Preparation of Waterborne Polyurethane-OMt Nanocomposites and Effect of Clay on UV Degradation

Engin Açıkalın,[*1,2] Oya Atıcı*[1]

Summary: Waterborne polyurethane polymers (WPU) have gained importance for some decades because of their environmentally friendly characteristics due to low or zero content of solvents. Polyurethane properties can be modified by changing segmental structure or incorporating inorganic fillers into the polymer matrix. Montmorillonite (Mt) clay which is a member of smectite family is widely used in polymer clay composites as a filler. In this work, linear WPU nanocomposites were synthesized using different polyols as soft segment via acetone process which has many advantages over the prepolymer mixing process in terms of reliable reproducibility and convenience for obtaining linear polyurethanes. Sodium modified montmorillonite (NaMt) clay was used without any chemical pretreatment. WPU nanocomposites were prepared via in-situ polymerization method by modification of sodium modified montmorillonite (NaMt) clay in polyol and following polyurethane reaction. Finally, spectroscopic, thermal, morphological characterizations and UV weathering tests carried out. As a result, different thermal and mechanical properties were observed due to different soft and hard segment content. Furthermore, increasing clay content caused lowering of resistance against UV degradation.

Keywords: acetone process; in-situ polymerization; NaMt; UV degradation; waterborne polyurethane

Introduction

Waterborne polyurethane (WPU) dispersions have been extensively studied and commercially important since the early 1970s. They can be formulated into coatings and adhesives containing little or no cosolvents.[1] Conventional polyurethane polymers are immiscible with water. However, waterborne polyurethane dispersions containing external or internal emulsifiers are able to be dispersed in water. External emulsifiers are not preferred due to problems in storage stability and coarser particle size. Therefore, emulsification in water is usually ensured by incorporation of ionic groups on polyurethane backbone as internal emulsifier. WPU dispersions having internal emulsifier groups are classified into three categories of anionic, cationic and nonionic.[2] Most commonly used types are anionic dispersions due to less co-solvent requirement, good pigment wetting property, high gloss and freeze- thaw stability. α, α-dimethylol propionic acid (DMPA) most often preferred internal emulsifier due to its advantage of having carboxyl groups with steric hinderance to prevent possible reaction with isocyanate groups. There are several techniques for preparing WPU dispersions such as acetone, prepolymer mixing, hot melt and ketamine-ketazine methods.[3] The most common synthesis

---

[1] Materials Institute, TUBITAK Marmara Research Center, 41470, Kocaeli, Turkey
E-mail: engin.acikalin@mam.gov.tr; enginacikalin@yahoo.com

[2] Department of Polymer Science and Technology, Istanbul Technical University, Maslak Istanbul Turkey

procedures are prepolymer mixing and acetone methods among them.[4] In acetone method, polymer chains are rearranged during dispersion stage and resulting polymer has linear structure which leads to be soluble in organic solvents. Besides, solvent removal is necessary after dispersion.

Montmorillonite (Mt) is a hydrated alumina-silica clay composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet. The Na^+ or Ca^{2+} residing in the interlayer can be replaced by organic cations such as alkyl ammonium ions via an ion-exchange reaction to make the hydrophilic silicate lipophilic and to render it good dispersion in the organic polymer phase.[5]

Polymer composites have been used frequently used in transportation, construction, electronics and consumer goods. Particle reinforced polymer composites are strongly affected by the dimension and microstructure of dispersed phase. Recently, there has been a high interest in the development of polymer-clay nanocomposites which are prepared in three methods including in-situ polymerization, solution dispersion and melt. Modification of untreated clay with surface active agent in order to enlarge the interlayer spacing of clay platelets is a crucial step for the preparation of polymer-clay nanocomposites. Otherwise making a composite out of untreated clay would not be a very effective use of material, because most of the clay would be stuck inside, unable to interact with the matrix.[6]

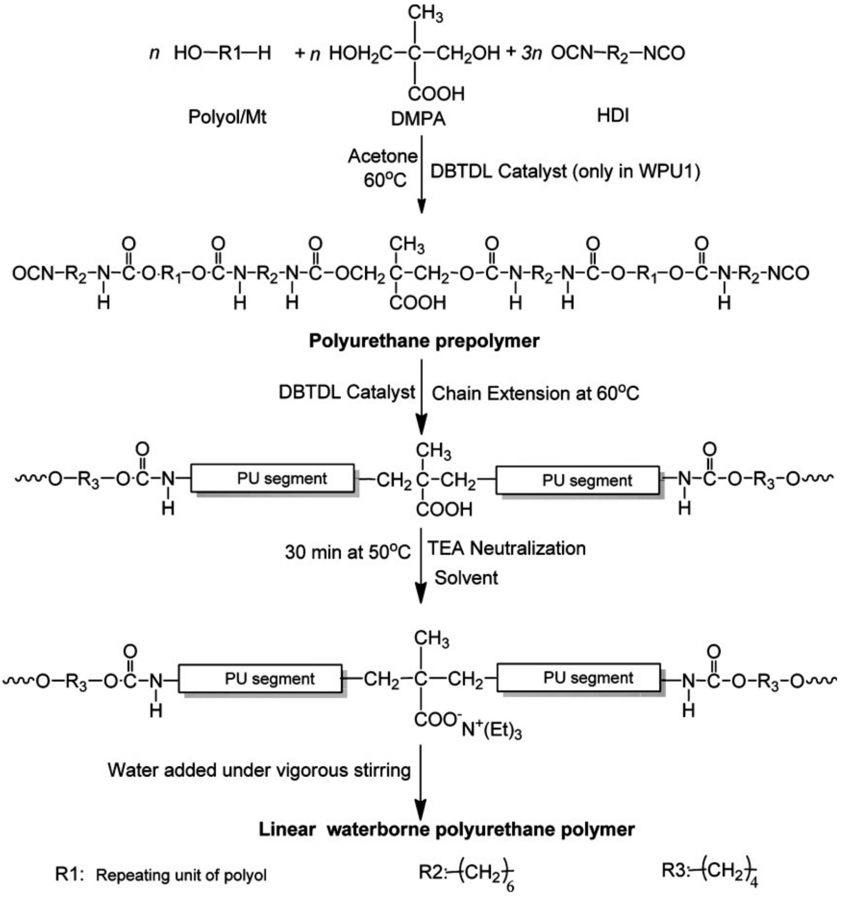
This study mainly focuses on two aspects. Firstly, the preparation of linear WPU polymers via acetone process using several type and molecular weight polyols were carried out. Linear WPU polymers were prepared by using two different polyol as the soft segment and BD was used as chain extender. DMPA was used as the internal emulsifier and HDI used as the isocyanate component for the experiments. Second aim is to prepare nanocomposites by using certain amounts of sodium modified montmorillonite clay (NaMt) via in situ method. In this manner, NaMt clay was modified with the polyol and the following polymerization procedure were carried out. Finally, spectroscopic, thermal, mechanical and morphologic characterizations were performed and solar radiation environmental tests were carried out to investigate the effect of NaMt content against photodegradation.

Experimental Part

Polyethylene glycol 600 (PEG 600, Merck), Poly(diethylene glycol/Trimethylolpropane-alt-adipic acid polyol) (PTAA, Sigma), Dimethyl propionic acid (DMPA, 98.5%, Fluka), 1,4-Butanediol (BD, Merck) and Cloisite Na^+ (NaMt, $Na_{0.65}[Al,Fe]_4Si_8O_{20}(OH)_2$, Southern clay) were vacuum dried overnight at 100°C before use. Hexamethylene diisocyanate (HDI 99.8%, Merck), Dibutyltindilaurate (DBTDL, Merck) and triethyl amine (TEA, 99%, Sigma) were used as received. Acetone (Merck, 99.8%, HPLC grade) was dried over 4 A° molecular sieves.

FTIR spectrums recorded on a Perkin-Elmer BXII with ATR spectrometer. ^{1}HNMR spectrums were recorded by Varian Unity Inova 500 MHz NMR spectrometer. Tensile tests were carried out using a Zwick Z250 SN5A tensile tester. Transmission electron microscope (TEM) micrographs were recorded using Jeol 100C electron microscope. Thermal analysis is carried out by using Exstar 6000 TGA/DTA 6300 Thermogravimetric Analysis (TGA) device with the heating rate of 10°C/min. X-Ray Diffraction (XRD) measurements were carried out by Shimadzu XRD 6000 spectrometer. Solar radiation weathering tests were performed by Atlas SC600 equipped with metal halide lamp which was operated with 1150W/m^{2}K irradiance value within full solar spectrum between 280–3000 nm wavelengths. Color measurements were carried out by Hunterlab Miniscan EZ spectrophotometer following solar radiation test.

The WPU polymers and nanocomposites were synthesized using acetone process (Scheme 1). Two different compositions



Scheme 1.
Preparation of WPU polymers and NWPU nanocomposites via acetone process.

were prepared by using PEG600 or PTAA polyols. PEG600 (or PTAA) were placed in a four necked flask equipped with a thermometer, a mechanical stirrer, a condenser and an inlet for pure argon. The flask placed in an oil bath with a temperature controller. In the case of nanocomposite preparation, certain amounts of NaMt clay (1, 3 and 5 w/w %) was swelled in the polyol component via melt technique by mechanical mixing for 15 hours at 80°C. Then, DMPA and acetone were added into the flask and stirred while heating at 60°C for 30 min to obtain homogeneous mixture. Next, DBTDL (0.5% total solid; only for WPU1) and HDI were added and mixture heated to reaction temperature. The reaction was carried out until certain amount of isocyanate content was reached. The content of free isocyanate was determined by dibutylamine back-titration method.[7] Once the desired free isocyanate content was reached, some acetone added into the flask to decrease the viscosity of the prepolymer mixture. Then, stoichiometric amount of BD chain extender was added into the mixture with additional acetone and DBTDL catalyst. The chain extension reaction was performed until all the free isocyanate groups terminated for 4h at 60°C. Then, TEA was added to neutralize the carboxyl groups of the polyurethane prepolymer. After 30 min neutralization at 50°C, deionized water was added dropwise into the polymer mixture and vigorous stirring. Finally, acetone was removed by distillation and WPU polymer and nanocomposite films were obtained after drying in a vacuum oven.

Results and Discussion

WPU Polymers

Prepolymer preparation stage of both WPU1 and WPU2 were performed with the molar ratio of polyol/DMPA/HDI as 1/1/3. DBTDL was used as catalyst only for the synthesis of WPU1 prepolymer. The ratio of BD/NCO was adjusted to 1/1 in the chain extension reaction. In addition, using DBTDL catalyst in chain extension stage was found more convenient because of lower reactivity of BD with isocyanate groups. DBTDL provided faster reaction between NCO containing prepolymer and BD in low temperature in the chain extension process. The detailed reaction conditions of the polymers synthesized were given in the following Table 1.

The FTIR spectrum of both WPU1 and WPU2 is shown in Figure 1. The most

Table 1.
Reaction conditions of WPU polymers and nanocomposites under mechanical stirring. (Polyol/DMPA/HDI molar ratio: 1/1/3, DBTDL: 0.5% on total solid, free NCO/BD: 1 (mol/mol), $[Et_3N]/[COOH]$: 1).

Experiment	NaMt content	Polyol type	DMPA	Prepolymer reaction time	Free NCO of prepolymer	Hard segment content[1]
	w/w %		w/w %	h	w/w %	w/w %
WPU1.0	0	PEG600	9.5	2	2.0	55
NWPU1.1	1	PEG600	9.5	2	2.0	55
NWPU1.3	3	PEG600	9.5	2	2.0	55
WPU2.0[2]	0	PTAA	2.5	3	2.5	25
NWPU2.1[2]	1	PTAA	2.5	3	2.5	25
NWPU2.3[2]	3	PTAA	2.5	3	2.5	25
NWPU2.5[2]	5	PTAA	2.5	3	2.5	25

[1] Hard segment content was calculated as [(HDI + DMPA + CE)/(Polyol + HDI + DMPA + CE)]*100.
[2] DBTDL catalyst was not used in the prepolymer reaction.

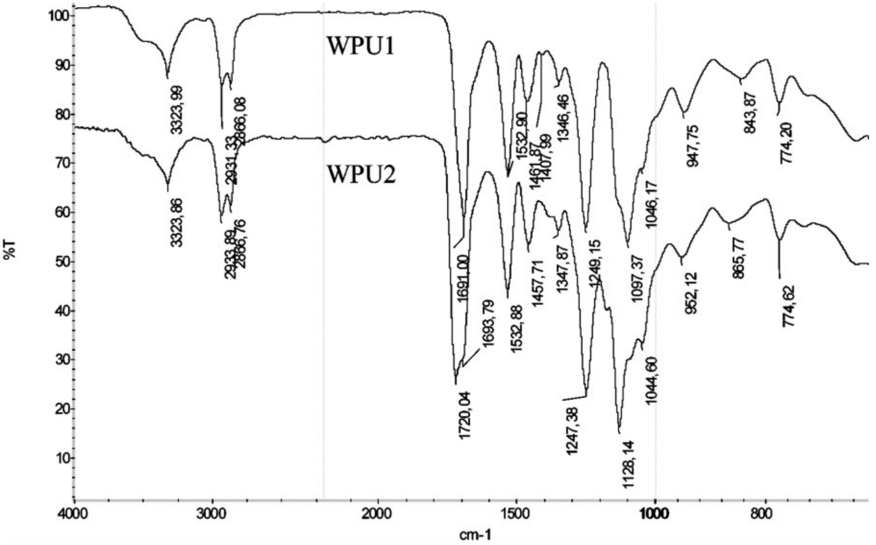


Figure 1.
FTIR spectra of WPU nanocomposites.

relevant bands corresponded to bonded N-H stretching at 3323 cm^{-1} sharp single peak, C-H stretching at 2931, 2866 cm^{-1} for WPU1 and 2933, 2866 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.[8]

H-bonded C=O stretching due to urethane at 1691 cm^{-1} for WPU1 and 1693 cm^{-1} for WPU2 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 WPU2 shifted to lower frequencies due to trans-cis isomerism. CN and NH stretching peaks were at around 1532 cm^{-1} for both WPU1 and WPU2. The symmetrical stretching peak of COO$^-$ belong to neutralized DMPA group was determined at 1406 cm^{-1} for WPU1. However, it wasn't clearly determined for WPU2. On the other hand, asymmetric N-CO-O stretching bands were identified at 1249 cm^{-1} for WPU1 and 1247 cm^{-1} for WPU4. C-O-C stretching bands were determined at 1097 cm^{-1} for WPU1 whereas 1128 cm^{-1} for WPU2 due to ester structure of PTAA polyol. The C-O-C peak was identified at 1128 cm^{-1}. Symmetric N-CO-O stretching bands were at 1039 cm^{-1} for both WPU1 and WPU2. Characteristic C-O-C stretching band was identified at 947 cm^{-1} for WPU1 and 952 cm^{-1} for WPU2. 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.

The ^{1}HNMR spectrum of both WPU1 and WPU2 was illustrated in Figure 2. The characteristic signal between 7.2–7.0 δ ppm was assigned to N-H proton of the trans conformer urethane groups.[4,9]

The peaks are observed at 6.8 and 5.8 δ ppm was attributed to N-H proton of the cis conformer urethane groups. The peak belongs to polyol protons are not identified clearly due to having dominated

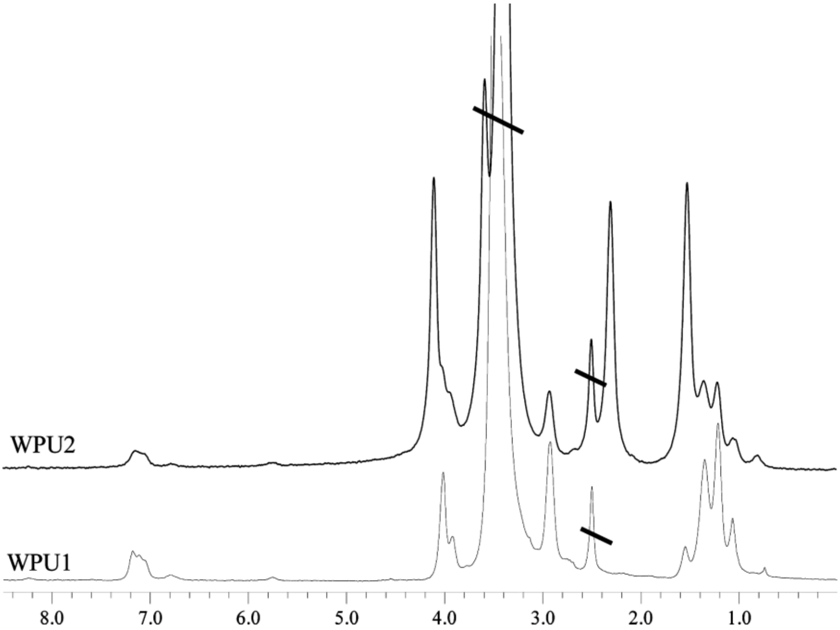


Figure 2.
^{1}HNMR of WPU nanocomposites.

by water peak absorbed by DMSO at around 3.5 δ ppm. However, ester protons of PTAA polyol in WPU2 are identified at 4.1, 3.6 and 2.3 δ ppm which are unique for the PTAA structure. The bands of methylene groups in 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 WPU2 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 peaks at 2.9 δ ppm are belong to methylene groups in TEA and urethane segments.[10] In addition, various methylene and methyl protons of urethane, TEA and DMPA segments are identified between at 1.3–1.0 δ ppm.

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 increasing to accommodate the additional salt groups at the interface.[11]

Particle size distribution of the linear WPUs is mainly affected by ionic dispersing group content in linear WPUs (Table 2). WPU1 polymer with higher DMPA content has relatively smaller particle size compared to WPU2. As a result, it canbe said that WPU1 polymer has a good penetration property compared to WPU2.

The weight average molecular weight (Mw), number average molecular weight (Mn) and polydispersity of WBPUs with different soft segments at the same molar ratios are also summarized in Table 2. WPU polymers prepared using different soft segments showed quite different results. Both Mw and Mn values of WPU2 are much higher than WPU1.

WPU Nanocomposites

In-situ intercalative polymerization method was used as the preparation method of the nanocomposites. In this method, NaMt is swollen in the liquid monomer itself or with the aid of solvent and polymer is formed between the intercalated sheets of the NaMt.[12] Structural hydroxyl group content determination of NaMt is performed by using TGA technique which is crucial for the evaluation of additional isocyanate corresponds to structural hydroxyl of NaMt. The degradation of structural hydroxyl group is identified between at 550–700°C. As a result, the structural hydroxyl content of the pure NaMt calculated as 3.73%.

All the nanocomposites were successfully prepared by using 1, 3 and 5% NaMt on weight basis over total solid of neat polymers except NWPU1.5. The preparation steps including melt blending of NaMt with polyol component for 15 hours at 80°C, in-situ polymerization reaction, neutralization/chain extension and dispersion were carried out respectively. During the preparation of the nanocomposites, the experiment with 5% NaMt (w/w) content caused gelling behavior 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 behavior was observed. This could be due to increasing of interaction expeditiously via higher amount of hydrogen bonding between NaMt and the growing polymer because of high hard segment content. As a result of rising hydrogen bonding

Table 2.
Particle size and molecular weight measurements of linear WPU polymers.

Polymer	Particle size (nm)	DMPA content (w/w %)	Mw (kDa)	Mn (kDa)	Mw/Mn
WPU 1	38.81	9.50	9.852	4.975	1.98
WPU 2	50.92	4.13	45.47	22.180	2.05

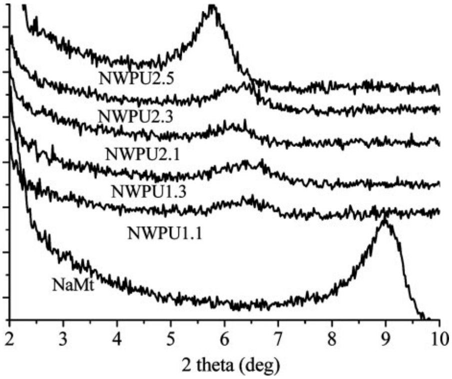


Figure 3.
XRD patterns of WPU nanocomposites.

tendency, rapid increase of viscosity of reaction medium was occurred.

The XRD diffractograms can be seen in Figure 3. The interlayer spacing of NaMt in the nanocomposites are increased to 3.78, 3.63 Å for WPU1 and 5.39, 4.42, 3.91 respectively.

The small differences could be due to Mw of the polyol which is relatively much higher in NWPU2 compared to NWPU1 series. According to XRD results it can be said that nanocomposites with intercalated architecture obtained.

TEM micrographs of the WPU1 and WPU2 series are illustrated in Figure 4. The dark lines in the micrographs represent the intersections of clay layers, and the spaces between the dark lines are interlayer spaces. It can be seen that NaMt layers well distributed in the WPU matrix which denote the dispersion of clay layers in the polymer and the formation of nanocomposites. Some clusters of agglomerated NaMt particles are observed which can be happened during sample preparation by solvent casting technique. At higher magnification, it is observed that the NaMt is mostly intercalated through WPU matrix instead of exfoliated architecture complying with the XRD results.

The thermal resistance of the NWPU nanocomposite films are analyzed by TGA. The thermograms of the nanocomposites are illustrated in Figure 5. Detailed results which are obtained from TGA are given in

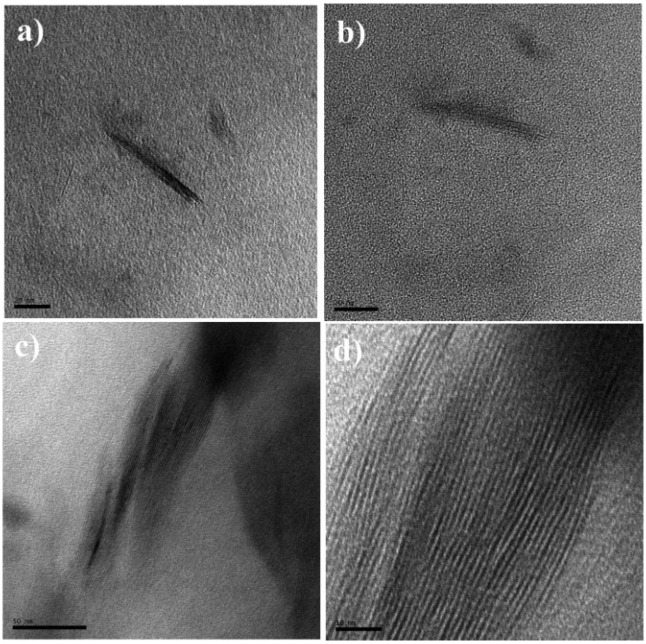


Figure 4.
TEM micrographs of WPU nanocomposites:a) NWPU1.1, b)NWPU1.3, c)NWPU2.1, d) NWPU2.3.

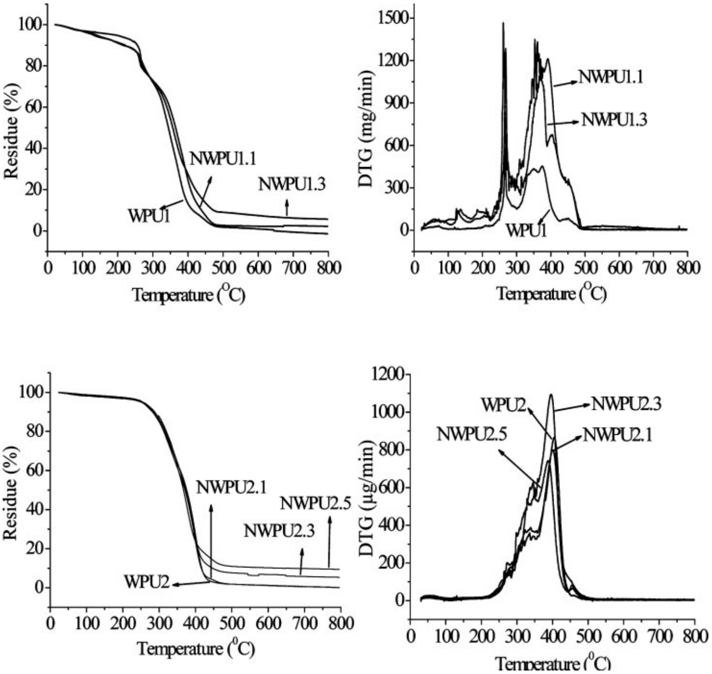


Figure 5.
TGA and DTG curves of WPU polymers and nanocomposites.

Table 3. In general, NaMt content increased the thermal stability of both linear WPU nanocomposites. T_D^{max} value of NWPU1 series rose with increasing NaMt content. However, in NWPU2 series, NWPU1.1 having 1% NaMt 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% NaMt is better in higher degradation temperatures by increasing of T_{80} and W_{450} values compared to neat WPU1 polymer. Unlike the NWPU1 series, weight percent of residue at maximum weight loss temperature (W_R) is increased with NaMt content in NWPU2 series. Besides, thermal resistance of NWPU2 series is developed in both low and high temperature degradation profiles by increasing T_{30}, T_{80} and W_{300}, W_{450} values

Table 3.
TGA results of WPU polymers and nanocomposites.

Sample	T_D^{max} (°C)	W_R (%)	T_{30} (°C)	T_{80} (°C)	W_{300} (%)	W_{450} (%)	Ash content
WPU1	375	27.11	307.07	385.10	45.68	13.02	0.00
NWPU1.1	391	17.25	315.21	407.33	58.87	23.91	2.33
NWPU1.3	403	12.25	312.06	421.22	54.34	27.58	5.80
WPU2	406	20.33	336.25	405.40	84.87	2.88	0.10
NWPU2.1	401	22.52	332.44	403.16	84.98	3.97	0.11
NWPU2.3	396	29.22	338.79	406.22	86.14	9.78	5.30
NWPU2.5	388	31.07	339.00	412.34	87.56	13.65	9.49

T_D^{max} Maximum weight loss temperature.
W_R Weight percent of residue at maximum weight loss temperature T_{30} and T_{80} The temperature at which 30% and 80% weight loss.
W_{300} and W_{450} Weight percent of residue at 300 and 450°C.

with increasing NaMt content and reached its maximum value with 5% NaMt content (NWPU2.5). In addition, ash content of both NWPU1 and NWPU2 series is increased with NaMt content which indicated interaction of the polymer and NaMt.

According to tensile tests, NaMt content has a remarkable effect on mechanical properties of the nanocomposites. The mechanical properties are summarized in Table 4. As the general trend, both stress and elongation at break values change with the NaMt content in all nanocomposites. Tensile tests show that both tensile strength and elongation at break values increase in the presence of NaMt, Elongation at break value increases almost by 50% for NWPU1 series and 100% for NWPU2 series with 5% NaMt content. However, tensile strength rises almost by 20% for NWPU1 series, 100% for NWPU2 series. The elastic moduli also increases with NaMt loading.

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 NaMt content. The test was carried out at 44°C for 500h. The weathering performance of the samples were examined by monitoring of light induced chemical changes via infrared absorbance characteristics using FTIR spectroscopy.[13,14] Several products containing carbonyl functions were 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 were evaluated by calculating carbonyl peak areas of the samples.

All the neat polymers and nanocomposites degraded during the test. 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 streching band at around 1530 cm^{-1}, N-CO-O + st C-O-C stretching at around 1249 cm^{-1} and 1040 cm^{-1}.

In the case of WPU polymers, WPU2 was more stable against photo degradation containing less hard segment and built of polyol with polyester units as well as having higher Mw compared to WPU1.

In the case of nanocomposites, it is observed that NaMt addition accelerates the degradation process. In NWPU1 series, 1% NaMt content doesn't cause significant change (NWPU1.1) whereas with 3% NaMt content, degradation rate raises by almost 12% (NWPU1.3) (Figure 6, Table 5).

Similar result is also observed for NWPU2 series. 1% content of NaMt increases the degradation rate by 6% (NWPU2.1) and 5% content of NaMt increased the rate up to 8% (Figure 7, Table 5).

In addition, color retention measurements were carried out using spectrophotometer.[15] Neat polymers were taken as reference and color change (ΔE values) were calculated (Table 5). If we consider the images of WPU polymers and nanocomposites, it could be said that color retention of neat polymers were much better if compared to nanocomposites. The ΔE values increase by rising of NaMt content of the nanocomposites.

Table 4.
Mechanical properties of WPU polymers and nanocomposites.

Sample	NaMt content (%)	E-Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
WPU1	–	1.77	0.51	102.10
NWPU1.1	1	2.24	0.55	116.28
NWPU1.3	3	2.25	0.64	148.41
WPU 2	–	3.03	0.67	80.09
NWPU2.1	1	2.50	0.91	142.05
NWPU2.3	3	3.43	0.98	165.99
NWPU2.5	5	4.46	1.14	154.32

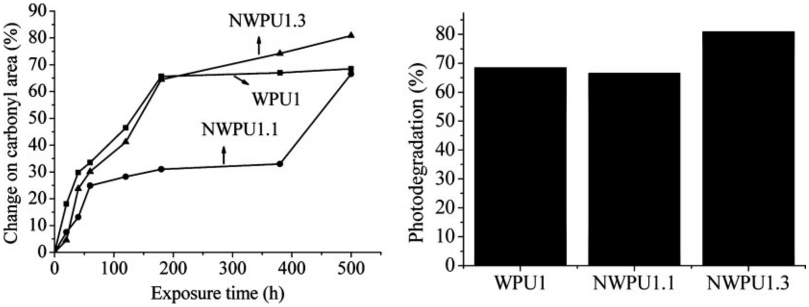


Figure 6.
Changes in carbonyl areas of WPU1 and NWPU1 series nanocomposites during solar radiation test.

Table 5.
Summary of percentage amount of changed peaks after solar radiation test.

Sample	NaMt content	ΔE	Changes of the carbonyl peak areas
	(%)		(%)
WPU 1	–	Control	68.46
NWPU 1.1	1	18.65	66.56
NWPU 1.3	3	21.55	80.86
WPU 2	–	Control	39.66
NWPU 2.1	1	9.95	46.19
NWPU 2.3	3	12.24	45.62
NWPU 2.5	5	15.82	48.45

Conclusion

Linear WPU polymers were synthesized by using two different type and molecular weight polyols as the soft segments via acetone process. Their nanocomposites were successfully prepared by using NaMt which is initially modified with polyol component by melt blending and following preparation of WPU nanocomposites were performed via in-situ intercalative polymerization. According to XRD and TEM analysis mostly intercalated and regionally exfoliated structure have been obtained. The nanocomposites were gained thermal resistance by shifting of degradation temperature and increasing ash content as NaMt content increases according to the TGA measurements. Tensile tests indicated significant improvement of toughness by the acting of NaMt particles as crosslinking points.

Solar radiation test showed that photodegradation were expected to be occured through hard segment units. In addition, increase in the rate of photodegradation was observed as NaMt content increases. This can be due to catalytic effect of transition metals such as Fe^{+2} and Fe^{+3} which are unexchangable cations and located intergallery spacing of NaMt.

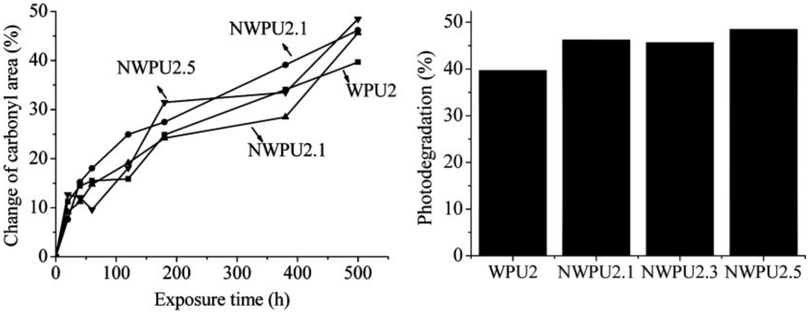


Figure 7.
Changes in carbonyl areas of WPU2 and NWPU2 series nanocomposites during solar radiation test.

[1] B. K. Kim, *Colloid Polym. Sci*, **1996**, *274*, 599–611.

[2] M. Szycher, "*Chapter 14: Waterborne Polyurethanes, Handbook of Polyurethanes*, CRC Press, USA **1999**, pp. 14–13.

[3] P. A. Liminana, A. A. Francisca, A. M. T. Palau, G. O. Barcelo, J. M. M. Martinez, *J. Adhes. Sci. Technol.*, **2006**, *20*(6), 519–536.

[4] M. M. Rahman, H. D. Kim, W. K. Lee, *J. Adhes. Sci. Technol.*, **2009**, *23*, 177–193.

[5] E. Açıkalın, O. Atıcı, Proceedings of the Polymer Processing Society 26th Regional Meeting, İstanbul, Türkiye, **2010**.

[6] E. Açıkalın, O. Atıcı, 1.Polimerik Nanokompozitler Sempozyumu ve Sergisi, İzmir, Türkiye, **2006**.

[7] ASTM D 2572 Standard test methods for Isocyanate groups in Urethane Materials or Prepolymers.

[8] L. C. Ciobanu, C. Ciabanu, D. Dorohoi, *High Perform. Polym.*, **2009**, *22*, 56–68.

[9] R. M. Versteegen, R. P. Sijbesma, E. B. Meijer, *Angew. Chem.*, **1999**, BNR: Z13388.

[10] M. J. Yeh, C. T. Yao, C. F. Hsieh, L. H. Lin, P. L. Chen, J. C. Wu, H. C. Yang, C. P. Wu, *Eur. Polym. J*, **2008**, *44*, 3046–3056.

[11] A. K. Nanda, D. A. Wicks, *Polymer*, **2006**, *47*, 1805–1811.

[12] S. S. Ray, M. Okamoto, *Prog. Polym. Sci.*, **2003**, *28*, 1539–1641.

[13] B. Singh, N. Sharma, *Polym. Degrad. Stab.*, **2008**, *93*, 561–584.

[14] R. Schwalm, C. Decker, F. Masson, Y. Heischkel, T. Jaworek, E. Beck, P. Enenkel, K. Menzel, RadTech Eur. 03, **2003**.

[15] ASTM D 2244 Standard Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates.