artış olduğunu göstermiştir. Kırılma noktasındaki uzama değeri %5 Mt içeriğinde NWPU1 için %50, hem NWPU2 hem de NWPU4 için %100 artış gösterirken NWPU3 serisi için değişiklik göstermemiştir. Ancak, çekme mukavemeti NWPU1 için yaklaşık %20, hem NWPU2 hem de NWPU4 için %100 ve NWPU3 için %500 artış göstermiştir. Mt içeriğinin artırılmasıyla, elastik modüllerde de artış gözlenmiştir. Mt parçacıkları çapraz bağlantı noktaları gibi davranarak nanokompozitin tokluğunu arttırmıştır.

Son olarak, solar radyasyon ve ozon testleri içeren çevresel iklimlendirme testleri uygulanmıştır. Foto bozunma ve oksidatif bozunma davranışları FTIR spektroskopisi kullanılarak incelenmiştir. Solar radyasyon testlerinde, katkısız polimerlerin fotobozunma davranışları birbirinden oldukça farklılık göstermektedir. Foto-bozunmanın katı blok üniteleri arasından olması beklenmektedir. Lineer WPU'larda, daha fazla sert blok ve poliether poliol bloğu içeren WPU1, ester/ester bloklu daha yüksek molekül ağırlıklı WPU4'e göre daha hızlı bozunma göstermiştir. Çapraz bağlı WPU-üre polimerlerinde, daha fazla dendritik yapı içeren WPU2, WPU3'e göre daha bozunabilir olduğu gözlenmiştir. Nanokompozitlerde ise, foto bozunmanın özellikle %5'lik Mt içerikli örnekte artış göstermiş ve renk değişimi de gözlenmiştir. WPU2'nin metilolamin gruplarından gelen ilave hidroksillerinden dolayı, WPU2'deki oksidatif bozunmanın daha hızlı olduğu görülmüştür. Diğer yandan, %5 Mt içeriği ile tüm nanokompozitlerde oksidatif bozunma azalmıştır.

Sonuç olarak, WPU polimerleri poliol türleri ve katı blok içeriklerine bağlı olarak değişik özellikler göstermektedir. Aynı zamanda, farklı termal ve mekanik özelliklere sahip dendritik WPU polimerlerinin hazırlanmasında HTMA'nın çapraz bağlama ajanı olarak kullanılabileceği ve bu yolla hazırlanan polimerlerden endüstride de faydalanabileceği belirtilmiştir. OMt kullanarak WPU nanokompozitlerinin WPU polimerlerinin mekanik ve termal özelliklerinin iyileştirilebileceği görülmüş ve WPU polimerlerin OMt ile hazırlanan nanokompozitlerinin foto bozunabilir polimerler olarak sanayide kullanım alanı bulabileceği ve polimerlerin OMt ile elde edilen nanokompozitleri ile oksidatif dayanımlarının arttırılabileceği kanısına varılmıştır.

1. INTRODUCTION AND AIM

During the last few years, WPU polymers have gained importance due to their superior properties with respect to solvent based polyurethane polymers and their compliance with environmental legislation (Oldring, 2001). Organic solvents hold health risks as well as requiring considerable expenditures in the area of safety technology due to the danger of fire and explosion (Westhues, 2007). Whereas WPU systems can be formulated with several polyols with or without crosslinkers, as they are based on WPUs.

To improve the properties or to reduce the cost of the polymeric materials; synthetic or natural inorganic compound fillers have been used traditionally. Traditional fillers are materials in the form of particles, fibers or plate-shaped particles (Pavlidou and Papaspyrides, 2008; Ajayan et al., 2003). Despite the fact that traditionally filled or reinforced polymeric materials are widely used in numerous applications such as filled polymers for damping, electrical insulators, thermal conductors and high-performance composites for uses in aircrafts are some examples of applications that make polymer composites very important commercial materials. Composites with tailored properties can be created when materials with synergistic properties are chosen, for example addition of high modulus brittle carbon fibers to low-modulus polymers and light-weight polymers with some degree of toughness can be achieved. it is commonly observed that the addition of these particles cause drawbacks in the resulting material, such as increases in the weight, brittleness and opacity of the resulting material. To overcome the limitations of traditional micrometer scale polymer composites, nanoscale filled polymer composites, in which the filler is less than 100 nm in at least one dimension, are developed recently (Figure 1.1) (Ajayan et al., 2003). Research and development of nanofilled polymers has increased greatly in recent years.

Nanocomposites are a new class of composites for which at least one dimension of the dispersed particles is in the nanometer scale (Ajayan et al., 2003). Isodimensional nanoparticles have their all three dimensions on the order of nanometers, nanotubes

or whiskers have two dimensions on the nanometer scale and the third dimension on larger scale. When two dimensions are on the larger scale and only one dimension is on nanometer scale layered crystals or clays are formed. Although there are many nanocomposite precursors, nanocomposites based on clay and layered silicates are the ones that have been investigated widely due to availability and intercalation chemistry that has been studied for a long time.

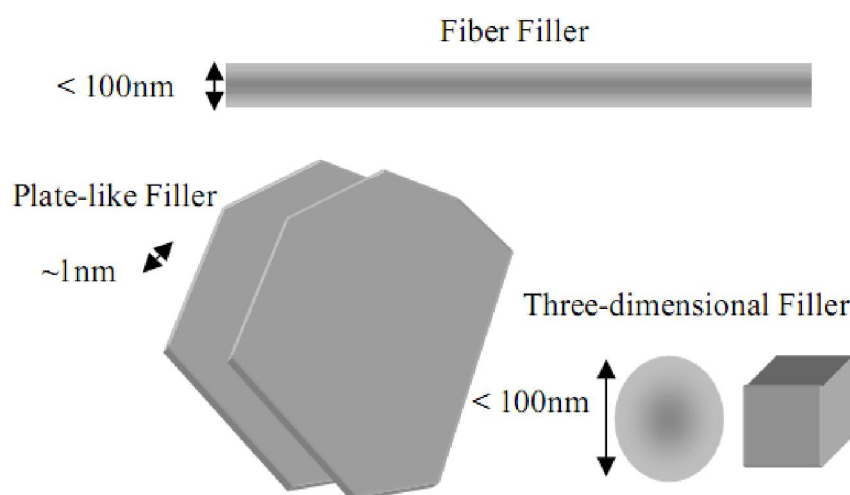


Figure 1.1 : Nanoscale fillers.

Although, nanocomposites have been prepared for centuries their specific preparation of and measuring of their properties is recent. Although a few commercialized products have been widely researched, Toyota is the first company to prepare commercial nylon nanocomposite with nanoscale clay (Cook and Myers, 2009).

The aim of this work is to synthesis of linear and crosslinked WPU polymers by two different processes including acetone and prepolymer mixing processes and to prepare their composites by using OMt to improve their properties and investigate their environmental degradation properties. Hence, it was thought that WPU/OMt composites would be prepared with better thermal resistance and with higher toughness. Additionally, it was conceived that the resulting composite materials to be tested in terms of their photooxidative and oxidative resistance to determine the final area of usage.

2. THEORY

2.1 Polyurethane Polymers

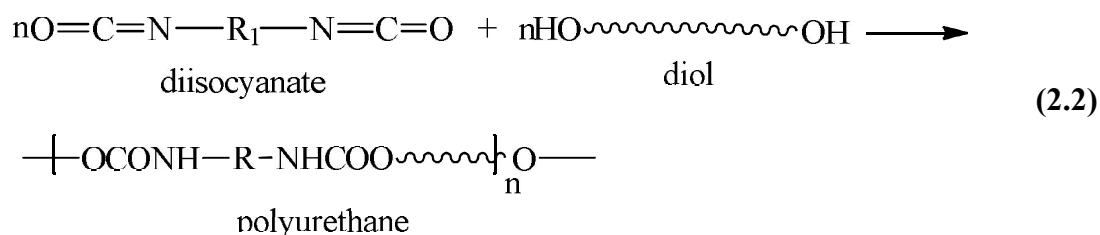
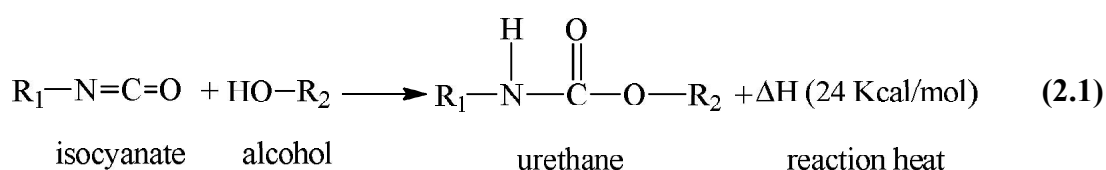
The polyurethanes include those polymers containing a plurality of urethane groups in the molecular backbone, regardless of the chemical composition of the rest of the chain (Szycher, 1999). Polyurethanes are wide variety of polymers with quite different compositions and different properties (Oertel, 1994). Polyurethanes are a class of polymers that are extremely versatile. A polyurethane chemist can design useful materials for many applications due to a wide variety of raw materials coupled with adaptable synthetic techniques (Ionescu, 2005). Polyurethanes can be divided into two categories when the practical and applicative reasons are considered. The first category is elastic polyurethanes such as flexible foams, elastomers, coatings, adhesives, fibers etc., the second category is rigid polyurethanes such as rigid polyurethane foams, structural foams, wood substitutes, solid polyurethanes etc. The classification of these categories is mainly based on the polyol structure. The general applications of polyurethanes are given in Table 2.1.

Table 2.1 : Applications of polyurethanes

Flexible Slab	Two components	Carpet	RIM	Solid	Rigid Foam	Flexible Molded
Furniture	Casting	Attached cushion	Auto	Elastomers	Insulation	Car seating
Bedding	Encapsulation	Unitary	Mechanical	Coatings	Appliances	Bedding
Auto	Sealants			Adhesives	Auto	
Carpet under layment				Medical		
Carrier media						

There is a very wide range of materials, which can be used to form polyurethanes. All of the items shown can be easily achieved with the proper choice of the starting materials, polymer design, processing conditions and application technique. Although polyurethanes certainly have limitations, it is reasonable to believe that no other class of polymers can match their usefulness, performance and versatility. The reaction of polyisocyanates and polyols create the urethane chemical linkages that form urethane polymers. Urethane linkage shown in (2.1 and 2.2) is the general structure of the basis of urethane chemistry.

With this route, the first urethane was synthesized by Wurtz as early as 1849. In 1937, following very systematic and intensive research works at IG Farbenindustrie, in Germany (2.1), Dr. Otto Bayer synthesized the first polyurethane, by the reaction of a diisocyanate with polyester having two terminal hydroxyl groups:



In a large number of industrial applications, polyurethanes are of great significance. Some of the applications are adhesives, elastomers and foams as well as materials for coatings.

Another specialty of polyurethane chemistry is the wide spectrum of properties found in its products. Because of this feature, polyurethanes are used in a wide range of applications, especially in coatings. Until recently, polyurethane coatings were primarily solvent based. Nowadays, they are used in waterborne systems as well as powder and UV-curable coatings. Primary structure in polyurethanes is based on both soft and hard segments (Figure 2.1). The ratio of hard segment/soft segment determines the properties of the final product. Variety of end products are obtained with several types of hard and soft segments.

Primary structure of polyurethane is composed of the backbone and compounds covalently connected to skeletal backbone which are determining the properties (Rogers and Long, 2003; Yang et al., 2007). A linear polyurethane chain built from high molecular weight polyol, isocyanate and chain extender can be seen in Figure 2.1. Polyol component of polyurethane is called as soft segment, while the isocyanate and chain extender are called as hard segment.

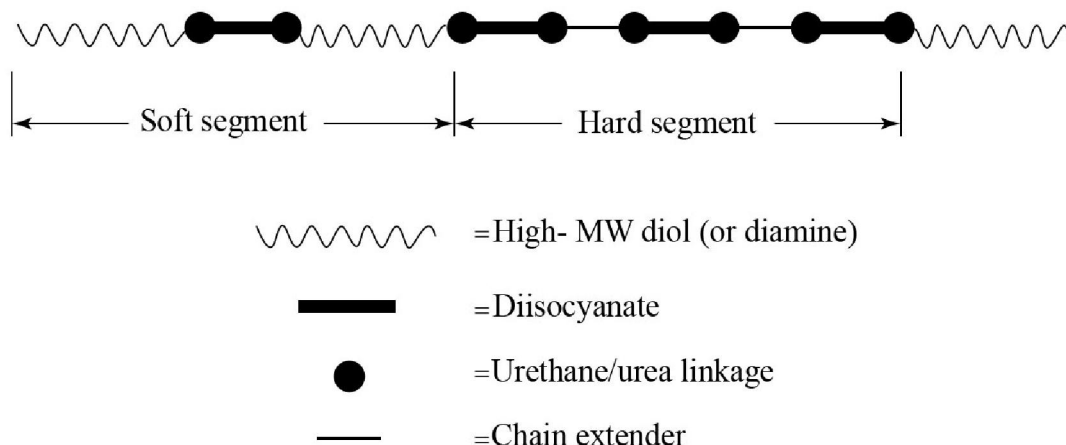


Figure 2.1 : Primary structure in polyurethanes: backbone structure (Rogers and Long, 2003).

In a polyurethane polymer high molecular weight nonpolar polyol compound (soft segment) and polar isocyanate and chain extender compounds (hard segment) are incompatible and tend to segregate into their micro domains which are named as hard block and soft block respectively (Figure 2.2). On the other hand, intermolecular hydrogen bonding is another factor for the phase segregation of polyurethanes. Addition order of raw materials during synthesis determines the sequence of the linkages. The formation of physical crosslinking which may appear caused by hydrogen bonding can be seen in Figure 2.2.

2.2 Raw materials and their selection

2.2.1 Isocyanates

The polymerization product of ethylene is polyethylene but polyurethane is not a result of urethane polymerization (Bock, 2001; Petrovic, 2005). Urethane is a specific chemical bond that covers a very small percentage of polyurethane bonds. Isocyanates are categorized in several ways but the widest delineation is aromatic versus aliphatic.

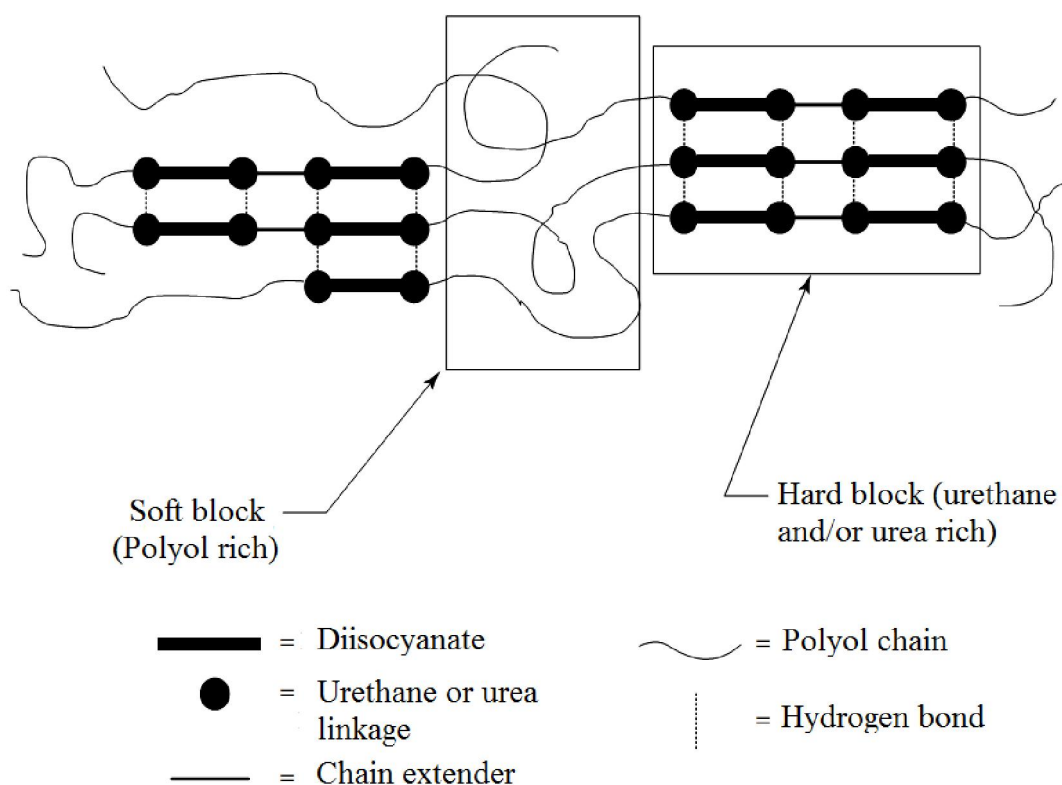
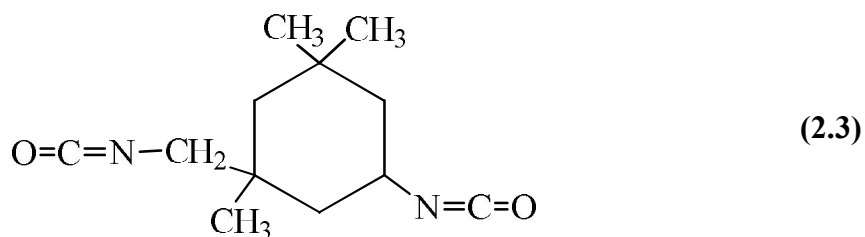


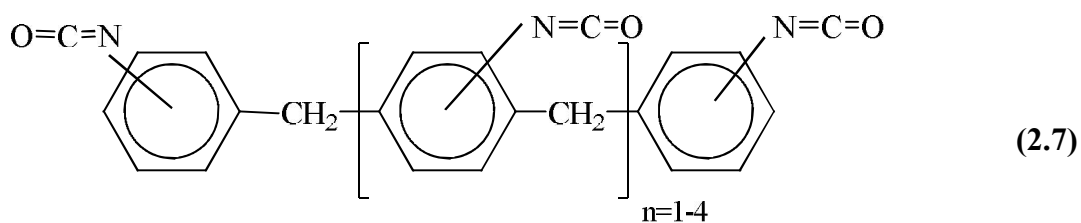
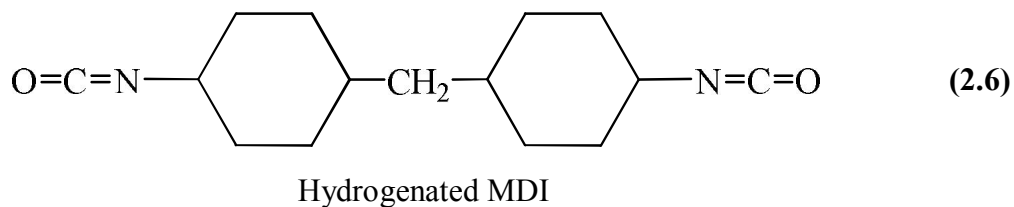
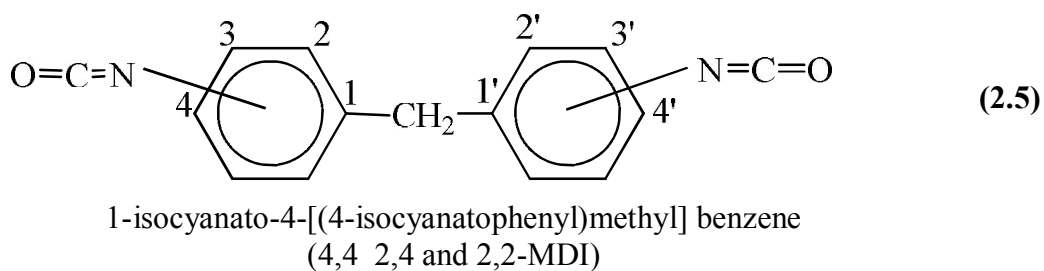
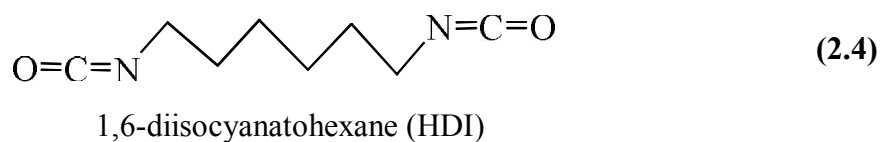
Figure 2.2 : Secondary structures in polyurethanes: hard and soft microdomains (Rogers and Long, 2003).

The largest worldwide volume of the manufactured isocyanates comprise aromatic methylene diphenyl diisocyanate (MDI), polymeric MDI (PMDI), and toluenediisocyanate (TDI). These compounds have two distinctive characteristics. First, they absorb ultraviolet (UV) radiation due to their aromatic structure. Many oxidative side reactions are triggered by this, particularly when atmospheric oxygen and water are present. Coloured quinodial and other delocalized moieties that cause a discoloration to yellow or brown are formed depending on the extent of reaction. Discoloration usually does not affect bulk physical properties unless the extent of oxidation is extreme but still discoloration is undesirable in most applications such as in foams and elastomers. This sensitivity to light is critical in coating applications, as it not only causes discolouration but also loss of surface gloss, crazing and many other problems. For coatings and other “thin cross-sectional” applications, another reason why light sensitivity is of broader importance is because UV radiation can penetrate a larger percentage of the material’s thickness, affecting not only the surface, but the bulk properties of the material as well, causing embrittlement, cracking, and peeling. It should be mentioned that despite aliphatic urethanes are dramatically less sensitive to light than aromatic formulations, they are still subject to

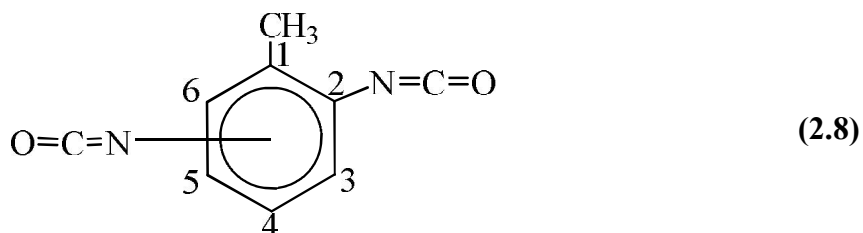
UV-induced degradation and are substantially tested accordingly. The important isocyanates are as follows (2.3-2.11):



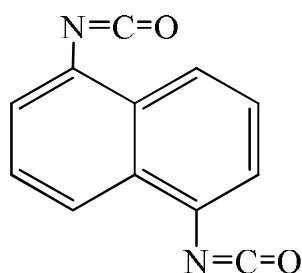
5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethyl-cyclohexane (IPDI)



Polymeric MDI (PMDI)

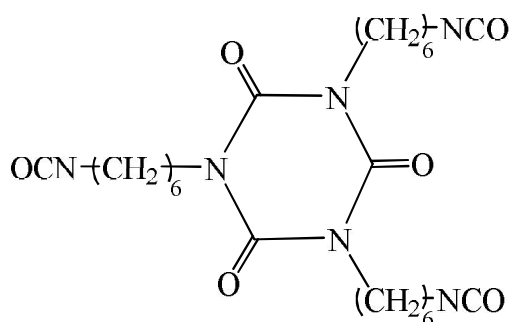


2,4(or 2,6)-diisocyanato-1-methyl-benzene (2,4 and 2,6-TDI)



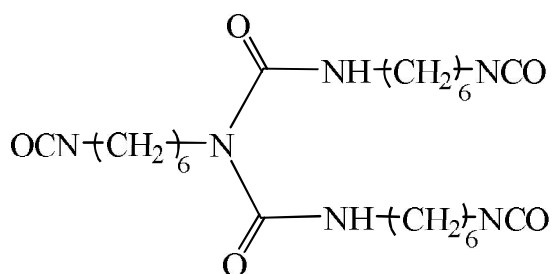
(2.9)

Isocyanic acid, 1,5-naphthylene ester (NDI)



(2.10)

HDI trimer



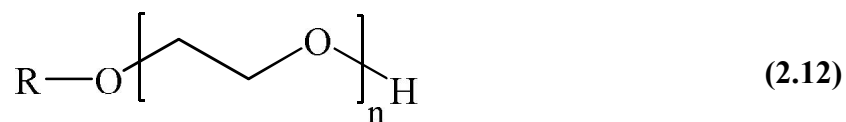
(2.11)

HDI biuret

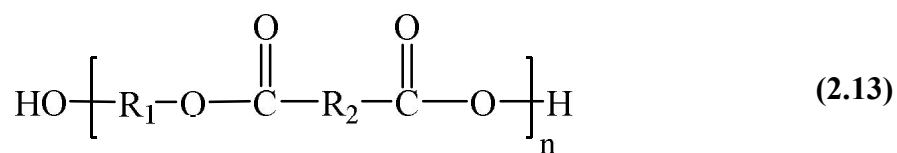
Being aware of the chemical effects of isocyanates is important (Thomson, 2005). The produced polyurethane will consist of polyols and isocyanates. The physical and chemical properties of the product will be determined by the ratio of polyols and isocyanates. Generally, the isocyanates make up the hard segments that pass on rigidity to the polymer.

2.2.2 Polyols

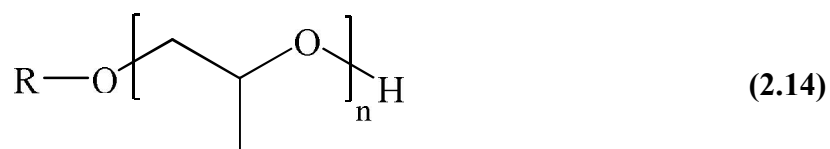
Polyols are the next important category of urethane starting components. The polyol imparts many properties to the finished polymer, such as flexibility, softness, low-temperature properties and processing characteristics (Rogers and Long, 2003). Some important polyols (2.12-2.20) are as follows;



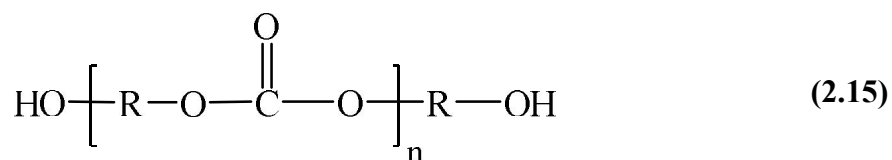
Polyethylene Glycol (C₂ polyether polyol)



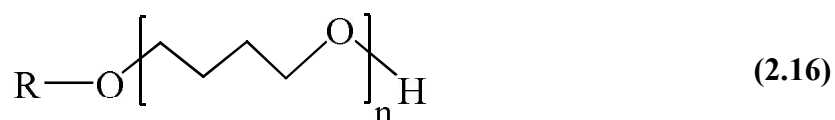
Polyester polyol



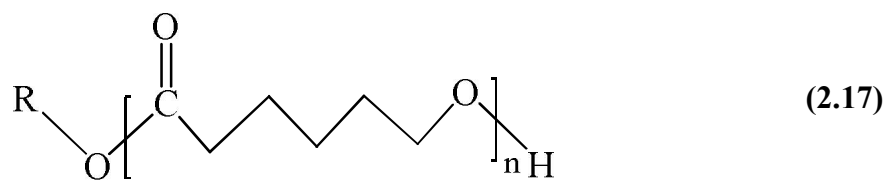
Polypropylene Glycol (C₃ polyether polyol)



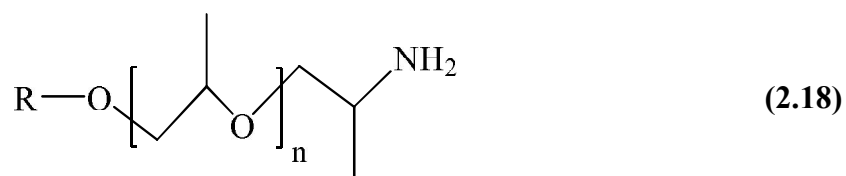
Polycarbonate polyol



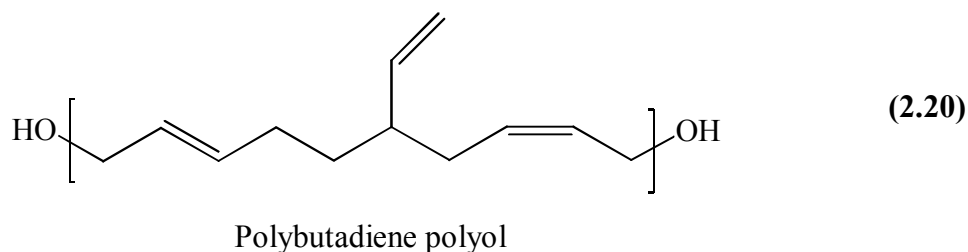
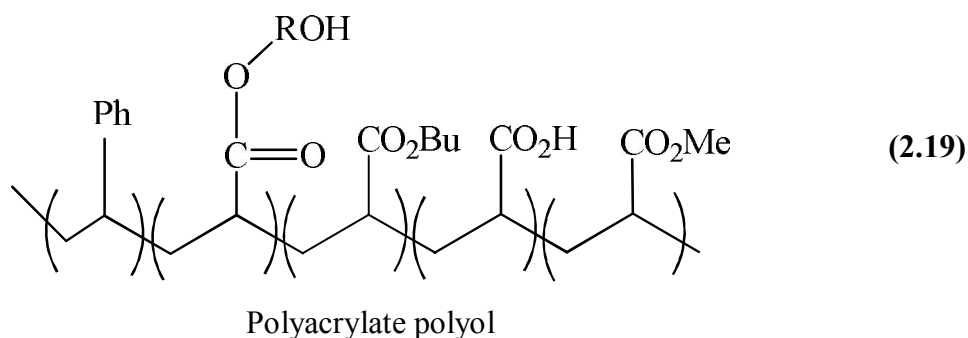
Polytetramethylene Glycol (C₄ polyether polyol)



Polycaprolactone polyol



Amine terminated polyether



The most common urethane-grade polyols are the polyethers made from ethylene oxide (EO), propylene oxide (PO), and tetrahydrofuran (THF), referred to as C2, C3, and C4 ethers, respectively, from the number of carbon atoms in each repeat unit (Ionescu, 2005, Oldring, 2001). To provide the enhanced reactivity of unhindered, primary OH groups, the C3 ethers are often capped with C2- ether end groups. In water-blown foams, random and mixed-block copolymers of ethylene oxide and propylene oxide are mainly as they implement better control of miscibility between polyol, isocyanate and water. They can also give better adjustment of processing characteristics such as reactivity, demold and flow properties.

The molecular weight of the oligo-polyols used in the synthesis of polyurethane varies between 300-10000 Daltons in the region of low molecular weight (MW) polymers (oligomers), the number of hydroxyl groups/molecule of oligo-polyol (the oligo-polyol functionality) being generally in the range of 2-8 OH groups/mol. Low functional polyols with high molecular weight of 2000-10000 Dalton and 2-3 hydroxyl groups per mol lead to an elastic polymer whereas oligo-polyols having around 3-8 hydroxyl groups per mole and low molecular weight of 300-1000 Daltons lead to a rigid crosslinked polyurethane.

When a diisocyanate reacts with a high molecular weight diol (such as polyether or polyester diol of Mw of 2000-4000) leads to very elastic linear polyurethanes (polyurethane elastomers). The urethane linkages (and urea linkages) generate the 'hard domain' or 'hard segment' of polyurethane elastomers because of the

possibility of association by hydrogen bonds. The ‘soft domain’ or ‘soft segment’ is represented by high mobility of high MW polyol which assures the high elasticity of the resulting polyurethane elastomers.

2.2.2.1 Polyacrylate polyols

Polyacrylate term comprises acrylic and/or methacrylic acid ester copolymers that bear hydroxyl groups (Westhues, 2007; Oldring, 2001). The hydroxyl groups required for reaction with isocyanate groups are generally introduced via functionalized esters of acrylic and methacrylic acid. In polyurethane coatings technology, polyacrylate polyols occupy a significant position. They are used for plastic coatings that require high flexibility and good chemical resistance, automotive finishing with long term resistance and top coats that require corrosion protection.

2.2.2.2 Polyester polyols

Polyester polyols are produced as a result of the polycondensation reaction of di- and polycarboxylic acids with an excess of polyfunctional alcohols (polyols) (Westhues, 2007; Oldring, 2001). Aromatic acids such as phthalic acid and isophthalic acid, the aliphatic acids such as adipic acid and maleic acid, and the cycloaliphatic acids such as tetrahydrophthalic acid and hexahydrophthalic acid are some of the most important polycarboxylic acids and their anhydrides which are available on an industrial scale for the manufacture of polyester polyols. The choice of raw materials, the molecular weight, the T_g and the functionality determine the properties of polyester polyols and of the polyurethane coatings in which they are used. Generally, good weather stability and high gloss coatings are obtained with saturated polyester polyols. Since aromatic polyesters tend to yellow when exposed to light, only the non-aromatic products yield good UV stability. However, unsaturated aliphatic/cycloaliphatic polyesters based on maleic anhydride represent an exception. Although they have a double bond, their UV stability is particularly high.

2.2.2.3 Polyether polyols

When ethylene oxide and/or propylene oxide is added to polyfunctional starter molecules, polyether polyols are formed (Westhues, 2007; Oertel, 1994). For starter molecules polyvalent alcohols such as ethylene glycol, 1,2-propanediol, glycerol and trimethylolpropane or amines such as ethylenediamine are used as a rule. The addition

of the alkene oxide is usually performed in an alkaline medium with sodium hydroxide as the base.

Key properties of the polyether such as the melting point, viscosity, hydrophilicity and compability can be controlled via the ratio of the ethylene oxide to propylene oxide. Due to their viscosity, polyether polyols are used mainly in solvent free coating systems. However, because of the poor weather stability of polyethers a consequence of oxidative polyether chain degradation their use is restricted to interior applications. On the other hand, these systems are characterized by particularly good resistance to hydrolysis and mechanical stability. For these reasons, they are often used in the construction sector for coatings on mineral substrates such as concrete.

2.2.2.4 Polycarbonate polyols

From the esterification reaction of carbonic acid and polyols, polycarbonate polyols are produced (Westhues, 2007; Szycher, 1999). The carbonate structure is introduced via phosgene or carbonic acid diesters in practice. Aromatic polycarbonates based on bisphenol A are not used in coating applications due to their poor solubility. On the contrary, linear aliphatic polycarbonates are used both as binders in high quality polyurethane and in the production of polyurethane binders, especially WPU. Aliphatic polycarbonate polyols have low viscosity and produce coatings with good weather stability and very good resistance to hydrolysis.

2.2.2.5 Polycaprolactone polyols

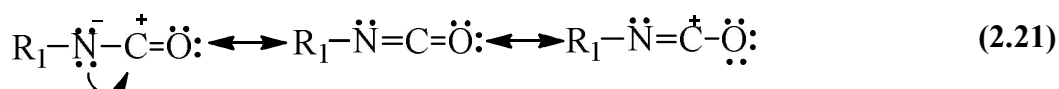
The ring opening polymerization of ϵ -caprolactone produces polycaprolactone polyols (Westhues, 2007; Oldring, 2001). In the manufacture of high molecular weight polyurethanes, polycaprolactone polyols are used as polyol building blocks. Another use of the ring opening polymerization of ϵ -caprolactone is for the modification of higher molecular weight polyols such as polyacrylate polyols. In addition to their viscosity, flexibility and weather stability are other technical advantages of polycaprolactone polyols.

2.2.3 Chain extenders

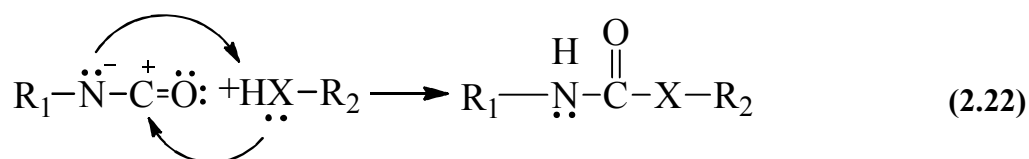
Chain extenders are low molecular weight compounds which ensure elastomeric properties to polyurethanes (Szycher, 1999). Chain extenders are generally hydroxyl and amine terminated. Linear polyurethanes are prepared by using difunctional compounds, whereas chain extenders with higher functionalities used for the production of crosslinked polyurethanes. Diols contribute the group of difunctional chain extenders for urethane-isocyanate prepolymers that is most widely used in the production of PU elastomers (Westhues, 2007). That group includes ethylene glycol, diethylene glycol, 1,6-hexanediol and 1,4-butanediol. Diamines such as, 6-hexamethylenediamine and 1,2-ethylenediamine can also be used as chain extenders, but for that case urethane chains are extended through urea groups. For the extension of urethane ionomers, aliphatic amines are frequently used. Chain extenders with hydroxyl end groups give relatively slow reaction than those containing amine end groups (Szycher, 1999).

2.3 Chemistry of isocyanates

By the following resonance structure, the high reactivity of the isocyanate group with hydrogen active compounds can be explained (2.21).



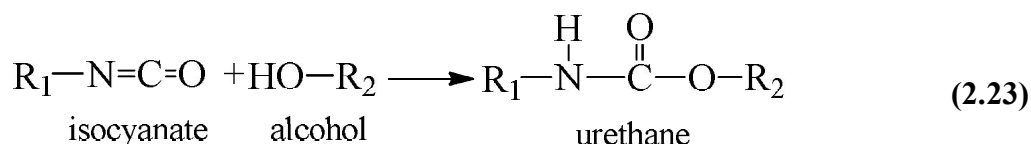
The oxygen atom has the higher electron density whereas the electron density of the carbon atom is the lowest (Ionescu, 2005; Petrovic, 2005; Krol, 2008). As a result, the carbon atom is charged positively, the oxygen atom negatively and the nitrogen atom has an intermediate negative charge. The reaction of isocyanates with hydrogen active compounds (HRX) is in fact an addition at the carbon – nitrogen double bond (2.22).



The electrophilic carbon atom is attacked by the nucleophilic centre of the active hydrogen compounds (the oxygen atom of the hydroxyl groups or the nitrogen atoms in the case of amines) and the hydrogen adds to the nitrogen atom of the –NCO groups. The electron donating groups decrease the reactivity against hydrogen active compounds whereas electron withdrawing groups increase the reactivity of –NCO groups. Aromatic isocyanates (R = aryl) are more reactive than aliphatic isocyanates (R = alkyl). The reactivity is significantly reduced by the steric hindrance at –NCO or HXR' groups.

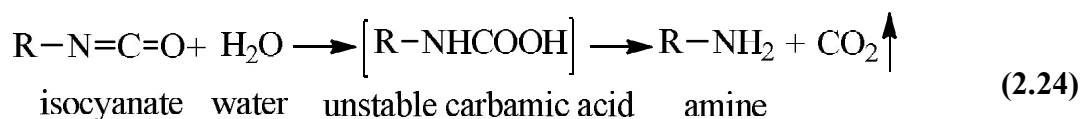
2.3.1 Reaction of isocyanates with alcohols

The most important reaction involved in polyurethane synthesis is the reaction between isocyanates and alcohols, which is an exothermic reaction leads to the production of urethanes as mentioned before (2.23).

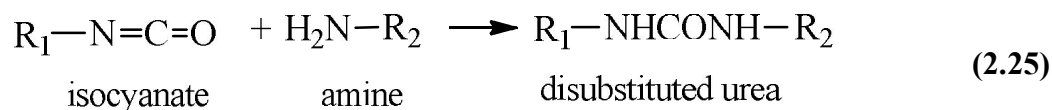


2.3.2 Reaction of isocyanates with amine and water

A urea group and gaseous carbon dioxide is formed due to the reaction between isocyanates and water (Ionescu, 2005). The cellular structure of polyurethane foams is generated by the gas produced with this reaction (2.24).



The reaction between the amine and other isocyanate molecules is very rapid and a symmetrical disubstituted urea is generated as a result of this reaction (2.25).



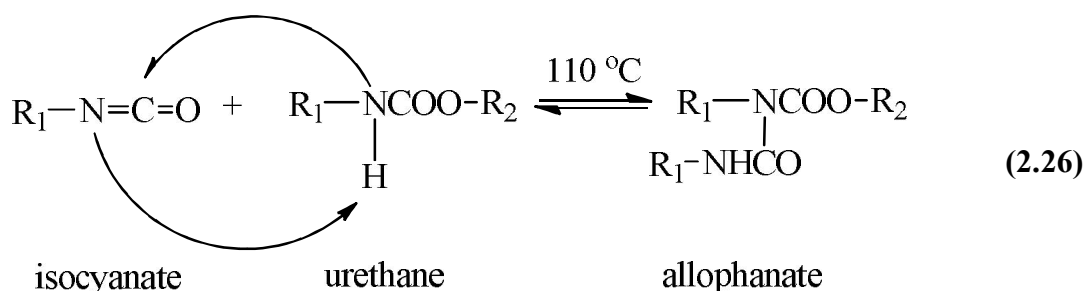
The reaction of isocyanate with water is more exothermic than the reaction with alcohols and the total heat release per mole of water is about 47 kcal/mol. It is obvious that one mole of water reacts with two –NCO groups, which is very

important in order to calculate the correct quantity of isocyanate needed for polyurethane formulations.

Polyurethane-urea polymers were also prepared by the reaction of urethane prepolymer and using of excess water as chain extender (Szycher, 1999). This preparation method leads to novel polyurethane-urea compositions especially high resistant to textile fiber-dressing solvents. By using of excess water, exothermic reaction heat modified as well as the urethane prepolymer chain extended.

2.3.3 Reaction of isocyanates with urethanes

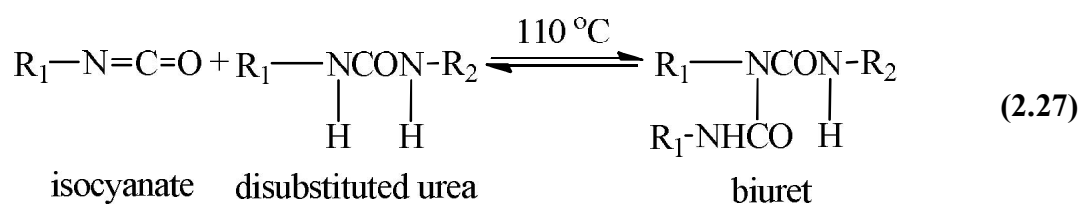
Due to the linkage of hydrogen atom to the nitrogen atom, urethane groups may be considered as hydrogen active compounds (Ionescu, 2005). Allophanate is formed by the reaction of an isocyanate with a urethane group (2.26).



The urethane group has much lower reactivity than the amine -N-H groups due to the electron withdrawing effect of the carbonyl groups and hence, higher temperatures (greater than 110°C) is necessary in order to promote the allophanate formation. It is crucially necessary to mention that the allophanate formation is a reversible reaction.

2.3.4 Reaction of isocyanates with urea groups

Biuret is generated with the reaction of the -N-H groups of urea with isocyanates, which is a similar to the allophanate formation (2.27) (Ionescu, 2005).

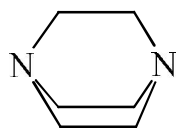


The reaction between urea and isocyanates is an equilibrium reaction and needs a higher temperature which is also similar to the allophanate formation. In

can be either nucleophilic (i.e. tertiary amines) or electrophilic (i.e. organometallic catalysts).

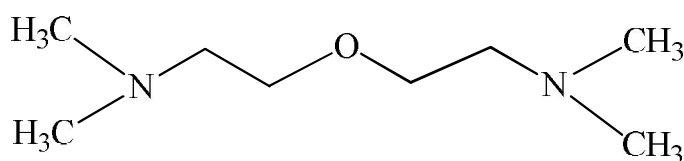
Usually in polyurethane reactions, trialkylamines, peralkylated aliphatic amines, triethylenediamine or diazobiscyclooctane (DABCO), N-alkyl morpholin, tindioctoate, dibutyl tindioctoate, dibutyltindilaurate catalysts are used. In the applications of foam generation and reaction injection molding applications combination of catalysts are required. Tin catalysts are stronger than amine catalysts. However, the important point is the amount of tin catalysts which is not usually exceeded 0.3% in the mixture due to its high reactivity rate.

In polyurethane foam manufacturing, water is considered as a chemical blowing agent because the generated gas is a consequence of a chemical reaction (Ionescu, 2005). The reaction between isocyanates and alcohols or water is catalyzed by tertiary amines with low steric hindrance, and some tin, lead or mercury compounds such as (2.31-2.36);



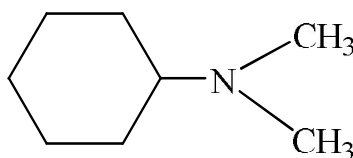
(2.31)

Triethylenediamine



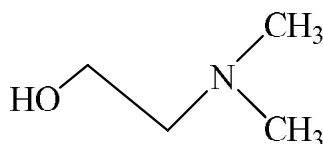
(2.32)

Bis (2-dimethylaminoethyl)ether



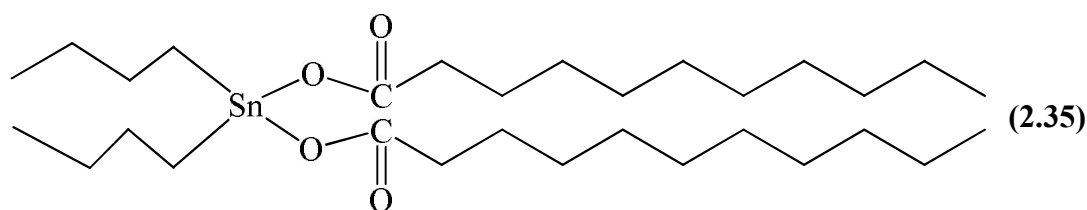
(2.33)

N,N-dimethyl cyclohexylamine

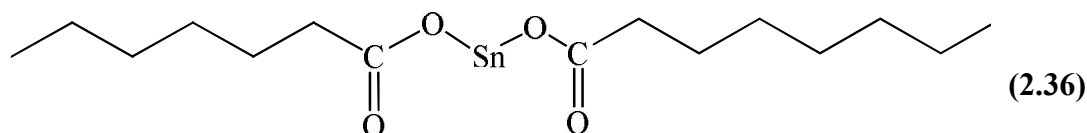


(2.34)

N,N-dimethyl ethanolamine

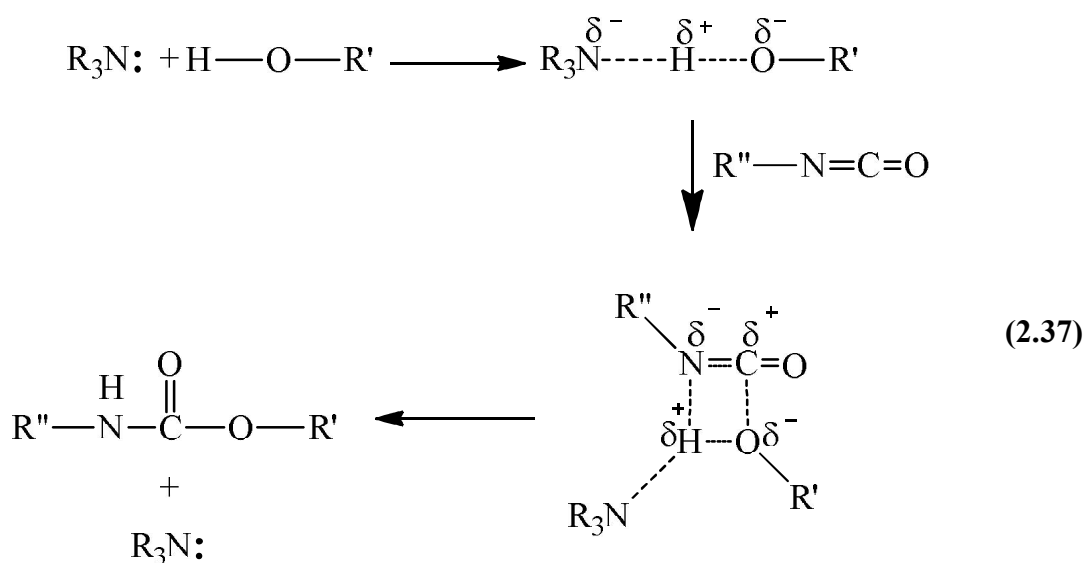


DBTDL

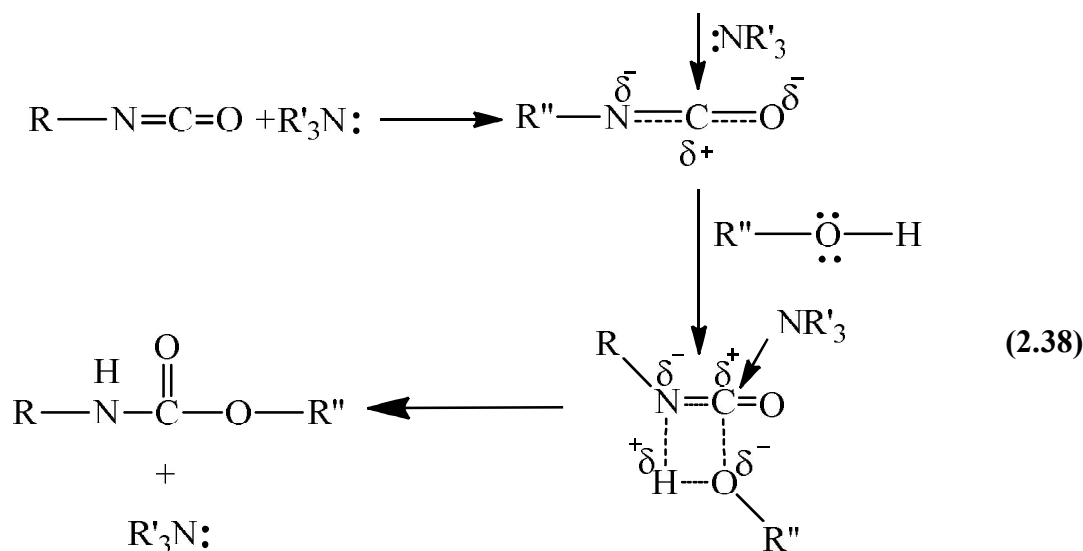


Stannous octoate

Two proposed mechanisms by which tertiary amines may catalyze these reactions (Rogers and Long, 2003). In the first, the amine and alcohol interact via a hydrogen bond, weakening and lengthening the O-H bond, making the oxygen atom more nucleophilic, and enhancing the likelihood of attack across the C=N bond (2.37). The second mechanism involves activation of the isocyanate carbon atom by Lewis acid-base coordination with the amine, exposing it to nucleophilic attack (2.38). The O-H group then adds across the C=N bond to form the urethane linkage and regenerate the catalyst. More important than the mechanism by which the tertiary amine catalysts function is how their molecular structure influences catalytic activity and selectivity.



Hydrogen Bonding Mechanism



Lewis Acid-Base Mechanism

2.4 Waterborne Polyurethane Dispersions

WPU is a colloidal binary system in which PU particles are dispersed in a continuous aqueous medium (Kim, 1996). Since 1960s WPUs have been on the market however it was early 1970s when they become commercially important. A technical advantage of aqueous dispersion is that the viscosity of the dispersion is generally independent of the molecular weight of the polymer. Hence, high solid content with a molecular weight high enough to form films with excellent performance can be achieved solely by physical drying. Thus, film formation can occur by simple evaporation of water even at room temperatures.

WPUs have been widely used in coatings and adhesives for flexible substrates (textile, leathers, papers and rubber) and textile, automotive industries as they are non-toxic, non-flammable and do not pollute air (Peruzzo et al., 2011; Rahman and Kim, 2006; Lee et al., 1997).

Commercial WPUs are predominantly linear polymers and hence, to improve water and solvent resistance properties it is generally necessary to use external crosslinking agents by post addition (Manock, 2000). A growing number of crosslinking agents are available in the market and diverse chemistries are being employed.

The continuity of cost reduction and control of volatile organic compound emissions lead to increase the use of aqueous-based resins, motivating the development of

WPU. (Cakic et al., 2009). Waterborne products present many of the features of solvent based coatings with many technological advantages such as low viscosity at high molecular weight and good applicability as coatings for different types of substrates, wood, concrete, leather, metal and some polymers. WPU have superior properties when compared with similar materials obtained from organic media.

WPU can be formulated into adhesives and coatings that contain little or no co-solvent. The quality and environmental advantages of WPU and the increase in the solvent prices expanded the usages of WPU in many areas such as textile coatings, fiber sizing, and adhesives for a number of polymeric materials and glass surfaces. They are essentially linear polymers. The water and solvent resistances of the produced films are needed to be improved. Modifications are predominantly directed to improvement of these properties. Improvements in these properties have been mainly accomplished by grafting of other polymers, external and internal crosslinkings and blending or interpenetrating polymer network formations.

The soft segment in the polyurethane backbone, which is the polyol component, may be polyfunctional polyether, polypropylene glycol, polytetramethylene glycol or polycaprolactone diol polyester polyol (PEPO), acrylic polyol (ACPO), polycarbonate polyol, castor oil or a mixture of these (Chattopadhyay and Raju, 2007; Chattopadhyay et al., 2006). A wide variety of branched or crosslinked polymers can be formed due to the adjustability of the functionality of free hydroxyl group-containing reactant or isocyanate.

The simplest polyols that are used in chain extension process are glycols, such as ethylene glycol, 1,4-butane diol (BDO) and 1,6-hexane diol (Kim, 1996). Due to the high concentration of urethane groups, the low molecular weight reactants result in hard and stiff polymers. On the contrary, when high molecular weight polymers are used as the main reactants, polymer chain with fewer urethane groups and more flexible alkyl chains are formed. For the hard segment in the polymer backbone, isocyanates are used. Variety of polyisocyanates, polyols and polyamines can be used for the preparation of WPU. For the selection of isocyanate, the reactivity with water is the most important criteria. Hence, aliphatic isocyanates that have lower reactivity and provide better control of the reaction such as 4,4-dicyclomethane diisocyanate (H_{12} MDI), isophorone diisocyanate (IPDI) and 1,6-hexamethylene diisocyanate (HDI) can be preferred.

2.4.1 Synthetic methods for waterborne polyurethanes

For WPU, several synthesis methods have been developed (Chattopadhyay and Raju, 2007; Kim 1996). In all of these processes, as first step, 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 react to form a medium molecular weight polymer (the prepolymer).

To allow the dispersion of the polymer in water, an emulsifier is usually added. The emulsifier can be a diol with an ionic group (carboxylate, sulfonate, or quaternary ammonium salt) or a nonionic group [poly(ethylene oxide)]. The various synthetic pathways differ on the critical step which is the dispersion process of the polymer in water and the buildup of the molecular weight.

WPU cannot be obtained by conventional synthesis methods, such as emulsion and suspension polymerizations, due to the high reactivity of isocyanate groups toward water (Sardon et al., 2011). Therefore, several processes have been developed for achieving WPU such as the acetone method, the prepolymer mixing method, the hot-melt method and the ketamine/ketazine method (Liminana et al., 2006; Barni, 2003). The most common procedures used are the acetone and prepolymer mixing processes, which have some differences in the experimental conditions and the nature of the reactants.

When preparing WPU, acetone process is one of the most important methods which is also used widely in industry. (Nanda and Wicks, 2006). The acetone process is the second widely used method after the prepolymer process for making WPU. The outstanding differences are in the chain extension and dispersion steps. In the beginning, the prepolymer is prepared in the same way as in the prepolymer mixing process, yet, acetone solvent is used instead of NMP, at a much higher level than when NMP is used. Diols or diamines are used to perform the chain extension process. By the slow addition of water to the polymer solution, the dispersion is affected and the dispersing groups are neutralized. After the dispersion step, the acetone is removed by distillation providing a product containing either very low or no Volatile Organic Compounds (VOCs). VOCs are low molecular weight organic compounds which can evaporate easily through coating films such as solvent molecules which can be harmful for the environment. Although acetone process is provided with this disadvantage, there are very few references related to this process

in literature. Sometimes a modified acetone process is used where some but not all of the acetone is replaced with NMP in the WPU.

2.4.1.1 Acetone process

Acetone process is the one of the most popular method among the synthetic methods of WPUs which consists of a two-step procedure. In the first step, hydrophilic and potentially charged groups are incorporated into the polymer backbone during the PU synthesis in acetone (Sardon et al., 2011). In a second step, water is added to the PU/acetone mixture. Acetone process is a universal technology for the production of WPUs (Kim, 1996; Oertel, 1994). For the chain extension of NCO-terminated polyurethane prepolymers, difunctional chain extenders are used in an organic solvent such as acetone, methyl ethyl ketone or tetrahydrofuran, followed by mixing with water to form dispersion and removal of the solvent by distillation. After removing the acetone, a fine dispersion containing no cosolvent is obtained. An organic solvent is used to control the viscosity during the chain extension step of this well established process. For this process, acetone is especially suitable as it is inert with the polyurethane forming reactions, miscible in water, and has a low boiling point. Wide scope of variation in structure and emulsion, high quality end products, wide variety of possibilities in terms of building up molecular weight of the polymer, the control of the average particle size and reliable reproducibility are some of the advantages of the acetone process. The main reason for these advantages is the accomplishment of the polymer formation in a homogeneous solution. Nevertheless, as chain extension is carried out in acetone, the resulting polyurethane is predominantly linear and soluble in water. The process is economically unfavorable due to the requirement of large amount of acetone distillation. Another disadvantage of the process is the low reactor volume yield because of the large quantities of solvent used in the process.

2.4.1.2 Prepolymer mixing process

The prepolymer mixing process prevents the usage of large amounts of solvent (Rahman et al., 2009; Kim, 1996). To form the emulsion hydrophilically modified NCO-terminated PU prepolymers are mixed with water. Prepolymer viscosity is crucial and must be limited or the dispersion step will be difficult. Hence, this process is suitable for low viscosity prepolymer. To reduce the viscosity, a small

amount of solvent can be added. With the addition of di- or polyfunctional chain extenders chain extenders to the aqueous dispersion, the chain extension process is accomplished. For the NCO-water reaction to be insignificant, the dispersion step must be carried out at low temperatures. Consequently, cycloaliphatic diisocyanates are most widely used due to their low reactivity with water. As the chain extensions are performed in a heterogeneous phase, they do not proceed in a quantitative way. Hence, the properties of WPU prepared by this process are generally inferior to those from acetone process.

2.4.1.3 Melt dispersion and ketimine/ketazine processes

In the melt dispersion process, sufficiently low viscosity, ionic and/or nonionic hydrophilically modified NCO prepolymers are placed in an aqueous dispersion (Westhues, 2007). The amine component used as the chain extender can either be added to the dispersion water or to the prepolymer dispersion following the dispersion stage. By contrast, in the ketimine/ ketazine process, the blocked diamine (ketimine) or (ketazine) hydrazine is mixed homogenously with the NCO prepolymer. After conversion to the aqueous phase, the diamine or hydrazine is released by hydrolysis and reacts spontaneously with the NCO prepolymer to produce chain extension.

2.4.2 Properties of waterborne polyurethanes

The properties of the WPU are primarily determined by the interactions between the hard and soft segments. The interactions between the ionic groups are secondarily affect the final properties. Recent studies showed that the segmented structure, ionic group content, molecular weight of the polyol, solids content, the type of chain extender and the hard/soft segments ratio, determines the WPU properties (Pacios et al., 2011).

Ionic and nonionic hydrophilic groups in WPU represent a synergistic effect (Oertel, 1994). The characteristic features of WPU are given in Table 2.2. The total hydrophilicity of the polymer can be lowered while maintaining the good dispersibility. Aqueous, emulsifier free dispersions can be synthesized with a wide range of particle size. The typical mean particle size of an WPU is between 10 and 500 nm which is relatively broad compared with other dispersions. However, true high molecular weight polymer solutions or viscous gels and coarse suspensions of

polymer particles in millimeter range can be prepared. The particle size decreases with increasing hydrophilicity, the viscosity increases and the dispersion becomes more stable. The mean particle size also depends on the molecular weight of the polyurethane. Due to the swelling of ionically modified particles by hydration, the film forming properties are excellent even at low temperatures. WPU with a higher solids content and a molecular weight are obtained by chain extension providing that is sufficient for forming films by physical drying alone, with an excellent property profile for many applications.

Polyurethane dispersions are being used increasingly in aqueous coating and adhesive systems (Westhues, 2007). Among the characteristic properties of these dispersions is the variability of the properties yielded by coatings, e.g. high film elasticity and hardness achieved at low curing temperatures. These features can be achieved because it is possible to produce defined hard and soft segments in the polymer. Hard and soft domains are produced during film formation as a result of this specifically induced incompatibility of the segments. The hydrophilic chain segments result in swelling and plasticization of the particles by water. This lowers the film forming temperature. However, water and solvent resistance of the WPUs are always inferior to the solvent-based polyurethane since the ionic segment in the polymer backbone (Jiu et al., 2011). Besides, long term stability of WPU systems has been a concern, since WPUs containing ester functionalities may hydrolyze over time due to the presence of water into formulation, leading to reduction in molecular weight of the WPU and ultimately colloidal instability and poorer film properties. In addition, WPUs exhibit inferior drying rate and slow development of adhesion. Now WPUs with high solid content and low ionic group are tracking much more attention. Although, WPUs are capable of providing films with acceptable properties for a number of applications, there is no doubt that a crosslinked film provides increased durability and chemical resistance when compared to uncrosslinked types.

Combination of WPUs with other types of dispersions provides further options for customizing the property profile. Such mixed dispersions include simple blends, but also dispersions with covalently bonded polyacrylate polyurethane molecules. Polyurethane-acrylate dispersions recently are the most studied mixed dispersion type.

Table 2.2 : Characteristic features of WPUs (Oertel, 1994).

	Dispersant shear force process	Acetone process	Prepolymer mixing process	Melt-dispersion process	Ketimine/ ketazine process	Solids self-dispersing process
Polyhydroxy compound	Polyether (liquid)	linear, variable	Polyethers, some polyesters	variable	variable	Variable softening of prepolymer > 40°C
Diisocyanate Glycols	TDI only small amounts	variable variable	TDI, IPDI, H ₁₂ MDI Dimethylol propionic acid	TDI, HDI, IPDI mainly ionic	variable variable	MW<8000
Dispersant Solvent	+ 5 to 10% toluene	- 40 to 70% acetone	- Often 10 to 30% NMP	-	- Possibly 5 to 30% acetone	-
Shear force mixer Temperature of dispersion	+ ~20°C	- ~50°C	- 20 to 80°C	- 50 to 130°C	- 50 to 80°C	- 15 to 30°C
Product before dispersion	nonionic NCO prepolymers	polyurethane	NCO prepolymer ionomer	ionic biuret prepolymers	NCO prepolymer + ketimine/ketazine	prepolymer
Procedure after dispersion	amine extension	acetone distillation	amine extension	polycondensation	possibly acetone distillation	curing agent added
End product	polyurethane-urea	polyurethane or polyurethane-urea	polyurethane urea ionomer	polyurethane-biuret	polyurethane-urea	polyurethane
Solvent contents of the final dispersion	2 to 8% toluene	<0.5%	often 5 to 15% NMP	-	possibly <2% acetone	-
Particle size (nm)	700 to 3000	30 to 100000	100 to 500	30 to 100000	30 to 1000	30 to 500
Post curing temperature	>100°C	-	-	30 to 150°C	-	>120°C

2.4.3 Selection of starting materials in waterborne polyurethanes

2.4.3.1 Selection of isocyanates

Almost all types of di- and/or higher functionality isocyanates can be used in WPU (Cakic et al., 2009). The critical point is that the isocyanate must be stable enough towards water hence the urethane bonds will be formed instead of urea bonds. TDI, MDI, IPDI, HDI etc are some of the few diisocyanates used commercially (Table 2.3). K1 and K2 are the reactivities of the two isocyanate groups in a diisocyanate structure. Aromatic isocyanates were neglected in earlier stages of WPU chemistry; however, nowadays they are used in some newly developed techniques.

The greater number of commercial WPUs are based on aliphatic isocyanates preferably to aromatic ones due to their low reactivity with water (Manock, 2000). Aromatic diisocyanates are of less use due to their high reactivity.

Table 2.3 : Reactivities of common isocyanates.

Isocyanate type	1st NCO group (K1)	2nd NCO group (K2)
TDI	400	33
MDI	320	110
HDI	1	0.5
H ₁₂ MDI	0.57	0.40
IPDI	0.62	0.23

2.4.3.2 Selection of polyols

Typically linear, difunctional polyols with molecular weights in the range of 500-3000 are suitable to be used (Cakic et al., 2009). The polyols used in WPU synthesis are of polyethers, polyesters, polycaprolactone, and polycarbonate origin. With respect to strength and oil resistance, etc. polyesters have some advantages over polyethers. The used polyols are linear or slightly branched. Short chains produce greater number of urethane links and hence different physical properties.

Polyester-based WPUs provide an extended range of properties from high to low modulus, solvent resistance, adhesion, good UV resistance and reasonable hydrolysis resistance (Manock, 2000). Because of this adjustability and cost effectiveness that make polyester types the most commonly used grades.

Polyether based WPUs offer good flexibility at low temperature, hydrolysis resistance and reasonable adhesion. Nevertheless, UV resistance is inferior to

polyester types. Polypropylene glycol polyethers are rather low cost raw materials and produce reasonable WPU. Although polytetramethylene glycol (PTMEG) is more expensive, it yields higher tensile strength.

Polycarbonate and polycarbonate-ester are used in high performance applications which require the optimum properties with respect to toughness, adhesion, hydrolysis and UV resistance. However, polycarbonate diols are very expensive and WPU based on this type of backbone are only viable in speciality applications. In addition to polyols short chain diols, e.g. 1,4 butanediol or 1,6 hexanediol or functionalised diols, can be used to modify properties.

2.4.3.3 Selection of chain extender

Extension of polyurethane chains with NCO terminating groups can be achieved by glycol forming urethane groups (Cakic et al., 2009; Rahman et al., 2009). Chain extenders play an important role in the morphology of polyurethane fibres, elastomers, adhesives, and certain integral skin and microcellular foams. They are low molecular weight hydroxyl and amine terminated compounds. The elastomeric properties of these materials come from the phase separation of the soft and hard segments of the polymer. The urethane hard segment domains act as crosslinks between the amorphous polyether (or polyester) soft segment domains. The reason why this phase separation occurs is; non-polar, soft segments that have low melting temperatures are incompatible with the polar hard segments with high melting temperatures. The soft segments are formed from high molecular weight polyols. They are mobile and are normally present in coiled formation. Whereas, the hard segments, which are formed from isocyanate and chain extenders, are stiff and immobile. The hard segments, which are covalently coupled to the soft segments, inhibit the plastic flow of the polymer chains and create elastomeric resiliency.

With mechanical deformation, some part of the soft segments is stressed by uncoiling, and the hard segments align in the direction of stress. The reorientation of the hard segments results in powerful hydrogen bonding and contributes to high tensile strength, elongation, and tear resistance values. The flexural, heat and chemical resistance properties are determined by the choice of chain extender. Ethylene glycol (EG), propylene glycol (PG), 1,4-butanediol (BD), 1,6-hexanediol (HD), cyclohexane dimethanol (CHD) and hydroquinone bis(2-hydroxyethyl) ether

(HQEE) are the most important chain extenders. All of these glycols form polyurethanes that form well defined hard segment domains by phase separation and are melt processable. This is the reason why polyurethanes have advantageous properties.

The timing of the chain extension stage is crucial and is dependent on the reactivity of the isocyanate group on the prepolymer, the prepolymer temperature and the temperature of the dispersion medium (Manock, 2000). The buildup of high molecular weight polyurethane is lead by the chain extension step with the ionic groups acting as an internal emulsifier to stabilize the polymer in the form of a particle.

2.4.3.4 Selection of internal emulsifier

WPU can be prepared by the emulsification of hydrophobic polyurethanes in water by the utilization of emulsification agents and protective colloids (Cakic et al., 2009). Conventionally, WPU are prepared in the form of an ionomer, especially an anionomer and hydrophilic centers are located in hard domains which are coupled with hydrophobic urethane and/or urea groups (Kim et al., 2003). As the polymer is dispersed in water, the hydrophilic segments are preferentially located on the surfaces of the particle and are swelled by water. Yet, the emulsifications with built-in hydrophilic groups propagate better dispersion. This process yields finer particle size, gives better stability of dispersion, the product's sensitivity towards water after evaporation is reduced although, strong shear forces are not required. The building of hydrophilic groups into the backbone is the replacement of other reactive ingredients (i.e., polyols, isocyanates) by special materials that contain ionic groups, ionic group precursors, or other water-soluble segments in their molecular structure. These units are called as internal emulsifiers or hydrophilic monomers. The most important compounds are the sulfonate diamines and diols, or dihydroxy carboxylic acids. DMPA is the most frequently used dihydroxy carboxylic acid as an ionic building block. The reason why this compound is the most frequently used dihydroxy carboxylic acid is; the the steric hindrance of the COOH group so that it minimizes the interaction with isocyanates. Because the DMPA controls the dispersibility and the resulting particle size, the level of DMPA is crucial (Sardon et al., 2011). Increasing the DMPA amount decreases the particle size until eventually a water

soluble polymer is formed. Also, increasing the concentration of the hydrophilic centers cause an increase in water sensitivity of the dried polymer film.

2.5 Polymer-Clay Nanocomposites

2.5.1 Layered silicates

The term clay is used to describe a group of hydrous aluminum phyllosilicate minerals which are typically less than 2 μm in diameter (Şen, 2007). Clays consist of a variety of phyllosilicate minerals rich in silicon and aluminum oxides and hydroxides that include variable amounts of structural water. Most of the clays are formed by the chemical weathering of silicate-bearing rocks by carbonic acid but some are formed by hydrothermal activity. There are many small particles present in soil but clays are distinguished by their small size, flake or layered shape, affinity for water and tendency toward high plasticity. Clay minerals are used in many important applications such as manufacturing, drilling, construction and paper production.

Unlike the common clay minerals, such as talc and mica, smectite clay can be exfoliated or delaminated and dispersed as individual layers, each ~ 1 nm thick. In the exfoliated form, the surface area of each nanoclay particle is ~ 750 m^2/g and the aspect ratio is >50 .

2.5.2 The chemical composition of layered silicates

The chemical composition of layered silicates is important when they are used as candidates for preparing nanocomposites (Ke and Stroeve, 2005). The final properties of the nanocomposite products are directly lead by the stable compositions. Kaolinite, Mt and illite (hydromica) are the three types of most popular or practical layered silicates of clay. Their chemical compositions are shown in Table 2.4.

Table 2.4 : Chemical compositions of layered silicate of clay minerals (Ke and Stroeve, 2005).

Name of clay	Chemical composition ($n\text{SiO}_2/n\text{Al}_2\text{O}_3$)	Type
Kaolinite	$\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$ or $2\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 4\text{H}_2\text{O}$	2:1
Mt	$(\text{Al}_2\text{Mg}_3)(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$	4:1
Illite	$(\text{K}, \text{Na}, \text{Ca}_2)m(\text{Al}, \text{Mg})_4(\text{Si}, \text{Al})_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ ($m < 1$)	4:1

Clays are different in chemical compositions: kaolinites have high content of alumina and low content of silica; Mts have low content of alumina and high content of silica; illites have high content of K₂O. The chemical composition of layered silicates of clay minerals is important as evidence for chemical analysis in order to identify the type of clay and also is a reference parameter for clay applications.

The classifications of layered silicates and compounds are shown in Table 2.5.

Table 2.5: Classifications of layered silicate and compounds (Şen, 2007).

Inorganic material	Examples
Layered compounds	MoS ₂ , V ₂ O ₅ , MoSe ₂ , WS ₂ , WSe ₂ , SnS ₂ , ZrSe ₂ , PbI ₂ , BN, BiI ₃
Layered silicates	Magadiite, bentonite, kaolinite, montmorillonite, saponite, sepiolite, vermiculite, talc (OH), hectorite, attapulgite, fluoromica, illite, chlorite

Additionally, these minerals are briefly classified according to their types and the relative content of the unit crystal lamellae (Table 2.6).

Table 2.6: Classifications of layered silicate crystals (Ke and Stroeve, 2005).

Unit crystal lamellae type	Family of clay	Examples of clay
1:1	Family of kaolinite Family of illite	Kaolinite, perlite clay, etc. Illite, etc.
2:1	Family of saponite ¹ Family of hydromica	Mt, saponite, vermiculite
2:2	Chlorite family and others	Chlorite
Mixed layer and chain structure	Family of saponite	Sepiolite, palygorskite, attapulgite

¹Previously also named as a family of NaMt while called montosaponite, since 1975, by the name committee of the international clay investigation committee.

The layered silicates are divided into three types according to the relative ratio of two unit crystal sheets (Table 2.6).

Its unit lamellar crystal is composed of one crystal sheet of silica tetrahedron combined with one-crystal lamellae of alumina octahedron (1:1 type).

Its unit lamellar crystal is composed of two crystal sheets of silica tetrahedron combined with one crystal sheet of alumina octahedron between them (2:1 type).

Its unit lamellar crystal is composed of four crystal sheets, in which crystal sheets of silica tetrahedron and alumina or magnesium octahedron are alternately arranged (2:2 type).

In mixed lamellar and chain-like structure, the lamellar hexagon rings composed of silica tetrahedron sheets are arranged opposite to one another in a right direction from the top down.

The most important layered silicate groups and their uses summarized below (Şen, 2007);

Kaolinite group has three members (kaolinite, dickite and nacrite) and a formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. Kaolinite type of layered silicates are used in ceramics, as a filler for paint, rubber and plastics and the largest use is in the paper industry that uses kaolinite to produce a glossy paper such as is used in most magazines.

The general formula of Montmorillonite (Mt) (Smectite) group is $(\text{Ca}, \text{Na}, \text{H}) (\text{Al}, \text{Mg}, \text{Fe}, \text{Zn})_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ where x represents the variable amount of water that members of this group could contain. Mt has a 2:1 layer structure. All tetrahedral sheets contain Si^{4+} ions. Aluminum is the normal ion in the central sheet, but about one-eighth of the octahedral containing Mg^{2+} act as a substituting ion for Al^{3+} . The negative charge caused by substitution is neutralized by various hydrated cations adsorbed to the surface of the sheets. The force of bonding between cations and the sheets is not very strong and depends on the amount of water present. In dry montmorillonite the bonding force is relatively strong. When wet conditions occur, water is drawn into the interlayer space between the sheets and causes the clay to swell dramatically (expanding clay). A characteristic feature of montmorillonite is the extensive surface for the adsorption of water and ions; therefore the cation exchange capacity of Mt is very high. Layers of the smectite group range in thickness from 0.98 to 1.8 nm or more. The uses are many and include a facial powder (talc), filler for paints and rubbers, an electrical, heat and acid resistant porcelain, in drilling mud and as a plasticizer in molding sands and other materials.

There are two types of Mt clay, Sodium and Calcium. Mt clays are also called Bentonite clays and vice versa. The name comes from the location of a commercial deposit near Fort Benton, Wyoming in the northwestern part of the U.S. Both clays are in the Smectite family of clays and are known as aluminum/silica colloidal mineral.

Illite (or the clay-mica) group is basically a hydrated microscopic muscovite. The general formula is $(\text{K}, \text{H})\text{Al}_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot x\text{H}_2\text{O}$, where x represents the variable

amount of water amount of water that this group could contain. A common constituent in shale and is used as a filler in paints and plastics and in some drilling mud.

2.5.3 Structure and properties of layered silicates

The commonly used layered silicates in PLS (Polymer Layered Silicates) nanocomposites belong to the same general family of 2:1 layered or phyllosilicate (Neş, 2004). Their crystal lattice dwells of two-dimensional layers where a central octahedral sheet of alumina or magnesia is binded to two external silica tetrahedron by the edge so that the oxygen ions of the octahedral sheet also belong to the tetrahedral sheets.

The thickness of the layer is around 1 nm, and the lateral dimensions of these layers can vary from 30 nm to several microns or larger, depending on the particular silicate. The layers are organized by themselves in order to form stacks with a regular van der Waals gap between called as interlayer or the gallery. Isomorphic substitutions within the layers (for example, Al^{3+} replaced by Mg^{2+} or Fe^{2+} , or Mg^{2+} replaced by Li^{1+}) generate negative charges that are counterbalanced by alkali and alkaline earth cations situated in the interlayer.

Because the forces which hold the stacks together are relatively weak, it is easy for the small molecules to intercalate between the layers. The hydrated cations of the interlayer can be exchanged with cationic surfactants such as alkylammonium or alkylphosphonium (onium) in order to render these these hydrophilic phyllosilicates more organophilic.

The surface energy of the modified clay (or organoclay, OMt) being organophilic, is lowered and is more compatible with organic polymers. Under well-defined experimental conditions, these polymers may be able to intercalate within the galleries. The most commonly used layered silicates are; Mt, hectorite, and saponite. The two types of layered silicates are; tetrahedral substituted and octahedral substituted. The negative charge is located on the surface of silicate layers for the case of tetrahedrally substituted layered silicates and hence, the polymer matrices can react interact more readily with these than with octahedrally-substituted material. The details of the structure and chemistry for these layered silicates are provided in Figure 2.3 and Table 2.7.

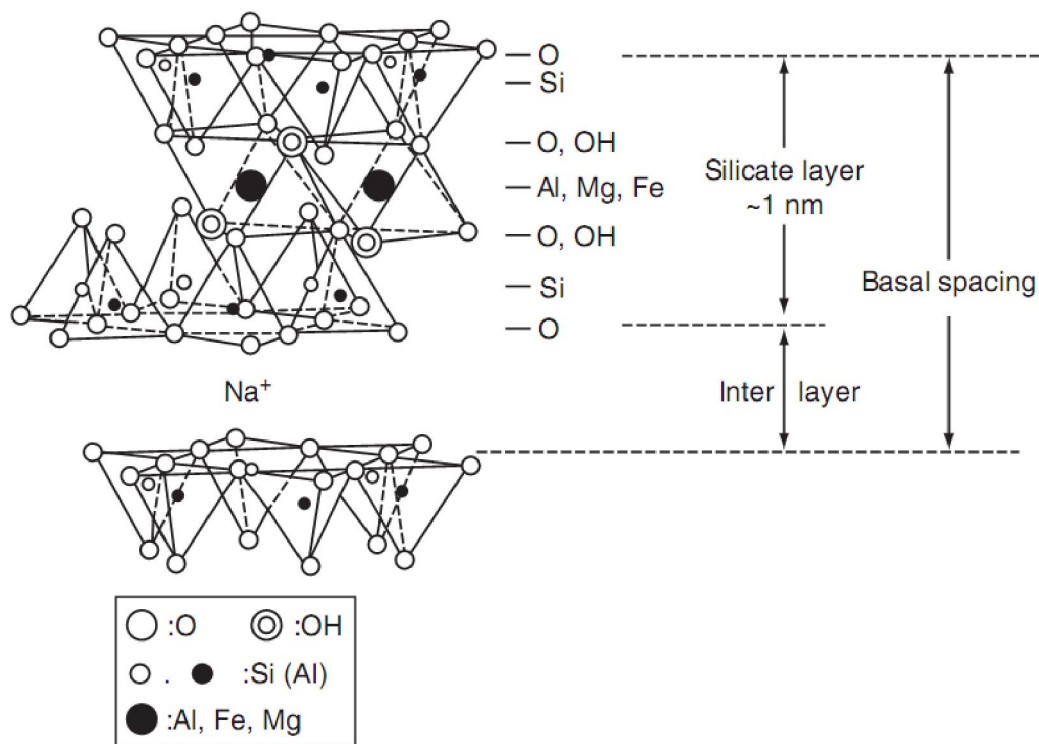


Figure 2.3 : Crystalsal structure of smectite clay (Hussain et al., 2006).

The layered silicates are characterized by a moderate surface charge which is called as cation exchange capacity (CEC). The CEC is generally expressed in terms of equiv./100 g (Neşe, 2004). This charge is different for each layer hence, an average value should be considered for the whole crystal. Although a few charge balancing cations are located on the external crystallite surface, the majority of the exchangeable cations are located inside the galleries.

Layered silicates have two specific characteristics that are generally considered for PLS nanocomposites. The first characteristic is the the ability of the silicate particles to disperse into individual layers. The second one is the ability to fine-tune their surface chemistry through ion exchange reactions with organic and inorganic cations. The degree of dispersion of the layered silicate in a particular polymer matrix depends on the interlayer cation hence, these two characteristics are interrelated.

Lately, researchers have been interested in montmorillonite (Mt, a layered silicate with lamellar shape, for the preparation of polymer-clay nanocomposites (Deng et al., 2007). This interest is due to the lamellar platelets of Mt display high in-plane strength, stiffness, and high aspect ratio.

Table 2.7: Chemical formula and characteristic parameters of commonly used 2:1 phyllosilicates (Neş, 2004).

2:1 phyllosilicates	Chemical formula ¹	CEC (mequiv/100 g)	Particle length (nm)
Montmorillonite	$Mx(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$	110	100-150
Hectorite	$Mx(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$	120	200-300
Saponite	$MxMg_6(Si_{8-x}Al_x)Si_8O_{20}(OH)_4$	86.6	50-60

¹M, monovalent cation; x, degree of isomorphous substitution (between 0.5 and 1.3).

Occasionally, Mt has a chemical structure with two fused silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of either magnesium or aluminum hydroxide. Organic cations such as alkylammonium ions can replace the Na^+ and Ca^+ ions residing in the interlayer galleries via a cationic-exchange reaction to render the hydrophilic layered silicate organophilic.

The layered silicates are modified in two ways, covalent bond formation on the edges and ion exchange with organic cations. Although there are a few reports which describe about the clay modified by organosilanes, typically long chain organoalkylammonium modified organophilic clays are used to make polymer-clay nanocomposites. These reports present the silylation of clays by organochlorosilane via covalent bond formation. It was reported that organoclays modified by a small amount of hexamethyldisilazane retards the intercalation of a polar polymer significantly, such as poly-(styrene-co-acrylonitrile), into the clay gallery. Mono and trifunctionalsilane grafted laponite clay platelets in water-based polymer-clay nanocomposites were presented (Herrera et al., 2006).

In similarity with polymer blends, any physical mixture of a polymer and silicate (or inorganic material in general) does not necessarily form a nanocomposite (Pavlidou and Papaspyrides, 2008). Normally, the separation into distinct phases occurs in most cases. For the immiscible systems, the poor attraction forces between the organic and inorganic components lead to relatively poorer mechanical properties. Consequently, a phase-separated composite is obtained that has properties similar to traditional microcomposites, when the polymer is unable to intercalate between the silicate sheets.

Different from the traditional class of polymer-filler composites, two types of nanocomposites can be obtained depending on the preparation method and the nature

of the components being used: Intercalated and exfoliated nanocomposites (Huh et al., 2009) (Figure 2.4).

In intercalated nanocomposites, the insertion of a polymer matrix into the layered silicate structure takes place in a crystallographically regular fashion and negligible of the clay to polymer ratio (Pavlidou and Papaspyrides, 2008; Mallick, 2007). The spacing between the silicate layers is between 2 and 3 nm.

In exfoliated nanocomposites, the individual layers of clay are separated in a continuous polymer matrix by average distances depending on the clay loading (Pavlidou and Papaspyrides, 2008; Mallick, 2007). Typically, the clay content of an intercalated nanocomposite is much higher than that of an exfoliated one. The spacing between the silicate layers is between 8 and 10 nm. This is the most desirable dispersion for improved properties.

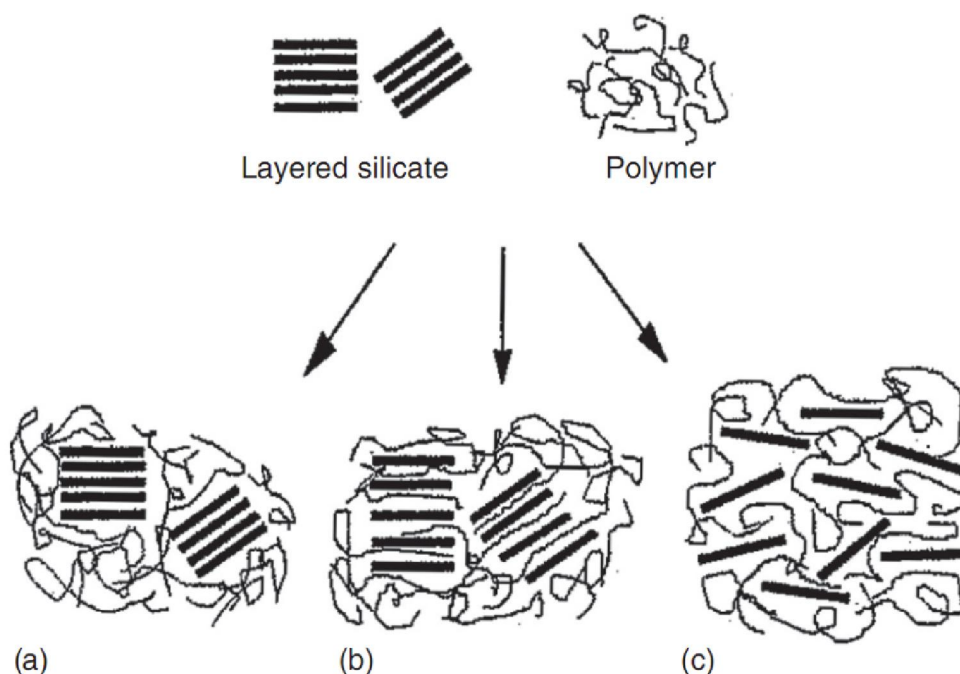


Figure 2.4 : Polymer-clay nanocomposite architecture: (a) phase-separated (microcomposite); (b) intercalated (nanocomposite); and (c) exfoliated (nanocomposite) (Alexandre and Dubois, 2000).

The homogeneous dispersion of clay and huge interfacial area between polymer and clay makes exfoliated polymer-clay nanocomposites especially desirable for improved properties (Kuan et al., 2005). In polymer-clay nanocomposites, to obtain better compatibility with polymers, the clay is modified via swelling agents that help to increase the interlayer spacing of the silicate sheets and modify the hydrophilic

clay to a more hydrophobic character which affects the properties of the final products.

When compared to pure polymers containing a small amount of layered silicate, polymer-clay nanocomposites generally exhibit improved mechanical and materials properties (Ray and Okamoto, 2003). Higher modulus, increased strength and heat resistance, decreased gas permeability and flammability, and increased biodegradability of biodegradable polymers etc are some of the examples of improving properties. Stronger interfacial interaction between the matrix and layered silicate compared with conventional filler-reinforced systems is considered to be the main reason for these improved properties.

The structure of the clay layers is not affected; the characteristics of the OMt basal reflections do not change for immiscible polymer/OMt mixtures (Kuan et al., 2005). The diffraction peak is shifted towards lower angle when the polymer is intercalated within the clay layers according to the Bragg's law. Nevertheless, the extensive layer separation associated with exfoliated structures disrupts the consistent layer stacking and causes a featureless diffraction pattern. There may be two reasons for the diffraction peaks to be no longer visible in the XRD diffractograms; too large spacing between the layers or because the nanocomposite is not ordered anymore (Pavlidou and Papaspyrides., 2008).

2.5.4 Preparation methods of polymer-clay nanocomposites

Two primary methods are utilized to prepare intercalated polymer-clay materials. These are shown schematically in Figure 2.5 as direct intercalation (melt and in solution blending) and as in situ polymerization of preintercalated monomers. Following are the most common techniques used for dispersing clays in polymers to make nanoclay-polymer composites (Kiliaris and Papaspyrides, 2010; Ajayan et al., 2003).

In direct intercalation (solution and melt processing) method, the clay is first exfoliated into single layers using a solvent in which the polymer is soluble. As the polymer incorporated, it is adsorbed in to the exfoliated clay platelets and when the solvent is evaporated, the structure of polymer molecules sandwiched between exfoliated sheets is created. The solution method has been widely used with water-soluble polymers, such as polyvinyl alcohol (PVA) and polyethylene oxide.

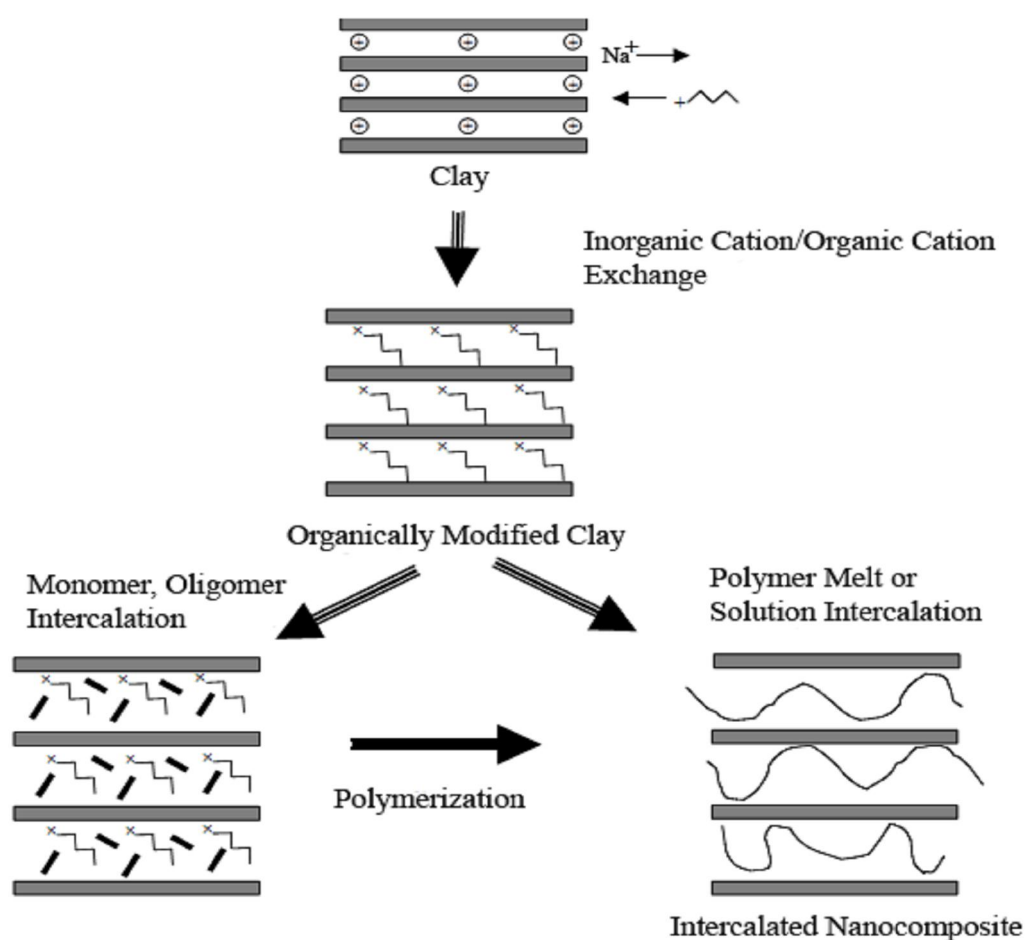


Figure 2.5 : Methods for creating intercalated polymer-clay nanocomposites (Ajayan et al, 2003).

In the melt processing method, the clay particles are dispersed in the polymer which is in the liquid state. The polymer molecules can enter into the interlayer space of the clay particles and the architecture resulted as either an intercalated or an exfoliated structure depending on the processing condition and the compatibility between the polymer and the clay surface. The melt processing method has been used with a variety of thermoplastics, such as polypropylene and polyamide-6, using conventional melt processing techniques, such as extrusion and injection molding. High shear stresses are created which is capable of delaminating the original clay stack into thinner stacks owing to the high melt viscosity of thermoplastics and the mechanical action of the rotating screw in an extruder or an injection-molding machine. Diffusion of polymer molecules between the clay layers in the stacks then tends to increase the interlayer spacing into intercalated or exfoliated form.

In In-situ polymerization method, the clay particle is dispersed into the liquid monomer, which is subsequently polymerized either by heat or by radiation (Mallick,

2007). The polymer molecules are formed in situ between the intercalated sheets of clay.

The in situ method is commonly applied on preparation of nanocomposites with thermoset polymers, such as epoxy and polyurethane. It has also been used with thermoplastics, such as polystyrene and polyamide-6 (PA-6), and elastomers, such as thermoplastic polyurethane and thermoplastic polyolefins (TPOs).

In situ polymerization method, standard polymerization methods are applied after dispersion of clay in the monomer or monomer solution. The important aspect of this method is the potential to graft the polymer onto the particle surface. Many different types of nanocomposites have been prepared by in-situ polymerization. The most important key is preparing appropriate dispersion of the clay in the monomer. This often requires modification of the particle surface because, although dispersion is easier in a liquid than in a viscous melt, the settling process is also more rapid.

2.5.5 Potential applications of nanocomposites

In the development of novel nanoscopic-pigment particles, the barrier properties of clay layers have been utilized (Yu et al., 2007). The novel nanoscopic-pigment particles exhibit improved oxygen, temperature and UV stability of organic molecules in addition to the normal leaching by a combination of soluble dyestuff and clay particles via ionic interactions. Additionally, the resultant coloured products are transparent because the primary particle size of the nano-pigments is lower than the wavelength of light. Employing their gas barrier properties and optical transparency, nanocomposites can be processed either as thin films for packaging or in bulk form for beverage bottles. Moreover, in a typical inkjet printer, layered silicate nanocomposite coatings are used as fast drying, high-quality, image-receiving layers. It was also shown that even the presence of filler incorporation at nano-levels show significant effects on the transparency and haze characteristics of films. When compared to conventionally filled polymers, nanoclay incorporation enhances the transparency significantly and reduces haze. Recently, commercial activities concerning polymer-clay nanocomposites increased considerably.

Polymer nanocomposites are widely used for automotive and packaging applications due to improved reinforcement, corrosion resistance, noise dampening, dimensional stability, scratch and wear resistance, and superior barrier properties etc. Due to their

lightweight, polymer nanocomposite parts lead to large fuel cost reductions as they are with an average 25% weight-saving over highly filled-plastics and 80% over steel. Polymer nanocomposites can also be used for under the hood and interior parts due to their good thermal stability, flame retardancy and heat distortion temperature. Superior gas barrier properties have been useful for various applications, such as packaging for processed meats, cheese, confectionery, cereals and boil in the bag foods, also extrusion coating applications in association with paperboard for fruit juice and dairy products, together with co-extrusion processes for the manufacture of beer and carbonated drinks bottles.

2.5.6 Commercial applications of nanocomposites

There are many examples of commercialized nanocomposites. A list of them are given below (Gupta et al., 2010);

- General Motors has used nanocomposites since 2002 in parts such as body side molding. A nanoclay-TPO composite is in use in the Hummer in 2005.
- Nanocomposite concentrates are being evaluated in films not only for enhancing barrier, but also to control the release and migration of additives such as biocides and dyes.
- PolyOne commercialized nanocomposite products in the Nanoblend™ family of concentrates and compounds for polyolefin resins. These composites are based on nanoclays and can reduce the amount of mineral fillers, often used as fire retardants that are required in many compounds.
- RTP offers nylon-based thermoplastics that are reinforced with nanoclays. They have also developed nanotube-based thermoplastic composites for the electronics industry in hard disk driven and wafer handling equipment.
- Bayer Polymers Durethan® polyamide 6 grade contains nano-sized, chemically modified layered silicates that are incorporated during the polymerization of the resin. The application is in barrier film, paper, and coatings.
- Honeywell Polymer has developed Aegis TM OX for high-barrier beer bottles and Aegis NC (Nylon 6/barrier nylon) for medium barrier bottles and films.

- Basell USA developed PP-based nanocomposites using Cloisite® nanoclay products from Southern Clay Products.
- Nobel Polymers-Forte™ nanocomposite. This is a polypropylene-based nanocomposite produced by Noble Polymers. It is one of the first commercializations of nanocomposites in the automotive industry and can be used in a variety of applications replacing talc-filled, glass-filled, or virgin polypropylene.
- Polykemi AB offers a PP-based nanocomposite called Scancomp®.
- Nanocyl recently launched NC9000, a nanotube-filled HDPE.
- Mitsubishi gas chemical company has developed M9, a high barrier property nanocomposite for the multi-layer films, juice and beer bottles, and containers.
- The use of multiwalled carbon nanotubes as a flame retardant in EVA has been reported.
- Solar cells: the U.S. Department of Energy at the Lawrence Berkeley National Laboratory and The University of California-Berkeley have developed a hybrid semiconductor-polymer photovoltaic device using nanometer-sized cadmium selenide rods.
- Thermoplastic nanocomposite foams: workers at Ohio State University have made dense plastic foams using nanocomposites made from polymer blends such as PMMA/PS and a nanoclay. These foams are lighter weight than solid plastics and have the potential to replace them in furniture and packaging applications.
- Putsch GmbH used nanofil to produce Elan XP, which is a blend of PP/PS.
- Chemtura's Polybound® X5104 is a maleated PP used as a coupling agent to improve physical and thermal properties of nanoclays, natural fibers, and glass in filled PP composites.
- Dyneon has developed hydrocarbon-based block copolymers as compatibilizers and coupling agents for polyolefin and styrenic nanocomposites produced by melt compounding nanoclays. These copolymers contain amine, epoxy anhydride, and acid, and are more efficient in enhancing the exfoliation and dispersion of organically modified clays.

- Nycoa has developed a nylon nanocomposite to meet CARB and U.S. EPA requirements for gas permeation in fuel tanks and fuel systems such as fuel hoses.
- U.S. Patent 6,942,897 describes a nanoparticle barrier-coated substrate and a method for making the same. The pigment nanoparticles may be talc, calcium carbonate, clay, silica, or plastic. This development may find application in paper, wood, wallboard, fiberglass, metal, and ceramics.
- U.S. Patent 6,646,026 B2 describes a method to enhance the ability to dye polymers by dispersion of nanocomposites into a polymer and reacting the nanocomposites with a dye. The nanomaterial may be a clay, silica, or an oxide of a metal such as silver or zinc.

2.5.7 Polyurethane-clay nanocomposites

The following steps are involved for a general polyurethane nanocomposite preparation method (Jana, 2007). Nanoparticles are predispersed in polyols in the first step. Secondly, to produce polyurethane nanocomposites, the polyol-nanoparticle suspension is reacted with diisocyanates. Several investigators followed this methodology. The preparation of polyurethane-clay nanocomposites by intercalating clay galleries with glycerol propoxylate polyol and reacting the clay-polyol mixture with MDI was performed (Wang and Pinnavaia, 1998).

These scientists used alkylammonium ions containing 12- and 18-carbon atoms in the alkyl chains to treat the clay particles. Polyurethane nanocomposites of organophilic mica, trihydroxy terminated oligo(propyleneoxide) polyol, diphenyl methane diisocyanate were prepared in the same manner (Zilg et al., 1999).

Nanocomposites of nano-silica were prepared by reacting a dispersion of polyol and nanosilica with diisocyanate, to obtain polyurethane nanocomposites (Petrovic et al., 2000). Besides, montmorillonite clay treated with trimethyl hexadecyl ammonium ion, prepared a dispersion of treated clay in poly(propylene oxide) glycol, and reacted clay-polyol mixture with toluene diisocyanate (Hu et al., 2001). On the other hand, Mt clay was modified with protonated 12-aminolauric acid and polymerized ϵ -caprolactone in the presence of treated clay (Chen et al., 2001). To achieve the nanocomposite product, the resultant material was mixed with a solution of separately prepared polyurethane.

Another approach to obtain polyurethane nanocomposites was developed for reactive nanoclay. Mt and bentonite are some of the examples of nanoclay particles that can be organically treated with alkyl ammonium ions containing hydroxylated alkyl groups, which participate in reactions with polymer chains carrying -NCO groups or diisocyanates. Alkyl ammonium ions carrying 1-OH, 2-OH, and 3-OH groups have been used to treat montmorillonite clay. In these cases, the -OH alcohol groups present in the alkylammonium ions associate a part of -OH groups in the overall stoichiometric ratio of isocyanate and hydroxyl groups. Polyurethane nanocomposites by allowing clay-polymer tethering reactions in solution under isothermal, well-stirred conditions were prepared (Tien and Wei, 2001). In that reaction, it was assumed that -CH₂OH groups of alkylammonium ions of organic treatment of clay reacted with -NCO groups on prepolymer chains. These scientists presented urethane linkage formation in the reactions between diphenyl methane diisocyanate and organically treated clay as an evidence for clay-polymer reactivity. On the other hand, polyurethane nanocomposite adhesives in solution were prepared in the same manner as Tien and Wei, but evidences of clay-prepolymer reactions were not found (Osman et al., 2003).

Besides, a third approach was developed in which organically treated clay and polymer were mixed in bulk and clay-polymer reactions took place during mixing (Pattanayak and Jana, 2005). Commercially available clay, Cloisite 30B (Southern Clay Products) was used as reactive clay and exploited the -CH₂CH₂OH groups in the structure of the quaternary ammonium ion, N⁺(CH₂CH₂OH)₂(CH₃)T, where T embodies an alkyl group with approximately 65% C₁₈H₃₇, 30% C₁₆H₃₃, 5% C₁₄H₂₉ to develop clay-polymer reactions.

During clay-polymer mixing, the extended chain polymers with residual -NCO groups were allowed to react with clay, the bulk polymerization methods avoid the use of solvents. Some advantages of bulk polymerization related to processing are as follows. (1) Clay dispersion can be promoted due to the larger shear forces during mixing. (2) Final products can easily be achieved by injection molding, film casting, or other techniques. (3) Single- and twin-screw extruders, which are conventional mixers, can be used for the production of nanocomposites. Thus, the method was developed in which all ingredients, including isocyanate, polyol, chain extender, and nanoclay are mixed and allowed to react. Prior intercalation of clay particles by

polyols or polymer chains is not required in these methods. However, there are some limitations for bulk polymerization methods such as hindered reaction rates of polymerization and clay-polymer tethering reactions due to diffusion constraints. Additionally, the reaction conditions are rarely isothermal. An additional temperature rise can trigger many side reactions such as biuret and allophanate formation.

Clay-polymer tethering via bulk polymerization have been attempted by other approaches. Nanoclay was treated with hydrochloride salt of organotin catalyst carrying $-NH_2$ end groups (Cao et al., 2005). This way, equivalent rates of chain extension reaction was achieved both inside and outside the clay galleries.

On the other hand, influence of polyurethane structure on the nature of polyurethane/clay nanocomposite have been studied by using varying amounts of trimethylol propane (TMP) as branching agent. The effect of hydroxyl groups in the modifier of organoclay on the structure of polyurethane-clay nanocomposites was studied (Rama and Swaminathan, 2010). They pointed out that incorporation of long alkyl chains in addition to tethering hydroxyl groups in the modifier structure of the clay is not significantly effective to improve the compatibility of linear polyurethane with the clay.

Waterborne polyurethane-clay nanocomposites have been studied especially for two decades. Similar to polyurethane-clay nanocomposites, organomodified clay is generally dispersed firstly in polyol component (Rahman et al., 2009; Rahman et al., 2011). However, there are some studies related to dispersion of clay in isocyanate component (Lee and Lin, 2006). In methods, improvements in physical properties including thermal, mechanical and gas barrier properties have been obtained. In addition, reinforcing with clay has been widely studied in adhesive related applications of waterborne polyurethanes as gas permeation barrier (Huh et al., 2009; Rahman et al., 2007a; Liminana et al., 2007).

3. EXPERIMENTAL

3.1 Materials

- PEG600 : Merck; Polyethylene glycol 600 (Mw=600). Used as polyol component in WPU synthesis. Vacuum dried overnight at 100°C before use. Hydroxyl value: 175 - 195 (mg KOH/g).
- PEG1500 : ABCR; Polyethylene glycol 1500 (Mw=1500). Used as polyol component in WPU synthesis. Vacuum dried overnight at 100°C before use. Hydroxyl value: 38 - 46 (mg KOH/g).
- PPG1000 : ABCR; Polypropylene glycol 1000 (Mw=1000). Used as polyol component in WPU synthesis. Vacuum dried overnight at 100°C before use. Hydroxyl value: 102 - 125 (mg KOH/g).
- PTAA : Aldrich; Poly(diethylene glycol/Trimethylolpropane-alt-adipic acid polyol (Mw=2300). Used as polyol component in WPU synthesis. Vacuum dried overnight at 100°C before use. Hydroxyl value: 60 (mg KOH/g).
- HDI : Merck; Hexamethylene diisocyanate (1,6-diisocyanatohexane) kept in dry conditions. Used as the hard segment of the polyurethane. Isocyanate content: %50 (w/w).
- NaMt : Southern clay; Cloisite Na⁺ sodium modified clay used as filler in the nanocomposites. Dried overnight in the oven at 100°C before use. CEC value: 92 mequiv/100 g having the formula Na_{0.65}[Al,Fe]₄Si₈O₂₀(OH)₂
- DMPA : Aldrich; Dimethyl propanoic acid (2,2-dimethyl-propionic acid). Used as carboxyl group source to prepare anionic WPU and as hard segment. Vacuum dried before use.

DBTDL	: Goldschmidt, Tegokat 218 (Dibutyltin dilaurate). Used as organometallic catalyst for polyurethane reaction.
TEA	: Sigma; Triethylamine. Used as neutralizing agent to neutralize carboxyl groups to prepare anionic WPU.
BD	: Merck; 1,4-Butanediol. Used as chain extender.
HMTA	: Industrial grade; Hexamethylene tetramine (1,3,5,7-Tetraazatricyclo-decane). Used as chain extender in WPU synthesis.
Acetone	: Merck; Extra pure, dried over 4Å molecular sieves.
NMP	: Merck; N-Methyl Pyrrolidone. Extra pure; dried over 4Å molecular sieves.
Water	: Deionized water. Deionized by using ion exchange process.
Dibutylamine	: Merck; N-Butylbutanamine. Extra pure; dried over 4Å molecular sieves. Used as reagent for determination of free NCO content of prepolymer.
Toluene	: Merck; Extra pure, dried over 4Å molecular sieves.
2-Propanol	: Merck; Extra pure, dried over 4Å molecular sieves.
HCl	: Merck; 38%, 0.1N solution with deionized water was prepared as titrant for determination of free NCO content of prepolymer.
Bromophenol blue	: Merck; The indicator solution was prepared as 0.10 g of bromphenol blue with 1.5 ml of 0.1 N sodium hydroxide solution and diluting to 100 ml with deionized water.

3.2 Instruments

- FTIR : Fourier Transform Infrared Spectroscopy (Perkin-Elmer BXII with ATR) was used for the monitoring of the reaction steps and final spectroscopic characterization.
- NMR : Proton Nuclear Magnetic Resonance spectra of linear WPU polymers were recorded with Bruker 250 MHz NMR Spectrometer and performed in DMSO-d₆ medium.
- : Proton Nuclear Magnetic Resonance spectra of crosslinked WPU polymers were recorded with Varian UNITY INOVA 500MHz NMR Spectrometer and performed in Trifluoroaceticacid medium.
- : Solid State Carbon Nuclear Magnetic Resonance spectra of crosslinked WPU polymers were recorded with frequency of 75.432 MHz by using Bruker Biospin Spectrometer. Powder samples were prepared using micromotor.
- XRD : X-Ray Diffraction Spectroscopy (Shimadzu XRD 6000) was used for spectral characterization of NaMt in the nanocomposites.
- DSC : Differential Scanning Calorimetry (TA Instruments Q1000) was used for thermal characterization. Temperature program: -100 to 400°C (10°C/min).
- TGA : Termogravimetric Analysis (Exstar 6000 TGA/DTA 6300) was used for thermal characterization. Temperature program: 30 to 800°C (10°C/ min) in N₂ and O₂ atmosphere.
- Particle Size Analysis : Dynamic light scattering device (Malvern Nano ZS) was used for particle size measurements
- Tensile Test : Tensile testing device (Zwick Z250 SN5A) was used for tensile testing of the specimens.

SEM-EDS	: Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (Jeol 6335F) was used for investigation of morphology of nanocomposites. Samples were treated into liquid nitrogen and cut to have their crosssectional images.
TEM	: Transmission Electron Microscope (Jeol 100C) was used for morphological investigations of solvent casted samples of linear WPU. In order to prepare solvent casted samples 1% (w/w) solutions of the samples in NMP solvent were casted on a teflon substrate.
	: Transmission Electron Microscope (FEI Company Tecnai G2 Spirit BioTwin 20-120kV High Res.11 Megapixel Morada Cam.) was used for morphological investigations of ultramicrotomed samples of crosslinked WPU.
Solar Simulator	: Atlas SC 600 having Metal Halide lamp was used for the weathering tests. The test was carried out according to MIL-STD-810G Method 505.4 with weathering program of 1150 W/m ² K irradiance value which simulates solar atmosphere between 280-3000 nm spectrums. The test was performed for 500h.
Ozone testing	: Anseros SIM 6050-T ozone generator, which works according to corona discharge principle, was used for ozone degradation tests. Ozone tests were performed in the conditions of 50pphm for 400h at 40°C.
Color measurement	: Hunterlab Miniscan EZ used for measurement of color difference after solar radiation testing. Color change values (ΔE) was calculated according to ASTM D 2244 standard.
Stereomicroscope	: Zeiss Stemi SV6 with x8-x50 magnification used for imaging after solar radiation test.
Digital Camera	: Sony DSC W120 used for digital imaging of the samples.

3.3 Preparation of WPU Dispersion

3.3.1 Preparation of linear WPU polymers via acetone process

A 250 ml round-bottom three necked flask with a mechanical stirrer with contact thermometer were placed in an oil bath. The polyol and acetone as a thinning solvent were charged into the flask and heated at 60°C. Then, DMPA was added as internal emulsifier and stirred for 30 minutes until it completely mixed in polyol. 0.5% of DBTDL (in weight basis in terms of sum of polyol, HDI and DMPA) and HDI added. Then the reaction was carried out under argon atmosphere until certain amount of free isocyanate remains. The free isocyanate content was determined by dibutylamine back titration method (ASTM D 2572). Then, the chain extender BD (and catalyst if needed) reacted for 4 hours at 60°C. After that, carboxyl groups ensured by DMPA in the prepolymer were neutralized by TEA at 50°C for 30 minutes. Then, certain amount of water was added via dropping funnel onto the prepolymer in the reaction flask with the ratio of 1 drop/sec during mixing and once the water addition completed the mixture was stirred vigorously at around 500 rpm. The amount of water was adjusted as the final WPU polymers to have 30% solid content. Finally, acetone was removed by vacuum distillation and 1 mm thick WPU films obtained after drying under vacuum for 1 day and in an oven at 50°C for 2 days in a teflon mold.

3.3.2 Preparation of crosslinked WPU-urea polymers via prepolymer mixing process

In prepolymer mixing process, the prepolymer preparation stage is exactly the same as in the acetone process. NMP solvent was replaced with some acetone as processing aid. Neutralization step with TEA was performed before chain extension after the prepolymer preparation stage. This is the main difference when it is compared to acetone process.

In the prepolymer mixing method, the prepolymer was synthesized until the certain amount of free isocyanate remains as explained above (see 3.3.1 title). Then carboxylic groups which are belong to DMPA units in the backbone were neutralized with TEA at 50 °C for 30 minutes. The neutralized polyurethane prepolymer was poured onto water with the dropping rate of 1 drop/1 minute in the precence of HMTA catalyst to obtain crosslinked WPU-urea polymer. Finally, 1 mm thick

crosslinked WPU-urea films were obtained after drying under vacuum for 1 day and in an oven at 50°C post curing for 2 days in a teflon mold.

3.3.3 Determination of NCO content of WPU prepolymer before chain extension

Free NCO content of polyurethane prepolymer was monitored by dibutylamine back titration method in prepolymer preparation stage of each polymer (ASTM D 2572). According to this method, 0.1 g of a prepolymer sample is weighed in a 250 ml erlenmeyer flask. Then, 25 ml of dry toluene is added and the sample is solved under magnetic stirring. After that, 25 ml of 0.1N di-n-butylamine solution in toluene is added and continued swirling for 15 minutes. Then, 100ml of isopropyl alcohol and 4-6 drops of bromophenol indicator solution in water is added into the flask. Finally, the mixture is titrated with 0.1N hydrochloric acid to a yellow end point.

3.4 Preparation of OMt

OMt was prepared by dispersing of NaMt into each polyol by melt blending technique. According to this method, certain amount of NaMt, which was initially dried overnight at 100°C under vacuum, was stirred magnetically at 80°C for 15h. Then, the dispersion of OMt in polyol was reserved for subsequent nanocomposite preparation.

3.4.1 Determination of hydroxyl content of NaMt

Hydroxyl content of the NaMt was performed by using TGA technique. After drying overnight in an oven at 120°C, structural water was calculated from TGA thermograms.

3.5 Preparation of NWPU nanocomposites

1, 3 and 5% (w/w) amount of clay was dispersed in polyol component for 15 hours at 80°C with magnetic stirring at 200 rpm to obtain fine polyol/NaMt mixture. NWPU composites were prepared by in-situ polymerization via either acetone or prepolymer mixing processes. Nanocomposite dispersions were distilled to remove acetone solvent. Finally, 1 mm thick crosslinked NWPU nanocomposite films obtained after drying (or post curing) under vacuum for 1 day and in an oven at 50°C for 2 days in a teflon mold.

4. RESULTS AND DISCUSSION

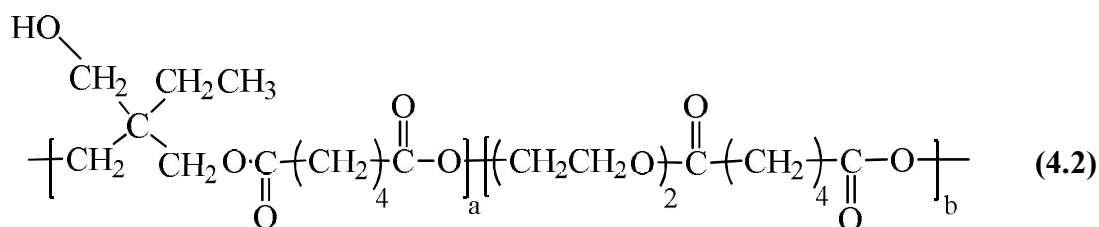
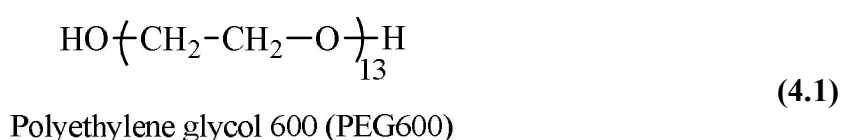
The results obtained from this work will be investigated as following sections:

- Synthesis of WPU polymers by using four types of polyols via acetone and prepolymer mixing processes and their characterization.
- Preparation of OMt by melt blending and nanocomposites by in-situ intercalation techniques and their characterization.
- Comparison of polymers and nanocomposites in terms of spectral, morphological and mechanical and thermal properties.
- Evaluation of environmental testing results.

4.1 Synthesis and Characterization of Linear WPU Polymers

4.1.1 Reaction conditions of linear WPU polymers

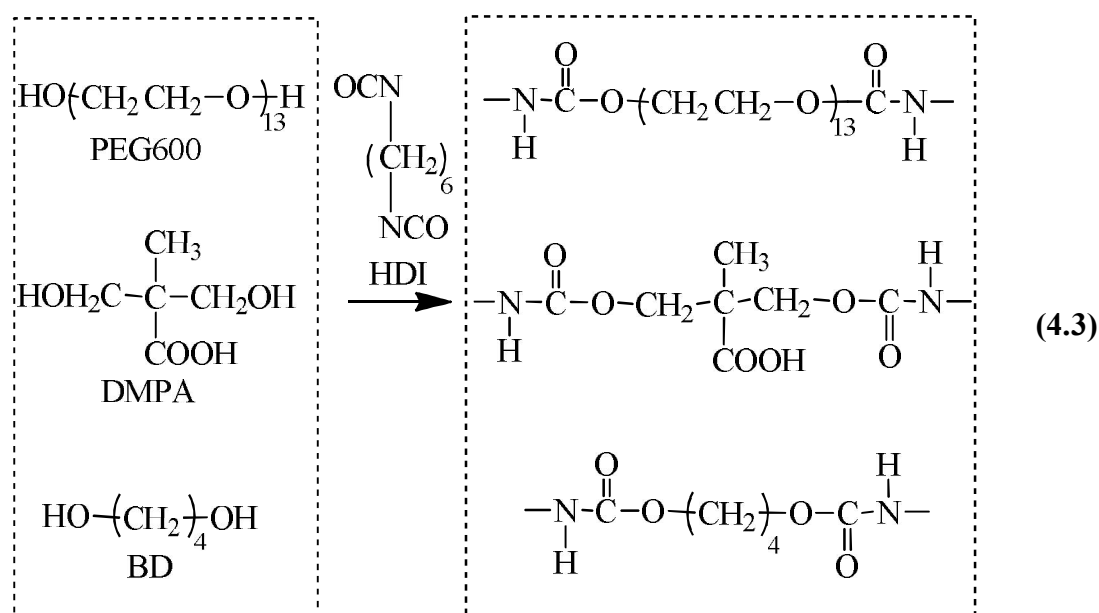
The main aim is to determine optimum reaction conditions of linear WPUs prepared using two different polyols. PEG600 (4.1) in WPU1 series was used as polyether polyol and PTAA (4.2) in WPU4 series was used as polyester/ polyether polyol.



Poly[di(ethylene glycol)/trimethylolpropane-alt-adipic acid] (PTAA)

Polyether polyols provide good temperature flexibility, hydrolysis resistance and reasonable adhesion depending on its molecular weights. However, polyester polyols offer wide range of properties such as solvent resistance, adhesion, good UV and

reasonable hydrolysis resistance unlike polyether polyols. HDI was used as hard segment component which is an aliphatic isocyanate having moderate reactivity in isocyanate family and used to prepare UV resistant polyurethanes. HDI also has a linear structure and which is suitable to obtain linear polyurethanes. DMPA were preferred as internal emulsifier which is to obtain anionic WPU. DMPA is the most often encountered ionic center due to its ability to provide steric hindrance to its carboxyl group to prevent any unwanted reaction with isocyanate groups. The chain extender component is also hard segment component of the segmented WPU which is decisive in terms of physical properties. BD which is simple linear diol was chosen as chain extender to obtain linear WPU polymers. Hydroxyl groups belong to polyols (PEG600 or PTAA), DMPA and BD have ability to react with isocyanate groups of the HDI in order to obtain polyurethane segments (4.3).



Synthesis of linear WPUs using two different polyols were carried out via acetone processes in which chain extension stage is made before neutralization stage (Figure 4.1). The acetone process was comprised mainly of four different stages including prepolymer preparation, chain extension (CE), neutralization and dispersion of the resulting polymer in water. In prepolymer preparation stage, one pot reaction of PEG 600 (for WPU1) or PTAA (for WPU4), DMPA and HDI were carried out in several molar ratios and experimental conditions to obtain prepolymer with isocyanate end groups. Then, neutralization of the carboxyl groups of DMPA with TEA was performed for solubilization in water and forming stable dispersion followed by the chain extension with BD.

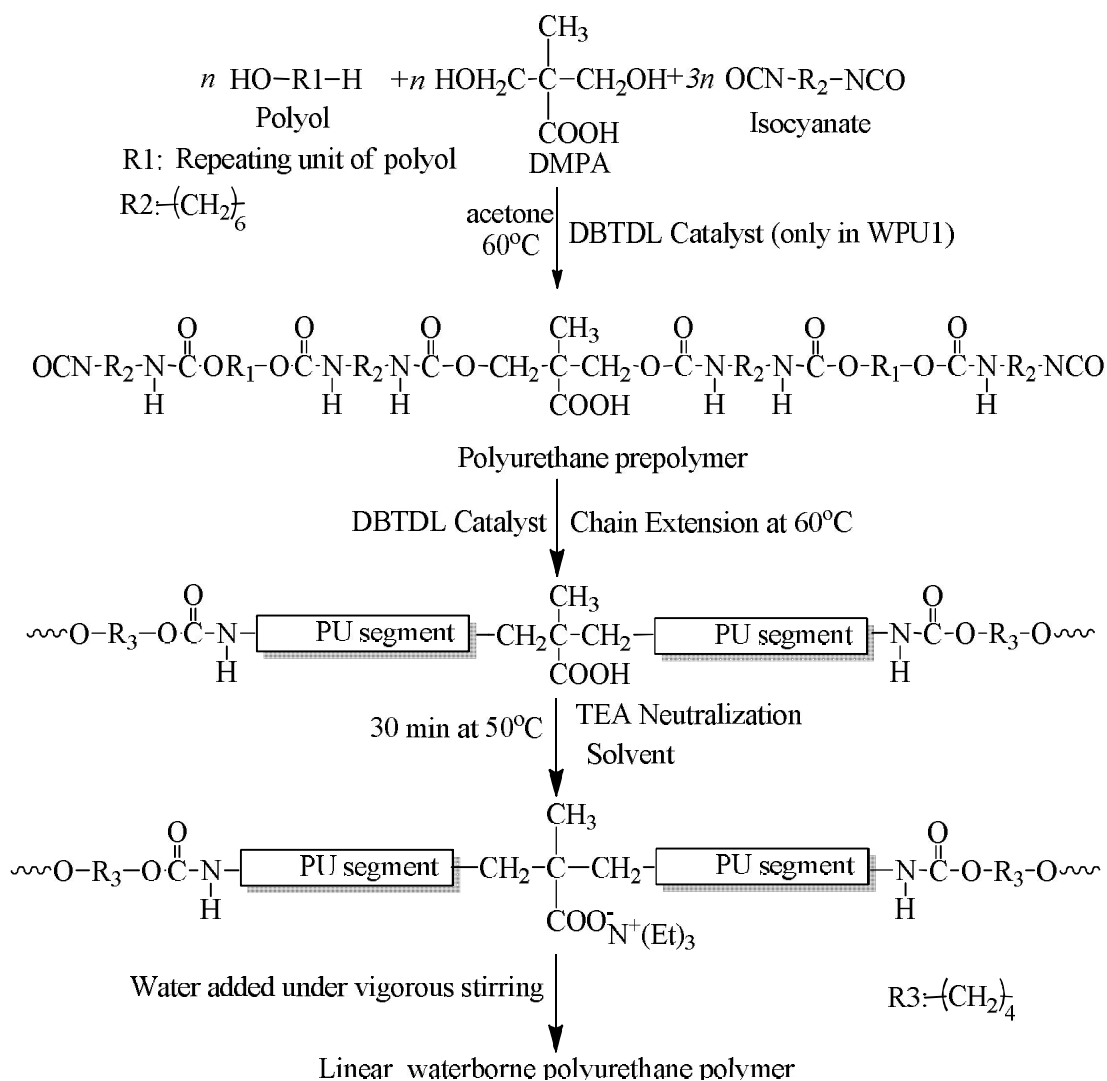


Figure 4.1 : The synthesis route of linear WPU polymers.

Firstly, WPU1 prepolymers were prepared via either magnetically or mechanically in the presence of DBTDL catalyst with the ratio of 0.5% on total solid in acetone media (Table 4.1). The prepolymer synthesis and subsequent chain extension reactions were performed at 60°C. The following neutralization step was carried out at 50°C. The ratio of [TEA]/[carboxyl group content of DMPA] was kept constant in all experiments. Initially, it was tried to prepare WPUs under magnetic stirring with the aid of very high amounts of solvent but uniform mixing was not obtained by stirring magnetically (WPU1.0 and WPU1.1). The prepolymer reaction time of WPU1.0 was very long due to mixing problems. When the solvent amount was reduced the reaction time was increased. However, inhomogeneous mixing was still encountered. Therefore, reproducibility was very poor. WPU1.0 was not able to form even stable film and WPU1.1 had poor film forming capability due to mixing problems experienced in chain extension and final dispersion stages. WPU1.2 was

formed more stable film than the previous trials and with better reproducibility owing to the mechanical stirring even though having the same polyol/DMPA/HDI mol ratio with WPU1.1. However, the film was not adequately strong and it was decided to change the prepolymer formulation.

Then, molar ratio of polyol/DMPA/HDI was changed to 1/1/3 and last experiments were carried out according to this formula. As a result of WPU1.3 experiment, the film was still soft and tacky which was containing chain extender BD/NCO as 2/1 in molar basis. Finally, the ratio BD/NCO was adjusted to 1/1 and proper WPU film obtained (WPU1.4). In addition, using catalyst in chain extension stage was found more convenient because of lower reactivity of BD compound with isocyanate groups. DBTDL provided faster reaction between NCO containing prepolymer and BD in low temperature in the chain extension process (WPU 1.5). Besides, it was tried to reduce chain extension reaction time by increasing the amount of DBTDL catalyst from 1% to 3%. However, gelation problem was experienced in the chain extension stage (WPU1.6). As a result of the experimental works, WPU1.5 was found the most appropriate sample in WPU1 series. The reaction conditions and results of the WPU1 polymers are given in Table 4.1.

WPU4 series were performed in acetone media by using PTAA polyol having poly (ether/ester) segments by mechanical stirring. The reaction conditions especially mixing method, which were experienced from WPU1 series, were applied on WPU4 series. However, WPU4 series prepared using PTAA polyol were indicated some different conditions than those prepared by using polyether polyols (PEG600, WPU1 series). The reaction conditions and results of the WPU4 polymers synthesized were also given in Table 4.1. The prepolymer preparation of the experiment firstly performed at 60°C in the presence of DBTDL catalyst. However, gelling behavior was observed after some time unlike the WPU1 series when catalyst used (WPU4.1). The reason could be the reactivity of polyester polyol segment against isocyanate component being higher than polyether polyols. Then, experiments were carried out without catalyst in the same condition with the first experiment (WPU4.2). The polymer film was poor if the prepolymer obtained with 3.6% free isocyanate content as a result of 2 hours reaction (WPU4.2). Next, the reaction time increased in order to decrease free isocyanate content at the end of the prepolymer preparation stage (Table 4.1).

Table 4.1 : Reaction conditions of linear WPU polymers (Polyol:10 g, [Et₃N]/[COOH]:1).

Code	Polyol type	Stirring	DMPA (on solid) (%)	Polyol/ DMPA/ HDI molar ratio	Prepolymer reaction time (h)	Catalyst in prepolymer reaction (on total solid) (%)	Free NCO in prepolymer (%)	BD/ free NCO molar ratio	Catalyst in CE reaction (on free NCO+ BD) (%)	CE reaction time ¹ (h)	Hard Segment ² (w/w %)
WPU1.0	PEG600	Magnetical	1.5	1/0.20/1.8	6	0.5	1.93	2/1	-	6	43.5
WPU1.1	PEG600	Magnetical	2.0	1/0.25/2	2	0.5	2.94	2/1	-	6	44.4
WPU1.2	PEG600	Mechanical	2.0	1/0.25/2	2	0.5	2.94	2/1	-	6	44.4
WPU1.3	PEG600	Mechanical	9.5	1/1/3	2	0.5	2.35	2/1	-	6	57.6
WPU1.4	PEG600	Mechanical	9.5	1/1/3	2	0.5	2.35	1/1	-	6	54.8
WPU1.5	PEG600	Mechanical	9.5	1/1/3	2	0.5	2.35	1/1	1	4	54.8
WPU1.6	PEG600	Mechanical	9.5	1/1/3	2	0.5	2.35	1/1	3	Gelation	54.8
WPU4.1	PTAA	Mechanical	4.1	1/1/3	2	0.5	-	-	-	-	-
WPU4.2	PTAA	Mechanical	4.1	1/1/3	2	-	3.6	1/1	-	5	25.6
WPU4.3	PTAA	Mechanical	4.1	1/1/3	3	-	2.5	1/1	2	3	24.8
WPU4.4	PTAA	Mechanical	4.1	1/1/3	3	-	2.5	1/1	3	Gelation	24.8

¹ CE: Chain extender.² Hard segment content was calculated as [(HDI+DMPA+CE)/(Polyol+HDI+DMPA+CE)]*100.

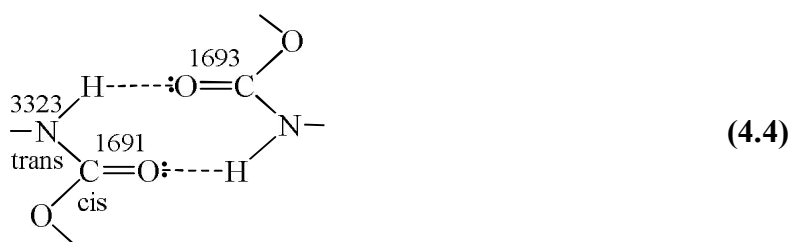
Finally, successful balance was obtained when the free NCO amount fixed to 2.5% after 3 hours reaction and using 2% DBTDL catalyst (WPU 4.3). In addition, CE reaction time was 5 hours without catalyst (WPU4.2). By using 2% DBTDL chain extension reaction time reduced to 3 hours (WPU4.3). Further addition of catalyst in chain extension stage resulted with gelation (WPU4.4). As a result of the experimental works, WPU4.3 was found the most appropriate sample in WPU4 series.

Consequently, the optimum conditions of the preparation of linear WPU polymers were determined. In terms of film formation capability WPU1.5 (WPU1) and WPU4.3 (WPU4) were chosen as the best compositions in order to prepare nanocomposites.

4.1.2 Characterization of of linear WPU polymers

4.1.2.1 FTIR analysis of linear WPU polymers

The FTIR spectra of both WPU1 and WPU4 are shown in Figure 4.2. The most relevant bands corresponded to bonded N-H stretching at 3323 cm^{-1} sharp single peak, C-H stretching at $2931, 2866\text{ cm}^{-1}$ for WPU1 and $2933, 2866\text{ cm}^{-1}$ for WPU4. On the other hand, the position of C=O bands depends very much on the hydrogen bond length which is a function of the local geometry, such as the linearity of the regarding bonds and the distance between groups (Ciobanu et al., 2010; Ren et al., 2003). The peaks of H-bonded C=O stretching bands are belong to urethane groups at 1691 cm^{-1} for WPU1 and 1693 cm^{-1} for WPU4 which is covered by the peak belong to bonded ester units of the PTAA polyol at 1720 cm^{-1} . The urethane C=O peaks of both WPU1 and WPU4 shifted to lower bands due to trans-cis isomerism (4.4).



This result is also compatible with the literature (Ciobanu et al., 2010). CN and NH stretching peaks are at around 1532 cm^{-1} for both WPU1 and WPU4. The symmetrical stretching peak of COO^- belong to neutralized DMPA group is

determined at 1406 cm^{-1} for WPU1. However, it is not clearly determined for WPU4. The assignments of most characteristic bands are given in Table 4.2.

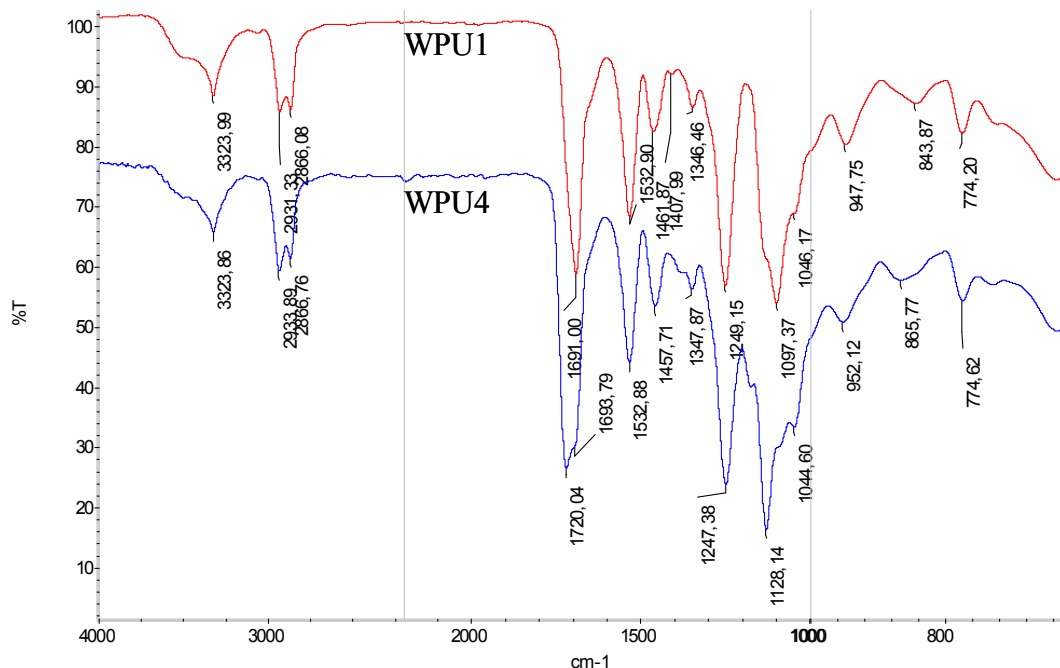


Figure 4.2 : FTIR spectra of linear WPU polymers.

Table 4.2 : Characteristics of the major IR bands of linear WPU polymers.

Assignment	Wavenumber (cm^{-1})	
	WPU1	WPU4
st N-H (bonded)	3323	3323
st C-H	2931, 2866	2933, 2866
st N=C=O	-	-
st C=O (urethane)	1691	1693
st C=O (bonded ester)	-	1720
st C=O (bonded ordered urea)	-	-
st C-N + δ N-H	1532	1532
st CH_2	1461	1457
st sym COO^-	1406	-
st sym CH_3	1346	1347
st asym N-CO-O + st C-O-C	1249	1247
asym st (C-O-C)	1097	1128
st sym N-CO-O + st C-O-C	1039	1039
sym st C-O-C	947	952

On the other hand, asymmetric N-CO-O stretching bands are identified at 1249 cm^{-1} for WPU1 and 1247 cm^{-1} for WPU4. C-O-C stretching band is determined at 1097 cm^{-1} for WPU1 whereas 1128 cm^{-1} for WPU4 due to ester structure of PTAA polyol. The C-O-C peak is identified at 1128 cm^{-1} . Symmetric N-CO-O stretching bands can be seen at 1039 cm^{-1} for both WPU1 and WPU4. Characteristic C-O-C stretching band is identified at 947 cm^{-1} for WPU1 and 952 cm^{-1} for WPU4. In all

cases, the absence of peak in the range of 2000-2300 cm^{-1} indicates that all isocyanate groups were reacted in the system and absence of urea peaks around 1640 cm^{-1} showed that there was no possible side reaction which may caused by moisture.

4.1.2.2 ^1H NMR analysis of linear WPU polymers

The ^1H NMR spectra of both WPU1 and WPU4 are illustrated in Figure 4.3. The characteristic signal between 7.2-7.0 δ ppm is assigned to N-H proton of the trans conformer urethane groups (Rahman et al., 2009; Versteegen et al., 1999).

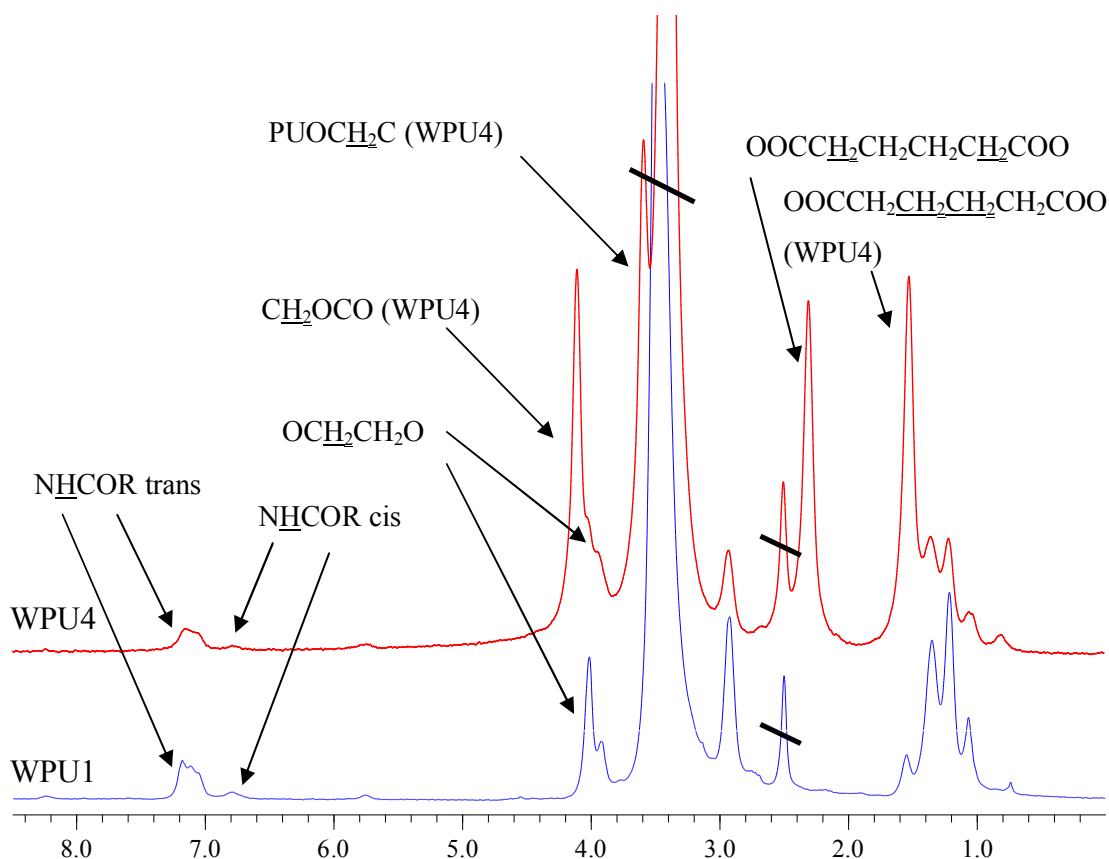


Figure 4.3 : 250 MHz ^1H NMR spectra of linear WPU polymers in DMSO- d_6 .

The peaks which are observed at 6.8 and 5.8 δ ppm is attributed to N-H proton of the cis conformer urethane groups. The peak, which belongs to polyol protons is not identified clearly due to having dominated by water peak absorbed by DMSO at around 3.5 δ ppm. However, ester protons of PTAA polyol in WPU4 are identified at 4.1, 3.6 and 2.3 δ ppm which are unique for the PTAA structure. The bands of methylene groups of neutralizing TEA and neutralized DMPA are identified at 2.9 and 1.0-0.74 δ ppm. On the other hand, methylene protons in polyether or BD structures of WPU1 and WPU4 and/or BD chain extender are denoted at

4.0- 3.9 δ ppm. Various protons belong to HDI unit are denoted between at 1.3 and 1.0 δ ppm respectively. Besides, the bands at 2.9 δ ppm are belong to methylene groups in TEA and urethane segments (Yeh et al., 2008). In addition, various methylene and methyl protons of urethane, TEA and DMPA segments are identified between at 1.3-1.0 δ ppm. The detailed assignment of chemical shifts can be seen in Table 4.3.

Table 4.3 : Characteristic ^1H NMR shifts of WPU1 and WPU4.

Segment	Assignment	Chemical shift (δ ppm)	
		WPU1	WPU4
Urethane trans	ROCONH	7.2-7.0	7.2-7.0
Urethane cis	ROCONH	6.8	6.8
Ester of polyol	PUOCH ₂ C	-	4.1
Polyether and BD	-O- CH ₂ CH ₂ -O- CH ₂ CH ₂ CH ₂ CH ₂ -O-	4.0-3.9	4.0-3.9
Ester of polyol	-CH ₂ -O-CO-	-	3.6
TEA and urethane	Water from DMSO-d ₆	3.5	3.5
	-NH ⁺ -(CH ₂ CH ₃) ₃ and ROCONH-CH ₂	2.9	2.9
	DMSO-d ₆	2.5	2.5
Ester of polyol	-OOCCH ₂ CH ₂ CH ₂ CH ₂ COO-	-	2.3
BD and ester of polyol	PU -O-CH ₂ CH ₂ CH ₂ CH ₂ -O-PU OOCCH ₂ CH ₂ CH ₂ CH ₂ COO	1.5	1.5
Urethane	ROCONH-CH ₂	1.3	1.3
Urethane	ROCONH-CH ₂ - CH ₂	1.2	1.2
DMPA and TEA	CCH ₃ COO ⁻ and -NH ⁺ -(CH ₂ CH ₃) ₃	1.1-1.0	1.1-1.0
Urethane	ROCONH-CH ₂ -CH ₂ - CH ₂ -		

4.1.2.3 Particle size analysis of linear WPU polymers

Particle size of the polymer dispersions is an important parameter which determines the film forming properties. Dispersions with larger particles have ability for rapid drying and preferred in surface coatings whereas, smaller particle sized ones are desirable when the deep penetration of the dispersion into a substrate is required (Rahman and Kim, 2006). In WPUs, the average particle size is primarily governed by the concentration of dispersing groups and process type and can be controlled by emulsification conditions such as impeller speed and temperature. The average particle size decreases with increased DMPA concentration as the overall surface area of the dispersed phase increases to accommodate the additional salt groups at the interface (Nanda and Wicks, 2006). Particle size distribution of the linear WPUs is mainly affected by ionic dispersing group content in linear WPUs (Table 4.4).

WPU1 polymer with higher DMPA content has relatively smaller particle size compared to WPU4. As a result, it can be said that WPU1 polymer has good penetration property compared to WPU4.

Table 4.4: Particle size analysis results of linear WPU polymers.

Polymer	Particle size (nm)	DMPA content (% w/w)	Process
WPU 1	38.81	9.50	Acetone
WPU 4	50.92	4.13	Acetone

4.1.2.4 GPC Analysis of linear WPU polymers

In polyurethane polymers, high molecular weight is a necessity to obtain sufficient mechanical properties. Average molecular weights of WPU polymers were measured by GPC method based on calibration curve of polystyrene standard. The weight average molecular weight (Mw), number average molecular weight (Mn) and polydispersity of WPUs with different soft segments at the same molar ratios were summarized in Table 4.5. WPU polymers which were prepared using different soft segments shows quite different results. Both Mw and Mn values of WPU4 are much higher than WPU1. However, molecular weight distribution of WPU1 lower than WPU4. The mechanical properties of linear WPUs are strongly affected by their molecular weights as which will be discussed in the following section.

Table 4.5: GPC results of linear WPU polymers.

Sample	Mw (Daltons)	Mn (Daltons)	Mw/Mn
WPU1	9.852	4.975	1.98
WPU4	45.470	22.180	2.05

4.1.2.5 Mechanical analysis of linear WPU polymers

Tensile tests were carried out to compare mechanical properties of the linear WPU polymers. The test were carried out according to the standart EN ISO 527-1. The specimens prepared as 1 mm thick in dog bone shape. Stress-strain curves of WPU1 and WPU4 polymers are depicted in Figure 4.4. Linear WPU polymers showed different properties due to having different polyol types and molecular weights. As is known, polyether polyols provide more flexible structure because of the mobility of ether bonds. However, polyester polyols generally accomodate more stiff-rigid behaviour due to limited mobility compared to polyether polyols. On the other hand, molecular weight plays an important role on physical properties of polymers

(Rahman et al., 2007a). Generally, as the molecular weight increases elongation at break decreases in WPU polymers (Jang et al., 2002). WPU4 was prepared using PTAA (Mw:2300) polyol with polyether/polyester units whereas WPU1 was prepared by PEG polyol with polyether units (Mw:600). Owing to the polyester units having more stiff rigid behaviour the WPU4 has higher elastic modulus and lower elongation values compared to WPU1 due to having different soft segment (Figure 4.4). In addition, the final molecular weight of WPU4 is four times higher than WPU1. Therefore, the elongation at break value of WPU4 is lower than WPU1 (Table 4.6).

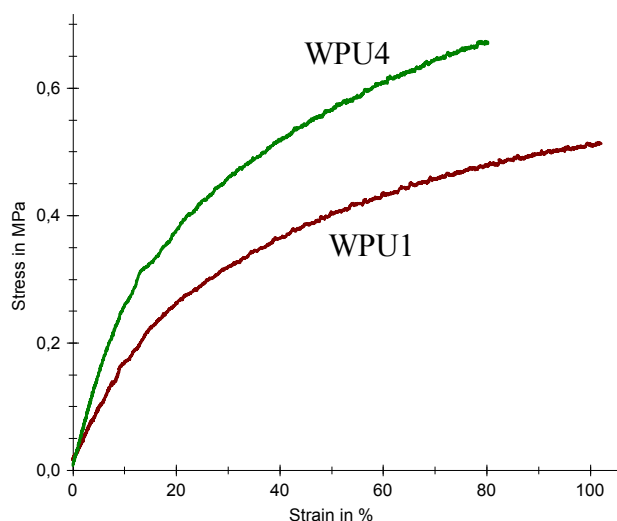


Figure 4.4 : Stress-strain curves of linear WPU polymers.

Table 4.6 : Mechanical properties of WPU polymers and nanocomposites.

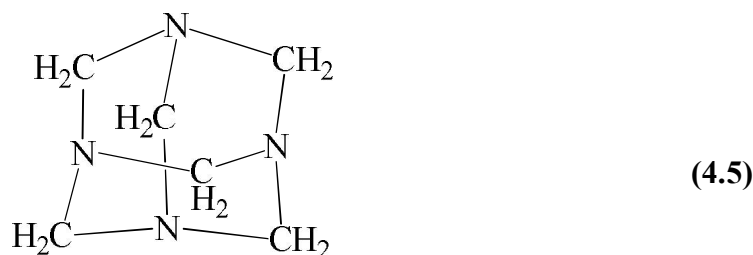
Sample	E-Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
WPU1	1.77	0.51	102.10
WPU 4	3.03	0.67	80.09

4.2 Synthesis and Characterization of Crosslinked WPU-urea Polymers

4.2.1 Reaction conditions of crosslinked WPU-urea polymers

The main aim is to investigate the effect of HMTA (4.5) as crosslinking agent and determine the optimum reaction conditions of crosslinked WPU-ureas prepared using two different polyols. PEG1500 in WPU2 series (4.6) and PPG1000 in WPU3 series (4.7) are both polyether polyols providing polyurethanes with quite different properties.

Similar to linear WPU synthesis, the prepolymer synthesis was performed by using HDI as hard segment together with DMPA which is also used as internal emulsifier in crosslinked WPU-urea synthesis.



Hexamethylenetetramine (HMTA)

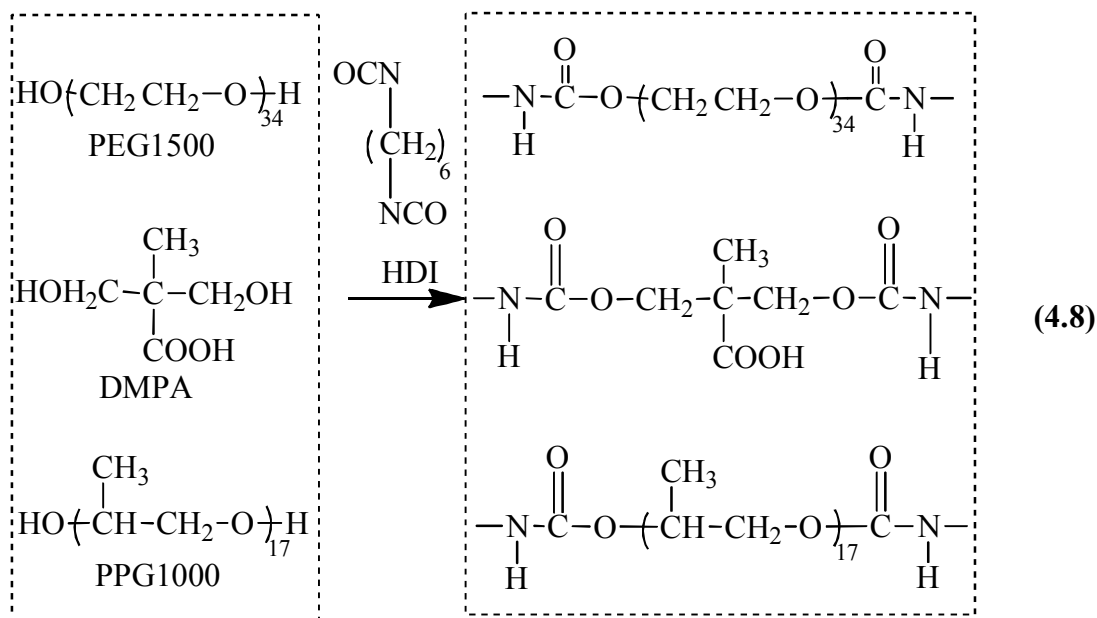


Polyethylene glycol 1500 (PEG1500)

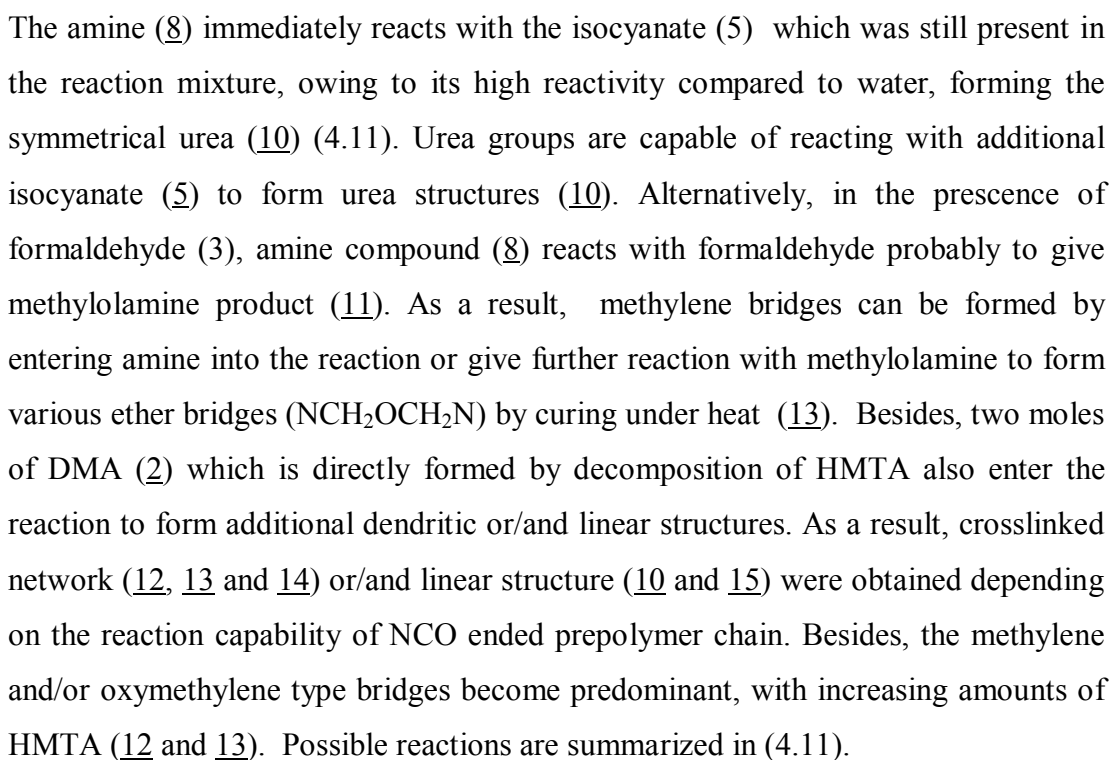
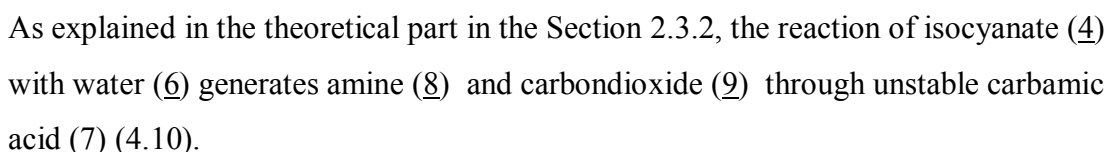


Polypropylene glycol 1000 (PPG1000)

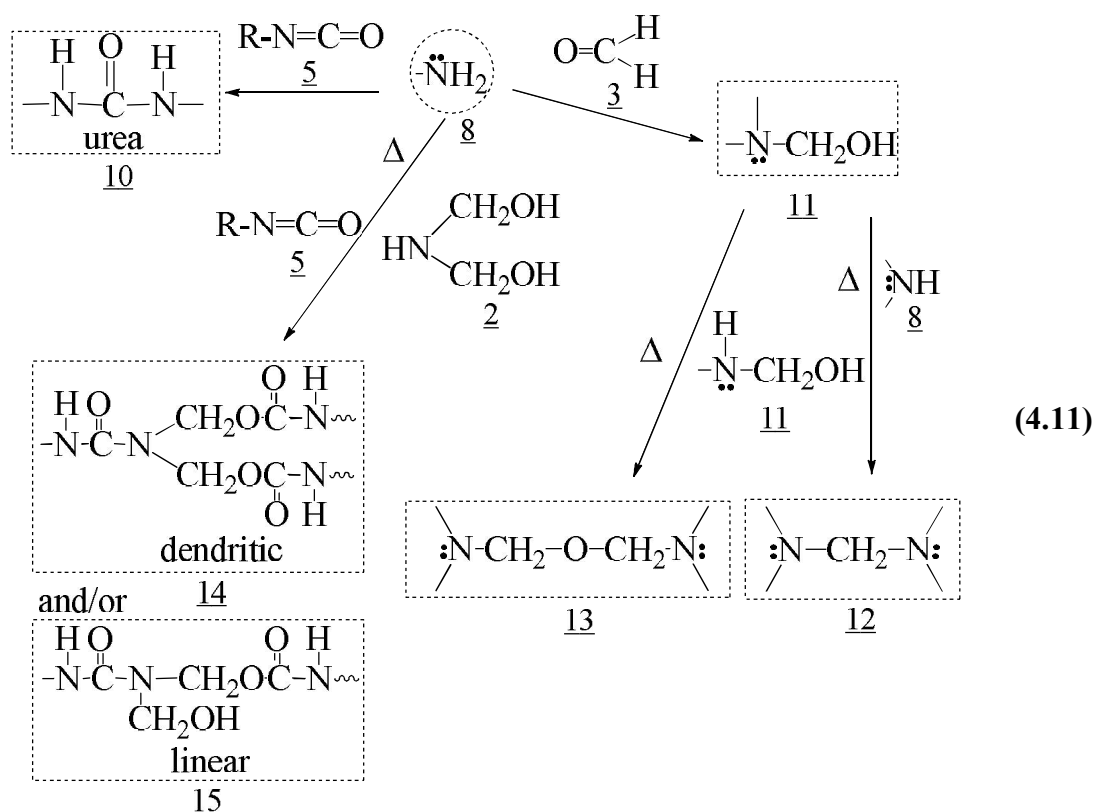
As a result, expected segments after the prepolymer reaction can be seen in (4.8).



Unlike the linear WPUs, water was used as chain extender to obtain crosslinked WPU-urea polymers (WPU2 and WPU3). In the presence of water, HMTA (1) hydrolyzes and decomposes into two moles of dimethylolamine (DMA) (2), one mole of formaldehyde (3) and two moles of ammonia (4) with the aid of heat which is shown in (4.9) (Pichelin et al., 1999; Kricheldorf et al., 2005).



Different from the linear WPU, crosslinked WPU-urea polymers (WPU2 and WPU3) were prepared via prepolymer mixing process. This type of process was composed of three stages including prepolymer preparation, neutralization and CE/dispersion. The neutralization and CE/dispersion stage was the single stage which differs from the acetone process. Another difference was the order of the neutralization stage being performed prior to chain extension.



Initially, the prepolymer was prepared. Then, subsequent chain extension with water (with or without HMTA) was followed by neutralization of the carboxyl groups of DMPA with TEA (Figure 4.5).

HMTA/water solution (4.9) was prepared by solving HMTA in certain amount of water in order to be used in the subsequent chain extension stage. pH measurements were applied in order to determine the basicity of the medium after ammonia liberation (4) and it was found that the initial pH value of deionized water was increased from 7.7 to 7.8 after addition of HMTA and again dropped at 7.7.

The prepolymer preparation stage performed in acetone media at 60°C for 2 hours in the presence of DBTDL catalyst with the ratio of 0.5% on total solid. The ratio of [TEA]/[carboxyl group content of DMPA] kept constant in all experiments (Table 4.7). Polyol/DMPA/HDI molar ratio kept constant as 1/1/3 which was experienced from previous experiments. Hard segment content was 30.5% for all experiments. Initially, the chain extension with water with the ratio of NCO/HMTA/water as 1/0.25/200 was performed in the one pot as adding onto prepolymer at 50°C. However, gelation is observed due to rapid reaction of water through free isocyanate (WPU2.1). Therefore, the same experiment was repeated and the prepolymer added onto HMTA/water solution in another pot at room temperature

in the chain extension stage (WPU2.3). In this manner, better control of chain extension is provided. Further reactions with the same conditions were performed by changing NCO/ HMTA/ water ratio (WPU2.2 and 2.4). The reaction conditions of WPU2 polymers which were carried out via prepolymer mixing processes using different ratios of HMTA as crosslinker and water as chain extender were given in Table 4.7.

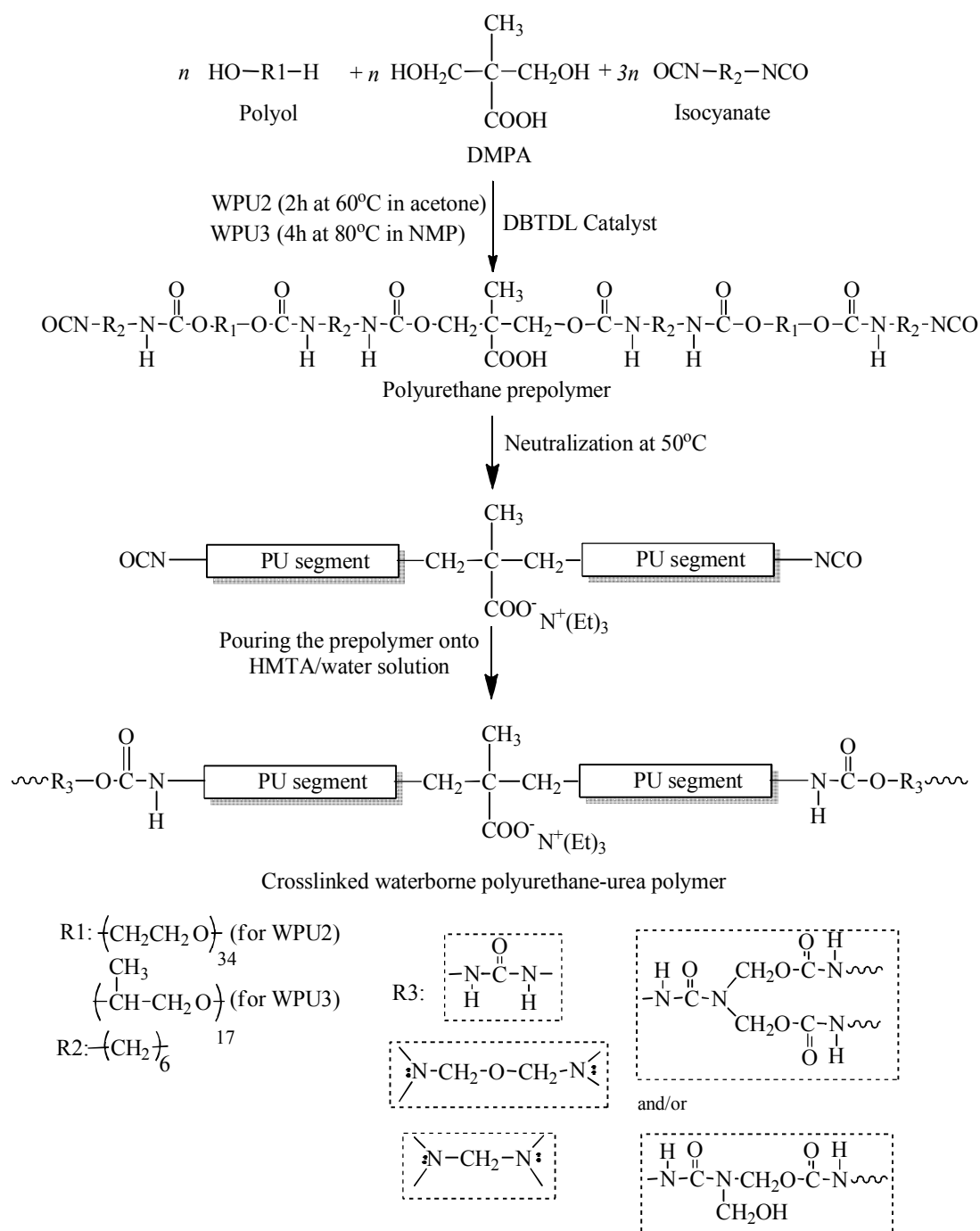


Figure 4.5 : The synthesis route of crosslinked WPU-urea polymers.

Table 4.7 : Reaction conditions of crosslinked WPU-urea polymers prepared by mechanical stirring (Polyol:10 g, [Et₃N]/[COOH]: 1).

Code	Polyol type	Solvent (Temperature)	DMPA (on solid)	Polyol/DMPA/HDI molar ratio	Prepolymer reaction time	Catalyst in prepolymer reaction (on total solid)	Free NCO in prepolymer	Free NCO/HMTA/Water molar ratio	Last dispersion step	CE reaction time ¹	Hard Segment ²
		(°C)	(%)		(h)	(%)	(%)			(h)	(w/w %)
WPU2.1	PEG1500	Acetone (60)	5.8	1/1/3	2	0.5	1/0.25/200	2/1	One pot	Gelation	43.5
WPU2.2	PEG1500	Acetone (60)	6.0	1/1/3	2	0.5	1/0/200	2/1	Two pots	½	44.4
WPU2.3	PEG1500	Acetone (60)	5.8	1/1/3	2	0.5	1/0.25/200	2/1	Two pots	½	44.4
WPU2.4	PEG1500	Acetone (60)	5.7	1/1/3	2	0.5	1/0.5/200	2/1	Two pots	½	57.6
WPU3.1	PPG1000	NMP (80)	7.4	1/1/3	4	1.0	1/0/200	1/1	Two pots	½	54.8
WPU3.2	PPG1000	NMP (80)	7.3	1/1/3	4	1.0	1/0.25/200	1/1	Two pots	½	54.8
WPU3.3	PPG1000	NMP (80)	7.2	1/1/3	4	1.0	1/0.5/200	1/1	Two pots	½	54.8

¹ CE: Chain extender.² Hard segment content was calculated as [(HDI+DMPA+CE)/(Polyol+HDI+DMPA+CE)]*100.

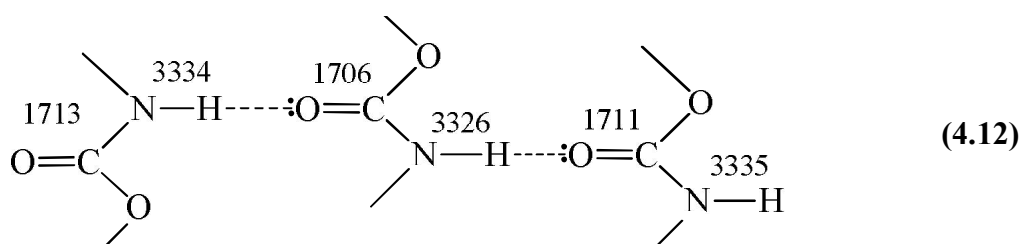
WPU3 series were carried out by using PPG1000 polyol which is having less reactivity through HDI compared to PEG1500 (Table 4.7). Therefore, the prepolymer preparation stage was carried out at 80°C for 4 hours in NMP solvent instead of acetone.

Besides, DBTDL catalyst ratio was raised to 1% on total solid. Polyol/DMPA/HDI molar ratio was kept constant as 1/1/3 and hard segment content is 39.7% for all experiments. The chain extension in water in the presence of HMTA (or not) was performed in another pot as experienced from WPU2 series. Similar to WPU2, several chain extension trials were carried out with various NCO/ HMTA/ water ratios (WPU3.1, WPU3.2, and WPU3.3).

4.2.2 Characterization of crosslinked WPU-urea polymers

4.2.2.1 FTIR analysis of crosslinked WPU-urea polymers

The FTIR spectrums of WPU2 series are shown in Figure 4.6. Characteristic peaks are also observed for WPU2 series. Bonded N-H stretching at 3334, 3326 and 3335 cm^{-1} for WPU2.2, WPU2.3 and WPU2.4 can be seen as a single peak. On the other hand, the FTIR spectrums of the products confirmed the presence of –CO-N- units from bound urea at 1632, 1646 and 1647 cm^{-1} for WPU2.2, WPU2.3 and WPU2.4. The stretching C–N and N–H bands are identified at 1534 cm^{-1} for WPU2.2 and WPU2.3 and 1535 cm^{-1} for WPU2.4. The C–O–C stretching bands can be seen at 1103, 1099 and 1095 cm^{-1} for the WPU2.2, WPU2.3 and WPU2.4. The urethane C=O peaks are identified at 1713 and 1711 cm^{-1} for WPU2.2 and WPU2.4 because of cis-cis or trans-cis isomerism. However, the hydrogen bonded C=O peak of WPU2.3 was identified at 1706 cm^{-1} due to trans-cis isomerism (4.12). This result is also confirmed in the literature (Ciobanu et al., 2010). The sharp peaks between at 1244-1245 cm^{-1} were belong to C–N units. The assignments of most characteristic bands were given in Table 4.8.



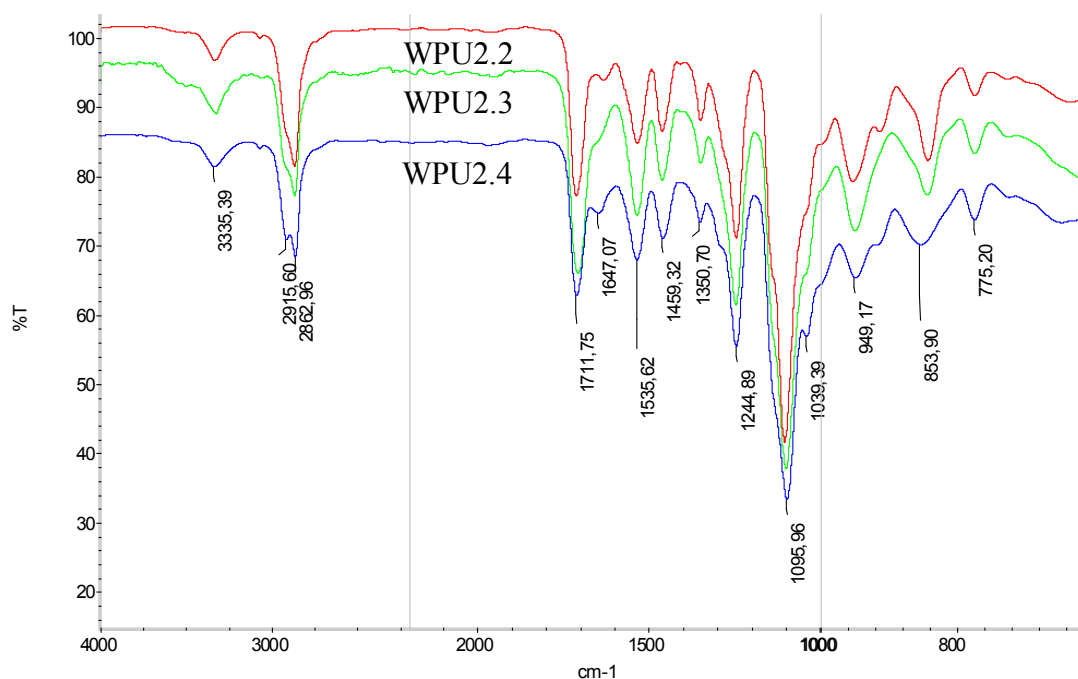


Figure 4.6 : FTIR spectra of WPU2 polymers.

Table 4.8 : Characteristic IR bands of WPU2 polymers.

Assignment	Wavenumber (cm-1)		
	WPU 2.2	WPU 2.3	WPU 2.4
st N-H (bonded)	3334	3326	3335
st C-H	2866	2866	2915, 2862
st C=O (urethane)	1713	1706	1711
st C=O (bonded urea)	1632	1646	1647
st C-N and N-H	1534	1534	1535
st CH ₂	1461	1461	1459
st sym (COO-)	1407	1404	1403
st sym CH ₃	1349	1349	1350
asym st N-CO-O + st C-O-C	1245	1245	1244
asym st (C-O-C)	1103	1099	1095
st sym N-CO-O + st C-O-C	1038	1040	1039
sym st C-O-C	953	950	949

The FTIR spectrums of WPU3 series are shown in Figure 4.7. Similar to WPU2 series, bonded N-H stretching can be seen at 3324 cm^{-1} for WPU 3.2 and 3320 cm^{-1} for WPU3.3. Unlike the WPU2 series, the -CO-N- urea bands are not identified which can be covered by large C=O bands at 1701 and 1679 cm^{-1} for WPU3.2 and WPU3.3 respectively. The C=O band of the WPU3.3 shifted to much lower frequency because of trans-cis isomerism (4.4). The assignments of most characteristic bands were given in Table 4.9.

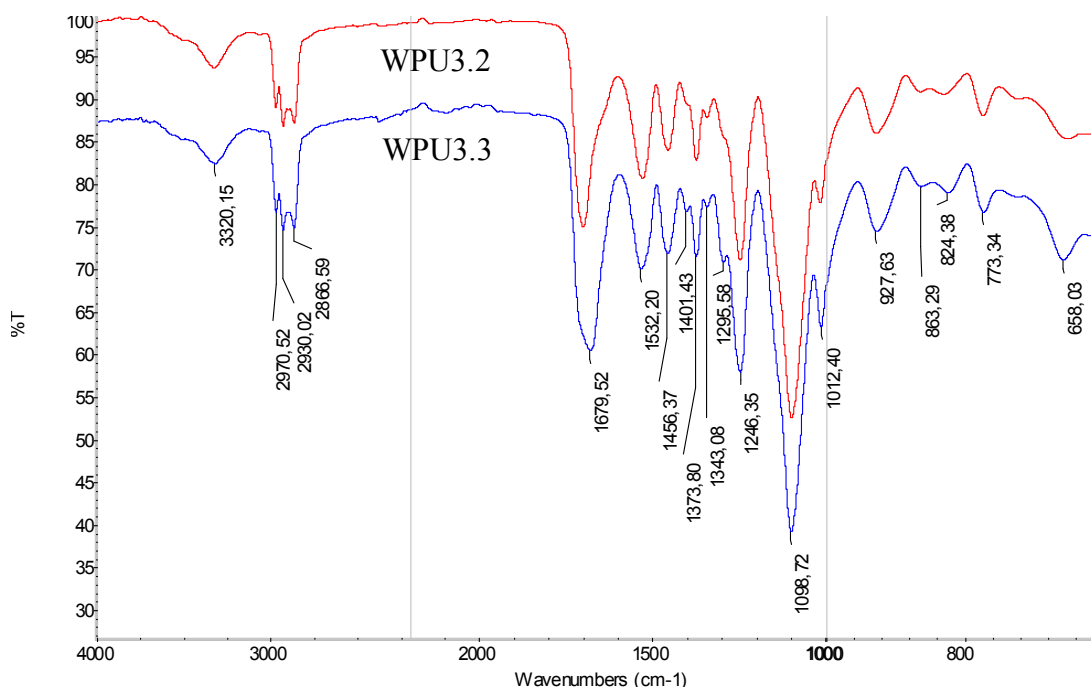


Figure 4.7 : FTIR spectra of WPU3 polymers.

Table 4.9 : Characteristic IR bands of WPU3 polymers.

Assignment	Wavenumber (cm ⁻¹)	
	WPU3.2	WPU3.3
st N–H (bonded)	3324	3320
st C–H	2971, 2929, 2865	2970, 2930, 2866
st C=O (urethane)	1701	1679
st C=O (bonded ordered urea)	not determined	not determined
st C–N and N–H	1529	1532
st CH ₂	1456	1456
st sym (COO ⁻)	1401	1401
st sym CH ₃	1373	1373
st asym N–CO–O + st C–O–C	1246	1246
asym st C–O–C	1097	1098
st sym N–CO–O + st C–O–C	1015	1012
sym st C–O–C	928	927

On the other hand, the C–O–C stretching band can be identified at around 1097 and 1098 cm⁻¹ and the sharp peaks at around 1246 cm⁻¹ denote C–N units of both WPU3.2 and WPU3.3.

4.2.2.2 ¹HNMR analysis of crosslinked WPU-urea polymers

¹HNMR analysis of WPU2 and WPU3 polymers are performed using trifluoroacetic acid and DMSO-d₆ solvents because of insolubility in common NMR grade solvents. In the case of WPU2 polymer, the peaks between at 8.1–7.9 δ ppm (WPU2.2 and

WPU2.3) and 8.1-7.6 δ ppm (WPU2.4) denote N-H proton of trans conformer urethane groups. However, the peaks between at 7.0-6.8 δ ppm (WPU2.2 and WPU2.3) and 7.0-6.7 δ ppm (WPU2.4) indicate N-H proton of cis conformer urethane groups. N-H proton of urea groups are identified at 6.7-6.5 δ ppm. The peak at around 4.8 δ ppm can be attributed to ether bridges ($\text{NCH}_2\text{OCH}_2\text{N}$) formed by methylolureas belong to WPU2.3 and 2.4. However, this peak is not identified for WPU2.2 which doesn't contain HMTA. In addition, the peaks between at 4.6-4.5 δ ppm can be related to methylene bridges (NCH_2N) which is also not identified for WPU2.2 whereas this is distinctive for WPU2.3 and WPU2.4. Besides, the signals belong to OH protons of DMA which are remained as unreacted and/or decomposed urea groups by hydrolytic attack can be identified at around 4.4 δ ppm. On the other hand, the peak belongs to methylene protons of DMA next to urea (NCH_2OCON) is identified at around 4.1 δ ppm which can be related to dendrinic or linear structure formed by DMA (WPU2.3 and WPU2.4). Methylene protons of polyether structure next to urethane carbonyl were denoted between at 4.0-3.9 δ ppm.

Methylene protons of DMA groups are identified at 3.6 δ ppm. Methylene protons of polyether polyol chain next to oxygen and methylene protons of DMA groups are identified between at 3.6-3.4 δ ppm. Methylene groups of neutralizing TEA and urethane group are identified at around 2.9 δ ppm. Besides, the peaks between at 1.4-1.1 δ ppm can be assigned to several methylene and methyl protons of TEA, DMPA and urethane segments. The ^1H NMR spectrums of WPU2 polymers are illustrated in Figure 4.8 and Figure 4.9. Detailed assignment are shown in Table 4.10.

In the case of WPU3 polymers, similar characteristics with WPU2 polymer are observed. The broad peak between at 7.2-6.6 δ ppm is related to trans conformer N-H proton of urethane groups, whereas the peaks between at 8.1-6.8 δ ppm denoted cis conformer N-H proton of urethane groups and N-H protons of urea groups. Urea bands are also identified at 5.5-5.2 δ ppm. Although, the peaks at around 4.8 δ ppm can be attributed to the ether bridges ($\text{NCH}_2\text{OCH}_2\text{N}$) formed by methylolureas and/or methylene bridges (NCH_2N).

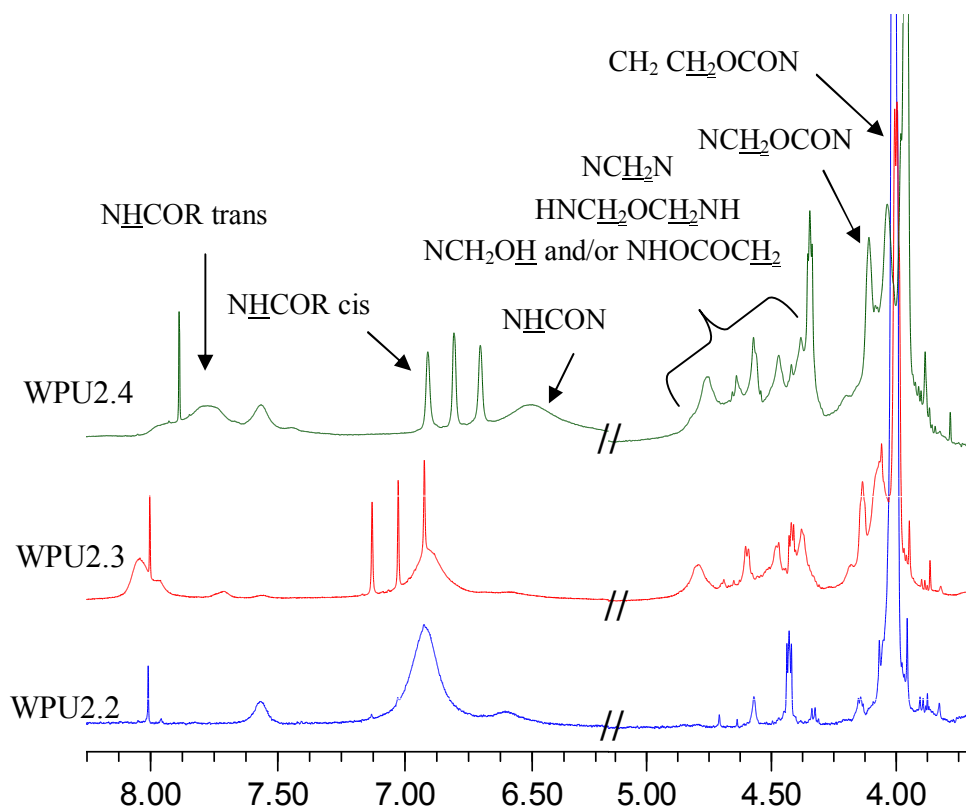


Figure 4.8 : 500 MHz ^1H NMR spectra of WPU2 between 8.5 and 3.7 δ ppm in Trifluoroacetic acid.

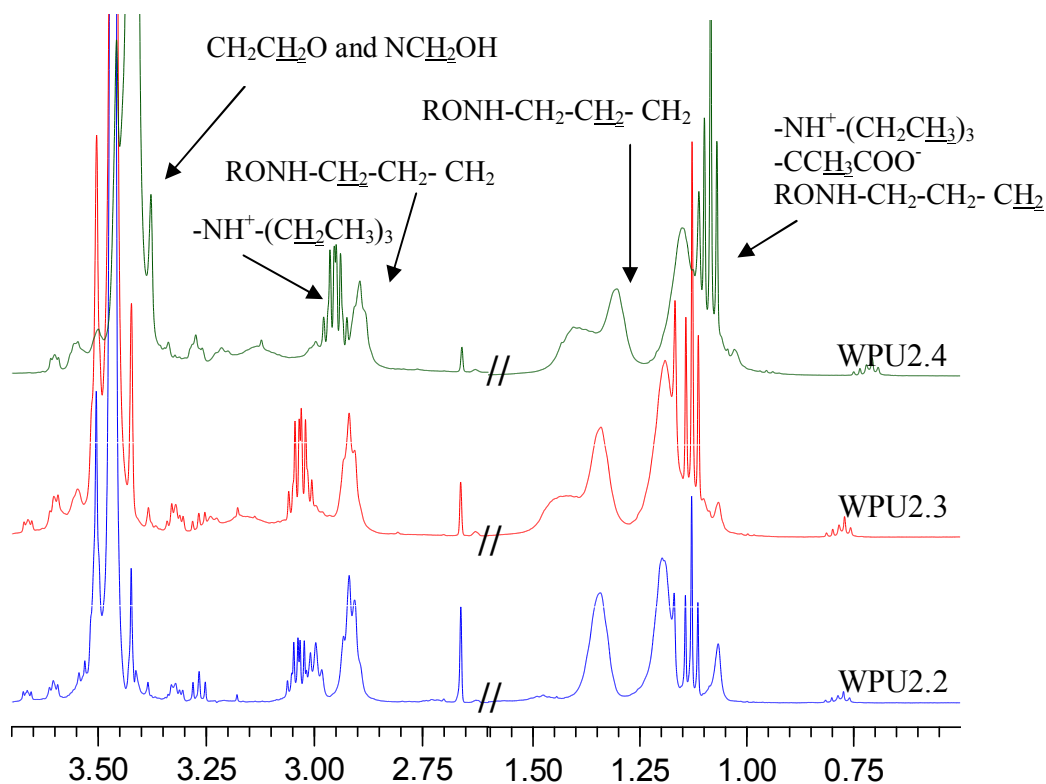


Figure 4.9 : 500 MHz ^1H NMR spectrum of WPU2 between 3.7 and 0.5 δ ppm in Trifluoroacetic acid.

Table 4.10 : Characteristic ^1H NMR shifts of WPU2 polymers.

Segment	Assignment	Chemical shift (δ ppm)		
		WPU2.2	WPU2.3	WPU2.4
Urethane-trans	-NH <u>C</u> OR-	8.1-7.9	8.1-7.9	8.1-7.6
Urethane-cis	-NH <u>C</u> OR-	7.0-6.8	7.0-6.8	7.0-6.7
Urea	-NH <u>C</u> ON-	6.7-6.5	6.7-6.5	6.7-6.5
Ether bridges	-HN-CH ₂ -O-CH ₂ -NH	-	4.8	4.8
Methylene bridges	-NCH ₂ N-	-	4.6-4.5	4.6-4.5
DMA or urethane	NCH ₂ O <u>H</u> and/or NHOCO <u>CH</u> ₂	4.4	4.4	4.4
DMA-urea	NCH ₂ OCON	4.1	4.1	4.1
Polyol	CH ₂ CH ₂ OCON	4.0-3.9	4.0-3.9	4.0-3.9
Polyol and DMA	CH ₂ CH ₂ OCH ₂ and NCH ₂ OH	3.6-3.4	3.6-3.4	3.6-3.4
TEA	-NH ⁺ -(CH ₂ CH ₃) ₃	3.1	3.1	3.1
Urethane	RONH-CH ₂ -CH ₂ - CH ₂	2.9	2.9	2.9
Urethane	RONH-CH ₂ -CH ₂ - CH ₂	1.4-1.3	1.4-1.3	1.4-1.3
TEA	-NH ⁺ -(CH ₂ CH ₃) ₃	1.2-1.1	1.2-1.1	1.2-1.1
DMPA	-CCH ₃ COO ⁻			
Urethane	RONH-CH ₂ -CH ₂ - CH ₂			

Besides, similar to WPU2 series the signals belong to OH protons of DMA which are remained as unreacted and/or decomposed urea groups by hydrolytic attack could be identified at around 4.7 δ ppm. Methylene protons of DMA next to urea (NCH₂OCON) which can be related to dendritic or linear structure formed by DMA and methylene protons next to urethane carbonyl (CH₂CH₂OCON) are identified between at 4.6-4.2 δ ppm. In addition, methylene protons of DMA groups (NCH₂OH) are determined at 4.1 δ ppm. Methylene protons of PPG polyol chain next to oxygen and methylene protons of DMA groups are associated between at 4.0-3.9 δ ppm. Methylene groups of neutralizing TEA and urethane group (NHCH₂) are identified between at 3.1-2.9. Besides, the peaks between at 1.4-0.7 δ ppm can be assigned to several methylene and methyl protons of TEA, DMPA, urethane and polyol segments (Figure 4.10 and Figure 4.11). Detailed assignments of the ^1H MNR shifts are given in Table 4.11.

As a result of the ^1H NMR analysis, despite the similar characteristics of the WPU2 and WPU3 polymers which are both entitled as crosslinked WPU-urea polymers have different structure. The dendritic structure of the WPU2 polymers are more obvious in the presence of HMTA which is due to higher reactivity of PEG1500 polyol (WPU2 series) compared to PPG1000 (WPU3 series).

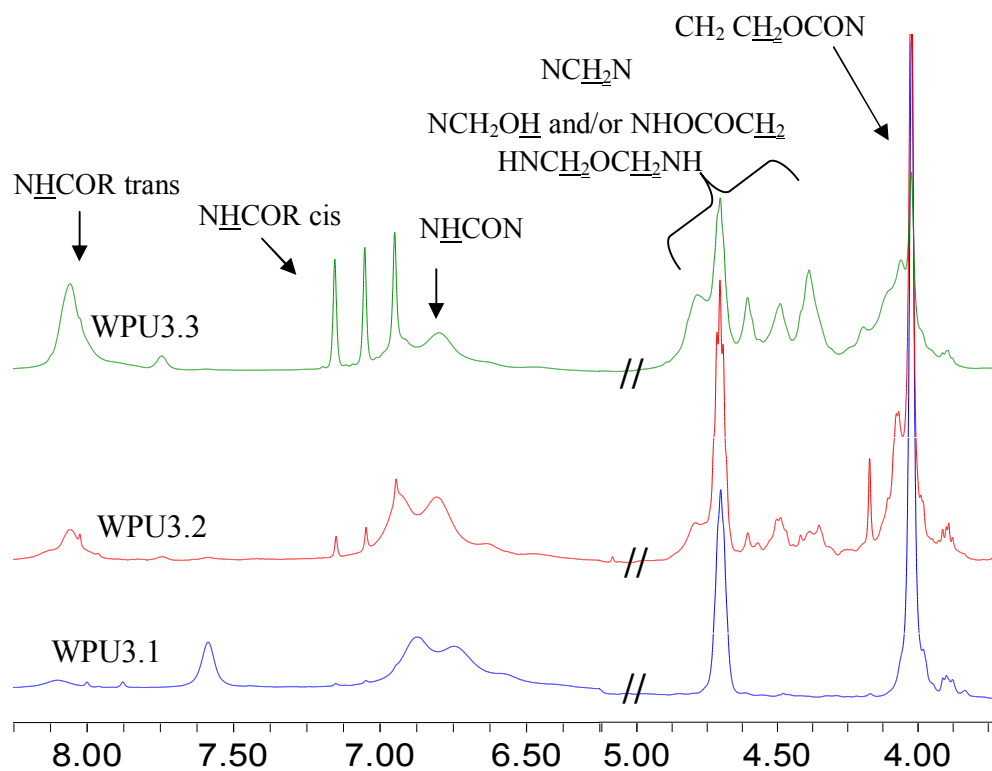


Figure 4.10 : 500 MHz ^1H NMR spectra of WPU3 polymers between 8.5 and 3.7 δ ppm in trifluoroacetic acid.

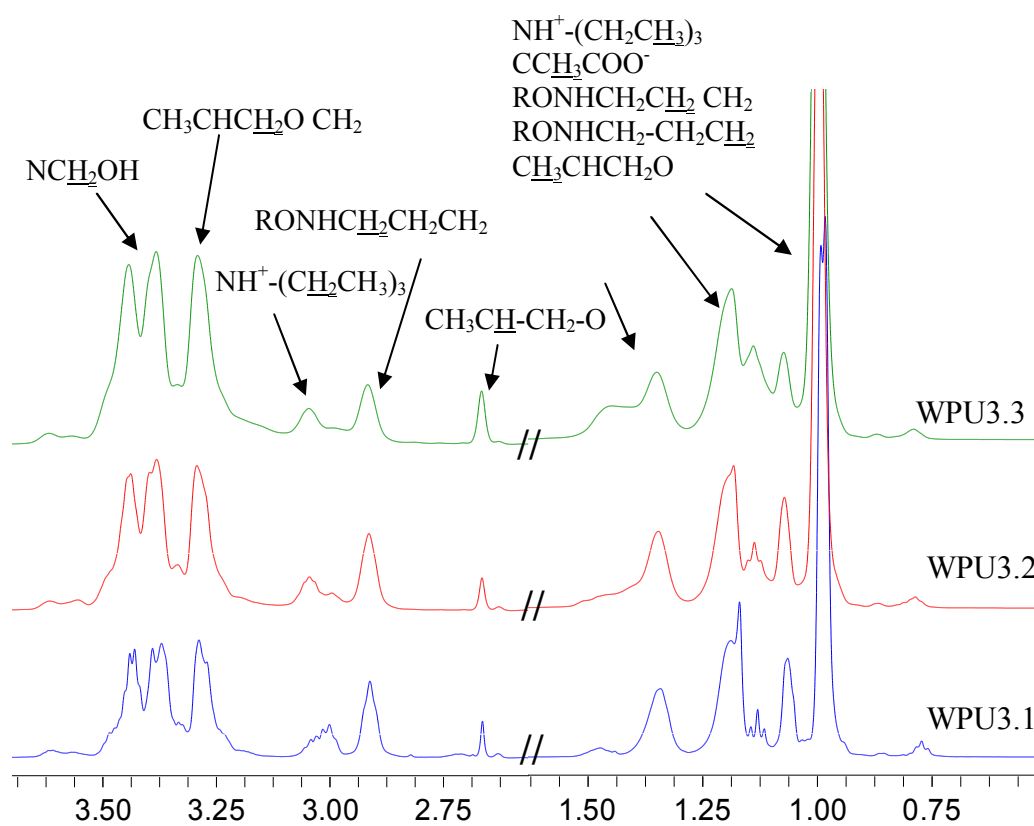


Figure 4.11 : 500 MHz ^1H NMR spectra of WPU3 polymers between 3.7 and 0.5 δ ppm in Trifluoroacetic acid.

Table 4.11: Characteristic ^1H NMR shifts of WPU3 polymers.

Segment	Assignment	Chemical shift (δ ppm)		
		WPU3.1	WPU3.2	WPU3.3
Urethane-trans	-NH <u>C</u> OR-	8.1-7.9	8.1-7.9	8.1-7.6
Urethane-cis and urea	-NH <u>C</u> OR-	7.0-6.8	7.0-6.8	7.0-6.8
Urea	-NH <u>C</u> ON-	6.8-6.6	6.8-6.6	6.8-6.6
Ether and methylene bridges	-HN-CH ₂ -O-CH ₂ -NH- and -NCH ₂ N-	-	4.8	4.8
DMA or urethane	-NCH ₂ OH and/or -NHOCOCH ₂ -	4.7	4.7	4.7
DMA-urea and polyol	-NCH ₂ OCON- and -CH ₂ CH ₂ OCON-	-	4.6-4.2	4.6-4.2
DMA	-NCH ₂ OH	-	4.1	4.1
Polyol	-CH ₃ CHCH ₂ O CH ₂ -	4.0-3.9	4.0-3.9	4.0-3.9
TEA and urethane	-NH ⁺ -(CH ₂ CH ₃) ₃ and RONH-CH ₂ -CH ₂ - CH ₂	3.1-2.9	3.1-2.9	3.1-2.9
Polyol	-CH ₃ CH-CH ₂ -O-	2.6	2.6	2.6
TEA	NH ⁺ -(CH ₂ CH ₃) ₃	1.4-1.1	1.4-1.1	1.4-1.1
DMPA	-CCH ₃ COO ⁻			
Urethane	RONH-CH ₂ -CH ₂ - CH ₂			
Urethane	RONH-CH ₂ -CH ₂ - CH ₂			
Polyol	-CH ₃ CH-CH ₂ -O-			

The results of the ^1H NMR analysis was tried to support by using ^{13}C NMR technique to determine the structure of the crosslinked WPU-urea polymers. The reason of characterization with solid state ^{13}C NMR spectra was the insolubility of the samples in common NMR solvents. Solid state ^{13}C NMR spectra of crosslinked WPU-urea polymers which were taken by using their powdered form can be seen in Figure 4.12 and Figure 4.13. The weak peak at around 178 δ ppm denoted neutralized carbon of COO⁻ groups. The broad peak between at 164 and 156 δ ppm belongs to carbonyl carbon of the urethane and urea groups. The unique peak at 125 δ ppm, which are observed as a result of the reaction in the presence of HMTA (WPU2.3 and WPU2.4) and not clearly observed in WPU3 series, are attributed to carbonyl carbons of the dendritic units in the WPU2 polymers. On the other hand, the peak at around 72 δ ppm belongs to polyol and/or ether bridges and the peaks between at 47 and 49 δ ppm show the methylene bridges of the network structure. In addition, the peak at around 66 δ ppm belongs to methylene carbons of the DMA structure. The peaks in upfield region denote the several carbon atoms in urethane, TEA and DMPA groups. The detailed assignments of chemical shifts can be seen in Table 4.12. As a result, ^{13}C NMR spectroscopy consolidates the ^1H NMR results and indicates that crosslinking with formaldehyde and DMA in WPU-urea polymers successfully obtained.

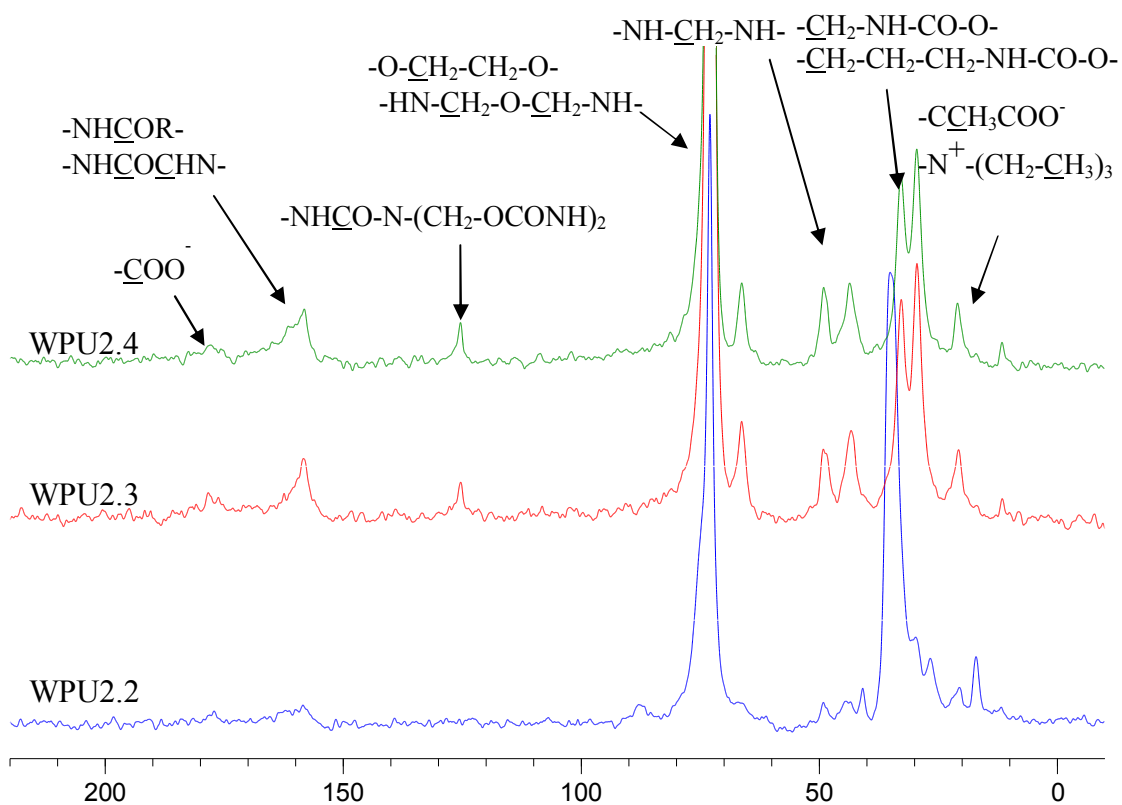


Figure 4.12 : Solid state 125.7 MHz ^{13}C NMR spectra of WPU2 polymers.

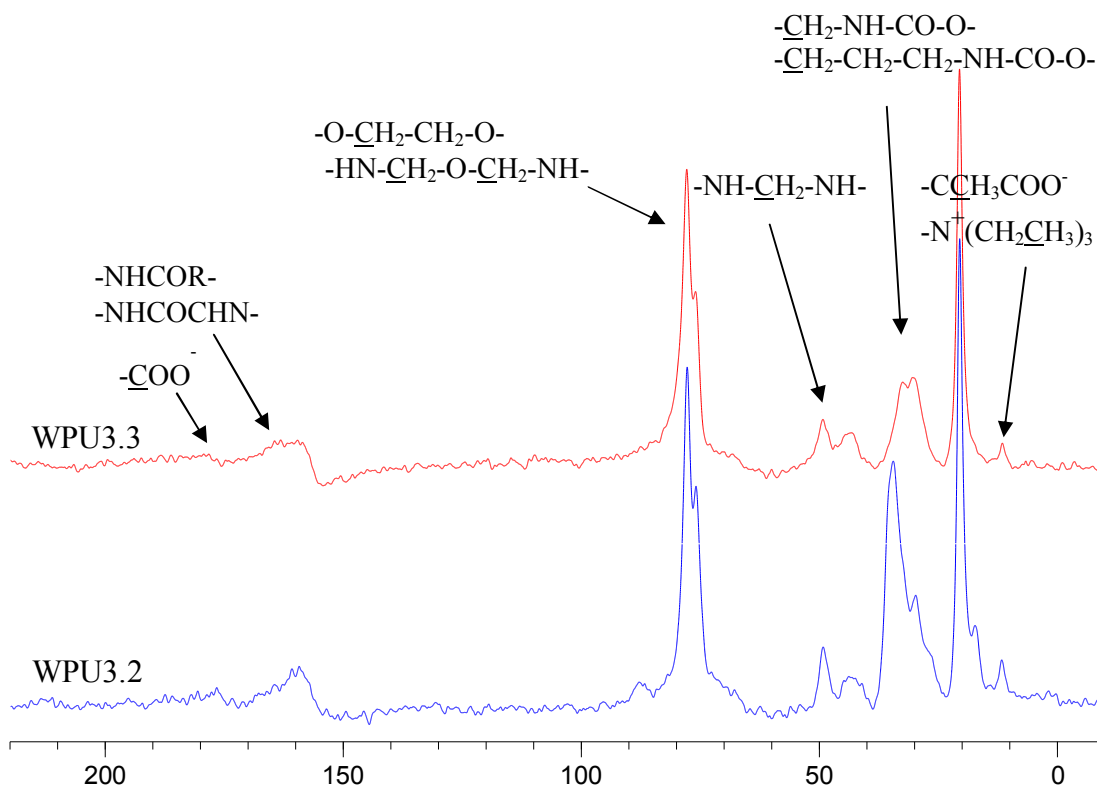


Figure 4.13 : Solid state 125.7 MHz ^{13}C NMR spectra of WPU3 polymers.

Table 4.12 : Characteristic ^{13}C NMR shifts of WPU2 and WPU3 polymers.

Segment	Assignment	Chemical shift (δ ppm)
DMPA	$-\underline{\text{C}}\text{OO}^-$	178.0
Urethane and urea	$-\text{NH}\underline{\text{C}}\text{OR}-$ and $-\text{NH}\underline{\text{C}}\text{OCHN}-$	164.0-156.0
Dentritic units	$-\text{NH}\underline{\text{C}}\text{O}-\text{N}-(\text{CH}_2-\text{OCONH})_2$	125.0
Polyol and/or ether bridge	$-\text{O}-\underline{\text{C}}\text{H}_2-\text{CH}_2-\text{O}-$	72.0
	$-\text{HN}-\underline{\text{C}}\text{H}_2-\text{O}-\underline{\text{C}}\text{H}_2-\text{NH}-$	
DMA	$-\text{NH}-\underline{\text{C}}\text{H}_2-\text{OH}$	66.0
Methylene bridge	$-\text{NH}-\underline{\text{C}}\text{H}_2-\text{NH}-$	47.0-49.0
Urethane	$-\underline{\text{C}}\text{H}_2-\text{NH}-\text{CO}-\text{O}-$	43.0
Urethane	$-\text{CH}_2-\text{CH}_2-\text{NH}-\text{N}-\text{CO}-\text{O}-$	32.8
Quarternal carbon (TEA)	$-\text{N}^+-(\underline{\text{C}}\text{H}_2-\text{CH}_3)_3$	
Urethane	$-\underline{\text{C}}\text{H}_2-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CO}-\text{O}-$	29.5
DMPA	$-\text{C}\underline{\text{C}}\text{H}_3\text{COO}^-$	20.7
Quarternal carbon (TEA)	$-\text{N}^+-(\text{CH}_2-\underline{\text{C}}\text{H}_3)_3$	11.6

4.2.2.3 Particle size analysis of crosslinked WPU-urea polymers

In the acetone method, the particle size distribution was determined by the DMPA concentration in linear WPUs that were already discussed in the Section 4.1.2.3. Generally, in the WPUs prepared by the prepolymer mixing method the relatively high viscosity of the prepolymer that inhibits its dispersion in water, giving a larger particle size, determines the particle size distribution (Liminana et al., 2006). In crosslinked WPU-urea polymers, WPU3 prepared by using PPG1000 polyol indicates relatively larger particle size compared to WPU2 prepared by using PEG 1500. It can be due to the structure of polyol rather than DMPA content. Methyl groups of PPG polyol ($\text{CH}-\text{CH}_3-\text{CH}_2-\text{O}$) are occupied relatively higher spacing compared to PEG type of polyol. As a result, WPU2 polymer has better penetration on substrate compared to WPU3 due to its lower particle size (Table 4.13).

Table 4.13 : Particle size analysis results of crosslinked WPU polymers.

Polymer	Particle size (nm)	DMPA content (% w/w)	Polyol type
WPU 2.3	47.62	5.83	PEG1500
WPU 3.2	83.74	7.90	PPG1000

4.2.2.4 Mechanical analysis of crosslinked WPU-urea polymers

Tensile tests were performed to investigate the effect of HMTA crosslinker on the mechanical properties of WPU2 and WPU3 series polymers. Similar to linear WPUs test specimens were prepared as with 1 mm thickness (EN ISO 527-1). Tensile test results of the polymer films are summarized in Table 4.14. Stress-strain curves are denoted in Figure 4.14 and Figure 4.15. As a general trend, elongation at break

values decreases with increasing HMTA ratio in both WPU2 and WPU3 series. However, WPU2.2 shows also high tensile strength as well as highest elongation value. Stress values indicates increasing trend as the HMTA ratio increases. Maximum stress values are elevated at highest HMTA ratio. This is due to increasing of crosslinking as the HMTA content increases through methylene or oxymethylene bridges which can be acted as crosslinking points. In addition, increasing dendritic structure which is established by reaction of DMA and urethane chains causes increasing of maximum stress value and decreasing of elongation at break. This result is also compatible with ^1H NMR results of which identifies crosslinked structure in HMTA containing samples (WPU2.3, WPU2.4, WPU3.2 and WPU3.3).

Table 4.14 : Mechanical properties of WPU2 and WPU3 with different HMTA ratios.

Sample	NCO/HMTA Ratio (%)	Tensile strength (MPa)	Maximum stress (N)	Elongation at break (%)
WPU2.2	-	0.79	2.76	119.6
WPU2.3	1/0.25	0.66	2.39	76.4
WPU2.4	1/0.50	1.18	4.74	65.5
WPU3.1	-	0.19	0.90	331.3
WPU3.2	1/0.25	0.17	1.48	72.0
WPU3.3	1/0.50	0.30	2.39	41.2

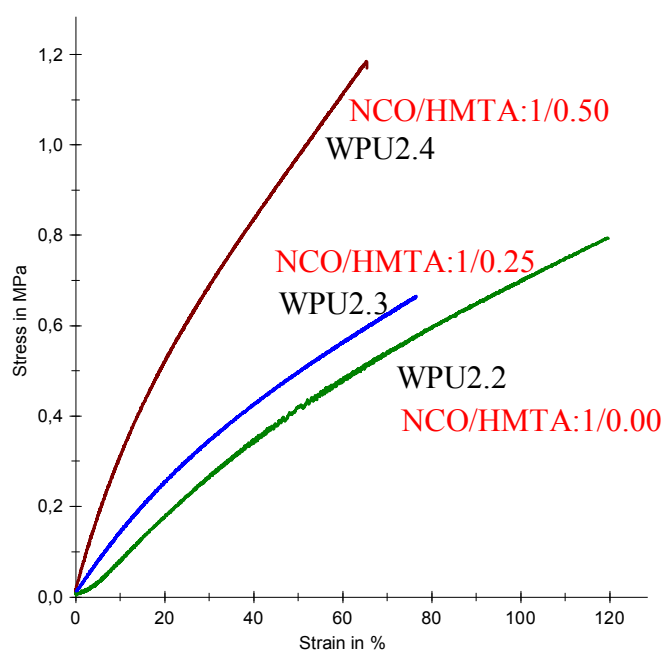


Figure 4.14 : Stress-strain curves of WPU2 polymer prepared with different HMTA ratios.

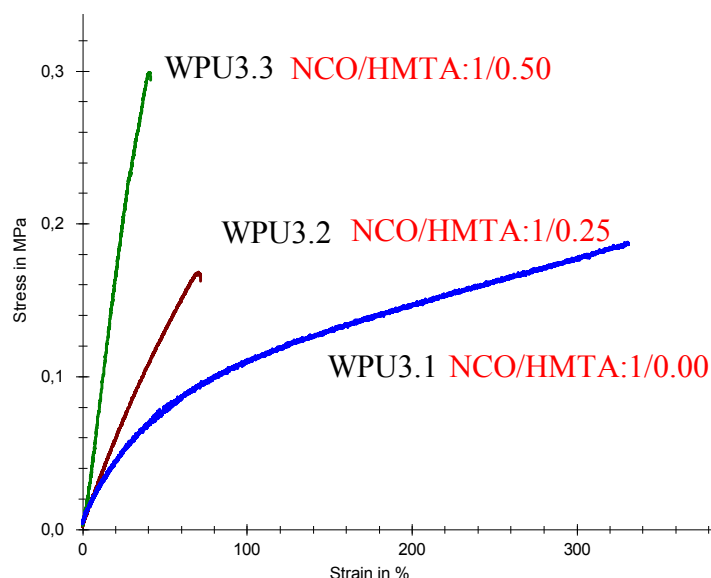


Figure 4.15 : Stress-strain curves of WPU3 polymer prepared with different HMTA ratios.

Consequently, the optimum experimental conditions of crosslinked WPU-urea polymers are determined in the presence of HMTA. All the samples were provided good film forming capability and both WPU2 and WPU3 polymers which are having crosslinked and linear segments methylene and/or ether type bridges through methylolurea groups. Besides, dendritic structure is established by the reaction of DMA and urethane chains by the increase of the rate of the HMTA. Although, WPU2 series indicates more dendritic structure owing to primary hydroxyl group in PEG1500 polyol with higher reactivity compared to PPG1000. However, WPU2.3 and WPU3.2 indicate moderate mechanical properties in terms of stress and strain values which were prepared using the ratio of NCO/HMTA: 1/0.25. Therefore, these compositions are chosen for composite preparation.

4.3 Synthesis and Characterization of Linear WPU and WPU-urea Nanocomposites

4.3.1 Preparation of OMt by melt blending method

Initially, NaMt was dried to remove absorbed moisture due to its capability of reacting with isocyanate segment. In addition, there is additional interlayer water aluminosilicate layers and cannot be removed by simple drying. The amount of water in NaMt was needed to be evaluated which has a reaction capability with isocyanate component.

TGA technique is widely used for the analysis of thermal degradation characteristics of Mt (Xie et al., 2001). According to the studies, dehydroxylation can be completed in several stages for Mt. Free water is removed at around 100°C. However, entire dehydroxylation can be completed between at 500-700°C.

Hydroxyl content determination of NaMt was performed using both TGA analysis technique and theoretically from its formula $[\text{Na}_{0.65}[\text{Al,Fe}]_4\text{Si}_8\text{O}_{20}(\text{OH})_2]$. The region of the degradation of structural hydroxyl group is identified between at 550-700°C. As a result, the structural hydroxyl content of the pure NaMt is calculated as 3.67% theoretically whereas 3.73% by using TGA analysis which are very similar (Figure 4.16). The additional isocyanate which is spent by structural hydroxyl group of the NaMt was calculated and added to the isocyanate content during the preparation of the nanocomposites.

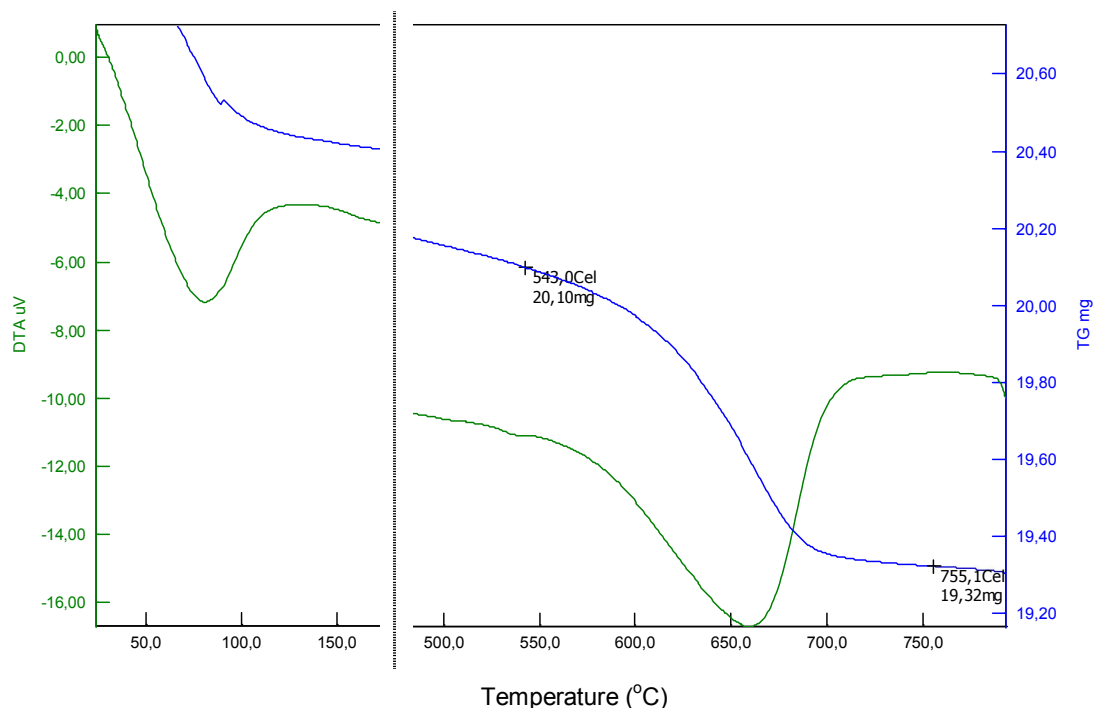


Figure 4.16 : Determination of structural hydroxyl in NaMt clay by using TGA.

There are intensive research related to the swelling of NaMt in glycols and polyols (Alemdar et al., 2000; Alemdar et al., 2005). In our study, the main idea is to intercalate the hydroxyl containing polyol within the galleries of the NaMt for the subsequent WPU nanocomposite formation. The aim of the dispersion at moderately elevated temperature is to provide better interaction of polyol into NaMt galleries by lowering the viscosity. Hence, polyol molecules would easily diffuse into interlayer galleries of NaMt.

The preparative works were performed in PEG1500 polyol as the matrix to examine intercalation properties of NaMt in polyol. Initially, the polyol component was dried by stirring overnight at 100°C under vacuum. Then, 1, 3 and 5% (w/w) NaMt was initially dispersed in polyol by melt blending technique without solvent for 15 hours at 80°C to obtain polyol-swelled OMt. Finally, XRD measurements were made to evaluate basal spacing of Mt. XRD patterns of the OMt can be seen in Figure 4.17.

According to this preparative studies, XRD analysis indicates that NaMt is successfully intercalated in PEG polymer. According to XRD results, the $2\theta=8.91$ value of NaMt which corresponds to 9.91Å interlayer spacing of NaMt shifts to around $2\theta=5$ which denoted 6-7 Å increase of the interlayer spacing.

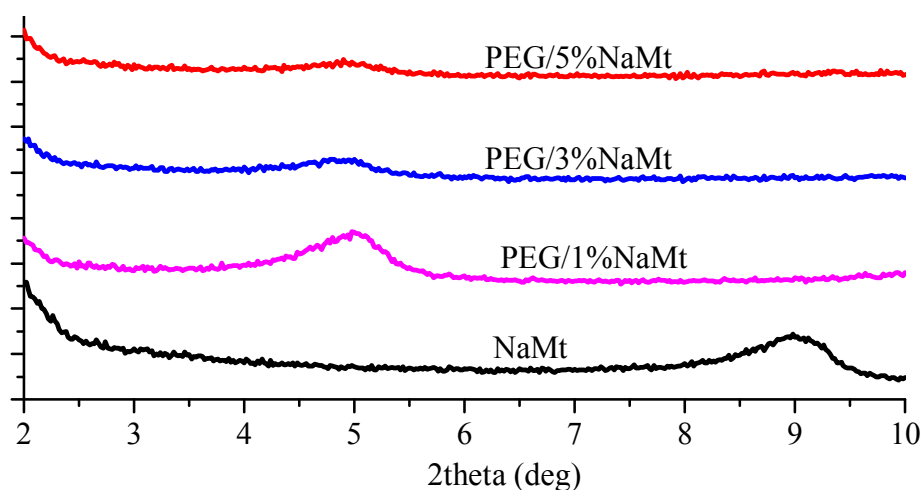


Figure 4.17 : XRD patterns of preparative dispersion study.

Finally, the rest of the OMt compositions including PEG600, PPG1000 and PTAA, were prepared under same conditions with PEG1500 and reserved in order to be used directly to obtain nanocomposites via in-situ intercalative polymerization.

4.3.2 Preparation of nanocomposites by in-situ polymerization method

In-situ intercalative polymerization method was used as the preparation method of the composites. In this method, OMt is swollen in the liquid monomer itself or with the aid of solvent and polymer is formed between the intercalated sheets of the NaMt. Several polymerization methods can be used with this technique depending on the final polymer type.

Linear WPU and crosslinked WPU-urea nanocomposites via in-situ polymerization method were prepared by using synthesis conditions of successful compositions of the linear WPU and crosslinked WPU-urea polymers. Synthetic methods of WPU1.5 and

WPU4.3 were chosen due to their good film forming capability to prepare linear WPU nanocomposites. Although, WPU-urea polymers all have good film forming property and synthetic methods of WPU2.3 and WPU3.2 were chosen which are containing free NCO/HMTA ratio of 1/0.25 with moderate crosslinking. The experiment codes of the neat polymers are taken as WPU1, WPU4, WPU2 and WPU3 which are named as NWPU1, NWPU4, NWPU2 and NWPU3 respectively.

The nanocomposites were prepared via in-situ polymerization method to obtain WPU or WPU-urea nanocomposites using OMt which had been initially prepared by melt blending into polyol. The preparation was performed including prepolymer synthesis, neutralization and chain extension stages with the addition of additional isocyanate corresponds to structural water by using the same polymerization procedures (Figure 4.18).

Linear WPU nanocomposites were attained by using BD chain extender (WPU1 and WPU4 series) whereas, crosslinked WPU-urea nanocomposites gained by using water as a chain extender in the presence of HMTA crosslinker (WPU2 and WPU3 series). All the nanocomposites were successfully prepared by using 1, 3 and 5%. The reaction conditions of the nanocomposites are summarized in Table 4.15.

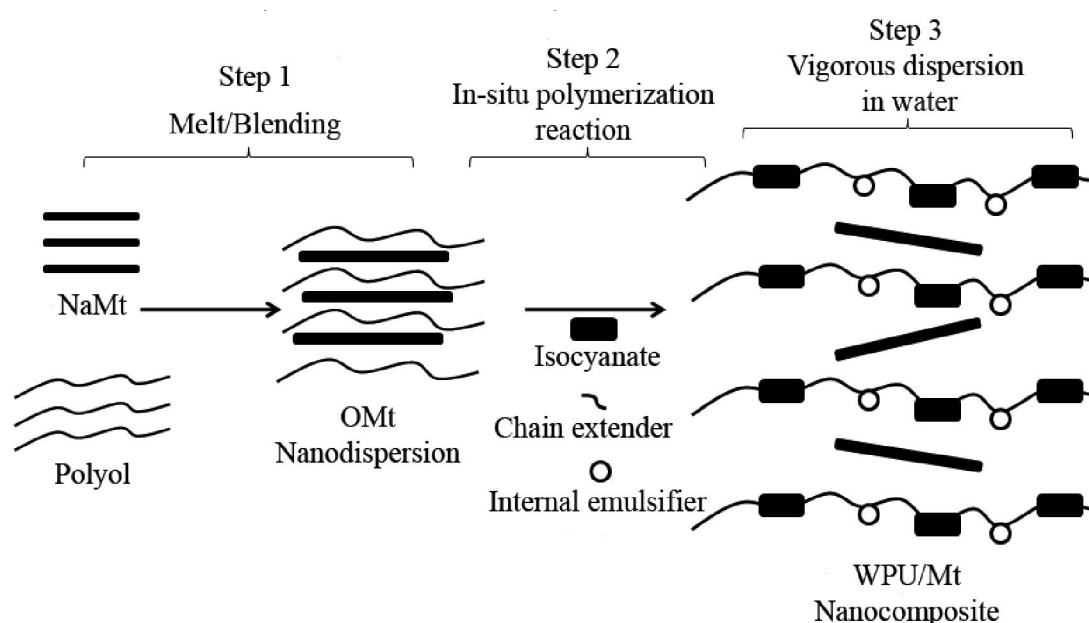


Figure 4.18 : Schematic representation of the preparation of nanocomposites by in-situ polymerization.

Table 4.15 : Reaction conditions of WPU and WPU-urea nanocomposites (Polyol:10 g, [Et₃N]/[COOH]: 1).

Exp ¹	Soft segment	Polyol/ DMPA/ HDI molar ratio	Prepolymer reaction time (h)	Catalyst in prepolymer reaction (on total solid) (%)	Free NCO in prepolymer (%)	Process type	CE	Catalyst in CE reaction (on free NCO+ BD) (%)	CE reaction time (h)	Hard Segment Content ¹ (w/w %)
NWPU1.1	PEG600	1/1/3	2	0.5	2.35	Acetone process	BD	1.0	4.0	54.8
NWPU1.3										
NWPU1.5										
NWPU2.1	PEG1500	1/1/3	2	0.5	2.00	Prepolymer mixing process	Water/ HMTA	-	0.5	30.5
NWPU2.3										
NWPU2.5										
NWPU3.1	PPG1000	1/1/3	4	1.0	2.50	Prepolymer mixing process	Water/ HMTA	-	0.5	39.7
NWPU3.3										
NWPU3.5										
NWPU4.1	PTAA	1/1/3	3	-	2.50	Acetone process	BD	2.0	3.0	24.8
NWPU4.3										
NWPU4.5										

¹ Hard segment content calculated as [(HDI+DMPA+CE)/(Polyol+HDI+DMPA+CE)]*100.

During preparation of the nanocomposites, the experiment with 5% Mt content (w/w) caused gelling behaviour in the latter period of the chain extension stage (NWPU1.5). Although, despite the experiment was repeated several times by increasing solvent, the same gelling behaviour was observed. This could be due to increasing of interaction expeditiously via higher amount of hydrogen bonding between OMt and the growing polymer because of high hard segment content. As a result of rising hydrogen bonding, rapid increase of viscosity of reaction medium was occurred.

The effect of Mt content on the nanocomposites was investigated firstly in terms of spectral, thermal, morphological, mechanical analysis and secondly the effect of environmental factors such as solar radiation and ozone on material properties are examined.

4.3.3 Characterization of nanocomposites

4.3.3.1 FTIR analysis of nanocomposites

FTIR analysis is one of the characterization methods of nanocomposites. The interaction of polymer and Mt can be identified by using FTIR spectrometry. FTIR analysis of NWPU nanocomposite films are performed using ATR equipped FTIR device similar to neat polymer films. The assignments of most characteristic bands of the nanocomposites, which are similar with neat polymers, are given in detail in Table 4.16.

The most relevant bands correspond to nonbonded N-H stretching at $3504\text{--}3510\text{ cm}^{-1}$ and bonded at $3322\text{--}3330\text{ cm}^{-1}$, C-H stretching between at $2862\text{--}2838\text{ cm}^{-1}$ and C=O stretching due to urea ($1629\text{--}1653\text{ cm}^{-1}$) and ester-urethane ($1689\text{--}1726\text{ cm}^{-1}$) groups. On the other hand, C-N and N-H stretching bands at around $1532\text{--}1539\text{ cm}^{-1}$, N-CO-O stretching bands at $1247\text{--}1249\text{ cm}^{-1}$, symmetric N-CO-O stretching bands between at $1095\text{--}1128\text{ cm}^{-1}$ and characteristic C-O-C stretching bands between at $1125\text{--}1174\text{ cm}^{-1}$ and $947\text{--}963\text{ cm}^{-1}$ are identified.

The FTIR spectrum of NaMt is depicted in Figure 4.19. Characteristic absorption bands of NaMt was identified as structural O-H stretching vibrations at 3625 cm^{-1} , Si-O stretching vibrations at around 1100 cm^{-1} and 987 cm^{-1} .

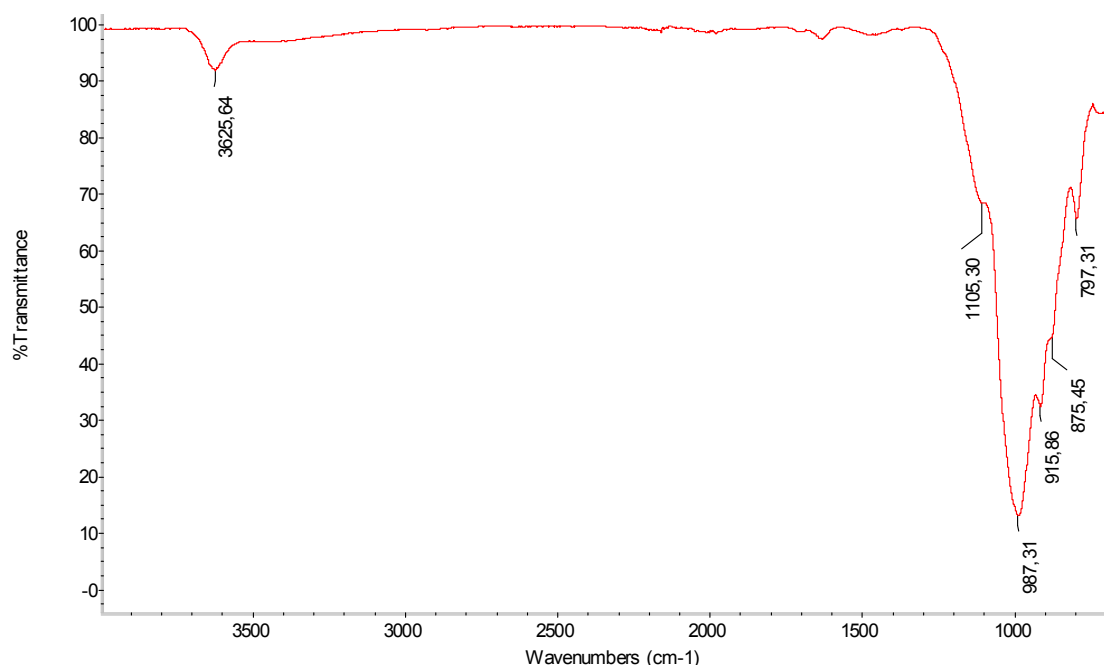


Figure 4.19 : FTIR spectrum of NaMt.

However, intra/intermolecular hydrogen bonded O-H stretching vibrations at around 3400 cm^{-1} , H-O-H deformation vibration due to adsorbed water between at $1640\text{--}1620\text{ cm}^{-1}$, Al-OH vibration at 915 cm^{-1} and Al-O, Mg-O at 875 cm^{-1} and 797 cm^{-1} , Si-O bending vibrations at around 520 and 460 cm^{-1} are not determined. Because, KBr technique was not suitable for FTIR characterization of film shaped WPU polymers. Owing to FTIR spectrums are recorded by using ATR equipped device hence the examination of the interaction between polymer and Mt might be limited.

The interaction of the polymers with NaMt was identified by investigation of changing bands at the region of structural O-H vibration of NaMt at around 3625 cm^{-1} . The change in the peak would be shifting of frequency or difference in the intensity. In all nanocomposites, structural O-H bands of NaMt are not determined which can be due to reacting with NCO groups with all the structural O-H groups of NaMt during in-situ polymerization (Figure 4.20, Figure 4.21, Figure 4.22, Figure 4.23). It is known that, FTIR bands of bonded NH bands are shifted towards to lower frequencies due to hydrogen bonding of Mt with polymer. In NWPU1 nanocomposites, the bands shifts from 3324 to 3322 cm^{-1} (NWPU1.1) and 3323 cm^{-1} (NWPU1.3). Similarly, in NWPU4 series the bands shifts from 3325 to 3322 cm^{-1} (NWPU4.3 and NWPU4.5).

Table 4.16 : Comparison of FTIR results of WPU polymers and their nanocomposites.

Assignment	WPU1	NWPU 1.1	NWPU 1.3	WPU2	NWPU 2.1	NWPU 2.3	NWPU 2.5	WPU3	NWPU 3.1	NWPU 3.3	NWPU 3.5	WPU4	NWPU 4.1	NWPU 4.3	NWPU 4.5
st N-H (bonded)	3324	3322	3323	3324	3326	3330	3330	3324	3331	3339	3339	3325	3325	3322	3322
st C-H	2934	2931	2929	2926	2932	2926	2926	2970	2968	2970	2970	2934	2939	2942	2938
	2862	2865	2865	2866	2868	2865	2867	2930	2930	2930	2930	2866	2869	2869	2866
								2865	2865	2864	2864				
st N=C=O	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
st C=O (urethane)	1689	1692	1694	1707	1717	1707	1708	1697	1700	1699	1697	1720	1728	1726	1726
st C=O (bonded ordered urea)	-	-	-	1648	1650	1653	1647	Not identified	Not identified	Not identified	Not identified	-	-	-	-
st C-N and N-H	1533	1533	1532	1535	1535	1539	1535	1531	1532	1534	1533	1534	1534	1534	1534
st CH ₂	1466	1461	1460	1464	1458	1460	1459	1455	1458	1457	1459	1458	1455	1456	1455
st sym (COO ⁻)	1411	1405	1400	1409	1409	1409	1407	1401	1402	1402	1403	1416	1416	1416	1419
st sym CH ₃	1347	1347	1347	1351	1349	1351	1350	1373	1372	1373	1372	1385	1384	1385	1384
								1344	1343	1343	1344	1348	1347	1351	1343
st asym N-CO-O and st (C-O-C)	1249	1249	1247	1248	1248	1248	1247	1246	1246	1247	1247	1249	1249	1249	1247
st (C-O-C)	1132	1132	1135	-	1125	-	-	-	-	-	-	1131	1175	1178	1174
st sym N-CO-O and st (C-O-C) or Si-O	1097	1100	1098	1101	1095	1095	1096	1097	1098	1095	1098	1086	1131	1131	1128
			1042	1039	1043	1039	1036	1015	1013	1013	1015	1044	1039	1078	1070
														1047	1047
st C-O-C	952	952	947	951	949	949	949	927	926	920	922	952	963	960	958

However, the opposite effect is observed for NWPU2 and NWPU3 those shift to higher frequencies which were also showing interaction of Mt with the neat polymer (Table 4.16).

On the other hand, the interaction of the polymers with Mt is also identified by investigation of the differences of the peaks which are observed at Si-O stretching region at around 1105 and 987 cm^{-1} . In NWPU1 series, C-O-C stretching vibrations shift from 1132 cm^{-1} to 1135 cm^{-1} (NWPU1.3) (Figure 4.20). In NWPU2 series, C-O-C stretching vibration at 1132 cm^{-1} becomes predominant (NWPU 2.1) due to effect of Si-O stretching band of NaMt (Figure 4.22). However, in NWPU3 series the intensity of the peak at 1017 cm^{-1} was belong to stretching vibration of N-CO-O + st(C-O-C) was drastically increased with the effect of Si-O stretching band (NWPU3.3) (Figure 4.23). The same effect was observed for NWPU4 series that significant change occurred at around 1043 cm^{-1} due to effect of Si-O stretching band of NaMt (NWPU4.1, NWPU4.3, NWPU4.5) (Figure 4.21).

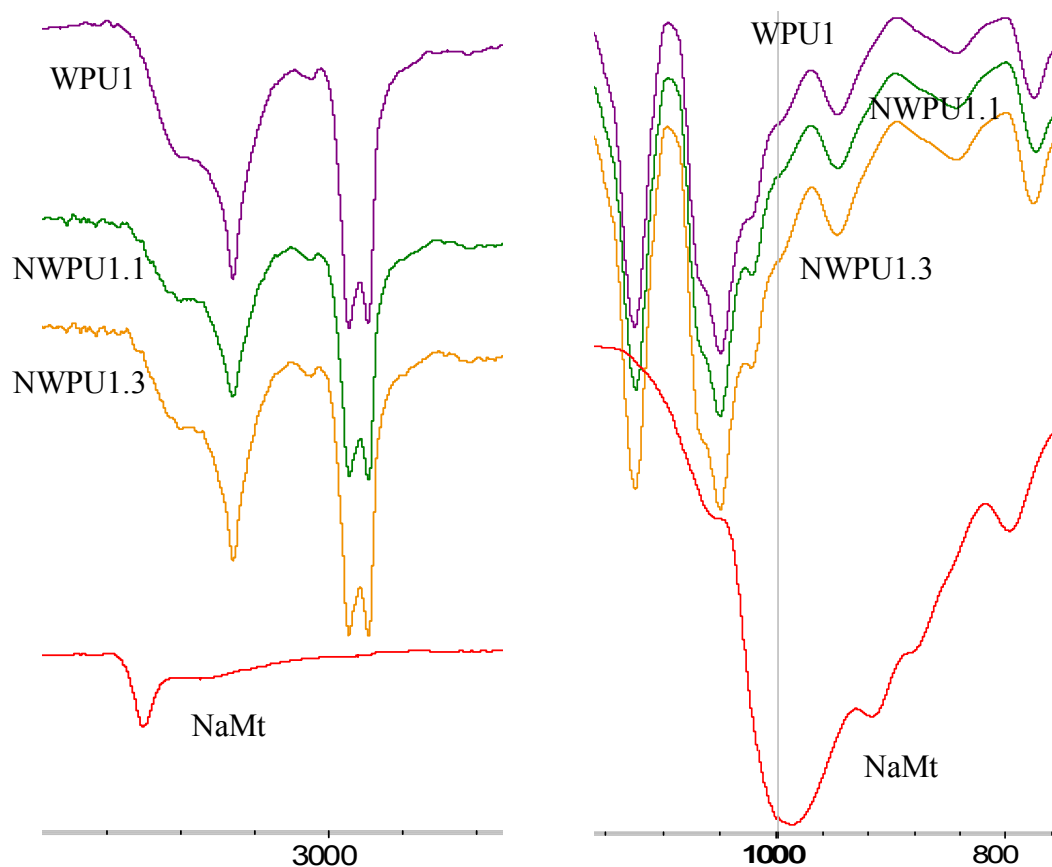


Figure 4.20 : FTIR spectra of NWPU1 series nanocomposites.

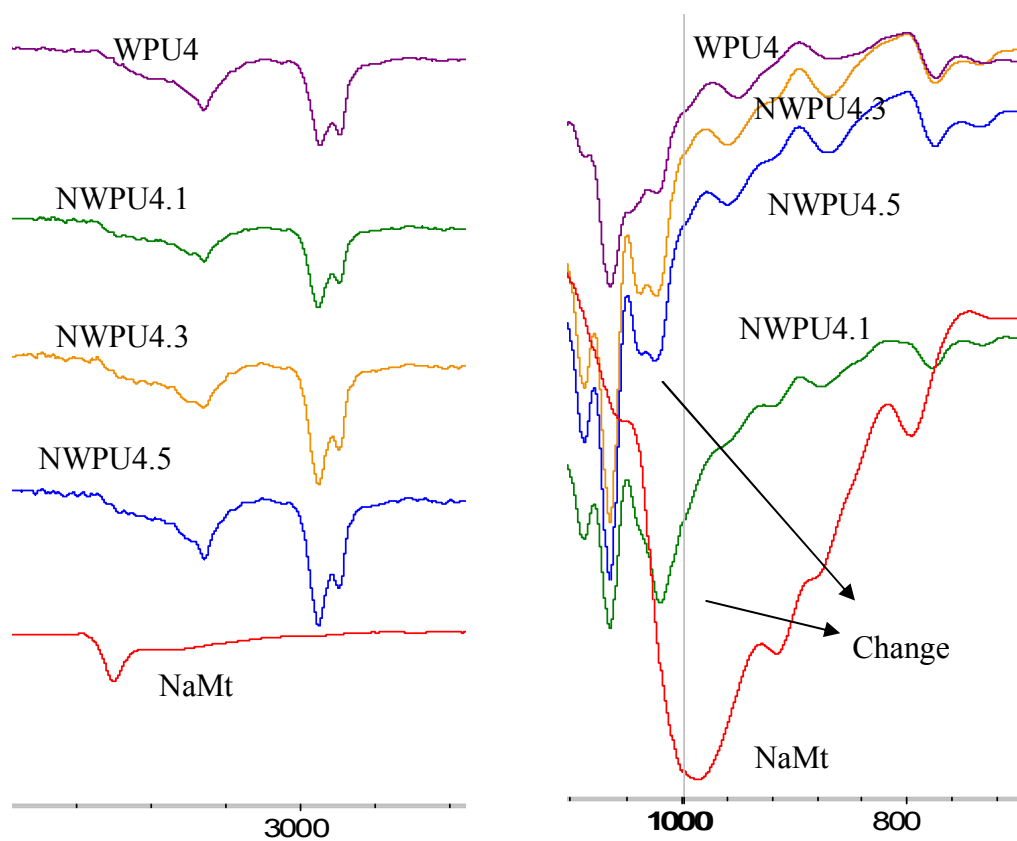


Figure 4.21 : FTIR spectra of NWPU4 series nanocomposites.

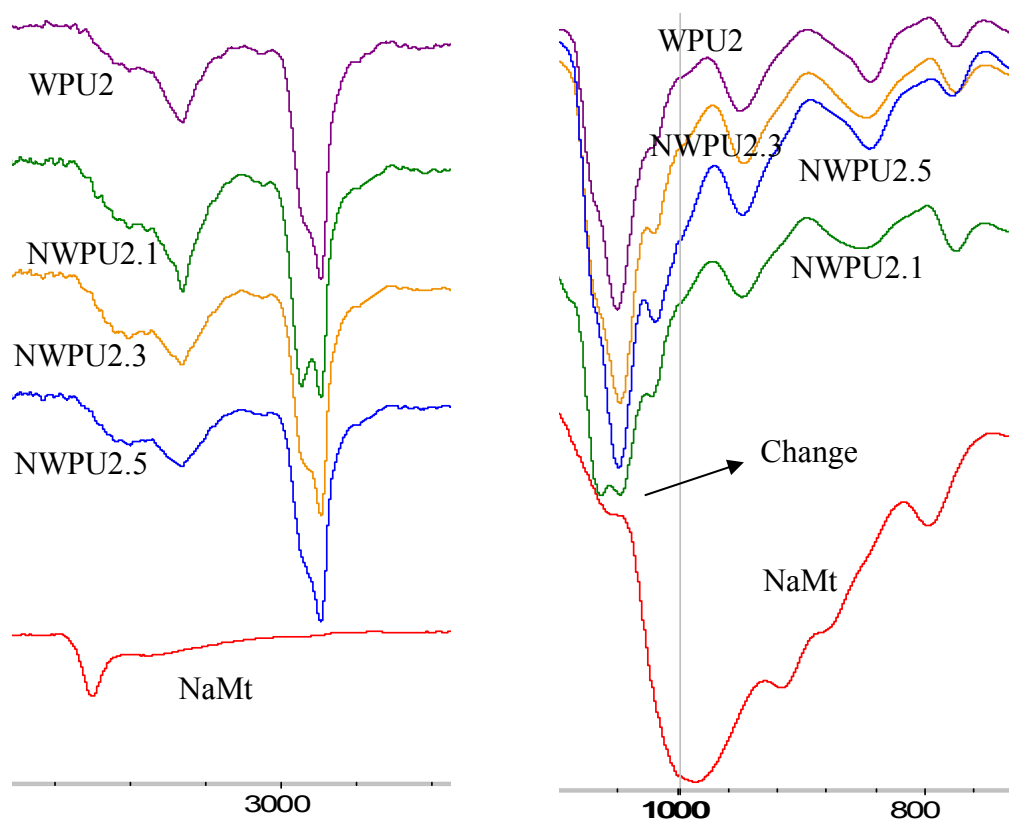


Figure 4.22 : FTIR spectra of NWPU2 series nanocomposites.

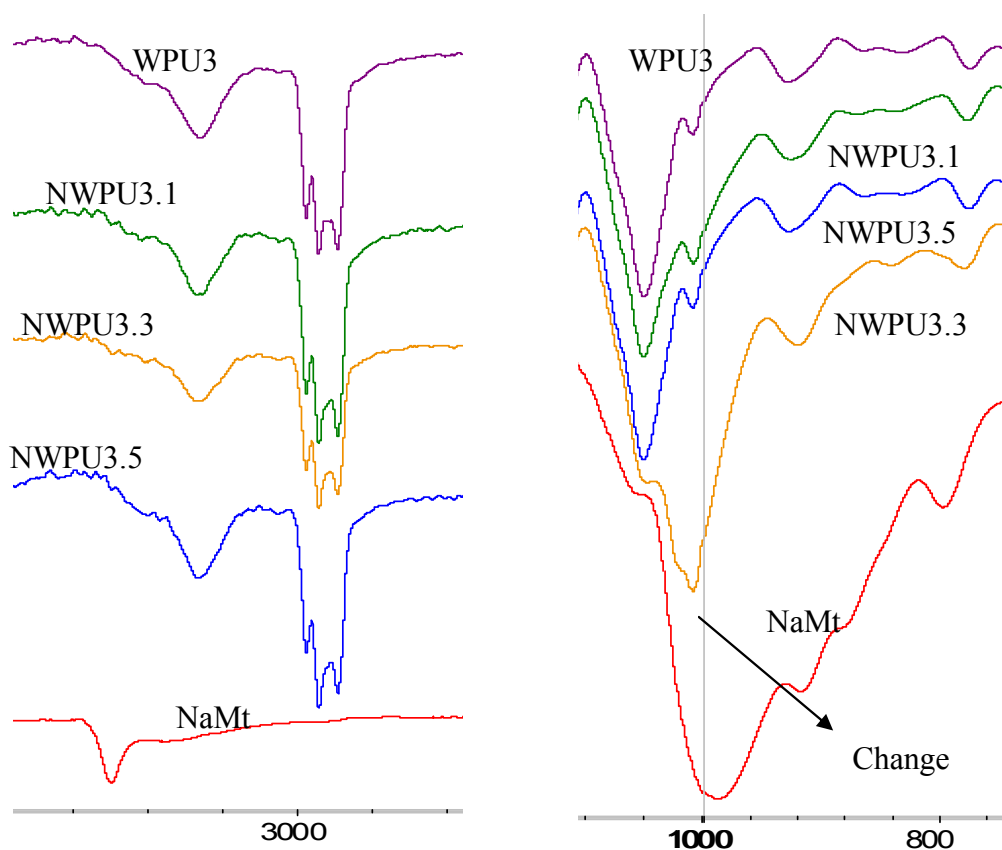


Figure 4.23 : FTIR spectra of NWPU3 series nanocomposites.

As a result, shifting of the bands and noticable change of the peaks by the addition of NaMt especially around characteristic Si-O stretching region of NaMt are the evidence of the interaction of polymer and Mt. However, changes in the peaks of the polymers around the Al-OH and Al-O and/or Mg-O regions of NaMt are not identified which might be suppressed by polymer peaks. In addition, the interaction of OMt on the polymer was not identified at around Si-O bending vibrations of NaMt which could be owing to limitations of ATR equipment.

4.3.3.2 X-Ray diffraction analysis of nanocomposites

X-Ray Diffraction analysis (XRD) is the primary method to investigate effectiveness of the dispersion of clay and architecture of the nanocomposites. According to Bragg's law, the interlayer spacing of clay layers examined in order to investigate the state of the dispersion (4.13).

$$\lambda = 2d \sin \theta \quad (4.13)$$

Initially, the XRD pattern of the NaMt was analyzed. The peak which is observed at $2\theta=8.91$ belong to XRD pattern of NaMt corresponds to $9.91\text{\AA}$ interlayer spacing. In linear nanocomposites, the interlayer spacing is increased to $3.6\text{-}3.8\text{\AA}$ in NWPU1 series whereas increasing of spacing varies between $3.9\text{-}5.4\text{\AA}$ in NWPU4 series. Although the values were similar, the small differences can be due to Mw of the polyol which was relatively much higher in NWPU4 compared to NWPU1 series. XRD patterns belong to the linear WPU and crosslinked WPU-urea nanocomposites are shown in Figure 4.24. Detailed XRD results can be seen in Table 4.17.

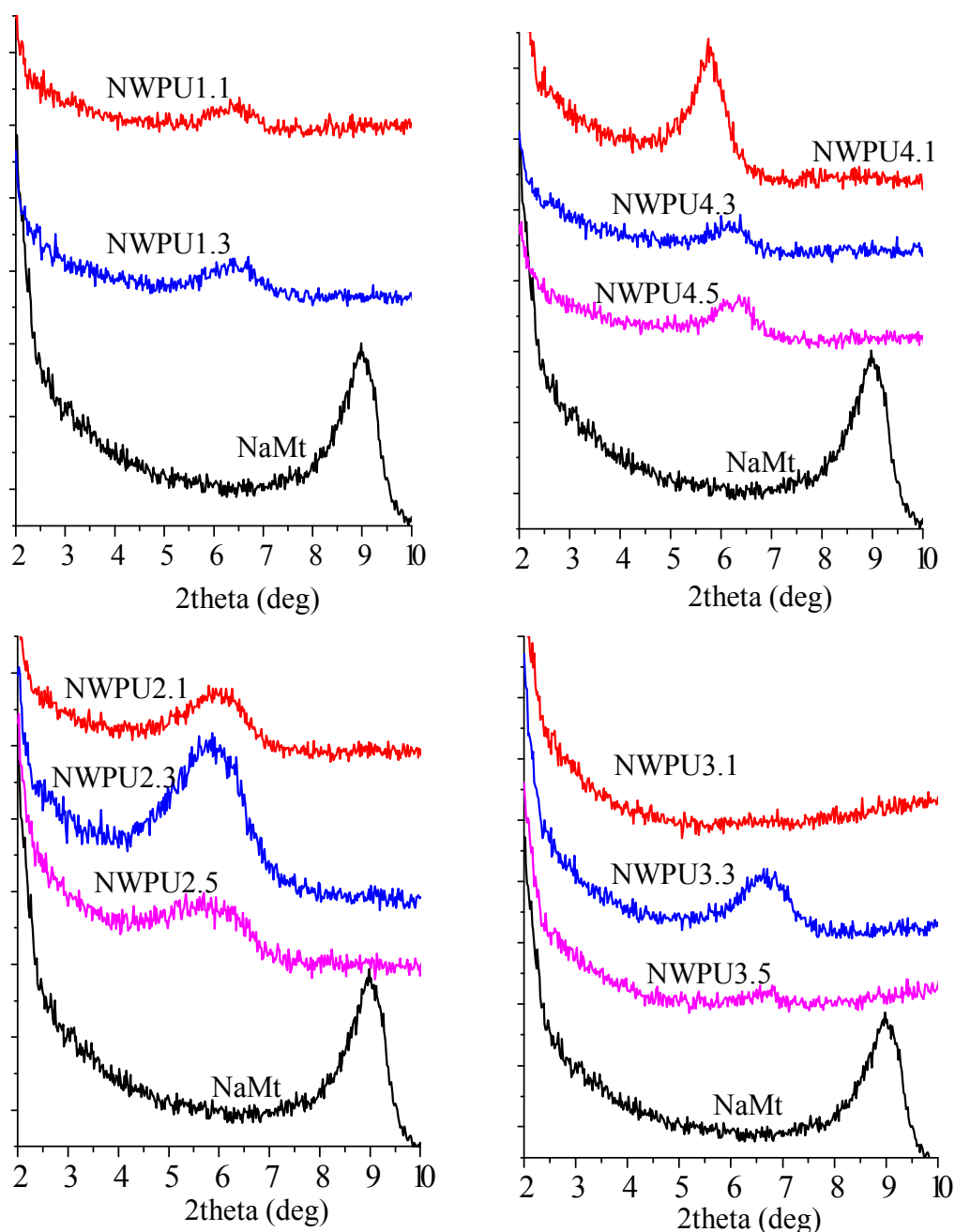


Figure 4.24 : XRD patterns of nanocomposites.

On the other hand, in the case of crosslinked NWPU2 and NWPU3 series, the increase in spacing is much higher in NWPU2 which varies between at 4.7-5.6 Å owing to the containing higher Mw polyol and intense crosslinking compared to NWPU3 having 3.1-3.6 Å increase. In addition, the lower increase in d-spacing of NWPU3 series compared to NWPU3 series can be due to having PPG soft segment which contains methyl group perpendicular to axis. Hence, this methyl group prevents entrance of the polymer into the galleries. On the other hand, there is no correlation between Mt content and increase in d-spacing in each series. Consequently, all composites have variety of increasing d-spacing values compared to pure NaMt and it can be said that nanocomposites with intercalated architecture obtained (Figure 4.24, Table 4.17).

Table 4.17 : XRD results of WPU/OMt nanocomposites.

	NaMt ¹ (%)	2Theta (deg)	d-spacing (Å)	Increase in d-spacing (Å)
NaMt		8.91	9.91	-
NWPU1.1	1	6.45	13.69	3.78
NWPU1.3	3	6.52	13.54	3.63
NWPU2.1	1	6.04	14.62	4.71
NWPU2.3	3	5.80	15.22	5.31
NWPU2.5	5	5.68	15.55	5.64
NWPU3.1	1	6.55	13.48	3.57
NWPU3.3	3	6.65	13.28	3.37
NWPU3.5	5	6.76	13.06	3.15
NWPU4.1	1	5.77	15.30	5.39
NWPU4.3	3	6.16	14.33	4.42
NWPU4.5	5	6.39	13.82	3.91

¹Based on total solid of WPU.

4.3.3.3 Morphological analysis of nanocomposites

Morphological analysis of the nanocomposites was performed by using electron microscopy including SEM and TEM techniques in order to obtain more accurate results and local examination of the nanocomposite architecture. SEM micrographs illustrate that the interaction between the Mt particles and WPU matrix. SEM analysis was performed through their cross sectional view in order to observe distribution of Mt in the polymer matrix. In order to achieve that, the samples were plunged into liquid nitrogen bath and fractured. All the samples were coated with a layer of gold before the investigation. Initially, the locations of the Mt particles in all samples were identified using EDS semi quantitative analysis and investigated using

SEM. Interaction of Mt particles in WPU matrix can be clearly seen in micrographs which was supporting previous XRD measurements. WPU matrix successfully penetrates into intercalated galleries of the clay. According to EDS analysis Mt particles have the elemental values of O: 34.72%, Mg: 0.97%, Al: 13.42%, Si: 44.58%, Fe: 6.31%. The result of EDS analysis belong to Mt which is located in NWPU4.1 nanocomposite is shown as an example in Figure 4.25.

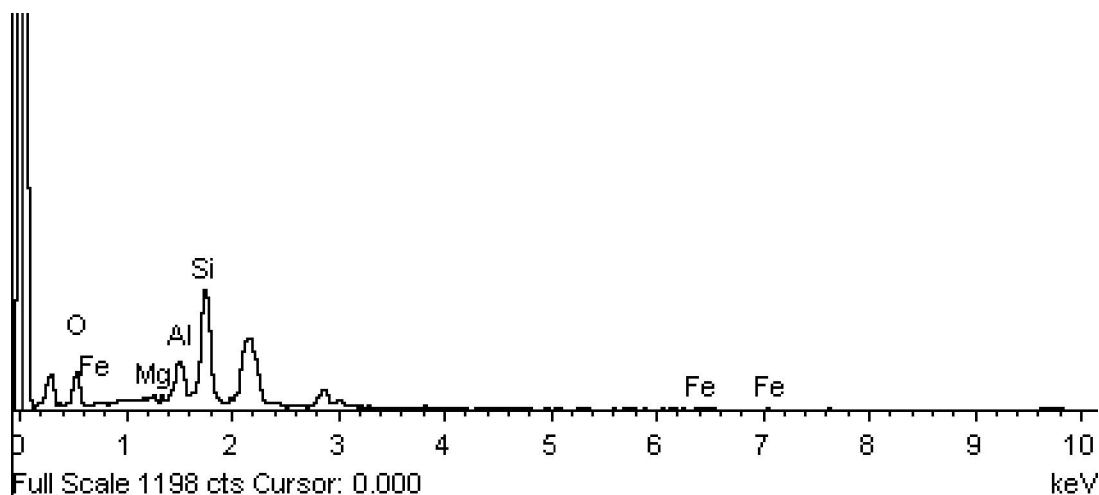


Figure 4.25 : EDS analysis of Mt clay.

The SEM images of the nanocomposite films are depicted in Figure 4.26. Initially, NaMt was investigated and layered structure of NaMt can easily be detected especially with x30000 magnification (Figure 4.26). Then, crosssectional nanocomposites samples were investigated. According to SEM micrographs of the nanocomposites, the Mt particles are mainly well distributed into the polymer film. Polymer matrix efficiently penetrates within the galleries of Mt particles in all linear WPU (NWPU1, NWPU4) and crosslinked WPU-urea (NWPU2, NWPU3) nanocomposites. However, there are also aggregated Mt particles, which are also observed. The aggregation tendency of Mt platelets increases by increase in Mt loading. As a result of the SEM analysis, it can be said that the architecture of the nanocomposites is intercalated.

On the other hand, SEM technique is limited for total identification of the morphology of Mt, which is located into the nanocomposites films. TEM analysis provides much more information regarding the architecture of nanocomposites. More local information is gained via TEM technique such as distribution of platelets of OMt particles.

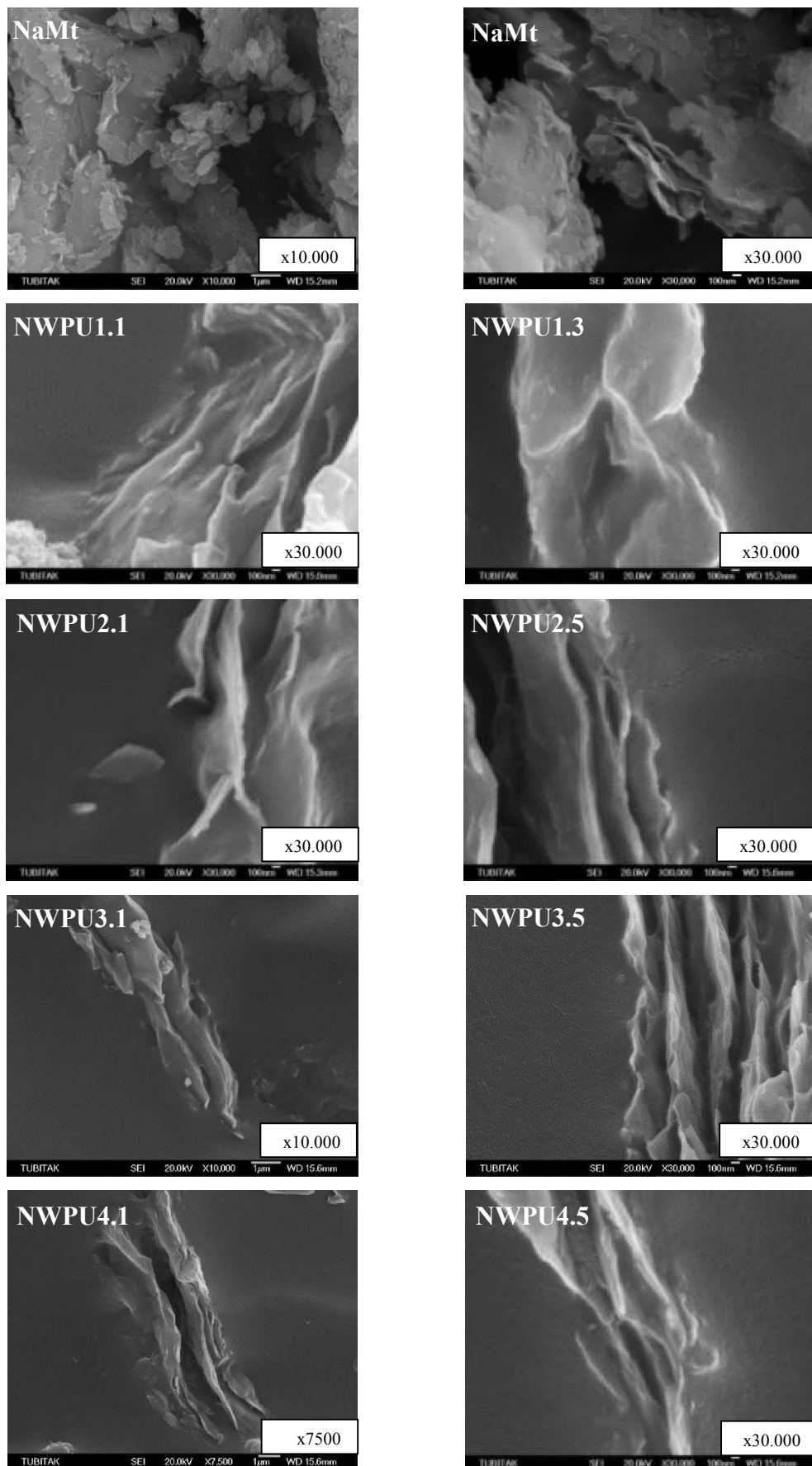


Figure 4.26 : SEM micrographs of Mt and nanocomposites.

In contrast to the XRD, conventional TEM analysis can directly provide more information in real space, in a localized area, and on morphology and defect structures, which are necessary for determining the nature of the nanocomposites. Because of limited information of XRD it is difficult to have determining conclusions about the structure of nanocomposites.

Linear WPU nanocomposite samples for TEM analysis were prepared by solvent-cast method. Dilute solutions of NWPU1 and NWPU4 series using NMP as a solvent with the ratio of 1% (w/w). Then, the solutions were dropped on a carbon-plated grid and finally they were dried in an oven at 60°C for a week. TEM analysis of crosslinked WPU nanocomposites (NWPU2 and NWPU3 series) was not performed by solvent casting method due to their insolubility in solvent. Their analysis was carried out by ultramicrotome sample preparation technique which includes cutting of extremely thin slices of the samples.

TEM micrographs of the nanocomposites of samples WPU1, WPU2, WPU3 and WPU4 series are illustrated in Figure 4.27 and Figure 4.28. The dark lines in the micrographs represent the intersections of clay layers, and the spaces between the dark lines were interlayer spaces. It was indicated that Mt layers well distributed in the WPU matrix which denote the dispersion of clay layers in the polymer and the formation of nanocomposites. There are some clusters of agglomerated Mt particles observed which could be happened during sample preparation by solvent casting technique. At higher magnification, it can be seen that the Mt is mostly intercalated through WPU matrix .

As a result, according to aforementioned SEM and XRD results, the NWPU nanocomposites can be apparently regarded as nanocomposites with mostly intercalated structures of Mt. The results are also accomodating with TEM micrographs which denote intercalated and partially exfoliated structures of the nanocomposites.

In addition, interlayer spacing of the nanocomposite samples were roughly calculated from the TEM micrographs. According to the measurements, the interlayer spacings were 0.84, 1.04, 0.95 and 1.47 nm for NWPU1.1, NWPU1.3, NWPU4.1 and NWPU4.3 respectively. However, the distance was around 13nm for WPU2.5.

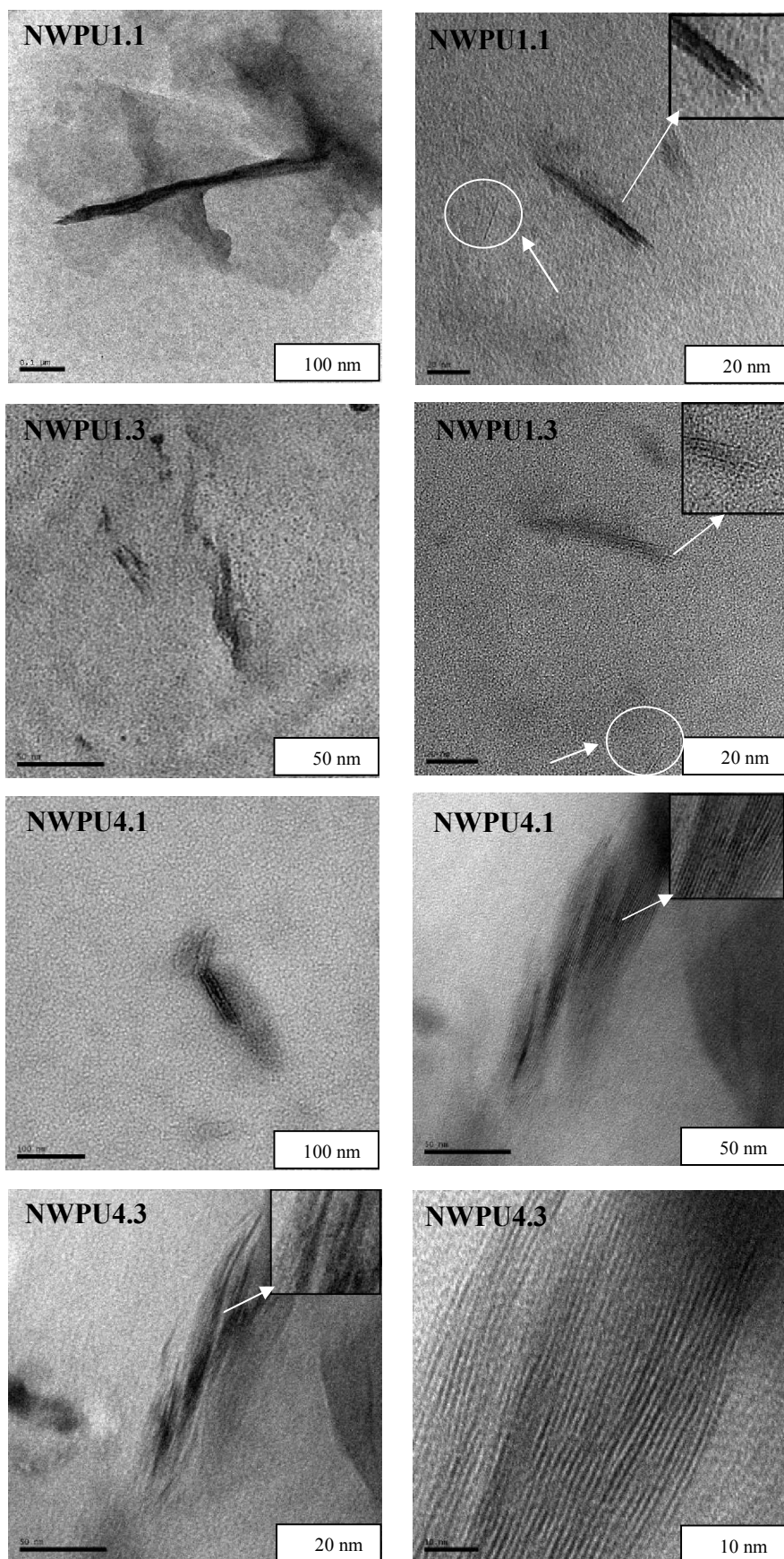


Figure 4.27 : TEM micrographs of linear WPU nanocomposites.

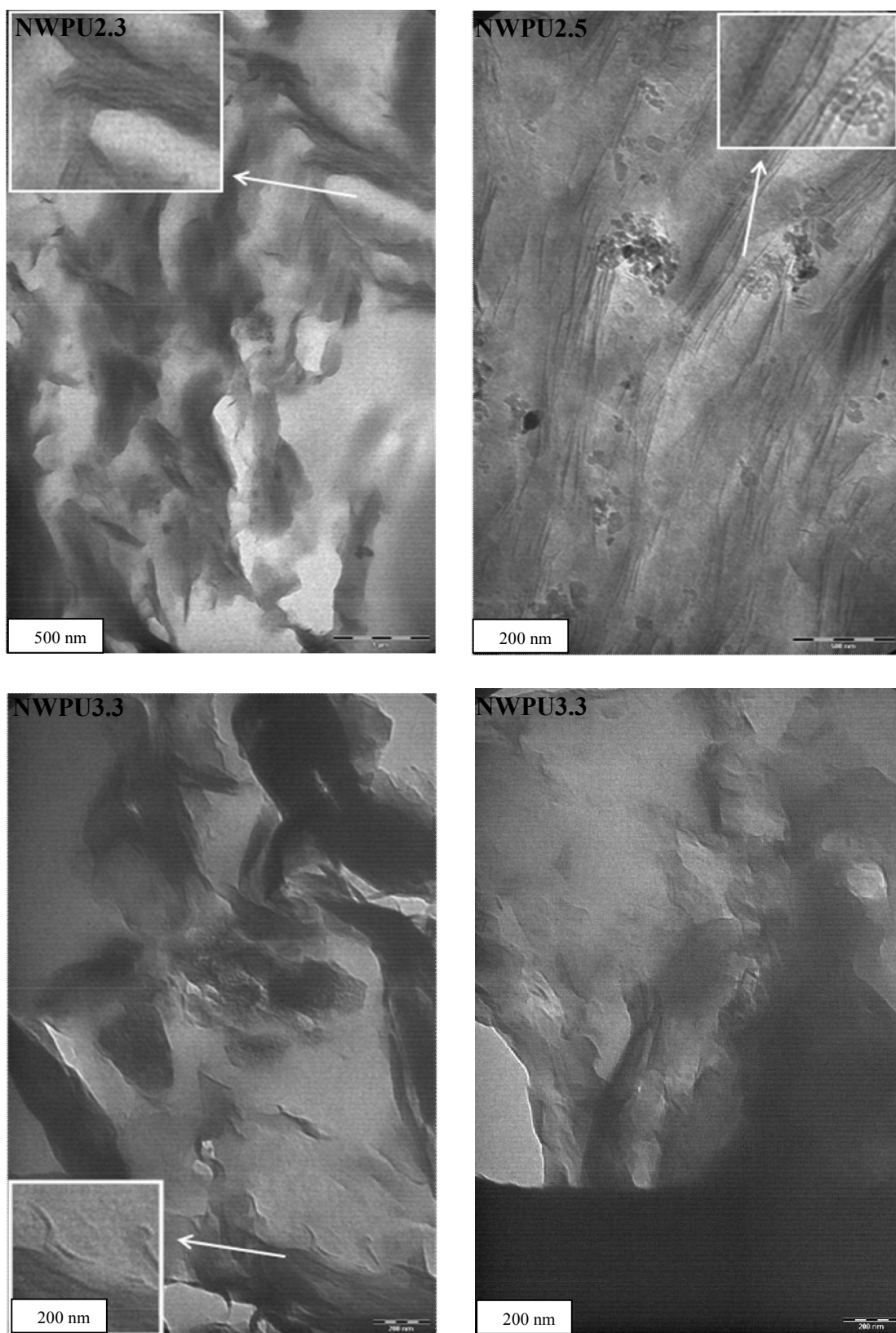


Figure 4.28 : TEM micrographs of crosslinked WPU-urea nanocomposites.

4.3.3.4 Thermal analysis of polymers and nanocomposites

The effect of Mt on thermal resistance of the nanocomposites was investigated by using TGA and DSC methods. Both TGA and DSC analysis were performed in nitrogen and oxygen atmosphere. Firstly, degradation profile of the neat polymers were examined. The results were quite different from each other depending on the type of soft segment, hard segment content, Mw or crosslinking .

TGA diffractograms of neat polymers are depicted in Figure 4.29. Low temperature degradation peaks at around 200-350°C denote the degradation of rigid segments formed by urethane and urea linkages. However, compounds which degrade above 350°C are the soft segments in WPU polymers (Cakic et al., 2009, Cakic et al., 2010; Cervantes et al., 2009). Therefore, investigation of the weight percent of residues at 300°C (W_{300}) and 450°C (W_{450}) is very important. The hard segment content (w/w) of the polymer and nanocomposites are as follows; WPU1>WPU3>WPU2>WPU4. If the W_{300} values are examined, the amount of residues are following the order of WPU4>WPU2>WPU3>WPU1 which is compatible with the literature.

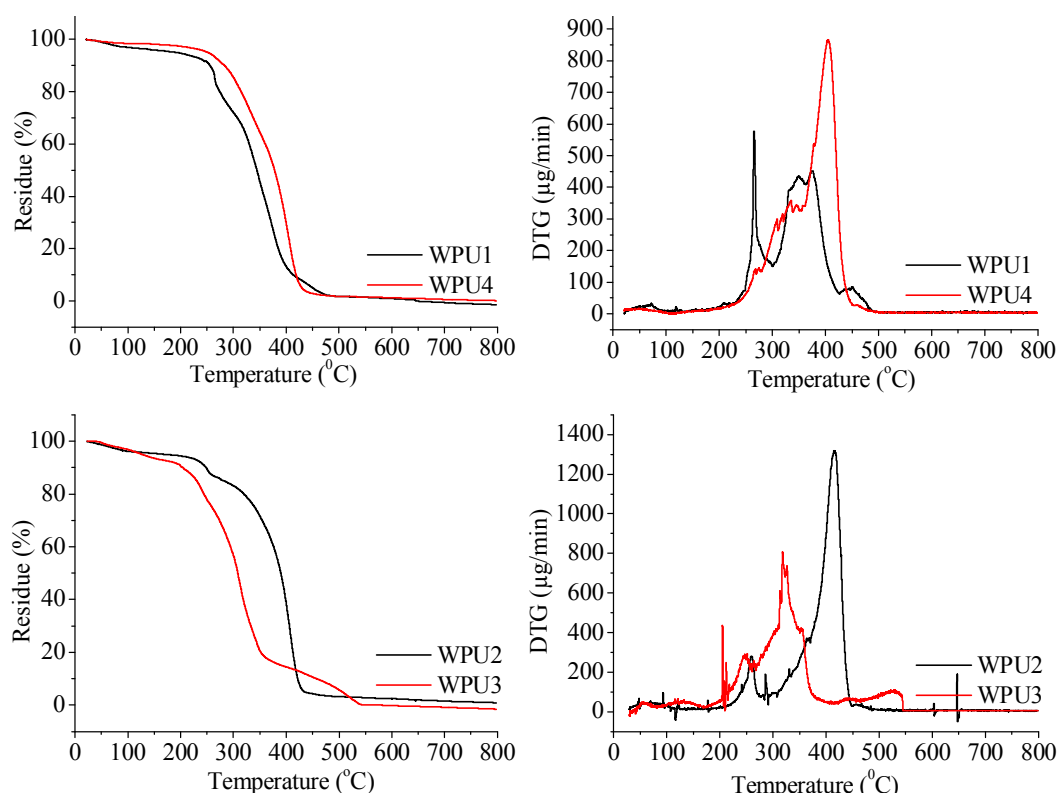


Figure 4.29 : TGA and DTG curves of WPU polymers in N₂ atmosphere.

The results of TGA analysis belong to neat polymers and nanocomposites which are extracted from the TGA thermograms are given in Table 4.18. If the linear WPU are considered, it could easily be seen that the thermal resistance of WPU4 was apparently better than WPU1. The maximum decomposition temperature ($T_D^{\max}$) of WPU4 is 406°C whereas 375°C for WPU1 (Table 4.18). In addition, both T_{30} and T_{80} values which are corresponded to the temperature at which 30% and 80% weight loss of WPU4 higher than WPU1. This can be due to WPU4 having higher Mw compared to WPU1. Besides, WPU4 having PTAA soft segment with ester units indicate better thermal resistance. However, if crosslinked WPUs are considered, thermal resistance of WPU2 was much higher compared to WPU3. The $T_D^{\max}$ and both T_{30} and T_{80} values of WPU2 are higher than WPU3 (Table 4.18). This can be due to soft segment of WPU2 (PEG1500) having primary hydroxyl group with higher reactivity, hence the ability of making intense crosslinking compared to soft segment of WPU3 (PPG1000). This result is also appropriate with the literature (Cakic et al., 2009).

Table 4.18 : TGA results of WPU polymers and nanocomposites in N₂ atmosphere.

Sample	$T_D^{\max}$ (°C) ¹	W_R (%) ²	T_{30} (°C) ³	T_{80} (°C) ³	W_{300} (%) ⁴	W_{450} (%) ⁴	Char (%)
WPU1	375	27.1	307.1	385.1	45.8	13.0	0.0
NWPU1.1	391	17.3	315.2	407.3	58.9	23.9	2.3
NWPU1.3	403	12.3	312.1	421.2	54.3	27.6	5.8
WPU2	409	24.5	354.3	412.2	71.6	38.1	0.8
NWPU2.1	413	25.0	357.7	417.2	72.2	41.3	0.9
NWPU2.3	410	29.6	362.6	417.9	74.5	43.6	5.3
NWPU2.5	407	32.8	359.1	417.2	73.2	42.0	4.9
WPU3	318	50.6	282.5	362.2	62.3	11.1	0.0
NWPU3.1	329	29.9	289.5	386.3	61.8	15.1	3.1
NWPU3.3	336	41.0	283.5	388.9	60.8	14.1	2.5
NWPU3.5	344	33.8	290.7	423.0	64.1	17.8	6.6
WPU4	406	20.3	336.3	405.4	84.9	2.9	0.1
NWPU4.1	401	22.5	332.4	403.2	85.0	4.0	0.1
NWPU4.3	396	29.2	338.8	406.2	86.1	9.8	5.3
NWPU4.5	388	31.1	339.0	412.3	87.6	13.7	9.5

¹ $T_D^{\max}$: Maximum weight loss temperature.

² W_R : Weight percent of residue at maximum weight loss temperature.

³ T_{30} and T_{80} : The temperature at which 30% and 80% weight loss.

⁴ W_{300} and W_{450} : Weight percent of residue at 300 and 450°C.

The thermal resistance of the NWPU nanocomposite films were also analyzed by TGA under nitrogen. The thermograms of linear WPU nanocomposites are illustrated in Figure 4.30 and their detailed analysis values were given in Table 4.18. In general, Mt content increases the thermal stability of both linear WPU nanocomposites. $T_D^{\max}$

value of NWPU1 series raises with increasing Mt content. However, the opposite effect occur for NWPU4 series. NWPU1.1 having 1% Mt content shows better thermal resistance in low degradation temperatures by increasing of T_{30} and W_{300} values whereas thermal resistance of NWPU1.3 having 3% Mt is better in higher degradation temperatures by increasing of T_{80} and W_{450} values compared to neat WPU1 polymer. Unlike the NWPU1 series nanocomposites, weight percent of residue at maximum weight loss temperature (W_R) is increased with Mt content in NWPU4 series nanocomposites. Besides, thermal resistance of NWPU4 series is developed in both low and high temperature degradation profiles by increasing T_{30} , T_{80} and W_{300} , W_{450} values with increasing Mt content and reach their maximum value with 5% Mt content (NWPU4.5). In addition, char residues of both NWPU1 and NWPU4 series increased with increasing Mt content which indicate also thermal stability of the nanocomposites.

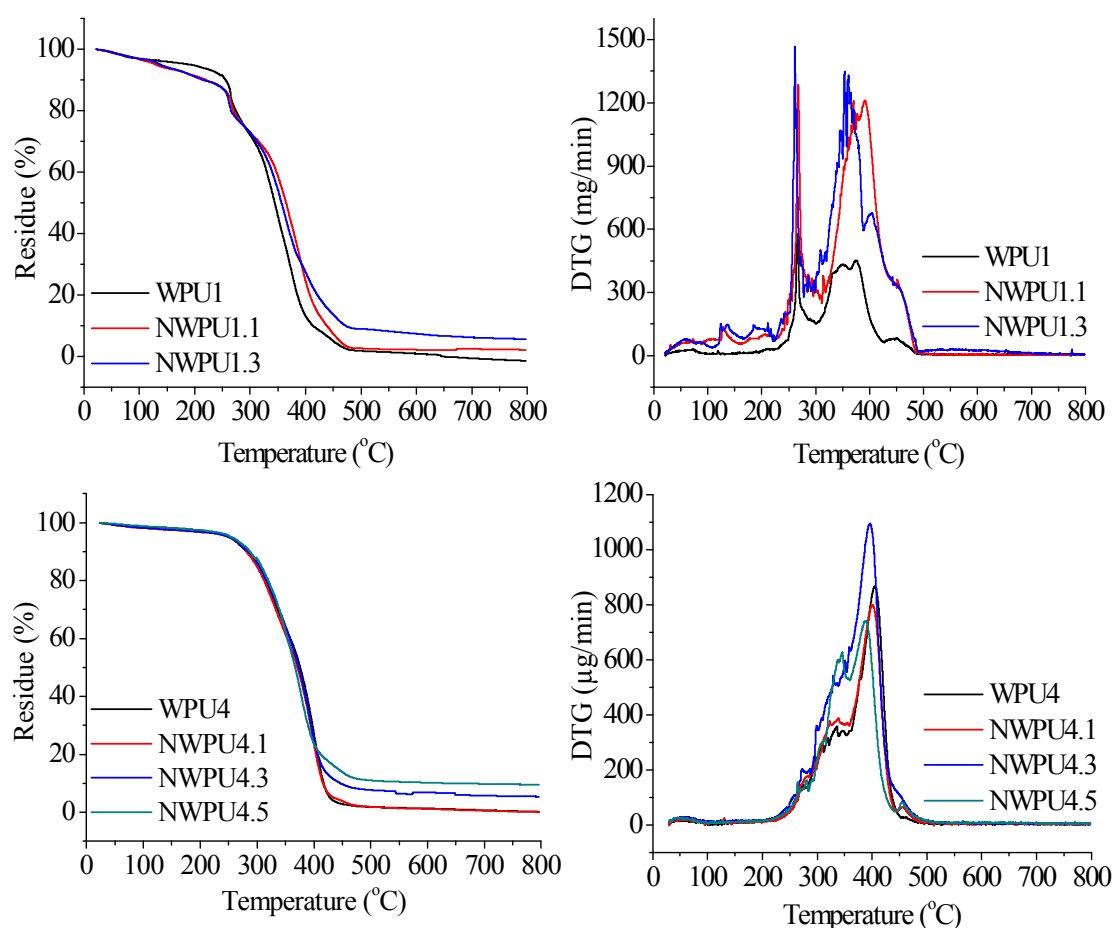


Figure 4.30 : TGA and DTG curves of linear nanocomposites in N_2 atmosphere.

The TGA thermograms of crosslinked WPU nanocomposites are illustrated in Figure 4.31 and detailed analysis values are given in Table 4.18. Similar results are

observed if the crosslinked WPU nanocomposites are considered. In NWPU2 series, thermal resistance increases to their highest value in both low and high temperature degradation values range with 3% Mt content (NWPU2.3) by increasing T_{30} , T_{80} and W_{300} , W_{450} values. However, $T_D^{\max}$ values are lowered with increasing Mt content. Similarly, in NWPU3 series, thermal resistance increase to their highest value in both low and high temperature degradation temperatures by increasing T_{30} , T_{80} and W_{300} , W_{450} values.

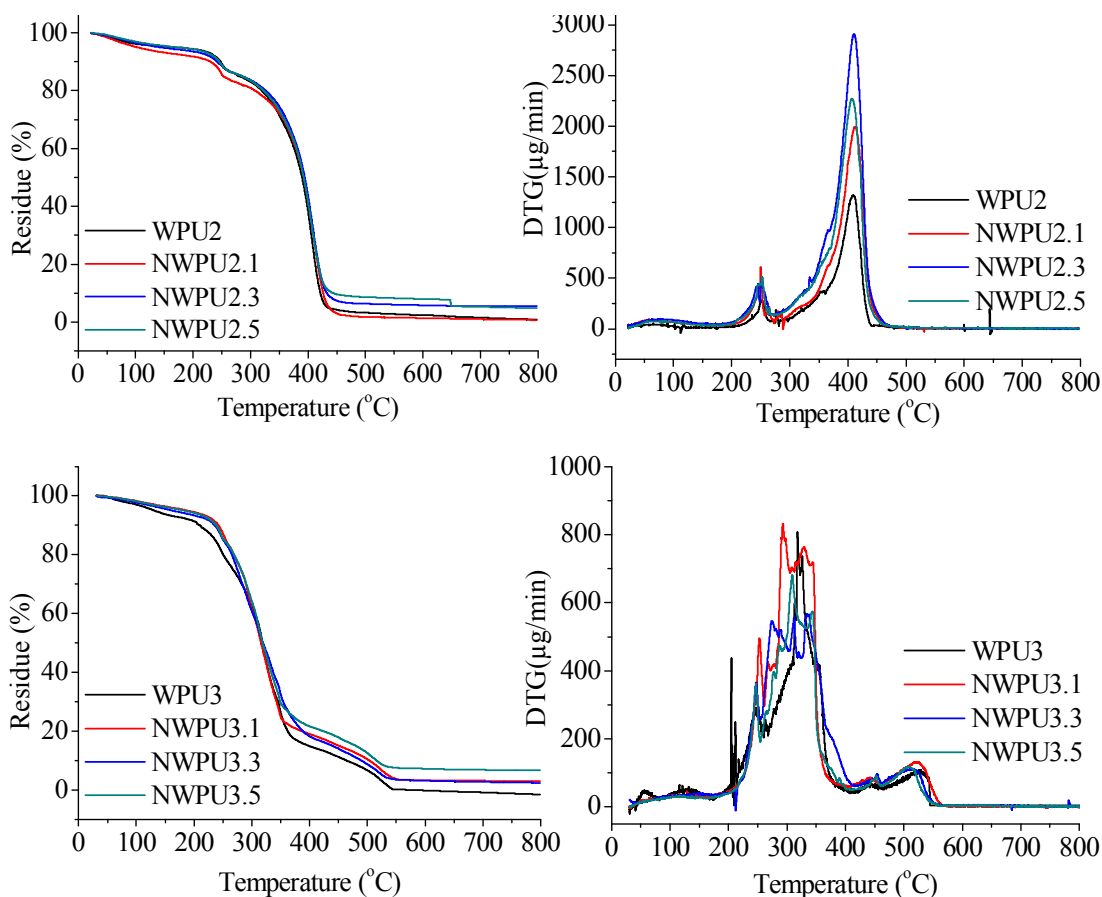


Figure 4.31 : TGA and DTG curves of crosslinked nanocomposites in N_2 atmosphere.

On the other hand, the increase rate reduces with 3% Mt content (NWPU3.3) and maximum increase is observed for NWPU3.5 having 5% Mt content (Table 4.18). The ash contents also confirm the increasing of thermal stability especially with 3% Mt (NWPU2.3) and 5% Mt (NWPU3.5).

The results indicate that Mt behaves as a barrier against thermal degradation in all nanocomposites were prepared by different soft segment and different processing conditions. It is observed that, thermal stability of the nanocomposites generally

showed tendency to increase by means of thermal insulation effect of clay. However, degradation profile is quite different for each group of polymers and nanocomposites. Consequently, the mechanism of the gained thermal stability of the nanocomposites can be explained by interactions of WPU with Mt particles having high thermal stability. Besides, chain motions of polymer molecules in these silicate layers are limited, therefore, thermal properties of the nanocomposite films increased. The results are consistent with the literature (Kim et al., 2005; Ni et al., 2004).

TGA curves of linear and crosslinked WPU polymers are shown Figure 4.32 which was performed under oxygen atmosphere. It is observed that degradation profile of the all WPU polymers are similar if the analysis is run whether under nitrogen or oxygen atmosphere. However, derivative curves (DTG), which are narrower than those analyzed under nitrogen, show that more rapid degradation is occurred.

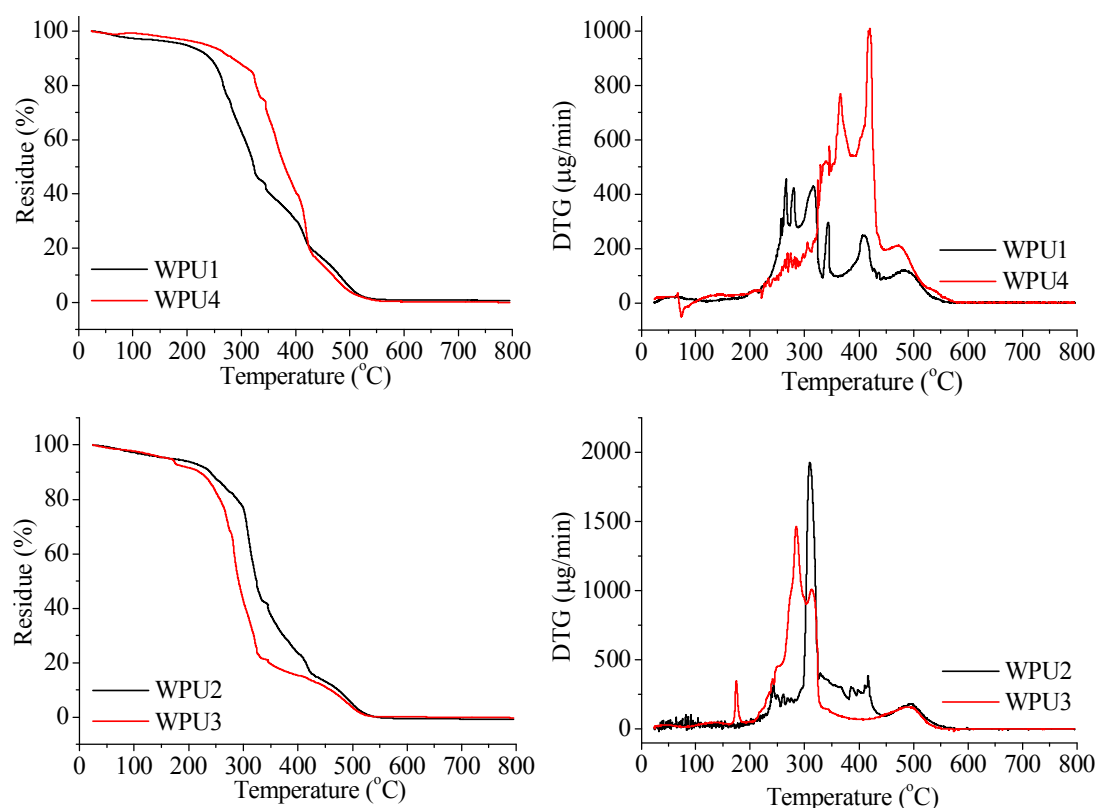


Figure 4.32 : TGA and DTG curves of WPU polymers in O₂ atmosphere.

On the other hand, degradation profiles of the neat polymers and the nanocomposites show slightly different behaviour under oxygen if compared to profiles under nitrogen atmosphere. Comparison of TGA data of the neat polymers and the nanocomposites under nitrogen and oxygen atmosphere were demonstrated in Table 4.19. According to decomposition data, decomposition rates of the neat

polymers change when the analysis performed under oxygen which can be clearly seen from the Table 4.19. The 30% weight loss temperatures (T_{30}) value decrease in WPU1, WPU2, WPU3 series polymers and their nanocomposites whereas, increase in WPU4 series. It can be due to WPU4 series polymer and nanocomposites having higher Mw, having ether-ester type polyol and having lowest hard segment content (Cervantes et al., 2009). The same effect is also observed at the residues at higher temperatures (W_{450}). Besides, at high temperature residues (T_{80}) and low temperature degradation point (W_{300}), thermal resistance increases under oxygen. This can be due to formation of metastable oxidation products such as isocyanurate and substituted urea which is consistent with the literature (Berta et al., 2006). In addition, dimerisation of isocyanates to carbodiimides prevents complete volatilisation of resulting chain fragments. Because, carbodiimides later reacts with alcohol groups to give relatively stable substituted ureas.

Table 4.19 : Comparison of TGA results of WPU polymers and nanocomposites in N_2 and O_2 atmosphere.

Sample	T_{30} in N_2 ($^{\circ}C$) ¹	T_{30} in O_2 ($^{\circ}C$) ¹	T_{80} in N_2 ($^{\circ}C$) ¹	T_{80} in O_2 ($^{\circ}C$) ¹	W_{300} in N_2 (%) ²	W_{300} in O_2 (%) ²	W_{450} in N_2 (%) ²	W_{450} in O_2 (%) ²	Char in N_2 (%) ²	Char in O_2 (%) ²
WPU1	307.1	284.2	385.1	428.6	45.8	63.4	13.0	16.2	0.0	0.7
NWPU1.1	315.2	298.4	407.3	432.6	58.9	69.4	23.9	17.4	2.3	0.1
NWPU1.3	312.1	291.0	421.2	450.1	54.3	67.1	27.6	20.1	5.8	2.4
WPU2	354.3	306.4	412.2	414.7	71.6	77.2	38.1	13.2	0.8	0.0
NWPU2.1	357.7	309.3	417.2	392.9	72.2	75.1	41.3	13.0	0.9	0.4
NWPU2.3	362.6	305.8	417.9	426.3	74.5	72.2	43.6	16.9	5.3	2.8
NWPU2.5	359.1	321.6	417.2	426.2	73.2	72.2	42.0	17.2	4.9	3.4
WPU3	282.5	273.0	362.2	347.1	62.3	42.7	11.1	11.2	0.0	0.1
NWPU3.1	289.5	267.5	386.3	363.2	61.8	28.7	15.1	12.9	3.1	1.0
NWPU3.3	283.5	266.5	388.9	416.1	60.8	30.7	14.1	16.1	2.5	2.4
NWPU3.5	290.7	276.3	423.0	432.6	64.1	58.0	17.8	17.4	6.6	5.1
WPU4	336.3	347.7	405.4	425.0	84.9	87.8	2.9	13.7	0.1	0.0
NWPU4.1	332.4	345.0	403.2	431.7	85.0	86.9	4.0	15.2	0.1	1.8
NWPU4.3	338.8	345.0	406.2	428.3	86.1	87.3	9.8	10.3	5.3	3.0
NWPU4.5	339.0	345.0	412.3	426.4	87.6	86.2	13.7	14.9	9.5	2.9

¹ T_{30} and T_{80} : The temperature at which 30% and 80% weight loss.

² W_{300} and W_{450} : Weight percent of residue at 300 and 450 $^{\circ}C$.

The nanocomposites were also analyzed under oxygen atmosphere in order to investigate the effect of Mt to their thermal resistance in the presence of oxygen. In general, similar effect was observed as in the analysis which were carried out in nitrogen. Thermal resistance of the nanocomposites increases in the presence of Mt. Besides, the general trend of the decomposition mechanism is quite similar to those

performed in nitrogen atmosphere. However, there are little differences in the decomposition temperatures.

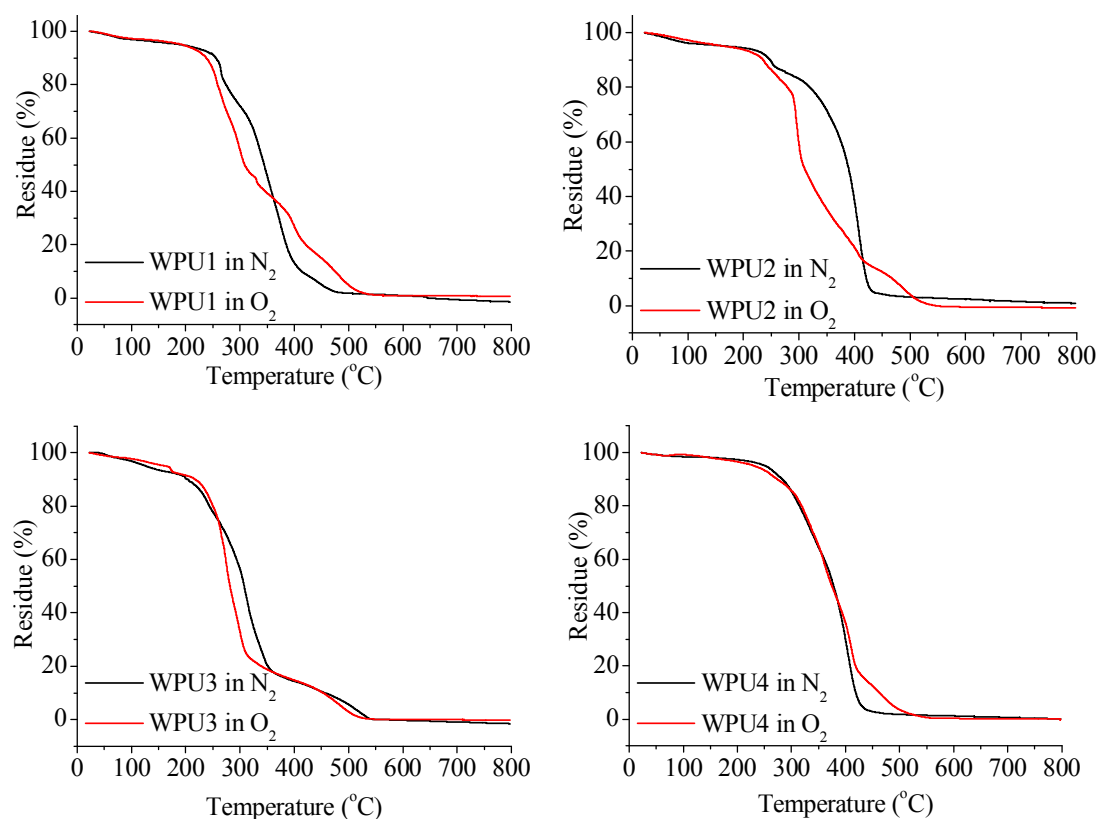


Figure 4.33 : Comparison of TGA curves of WPU polymers in N_2 and O_2 atmosphere.

In the case of linear WPU nanocomposites, low temperature degradation values increase for NWPU1 series by increasing W_{300} and T_{30} values in the presence of Mt. There is an increase in T_{300} values whereas no increase observed in W_{300} values of NWPU4 series (Figure 4.34). In the case of crosslinked WPU nanocomposites, low temperature degradation values of NWPU2 such as T_{30} increase whereas W_{300} values decrease in the presence of OMt. However, little increase in T_{30} values is observed for NWPU3 (NWPU3.5) and dramatic increase in W_{300} values of NWPU3 is determined (NWPU3.5). Besides, dramatic increase is detected in high temperature degradation values such as T_{80} and W_{450} in NWPU3 series (NWPU2.5). Detailed TGA data can be seen in Table 4.19.

This results is also compatible with the literature which has been proved that the introduction of clays into polymeric matrices can improve their thermal stability due to its barrier effect which delays the release of degradation products compared to neat polymer (Cervantes et al., 2009; Kiliaris et al., 2010).

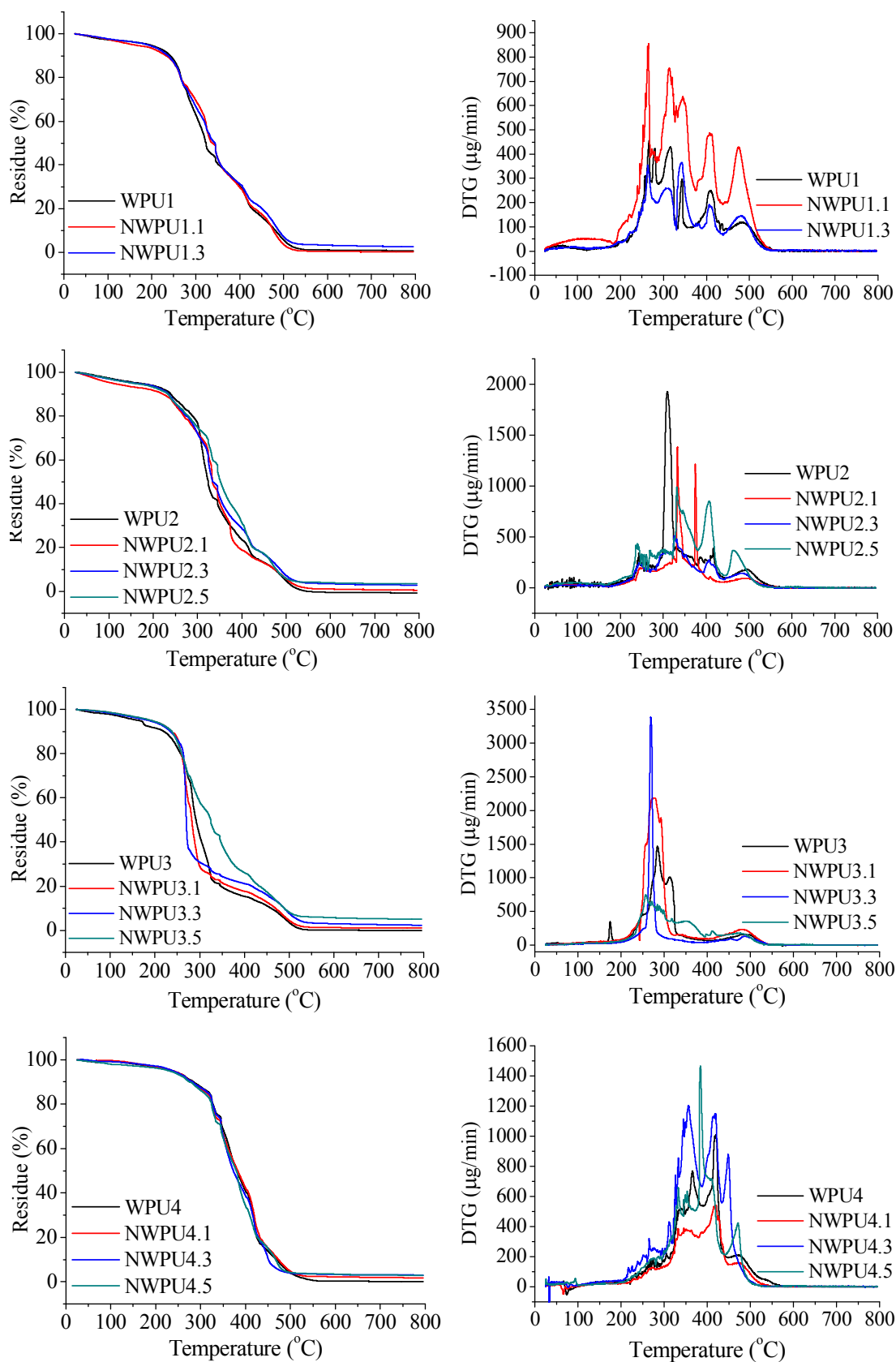


Figure 4.34 : TGA and DTG curves of nanocomposites in O_2 atmosphere.

The thermal characteristics of the neat polymers and nanocomposites were also evaluated by DSC analysis. DSC curves of neat polymers are depicted in Figure 4.35 and detailed results were given in Table 4.20. The DSC curves of WPU polymers indicate two glass transition temperature (T_g), one was at low temperature which belongs to soft segment and other belongs to hard segment.

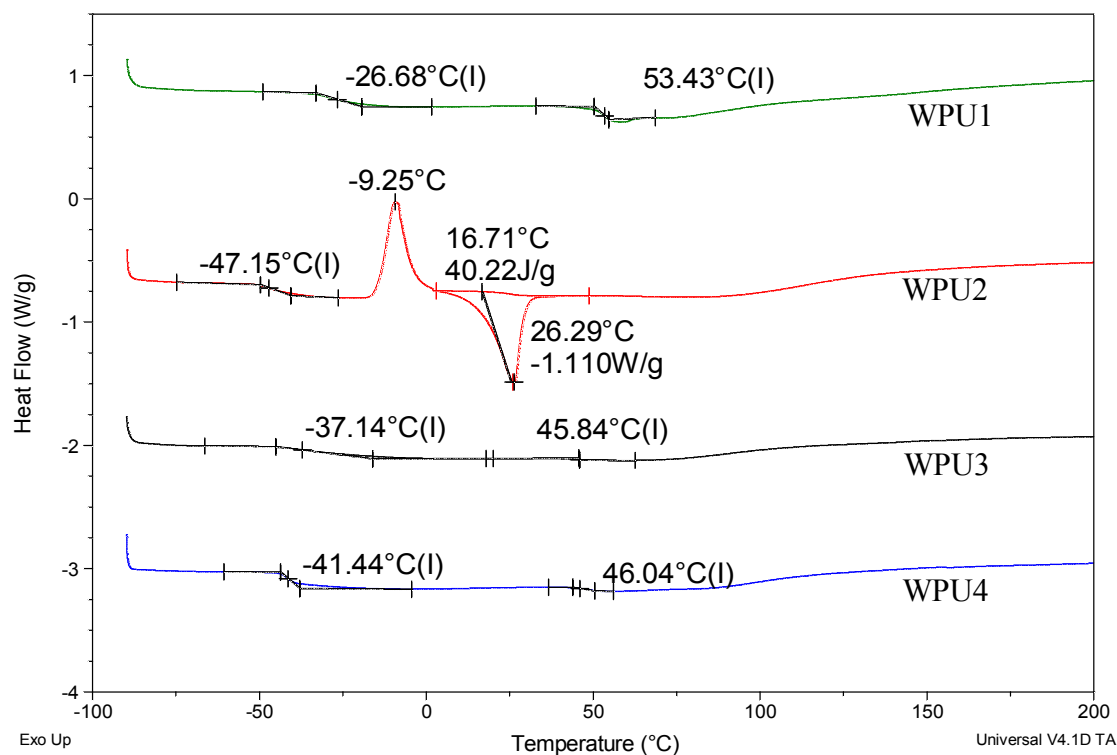


Figure 4.35 : DSC curves of linear and crosslinked WPU polymers.

In the case of linear WPU polymers, T_{g1} and T_{g2} values of WPU1 are higher than those of WPU4. The reason of increasing T_g of soft segment (T_{g1}) is having greater number of hard segment residing within the soft phase. Therefore, the mobility of soft segment is suppressed by the hard segment. This result is also compatible with the literature (Kim et al., 2000; Miller et al., 1985). However, thermal decomposition temperatures (T_{d1} and T_{d2}) of WPU4 is higher than WPU1 also owing to WPU1 having higher hard segment content compared to WPU4. Because, degradation of hard segment content is preferential which is also meets TGA results.

In the case of crosslinked WPU-urea polymers WPU2 has lower T_g values if compared to WPU3 which can be due to WPU2 having higher dendritic structure through DMA units which is also confirmed by NMR analysis. This hyperbranched architecture of WPU2 causes lowering of T_g values due to increasing of chain flexibility (Elrehim et al., 2005). This result is also compatible with mechanical

analysis results. Exothermic crystallization peak is observed in WPU2 polymer at -9.25°C. However, it is not observed for WPU3. This can be due to crystallization of polyol segments (PEG1500) in dendritic structure of WPU2 through DMA which is confirmed by NMR analysis.

Table 4.20 : DSC values of WPU polymers and nanocomposites.

Sample	Tg ₁ (°C) ¹	Tc (°C) ²	Tg ₂ (°C) ¹	Td ₁ (°C) ³	Td ₂ (°C) ³
WPU1	-26.7	-	53.4	268.3	350.1
NWPU1.1	-32.0	-	49.0	266.9	326.1
NWPU1.3	-29.7	-	45.7	265.4	353.1
WPU2	-47.2	-9.2	16.7	250.6	351.9
NWPU2.1	-40.1	-10.8	17.0	247.9	335.7
NWPU2.3	-43.7	-2.6	17.3	250.3	349.5
NWPU2.5	-43.0	-2.2	17.4	252.1	330.7
WPU3	-37.1	-	45.8	258.2	338.9
NWPU3.1	-39.9	-	41.5	273.6	342.6
NWPU3.3	-40.7	-	41.4	269.4	332.7
NWPU3.5	-40.3	-	41.4	268.6	335.9
WPU4	-41.4	-	46.0	289.3	383.9
NWPU4.1	-36.3	-	49.4	263.1	395.2
NWPU4.3	-40.6	-	47.0	258.4	360.5
NWPU4.5	-39.8	-	57.7	241.5	341.6

¹Tg: Glass transition temperature.

²Tc: Crystallization temperature.

³Td: Decomposition temperature.

The effect of Mt content was also investigated for the nanocomposites by using DSC. In the case of linear WPU nanocomposites, Tg₁ and Tg₂ values both decrease with Mt content for NWPU1 series (Table 4.20). The reduction is 3-4°C for the soft segments (Tg₁) whereas 4-8°C for the hard segments. This can be due to changing of Mw in the presence of Mt. On the contrary, in NWPU4 series Tg₁ and Tg₂ values were raised especially with 1% Mt content (NWPU4.1) (Tg₁) by 2-6 °C and with 5% Mt content (NWPU4.5) (Tg₂) by 1-11°C. DSC curves of nanocomposites are depicted in Figure 4.34.

In the case of crosslinked NWPU2 nanocomposites, both Tg₁ and Tg₂ values raise with increasing Mt content (NWPU2.1, NWPU2.3, NWPU2.5). In addition, it was identified that crystallization temperature (Td) shifted from -9.25°C to -2.64°C (NWPU2.3) and -2.15°C (NWPU2.5). This result showed that Mt particles are successfully interacted with WPU2 polymer. On the contrary to NWPU2 series, both Tg₁ and Tg₂ values decrease with increasing OMt content in NWPU3 series. On the other hand, decomposition temperatures (Td₁ and Td₂) of all NWPU1, NWPU2,

NWPU3 and NWPU4 series change in the presence of Mt which indicate the interaction of Mt with polymers which indicates interaction of Mt with polymer matrix.

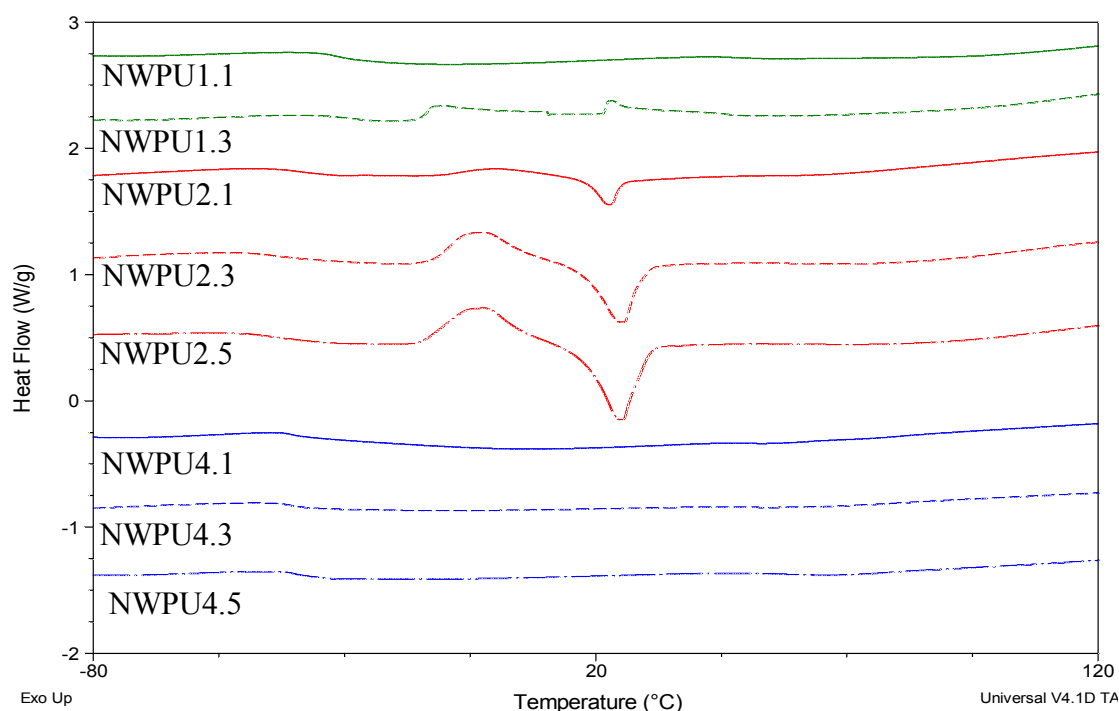


Figure 4.36 : DSC curves of nanocomposites.

As a result of thermal analysis, the effect of Mt content on thermal resistance of the nanocomposites are successfully investigated. Both TGA and DSC results show that thermal resistance of WPU nanocomposites raise by using certain amounts of Mt.

4.3.3.5 Mechanical analysis of nanocomposites

Tensile tests were performed to investigate the effect of Mt on mechanical properties of the nanocomposites. Mechanical properties of the linear and crosslinked neat polymers have already discussed. Their properties are highly dependant on type of soft segment, Mw of the resulting polymer, hard segment content for linear WPUs (WPU1 and WPU4). However, degree of crosslinking is the main factor affecting the mechanical properties for WPU2 and WPU3 series. The specimens were prepared as 1 mm thick in dog bone shape as explained before (EN ISO 527-1 and 2). It is observed that, Mt shows a remarkable effect on mechanical properties of the nanocomposites. As a general trend, both stress and elongation at break values change with the clay content in all nanocomposites. However, increasing or decreasing rate changes depending on the polymer type. The mechanical properties

are summarized in Table 4.21. Stress-strain curves of WPU polymers and their nanocomposites are presented in the Figure 4.37 and Figure 4.38.

Table 4.21 : Mechanical properties of WPU polymers and nanocomposites.

Sample	Mt content(%)	E-Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
WPU1	-	1.77	0.51	102
NWPU1.1	1	2.24	0.55	116
NWPU1.3	3	2.25	0.64	148
WPU2	-	1.40	0.66	76
NWPU2.1	1	2.31	0.82	54
NWPU2.3	3	2.68	1.02	67
NWPU2.5	5	8.06	1.18	91
WPU3	-	0.28	0.17	72
NWPU3.1	1	1.87	0.93	70
NWPU3.3	3	2.67	0.89	58
NWPU3.5	5	1.53	0.93	68
WPU 4	-	3.03	0.67	80
NWPU4.1	1	2.50	0.91	142
NWPU4.3	3	3.43	0.98	166
NWPU4.5	5	4.46	1.14	154

In the case of linear NWPU nanocomposites, tensile strength increases from 0.51 MPa (WPU1) to 0.64 MPa (NWPU1.3) in NWPU1 series. Elongation at break value also increases from 102% (WPU1) to 148% (NWPU1.3). In addition, elastic modulus increased from 1.77 MPa (WPU1) to 2.25 MPa (NWPU1.3). However, in NWPU4 series, tensile strength increases almost twice from 0.67MPa (WPU4) to 1.14MPa (NWPU4.5). Elongation at break value also increases nearly twice from 80% (WPU4) to 154% (NWPU4.5). The elastic modulus initially decreases to 2.50 MPa (NWPU4.1) but raises to 3.43 MPa (NWPU4.3) and 4.46 (NWPU4.5) with increasing OMT content.

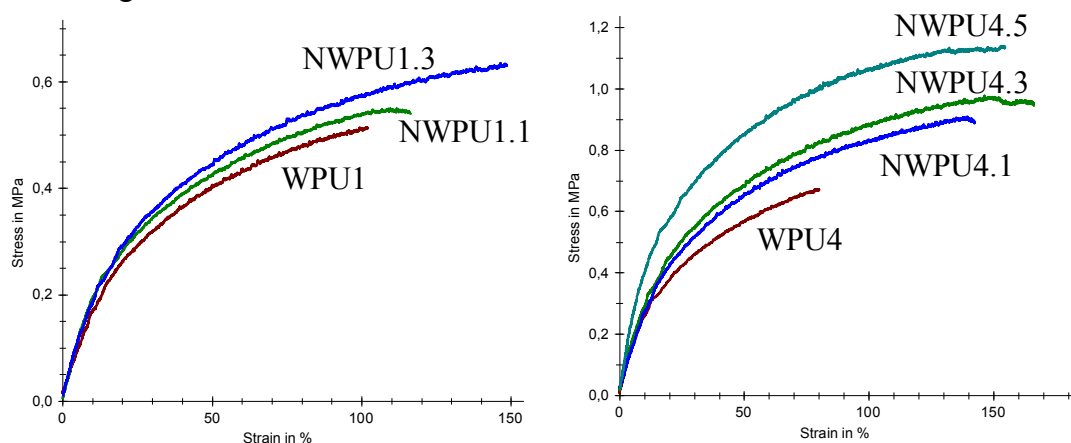


Figure 4.37 : Stress-strain curves of linear nanocomposites.

This result is also compatible with the XRD results in which NWPU4 series having higher increase in d-spacing compared to NWPU1 series proved to have better interaction of OMt with the polymer.

On the other hand, in the case of crosslinked NWPU nanocomposites, in NWPU2 series tensile strength increases almost twice from 0.66 MPa (WPU2) to 1.18 MPa (NWPU2.5). Elongation at break value increases from 76% (WPU2) to 91% (NWPU2.5). Although, little decrease to 54% (NWPU2.1) and 67% (NWPU2.3) is also observed. The elastic modulus increases from 1.40 MPa (WPU2) to 2.68 MPa (NWPU2.3). In addition, drastical increase to 8.06 MPa is observed (NWPU2.5) .

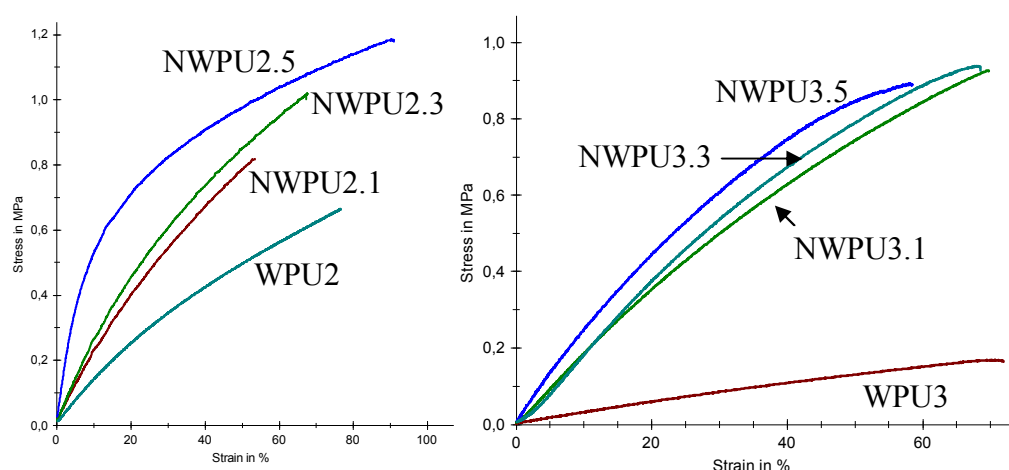


Figure 4.38 : Stress-strain curves of crosslinked nanocomposites.

However, quite different from NWPU2 nanocomposites, in NWPU3 series distinctive behaviour was observed. Tensile strength dramatically increases from 0.17 MPa (WPU3) to 0.93 MPa (NWPU3.1) with 1% content of Mt. Although, little decrease to 0.89 MPa (NWPU3.3) is observed and again increased to 0.93 MPa with increasing Mt content (NWPU3.5). However, in NWPU3 series, a little decrease on elongation at break values are observed with increasing Mt content. It decreases from 72% (WPU3) to 70% (NWPU3.1) and 58% (NWPU3.3) and again increases to 68% (NWPU3.5). The elastic modulus drastically increases from 0.28 MPa (WPU3) to 1.87 MPa (NWPU3.1) and 2.67 MPa (NWPU3.3). Besides, little decrease to 1.53 MPa is observed (NWPU3.5). The reason of showing quite different mechanical properties of NWPU3 series from NWPU2 series can be due to their quite different structure as well as worse interaction with Mt compared to NWPU2 series. This can also be identified from the XRD results which indicated the increase in d-spacing values of NWPU3 were lower than those of NWPU2 series. The comparative results

of tensile strength, elongation at break and elastic modulus values are depicted in Figure 4.39, 4.40 and 4.41.

Consequently, the effect of Mt on mechanical properties of the nanocomposites are investigated in terms of tensile strength, elastic modulus and elongation at break. As a result, unlike the traditional composites elongation at break values improve as well as the tensile strength owing to the reaction between hydroxyl groups of Mt compound and isocyanate segment. In addition, swelled clay can be regarded as a crosslinking center of polyurethane polymer, promoting not only the toughness but also the elongation of the nanocomposites. These results were consistent with the literature (Rama and Swaminathan, 2010; Rahman et al., 2007b; Kuan et al., 2004; Ma et al., 2001).

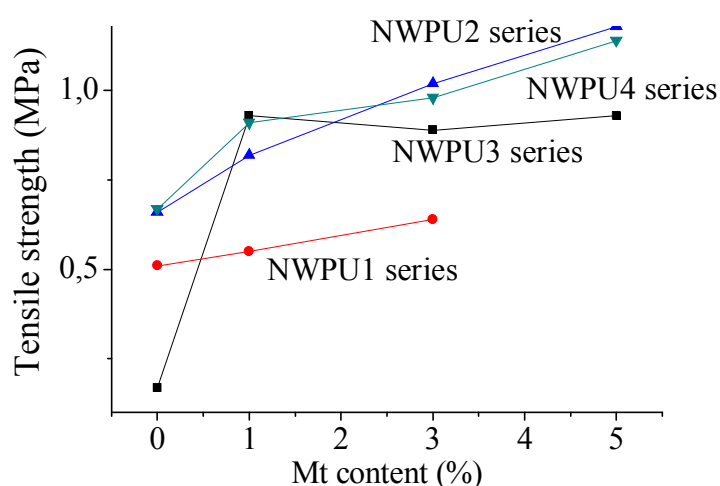


Figure 4.39 : The change of tensile strength values with Mt content.

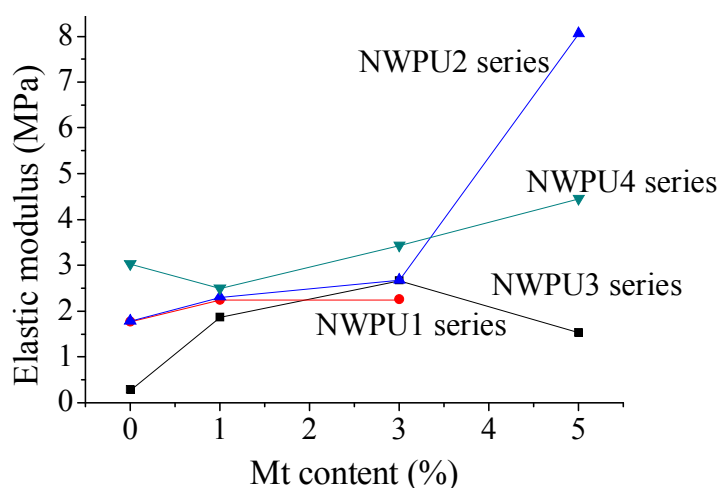


Figure 4.40 : The change of elastic modulus value with Mt content.

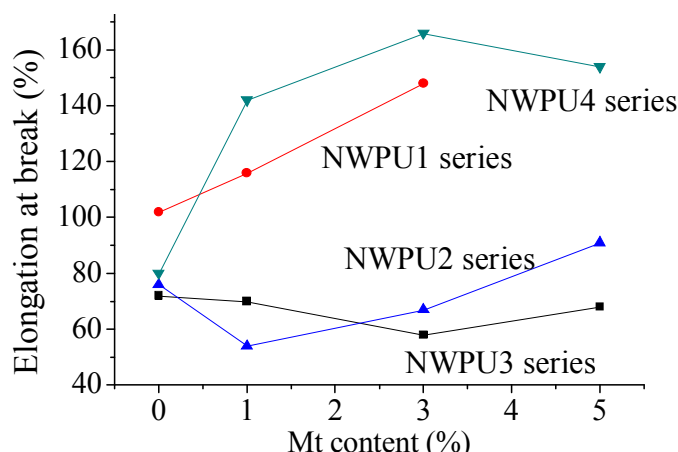


Figure 4.41 : The change of elongation at break values with Mt content.

4.4 Environmental Testing of WPU Polymers and Nanocomposites

The durability of the polymeric materials are studied under several weathering simulation conditions. The durability of these materials depends on the duration of interaction with the environment. Photo and oxidative degradation is the most important issues especially for polymers, which are applicable for outdoor usage. Among these environmental factors, the most applicable determination of photodegradation is performed by using UV irradiation.

4.4.1 Solar radiation testing

The aim of the solar radiation testing of WPU polymers and nanocomposites is to investigate the effect of accelerated solar atmosphere depending on polymer type and the presence of Mt. The test carried out at 1120 W/m²K irradiation and 44°C with 20h irradiated zone and 4 hours dark zone for per cycle.

All the neat polymers and nanocomposites degrade during the test. Although, FTIR spectrum of WPU4 is given as an example which is shown in Figure 4.42. Drastic changes are observed from the FTIR spectrums in structural bands of the WPU polymers such as N-H stretching bands at around 3300 cm⁻¹, C=O stretching at around 1700 cm⁻¹, C-N + δ N-H stretching band at around 1530 cm⁻¹, N-CO-O + st C-O-C stretching at around 1249 cm⁻¹ and 1040 cm⁻¹.

The weathering performance of the samples were examined by monitoring of light induced chemical changes via infrared absorbance characteristics using FTIR spectroscopy (Singh and Sharma, 2008; Schwalm et al., 2003). Several products containing carbonyl functions are expected to be manifested. Therefore, the increase

was occurred in the region where C=O absorbance of several decomposition products (around 1700 cm^{-1}). The results are evaluated by calculating carbonyl peak areas of the samples.

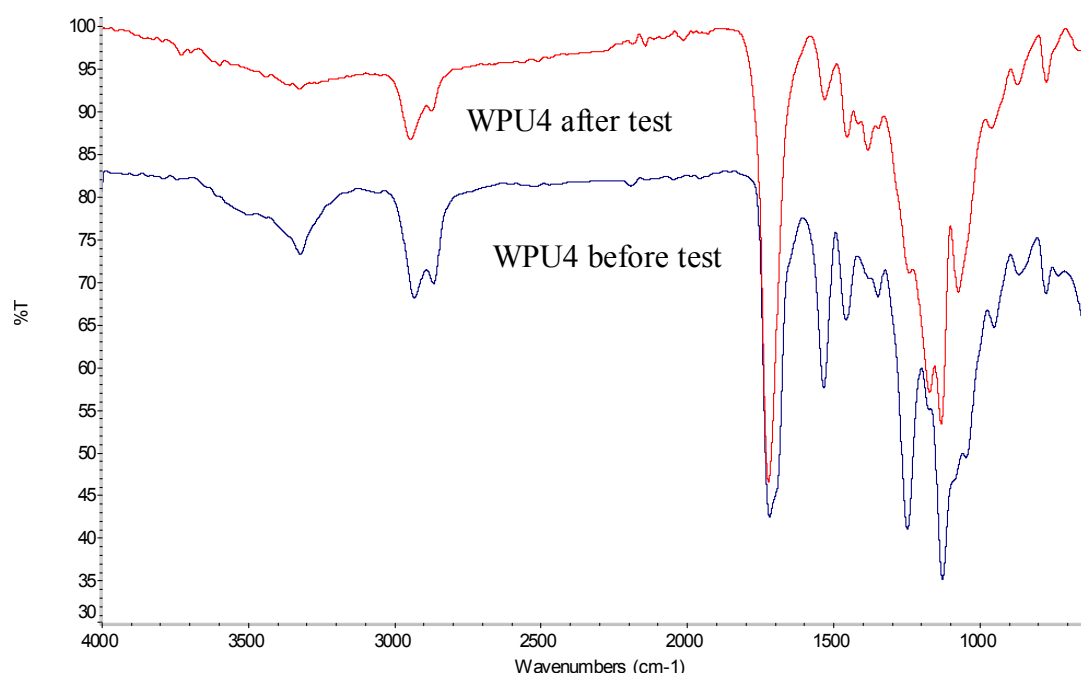
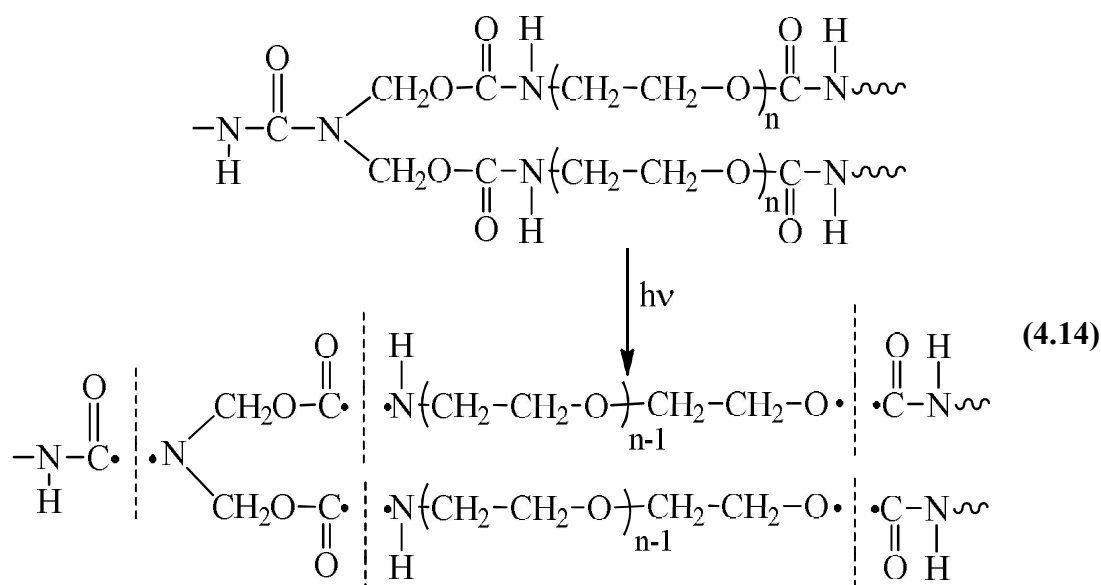
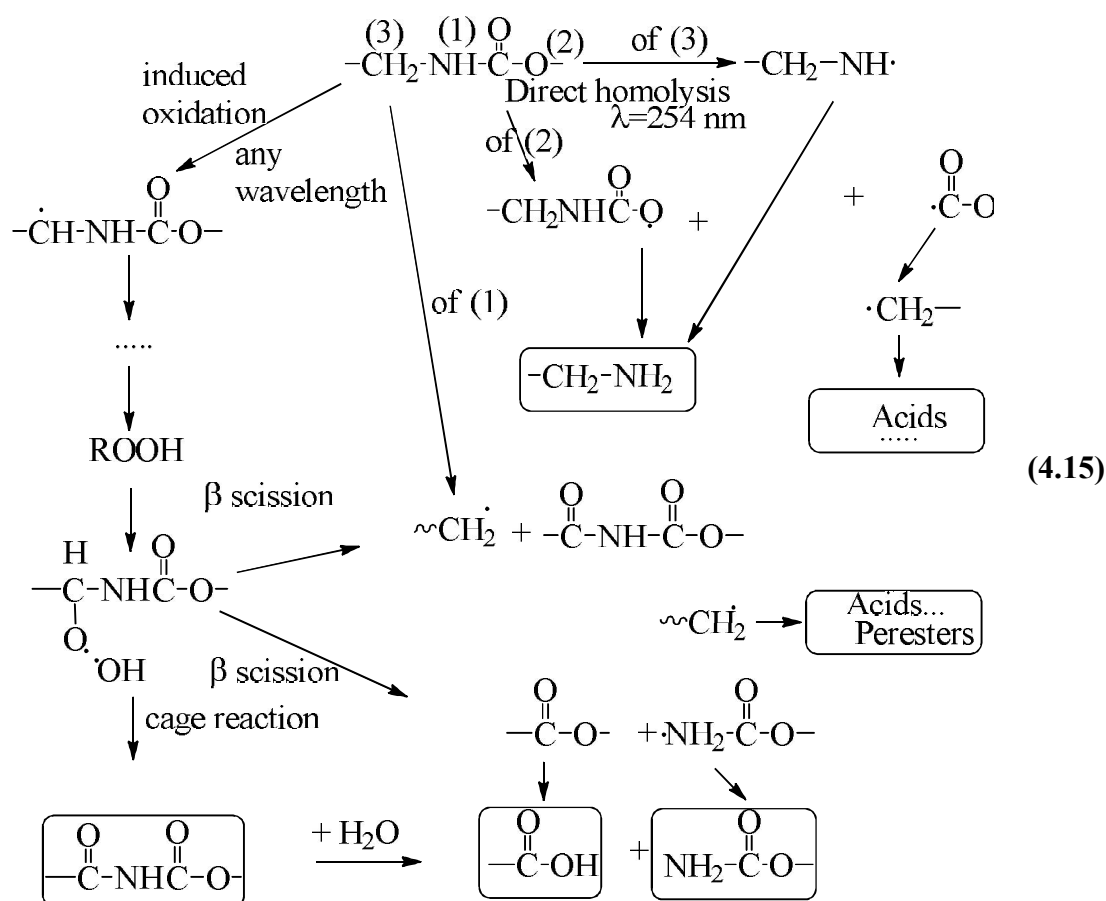


Figure 4.42 : Changes of FTIR spectrum of WPU4 during solar radiation test.

The degradation behavior of neat WPU polymers is quite different from each other. As is known, polyethers are more susceptible to light and free radical initiated oxidative degradation compared to polyesters. On the other hand, photodegradation of the WPU polymers are expected to be occurred through hard segment units (4.14 and 4.15) (Rosu et al., 2009; Wilhelm and Gardette, 1997).





In the case of linear WPU polymers, WPU4 is more stable against photo degradation having less hard segment content and containing polyol with polyester units as well as having higher Mw compared to WPU1 (Figure 4.43).

As a result, in the case of linear WPU polymers, the ratio of hard segment contents which are following as, $\text{WPU1} > \text{WPU4}$ (w/w) is effective. However, in the case of crosslinked WPU-urea polymers, dendritic structure is significant in the event of photodegradation.

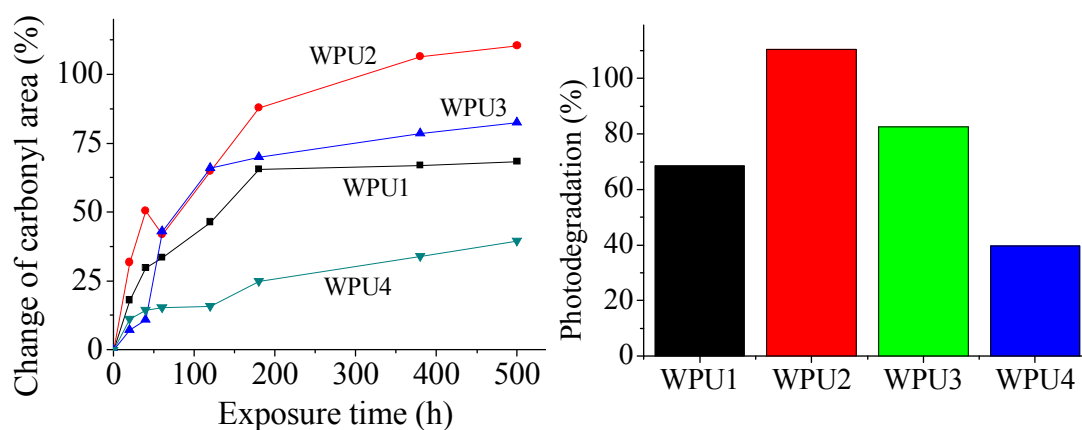


Figure 4.43 : Changes in carbonyl areas of WPU polymers during solar radiation test.

In the case of linear WPU nanocomposites, Mt addition accelerates the degradation process. In NWPU1 series, 1% Mt content does not show significant change (NWPU1.1) whereas with 3% Mt content, degradation rate raises by almost 12% (NWPU1.3) (Figure 4.44). Similar result was also observed for NWPU4 series. 1% content of Mt increases the degradation rate by 6% (NWPU4.1) and 5% content of Mt increases the rate upto 8% (Figure 4.45).

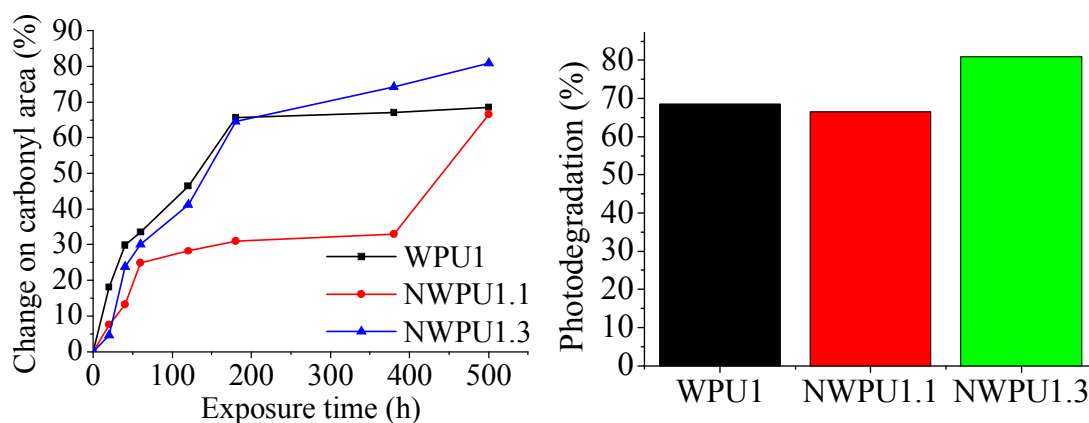


Figure 4.44 : Changes in carbonyl areas of WPU1 and NWPU1 nanocomposites during solar radiation test.

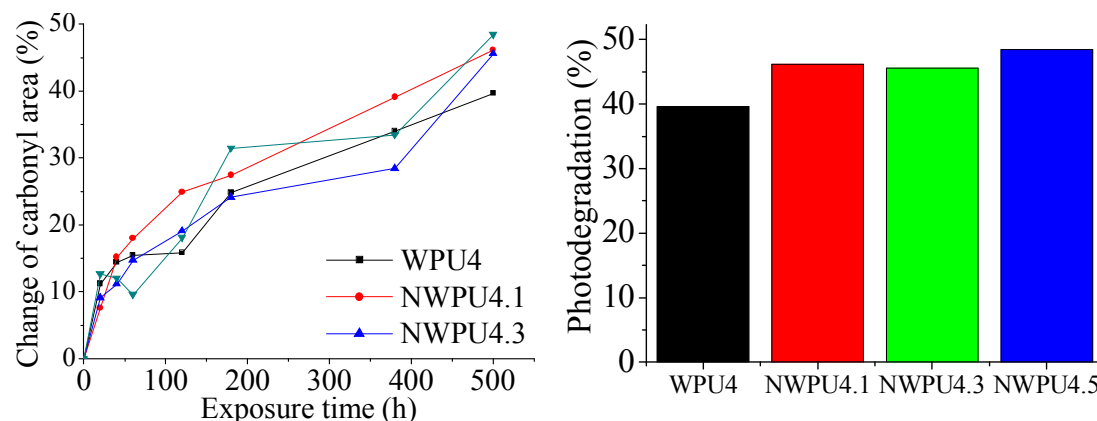


Figure 4.45 : Changes in carbonyl areas of WPU4 and NWPU4 nanocomposites during solar radiation test.

In the case of crosslinked WPU nanocomposites, the NWPU2 series indicate different characteristics if compared to NWPU3 series. Increasing Mt content of NWPU2 series is resulted with very rapid degradation rate (Figure 4.46). NWPU2 with 1% Mt is degraded nearly twice percent (NWPU2.1) and higher Mt content is resulted with 300% increase in degradation compared to neat polymer. The degradation rate of the NWPU2 series increases dramatically with increasing Mt content. However, in NWPU3 series 1% and 3% Mt content does not show significant change (NWPU3.1 and NWPU3.3).

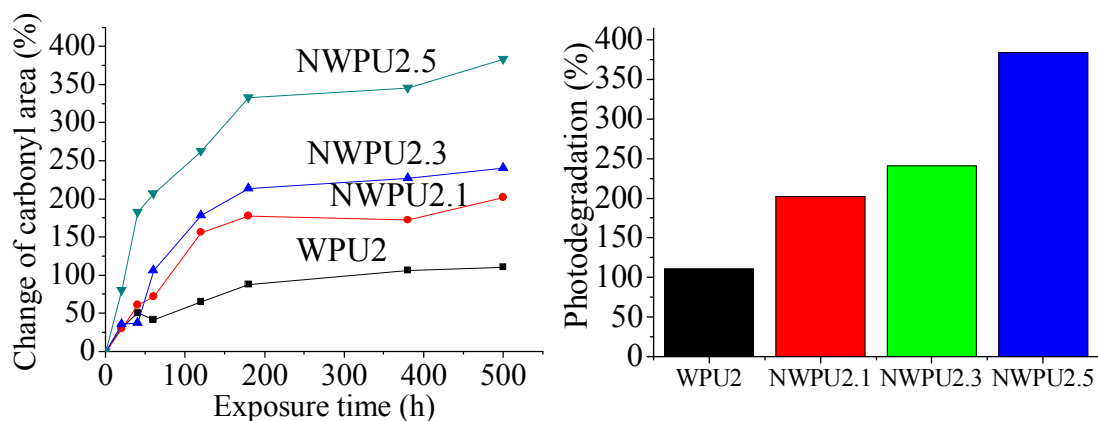


Figure 4.46 : Changes in carbonyl areas of WPU2 and NWPU2 nanocomposites during solar radiation test.

In NWPU3 series, 5% increase of degradation is gained by NWPU3.5 containing 5% Mt (Figure 4.47). The difference can be due to NWPU3 series having less dendritic structure which is also compromised by NMR and DSC measurements.

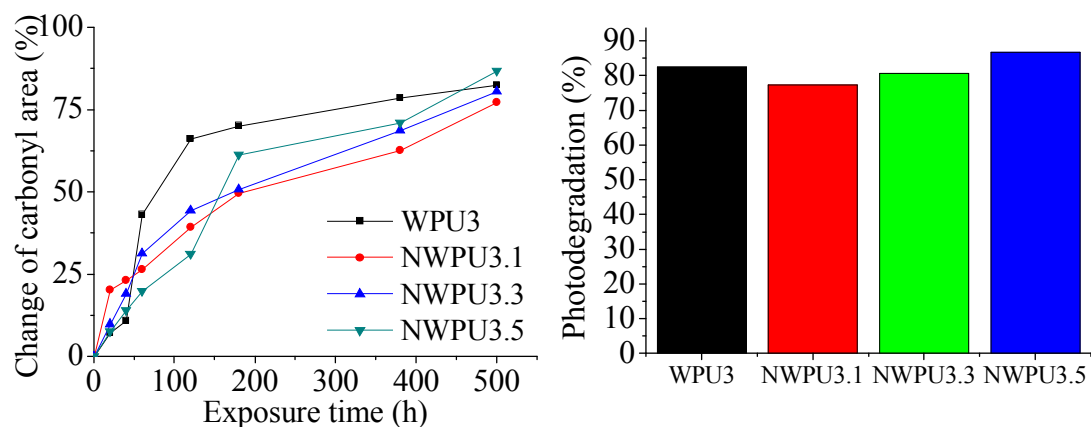


Figure 4.47 : Changes in carbonyl areas of WPU3 and NWPU3 nanocomposites during solar radiation test.

In addition, color retention measurements were carried out using spectrophotometer (ASTM D 2244). Neat polymers were taken as reference and color change (ΔE values) was calculated (Table 4.22, Figure 4.48, Figure 4.49). If the images of WPU polymers and nanocomposites are considered, it can be said that color retention of neat polymers are much better if compared to nanocomposites. The ΔE values increases by rising of Mt content showing that the color difference increases as the Mt content raises. The stereomicroscope images of the final conditions of WPU polymers and nanocomposites after solar radiation test are given in Figure 4.48. Among the samples, the drastic change is perceptible especially for NWPU2 series nanocomposites which is more likely to have dendritic structure.

Table 4.22 : Summary of change on peak areas and color values after solar radiation and ozone tests.

Sample	Mt content (%)	ΔE	Changes of the carbonyl peak areas (%)	
		Solar radiation	Solar radiation	Ozone
WPU 1	-	Control	68.46	22.64
NWPU 1.1	1	18.65	66.56	29.21
NWPU 1.3	3	21.55	80.86	17.58
WPU 2	-	Control	110.44	26.57
NWPU 2.1	1	8.42	202.17	28.02
NWPU 2.3	3	10.53	241.13	27.54
NWPU 2.5	5	11.12	383.63	23.58
WPU 3	-	Control	82.51	17.87
NWPU 3.1	1	9.61	77.24	17.93
NWPU 3.3	3	12.08	80.59	33.91
NWPU 3.5	5	9.86	86.78	13.63
WPU 4	-	Control	39.66	10.53
NWPU 4.1	1	9.95	46.19	19.40
NWPU 4.3	3	12.24	45.62	10.59
NWPU 4.5	5	15.82	48.45	4.28

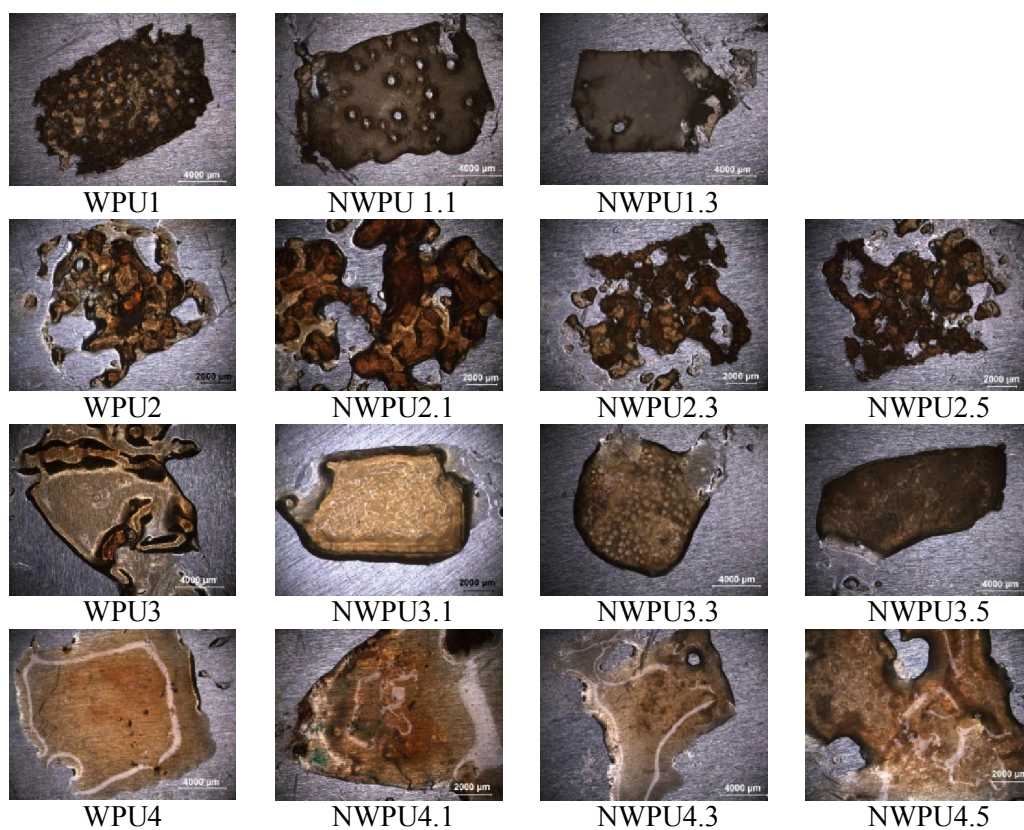


Figure 4.48 : Stereomicroscope images of WPU polymers and nanocomposites after solar radiation test.

Code	Before test	After test
WPU1		
NWPU 1.1		
NWPU1.3		
WPU2		
NWPU2.1		
NWPU2.3		
NWPU2.5		
WPU3		
NWPU3.1		
NWPU3.3		
NWPU3.5		
WPU4		
NWPU4.1		
NWPU4.3		
NWPU4.5		

Figure 4.49 : Images of WPU polymers and nanocomposites before and after solar radiation test.

The mechanism of more rapid degradation of nanocomposites can be firstly decomposition of modifier polyol segments within the galleries of OMt with greater increase of crystallographic defects within the layers of OMt. In addition, acceleration of photo-degradation in the presence of OMt can be caused by the transition metals such as Fe^{+2} and Fe^{+3} , which are unexchangeable cations located intergallery spacing of the OMt. This is a secondary factor leads to a catalytic effect on scission of polymer chains with the formation of products with carbonyl groups (Figure 4.50). This result is compatible with the literature (Kumar et al., 2009; Pandev et al., 2005; Qin et al., 2004; Singh et al., 2010; Woo et al., 2007).

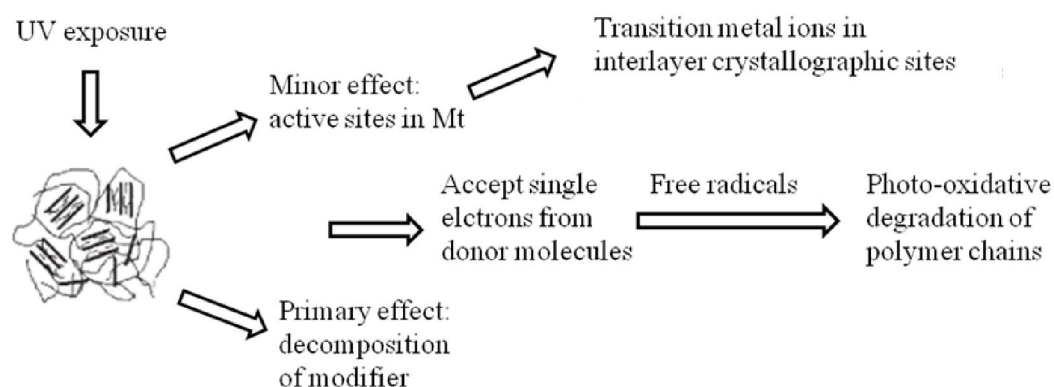


Figure 4.50 : Schematic representation of catalysis mechanism of photooxidative degradation of nanocomposites.

As a result, nanocomposites indicate higher degradability than neat polymers under solar radiation. If photo-degradation behavior of nanocomposites is considered, it can be said that all nanocomposites demonstrate worse performance than neat polymers.

4.4.2 Ozone testing

The aim of the ozone testing of WPU polymers and nanocomposites is that to investigate the effect of oxidation by ozone depending on polymer type and the presence of Mt. The test is carried out at 40°C with 0.50 ppm ozone concentration for 400 hours (ASTM D 1149). The weathering performance of the samples was examined by monitoring of infrared absorbance characteristics using FTIR technique as performed in solar radiation testing. The oxidative degradation profile was investigated by monitoring C=O absorbance around 1700 cm^{-1} (Peng et al., 2009).

The effect of ozone on polymers is relatively slow and they retain their properties for a rather long time compared to effect of solar radiation. The effect of ozone on

aliphatic polyurethanes is very low compared to polymers containing double bonds. Reaction of ozone with polymers is occurred on main chains containing double bonds, aromatic rings or saturated hydrocarbon links. The presence of ozone in the air, even in very small concentrations, markedly accelerates the aging of polymeric materials. Degradation with ozone was relatively slow and less harmful than solar radiation test for WPU polymers. This can easily be understood from the FTIR spectra of WPU2 polymer, which is denoted in Figure 4.51.

Little changes are observed from the FTIR spectrums in the structural bands of the WPU polymers such as urethane and urea C=O stretching at around 1700 cm^{-1} and 1640 cm^{-1} . In addition, little changes on C-N + δ N-H stretching band at around 1530 cm^{-1} , N-CO-O + st C-O-C stretching at around 1249 cm^{-1} and 1040 cm^{-1} are also observed. However, these changes were minor compared to solar radiation testing. Dimensional stability of the samples was good at the end of the test unlike the samples which were sticky after solar radiation testing. Similar to solar radiation test, effect of ozone was monitored by changes of carbonyl peak and the results were evaluated by calculating carbonyl peak areas of the samples.

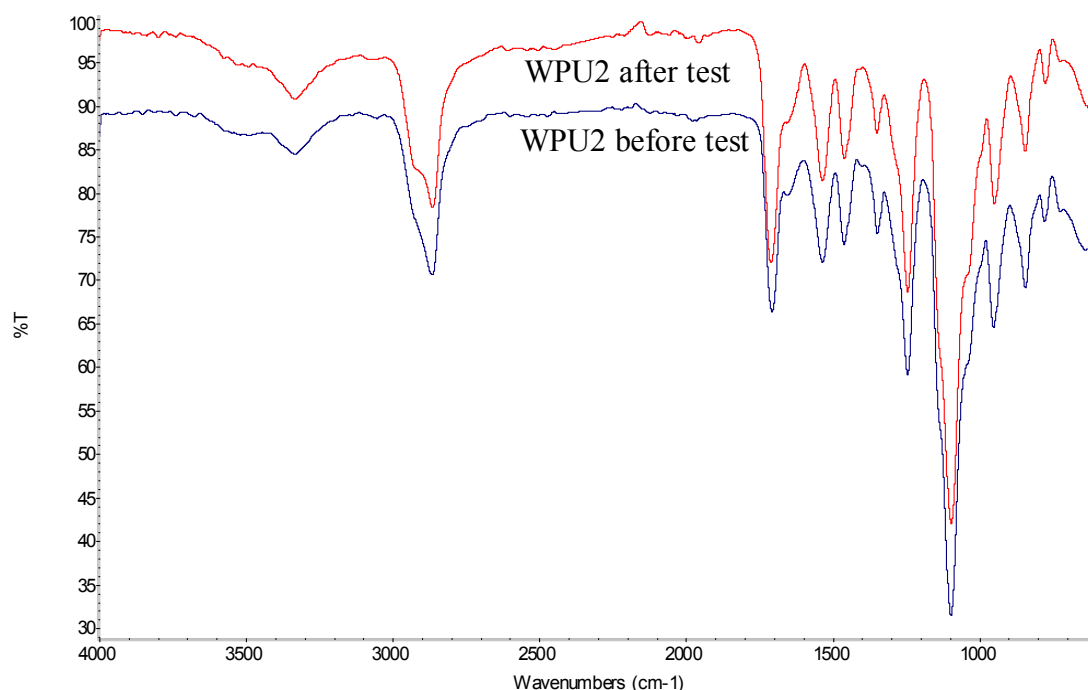
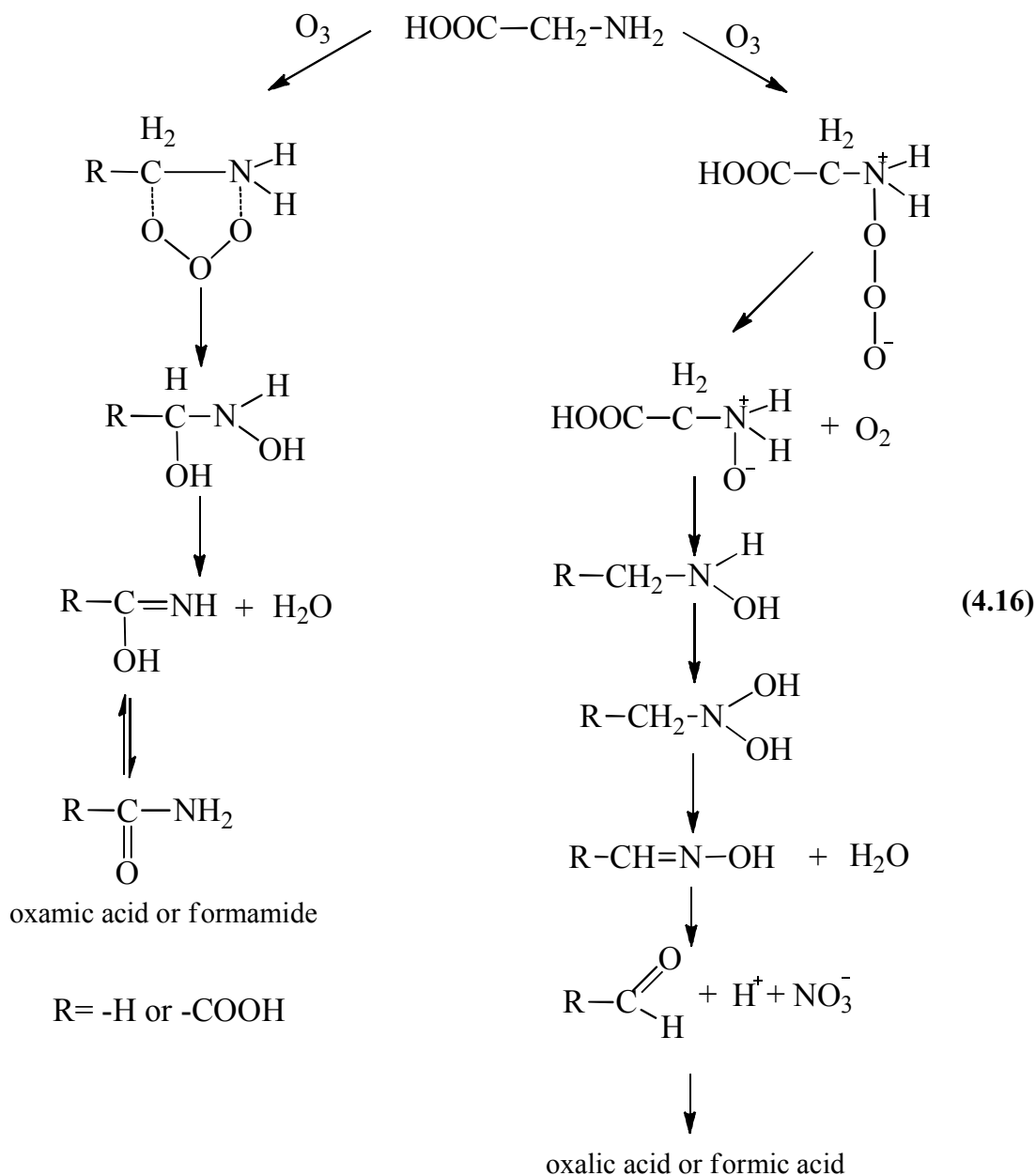


Figure 4.51 : Changes of FTIR spectrum of WPU2 during ozone test.

The possible mechanism of oxidative degradation of linear WPU polymers caused by ozone is shown in (4.16). Functional groups such as urethane can be affected by ozone. The mechanism on WPU polymers can be explained by attack of ozone

through hard segments (4.15). As a result, several degradation products with carbonyl group were supposed to be formed (4.16). Therefore the main change was observed at carbonyl band of FTIR spectra (Figure 4.51).



Initially, linear WPU and crosslinked WPU-urea polymers were investigated in terms of ozone induced oxidative degradation.

In the case of linear WPU polymers, oxidative degradation of WPU4 containing PTAA polyol is much lower than WPU1 containing PEG600 polyol which is a similar result with solar radiation testing (Figure 4.52, Table 4.22). This can be due to WPU4 polymer which contains higher Mw and includes lower hard segment content compared to WPU1.

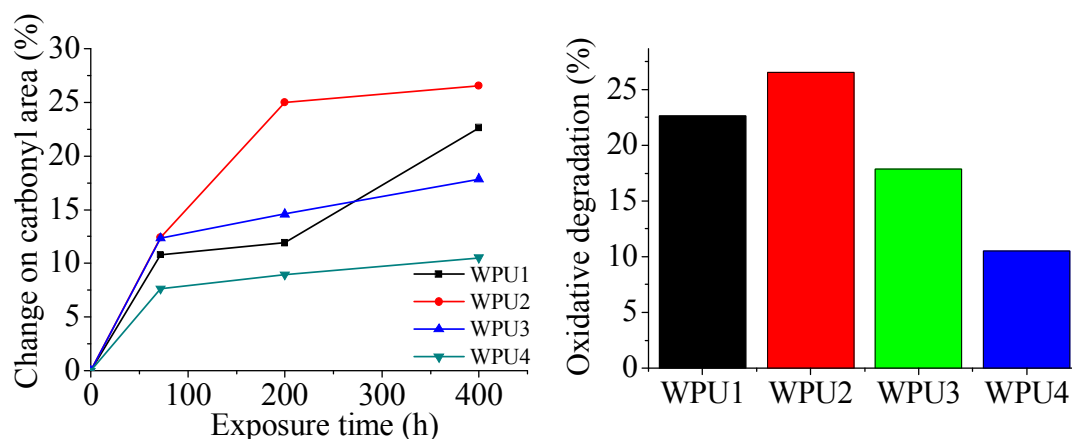
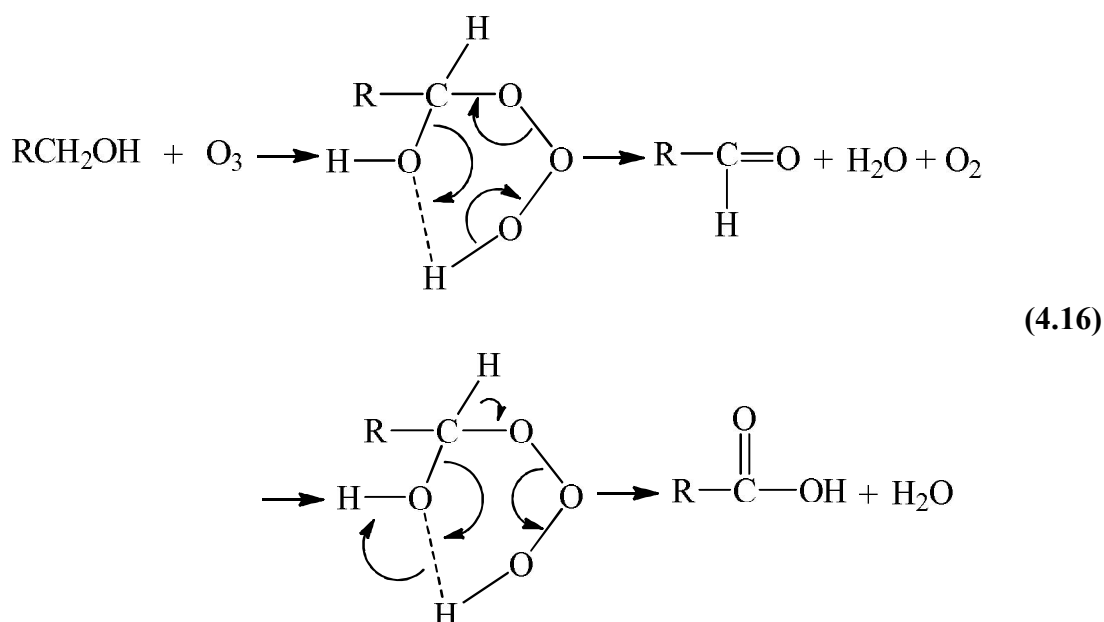


Figure 4.52 : Changes in carbonyl areas of WPU polymers during ozone test.

In the case of crosslinked WPU2 polymers, ozone degradation is accelerated by OH groups which are being attacked by ozone. OH functions came from methylolamine groups in WPU2 polymers which is confirmed by NMR analysis can be susceptible of accelerating ozone degradation (4.16).



In the case of linear WPU nanocomposites, in NWPU1 series, degradation of the sample with 1% Mt content is higher than the WPU1 neat polymer (NWPU1.1). However, drastic decrease is observed by rising Mt content to 3% (NWPU1.3). Similar behaviour is detected for NWPU4 series. Degradation of the sample with 1% Mt content is higher than the WPU4 neat polymer (NWPU4.1). However, it was observed that the rate of degradation of the sample with 3% is nearly the same with WPU4 neat polymer (NWPU4.3) and degradation rate is lowered significantly with

5% Mt content (NWPU4.5). The ozone test results of NWPU1 and NWPU4 series are depicted in Figure 4.53, Figure 4.54 and Table 4.22.

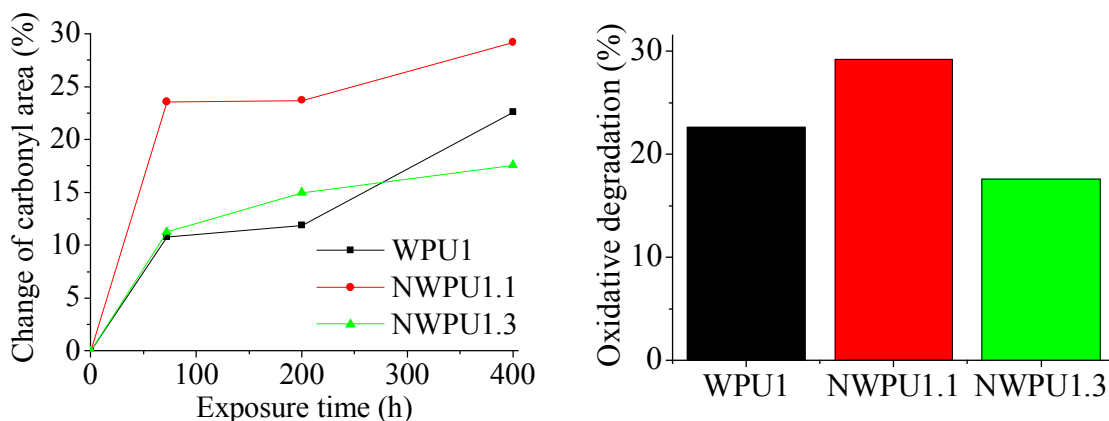


Figure 4.53 : Changes in carbonyl peak areas of WPU1 polymer and NWPU1 nanocomposites during ozone test.

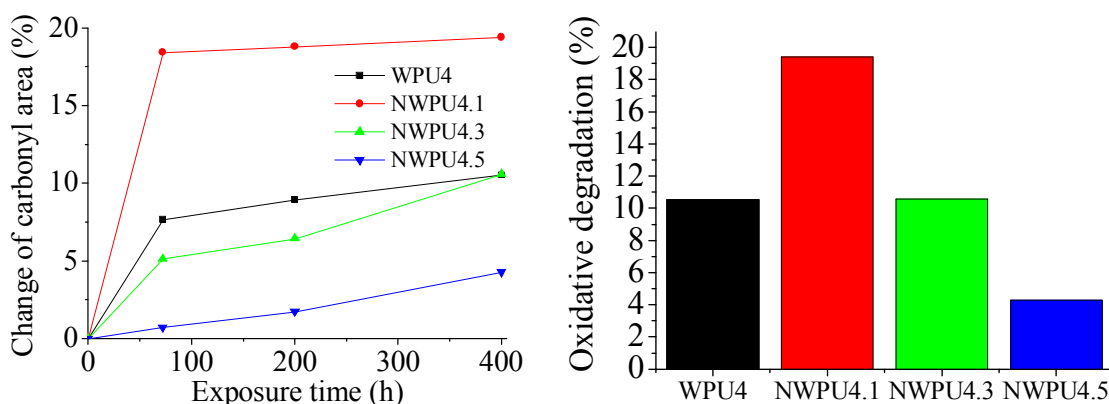


Figure 4.54 : Changes in carbonyl peak areas of WPU4 polymer and NWPU4 nanocomposites during ozone test.

In the case of crosslinked NWPU2 nanocomposites the similar results are obtained with linear WPU nanocomposites. Degradation rate initially increases in small ratio with 1% Mt content (NWPU2.1) and decreases to the similar ratio with the neat WPU2 polymer as the OMt content increases to 3% (NWPU2.3). However, it decreases to its lowest rate with 5% Mt content (NWPU2.5). Similarly, in NWPU3 series, degradation rate increases at especially with 3% OMt content (NWPU3.3) and decreases to its lower rate with 5% Mt content (NWPU3.5). The ozone test results of NWPU2 and NWPU3 series nanocomposites are depicted in Figure 4.55, Figure 4.56 and Table 4.22.

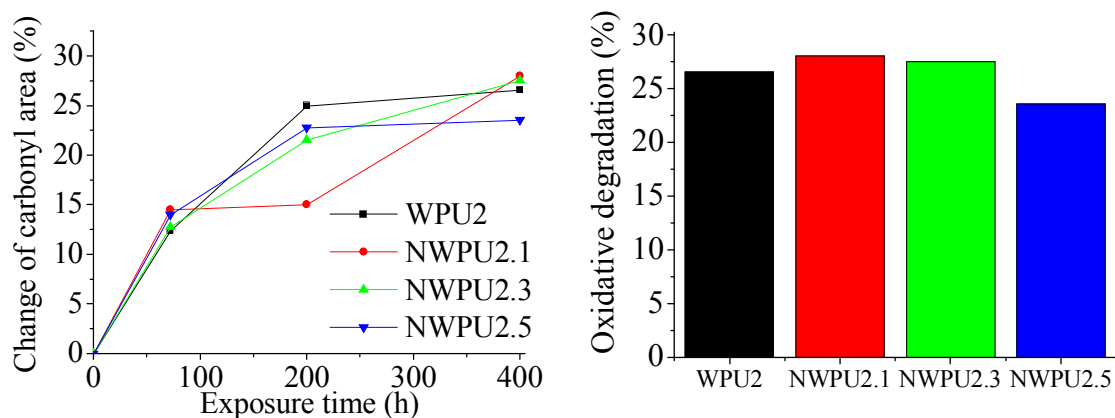


Figure 4.55 : Changes in carbonyl peak areas of WPU2 polymer and NWPU2 nanocomposites during ozone test.

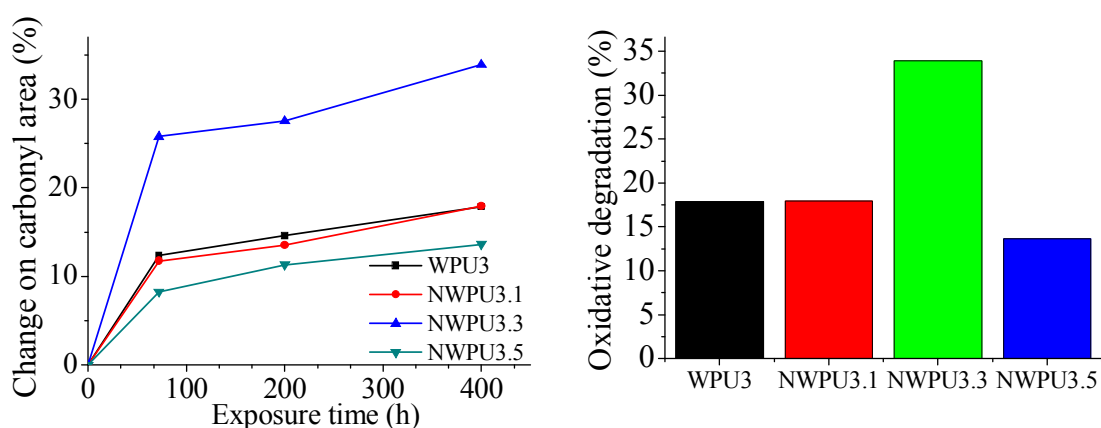


Figure 4.56 : Changes in carbonyl peak areas of WPU3 polymer and NWPU3 nanocomposites during ozone test.

The sample photos before and after test were shown in the Figure 4.57. According to images, discoloration of the is reduced with increasing content of Mt in the all nanocomposites including linear WPU (NWPU1, NWPU4) and crosslinked WPU-urea nanocomposites.

As a result of the ozone test, Mt particles behave as a barrier against diffusion and retards the penetration of oxidizing species generated by ozone due to high aspect ratio of Mt. It could be related to the surface area of the interaction of OMt with the polymer matrix. It is interesting that the barrier effect of OMt is unsuccessful even have opposite effect with 1% and/or 3% Mt content (NWPU1.1, NWPU2.1, NWPU2.3, NWPU3.1, NWPU3.3, NWPU4.1, NWPU4.3). This can be due to crystallographic defects and catalytic effect caused by OMt as explained in solar radiation testing as well as the degradation of modifier polyol segments within the galleries of Mt particles.

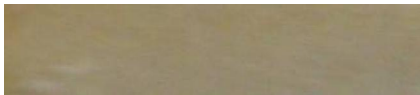
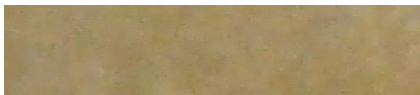
Code	Before test	After test
WPU1		
NWPU 1.1		
NWPU1.3		
WPU2		
NWPU2.1		
NWPU2.3		
NWPU2.5		
WPU3		
NWPU3.1		
NWPU3.3		
NWPU3.5		
WPU4		
NWPU4.1		
NWPU4.3		
NWPU4.5		

Figure 4.57 : Images of WPU polymers and the nanocomposites before and after ozone test.

5. CONCLUSION AND RECOMMENDATIONS

The aim of this work is to synthesis WPU polymers by two different processes including acetone and prepolymer mixing processes and to prepare their composites by using OMT to improve their properties and investigate their environmental degradation properties.

Linear WPU polymers (WPU1 and WPU4) were synthesized by using two different type and Mw polyols (PEG600 and PTAA) as the soft segments via acetone process. The optimum synthesis conditions of prepolymer were determined by several trial and error periods. Initially the experiments were carried out by magnetic stirring. However, it was changed with mechanical stirring after several trials. Besides, several hard and soft segments as well as different ratio of catalysis were tried. The appropriate mole ratio of polyol/DMPA/HDI was found as 1/1/3 for film preparation and the same ratio was used for all experiments. The neutralization ratio of [TEA]/[DMPA] was kept constant as 1/1 for all experiments. DBTDL catalysis were used as 1% (on total solid) for only WPU1 in prepolymer preparation stage and as 3% (on free NCO+ BD) for both WPU1 and WPU4 for the chain extension stage. The suitable reaction temperature was taken as 60°C for the prepolymer preparation stage of all linear WPUs due to using acetone as processing solvent. FTIR and ¹HNMR analysis results showed that desired linear WPU polymers obtained. FTIR analysis showed that linear WPU polymers with trans-cis isomerism indicated characteristic bands such as N-H stretching at 3323 cm⁻¹, urethane C=O at around 1690 cm⁻¹, C-N and N-H stretching at 1532 cm⁻¹ and asymmetric and symmetric stretching N-CO-O and C-O-C at around 1247 and 1249 cm⁻¹ respectively. ¹HNMR results showed characteristic shifts of trans and cis urethane at 7.1 and 6.8 δ ppm respectively. The molecular weights of WPU1 and WPU4 were calculated as 10.000 and 40.000 Daltons respectively. The tensile strength of WPU4 was higher than WPU1 owing to its higher Mw and having ether-ester type polyol whereas elongation at break value was lower than WPU4 due to having lower hard segment.

Crosslinked WPU-urea polymers (WPU2 and WPU3) were synthesized by using two different type and Mw polyols (PEG1500 and PPG1000) as the soft segments via prepolymer mixing process by using water as chain extender. The same ratio of polyol/DMPA/HDI was kept as 1/1/3 as linear WPU polymers. The prepolymer preparation reaction conditions of crosslinked WPU-urea polymers was determined as 2 hours at 60°C with %0.5 catalyst (on total solid) for WPU2 whereas 4 hours at 80°C with %1 catalyst (on total solid) for WPU3 due to low reactivity of PPG1000. The neutralization ratio [TEA]/[DMPA] was also kept constant as 1/1.

DMA and methylolurea which were obtained by the solvation of HMTA used as crosslinking agent. Similar spectral results with linear WPU polymers were obtained for crosslinked WPUs. However, some spectral results especially from ^1H NMR and ^{13}C NMR spectroscopy distinguished that different structures were gained for crosslinked WPUs. In chain extension stage, crosslinked structures were obtained as a result of reaction between NCO ended prepolymer and DMA. In addition, methylene and/or ether bridges were also gained by the reaction with methylolurea. Crosslinked WPU-urea polymers with different properties were obtained depending on the HMTA ratio and reactivity of polyol. Tensile tests showed that tensile strength increased as the HMTA ratio increased. According to ^1H NMR analysis, NCH_2OCON band at 4.4 δ ppm and 4.8- 4.5 δ ppm belong to methylene and/or ether bridges as well as 125 δ ppm bands in ^{13}C NMR spectrums became apparent with increasing HMTA content which was showing that WPU2 was more likely to be dendritic structure compared to WPU3 polymer. This result was also supported by DSC analysis and mechanical tests.

Particle size distribution of neat polymers were depend on DMPA content for linear WPU polymers which was higher for WPU1 than WPU4 owing to higher DMPA content. However, it depended on rather soft segment type for crosslinked WPU-urea polymers that WPU3 containing PPG1000 polyol was higher particle size compared to WPU2. WPU1 and WPU2 polymers would have higher penetration ability compared to WPU4 and WPU3 due to lower particle size distribution.

According to TGA analysis thermal resistance of neat WPU polymers were inversely proportional to their hard segment content which were as follows; $\text{WPU4} > \text{WPU2} > \text{WPU3} > \text{WPU1}$. In addition, in linear WPU polymers, WPU4 having higher Mw compared to WPU1 and WPU4 having ester units caused higher thermal

stability. In addition, in crosslinked WPU-urea polymers, WPU2 was more thermally resistant due to having higher crosslinked structure compared to WPU3. On the other hand, thermal stability of nanocomposites was higher than neat polymers. DSC results, of linear WPU polymers showed that T_g of WPU1 was higher than WPU4 because of having higher hard segment content which limited the mobility of the soft segment of the WPU. However, T_g values of WPU2 polymer was lower than WPU3 due to WPU2 containing higher dendritic structure compared to WPU3. In addition, crystallization temperature (T_c) was observed in WPU2 due to having more ordered structure compared to WPU3.

The preparation of the nanocomposites were carried out by using OMt. Firstly, structural OH content of NaMt was determined by TGA to be added additional corresponding HDI. NaMt was initially modified with polyol component by melt blending to obtain OMt and following preparation of WPU nanocomposites were performed via in-situ intercalative polymerization.

FTIR analysis of nanocomposites showed that interaction of NaMt with WPU matrix were indicated changing of structural O-H vibration of NaMt at around 3625 cm⁻¹. The change was shifting of frequency and/or difference in the intensity. In addition, C-O-C stretching vibration bands of the polymers changed with the effect of Si-O stretching vibration bands of NaMt. XRD analysis denoted the increase of interlayer spacing depending on the type and structure of polymers and resulting nanocomposites were in intercalated architecture. The increase of d-spacing was slightly lowered by rising Mt content such as 3.78Å (NWPU1.1), 3.63Å (NWPU1.3), 3.57Å (NWPU3.1), 3.37Å (NWPU3.3), 3.15Å (NWPU3.5), 5.39Å (NWPU4.1), 4.42Å (NWPU4.3) and 3.91Å (NWPU4.5). However in NWPU2 series, it was increased by rising Mt content such as 4.71Å (NWPU2.1), 5.31Å (NWPU2.3) and 5.64Å (NWPU2.5). XRD results were consolidated by SEM and TEM micrographs. However, regional exfoliation were observed. TEM analysis of crosslinked NWPU2 and NWPU3 was not be able to be performed by solvent cast method due to their insolubility. Therefore, their TEM analysis were performed by using ultramicrotome technique.

According to TGA results under nitrogen atmosphere, thermal resistance of linear NWPU1 nanocomposites having 1% Mt content showed better thermal resistance in low degradation temperatures whereas 3% Mt was better in higher degradation

temperatures. However, in NWPU4 series the sample with 5% Mt content had better resistance. Similar results were observed in crosslinked WPU nanocomposites. In NWPU2 and NWPU3 series, thermal resistance increased its highest value in both low and high temperature degradation temperatures range with 3% Mt content in NWPU2 whereas with 5% Mt for NWPU3 series. TGA analysis under oxygen atmosphere showed slightly different results on neat polymers and nanocomposites. Their degradation temperature shifted under oxygen compared to nitrogen. However, same trend was observed with those analyzed under nitrogen in the presence of Mt. According to DSC measurements, T_g values of the linear WPU nanocomposites decreased (NWPU1, NWPU3) or raised (NWPU4, NWPU2) in the presence of OMt which could be due to changing of M_w. In addition, changing of T_c values in NWPU2 and T_d values in all nanocomposites indicated the interaction of polymer with Mt.

According to the tensile tests, all the nanocomposites indicated increase in stress and strain values except NWPU3 series showing that toughness increased in the presence of OMt. Tensile tests indicated that in the presence of OMt both tensile strength and elongation at break values were increased. Elongation at break value increased almost by 50% for NWPU1 and 20% for NWPU2 and 100% for NWPU4 with 5% OMt content and was not changed for NWPU3 series. However, tensile strength raised almost by 20% for NWPU1, 100% for both NWPU2 and NWPU4, 500% for NWPU3. WPU3 showed drastic increase in tensile strength whereas no improvement in elongation. It was thought that WPU3 had worse interaction with Mt compared to NWPU2 series. This was also identified from the XRD results which indicated the increase in d-spacing values of NWPU3 were lower than those of NWPU2 series. The elastic modulus of all nanocomposites also increased with Mt loading. Mt particles behaved as crosslinking points and improved toughness of the nanocomposites.

Environmental weathering tests were executed including solar radiation and ozone tests. The photo-degradation behaviour of neat WPU polymers was quite different from each other according to solar radiation test. Photodegradation were expected to be occurred through hard segment units. In linear WPU polymers, WPU1 polymer indicated rapid degradation due to containing polyether polyol segment compared to WPU4 containing ether/ester segmented polyol as well as WPU1 having higher hard

segment content. In addition, WPU4 containing higher Mw compared to WPU1. In crosslinked WPU-urea polymers, WPU2 was more degradable than WPU3 because of having more dendritic units susceptible to accelerating photodegradation. On the other hand, in the presence of OMt, the photodegradation was accelerated from 68.5% to 80.9% (NWPU1 series), 110.4% to 383.6% (NWPU2 series), 82.5% to 86.9% (NWPU3 series) and 39.7% to 48.5% (NWPU4 series) with 5% Mt content showing the greater photodegradation. NWPU2 series were drastically affected in the presence of Mt which was already least resistant to solar radiation. In addition, discoloration was also confirmed the accelerated degradation of in the presence of OMt. As a result, the effect of OMt clay on photodegradation was determined which behaved as photodegradation agent in WPU matrix. Therefore, the NWPU nanocomposites can be used as photodegradable polymers which has gained importance in recent years.

Oxidative degradation with ozone slightly effects WPU polymers and nanocomposites compared to photodegradation through solar radiation. Ozone degradation was accelerated by urethane groups in the backbone for linear WPUs and urethane or urea groups as well as OH groups came from methylolamine groups which were being attacked by ozone for crosslinked WPU2 and WPU3 polymer. In the presence of OMt, drastic decrease of oxidative degradation of the all nanocomposites was observed at their highest value of OMt content. As a result of the ozone test, with the ratio of 5% Mt (w/w) particles behaved as a barrier against diffusion and retarded the penetration of oxidizing species which could be important where the oxidation prevention is necessary.

As a conclusion;

- Depending on the polyol type and hard segment content linear WPU polymers were indicated different properties,
- It was shown that HMTA can be used as crosslinking agent in WPU polymers to prepare dendritic WPU polymers with different thermal and mechanical properties which can be found an industrial usage,
- WPU/OMt nanocomposites can be prepared by starting from direct organomodification of Mt clay which can reduce the processing time and cost of the production.

- Mechanical and thermal properties of WPU polymers can be improved by the preparation of their nanocomposites using OMt,
- WPU polymers can be used as photodegradable polymers by the preparation of their nanocomposites with OMt to be used for several industries where the green chemistry can take place.
- WPU polymers can be gained oxidative resistance by the preparation of their composites with OMt.

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Banqueting personnel

▪ Reward: Development and Testing of Radar Absorbing Materials (TUBITAK MAM, 2008).

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