

Preparation of Polyurethane Silicon Oxide Nanomaterials as a Binder in Leather Finishing

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Abstract: Leather finishing processes using toxic organic solvent based produce volatile organic compounds (VOC), chronic exposure to this chemicals effect on workers' health causing many diseases especially lung cancer. So, polyurethane water-based was synthesized for application in leather finishing instead of organic solvent based because it's economic and safety for industry and workers. Preparation of water-based polyurethane (PU) depends on the reaction of polyethylene glycol (PEG, 300) with isophorone diisocyanate (IPDI) and the reaction of IPDI-1,4-butanediol (BDO) together with dimethylolpropionic acid (DMPA), was synthesized by poly-addition polymerization reaction. PU was then modified with different amounts of silicon dioxide nanoparticles (1-5 % SiO₂), used as a binder in leather finishing. Leather coated was characterized physically, chemically and thermally by FTIR, GPC, DLS, TEM, SEM and TGA. The results reveal that, water vapor permeability (WVP) of leather coated with PU modified with SiO₂ showed improvement due to the existence of SiO₂ particles which increases the interspaces of the polyurethane coating. SEM showed that when the amount of SiO₂ nanoparticles increases, there is uniform nanoparticles accumulated can be observed. EDX prove the presence of Si and O₂ elements and the formation of SiO₂ nanoparticles. Mechanical properties discussed that tensile strength; tear strength and elongation at break % increase with increase SiO₂ concentration until 3 % SiO₂ nanoparticles. TGA showed an improvement of thermal stability of coated leather modified with SiO₂. Therefore, this study succeeded in preparation of safe, ecofriendly of water-based polyurethane binders which modified with SiO₂ for using in leather finishing.

Keywords: Coated leather, Fibers, Leather finishing, Silicon dioxide nanoparticles, Water-based polyurethane

Introduction

Leather finishing is one of the most significant stages, responsible for the enhancement the leather appearance, it provides the performance characteristics expected of finished leather that required for end users. Leather finishing shows an important role in the final form of the produced leather such as color, fullness, elasticity, gloss, fastness and stability [1-3].

Binders are products accomplished to form a thin film upon drying on the surface and signify the basic element in an aqueous leather finishing formulation. Four types of binders having altered chemical base are used in leather finishing: acrylic, protein, butadiene and polyurethane. All of them have precise properties according to their chemical structure. Hence, choosing the most suitable binder to obtain the desirable effects is very essential [3-8].

Preparation of cationic organosilicone/polyurethane micro-emulsion and its application in leather finishing processes was investigated by Yiding [4]. The WPU/HPMS micro-emulsion is a good finishing agent; provides leather with brilliance, gentleness and soft surface thus improving the quality of leather. The current finishing agents have many disadvantages as; unstable properties at different temperature, poor coverage, low chemical resistance and mechanical properties. Emissions of VOC and wastewaters was one of critical environmental problems in the leather finishing

process, hence, it is essential to reduce the content of solvents used in the finishing recipes. Solvent based finishes must be limited owing to their toxicity, negative effects on the environment and in terms of safety. Aqueous finishing, present advantages as inflammability for products to be used, or stored, healthy environment and working place, reduction of atmospheric emissions of VOC and waste products [9,10]. To overawed these problems, this research aims to prepare water-based polyurethane finishing binders modified with silicon dioxide nanoparticles (SiO₂), which have many advantages as small nano-size that can bind with leather surface and impart better characters such as softness, flexibility and donated with many dominating properties.

Nowadays, many studies concentrated on the preparation of composite materials having nanoparticles or hybrids in ceramics industry and polymer technology [11]. Recently, mixture of organic/inorganic (waterborne polyurethane-silica) via sol-gel process has concerned great consideration in the area of nanomaterial science due to prospective for improvement of new materials with useful and unique properties, by controlling at the molecular structural level. Despite of the inorganic silicon nanoparticles is brittle; it shows a number of valuable properties for surface as hardness, transparency, higher thermal stability and physical properties. In conflicting, the organic polymer shows good flexibility, low density, easy processing but are thermally unstable [11-16].

Polyurethane polymeric materials (PUs) are distinctive with a varied range of physical and chemical properties [17]. Polyurethane designated to accommodate the highly varied needs of modern technologies as adhesives, coatings and

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thermoplastic elastomers [18-27]. The assessment of finishing application as aliphatic polyurethane dispersions and polyurethane/polyacrylate (PUA) composite emulsions was studied by Chai and Zhang [21]. The results show that the anionic PU dispersions, the core-shell and interpenetrating PUA composite emulsions showed fine good film forming and strong adhesive force to leather. Characterization of the bought SiO_2 nanoparticles and possibility for application in leather coating was studied by Sudhakar [27]. It was revealed that the silica sol-gel nanoparticles coated leather exhibited enhanced water vapor permeability and increased linkage in base coat application.

Also, waterborne PUs have received increased attention recently because it gave healthy and fire-resistant products. Some disadvantage of PUs such as low mechanical strength and water resistance which can be improved by modifying them with (SiO_2).

In this research, preparation of water-based polyurethane and its modification with different ratios of silicon dioxide nanoparticles via the sol-gel process and its application on leather surface was discussed then evaluation of the leather properties before and after coating.

Experimental

Materials

Crust bovine leather was supplied by Hafez-Abaas; medium tannery (Misr-Elkadima, Cairo, Egypt). Polyethylene glycol with molecular weight (300) (PG300), isophorone diisocyanate (IPDI), 2,2-bis(hydroxyl methyl) propanoic acid (DMPA), N,N-dimethyl formamide (DMF), dibutyltin dilaurate (DBTDL) and 1,4 butanediol (BD) were provided by Acros, ethylene diamine (ED), triethyl amine (TEA), ethanol and ammonium hydroxide were supplied by S. D. Fine-Chem Ltd. Tetraethoxysilane (TEOS) for in situ sol-gel was provided by Sigma-Aldrich (Germany).

Preparation of Silica Sol-gel Nanoparticles

Silicon dioxide nanoparticles (SiO_2) were synthesized by sol-gel method from TEOS, ethanol and de-ionized water in presence of ammonia as catalyst at room temperature [25, 26]. Simple step based on hydrolysis and condensation process of TEOS in ethanol and water mixture in alkaline condition at room temperature. An experiment was carried out by taking 20 ml of ethanol in 50 ml beaker, followed by 2 ml of TEOS, 25 ml deionized water and 4 ml of concentrated ammonia solution. The mixture was stirred for 30 min, at the end milky white solution was obtained then centrifuged. This resulted in fine white powder, which was characterized by TEM, EDX, FTIR and confirmed as (SiO_2).

Preparation of Water-based Polyurethane (PU) as a Binder in Leather Finishing

Preparation of polyurethanes binders were carried out with

the following constituents as shown in Table 1. Polyurethane was prepared by reaction of PG300 with DMPA and BD dissolved in DMF in 250 ml three necked round bottom flask fitted with mechanical stirrer, thermometer nitrogen gas inlet and reflux condenser. The mixture was heated at 90°C for about 30 min. After complete mixing IPDI and DBTDL as a catalyst were slowly added to the flask to maintain the reaction temperature at 90°C for 3 hours (Scheme 1).

The mixture was cooled to 50°C and added TEA for 30 min, the neutralization reaction was proceeded at the same temperature for 30 min. Afterward, EDA was added to dispersion and the temperature was kept at 50°C for about 30 min to complete the chain extension reaction.

From Table 1 it was found that (PU8=PU) is the best water-based polyurethane prepared due to its complete solubility in water and it was applied as a binder in leather finishing.

The Application in the Leather Finishes with SiO_2

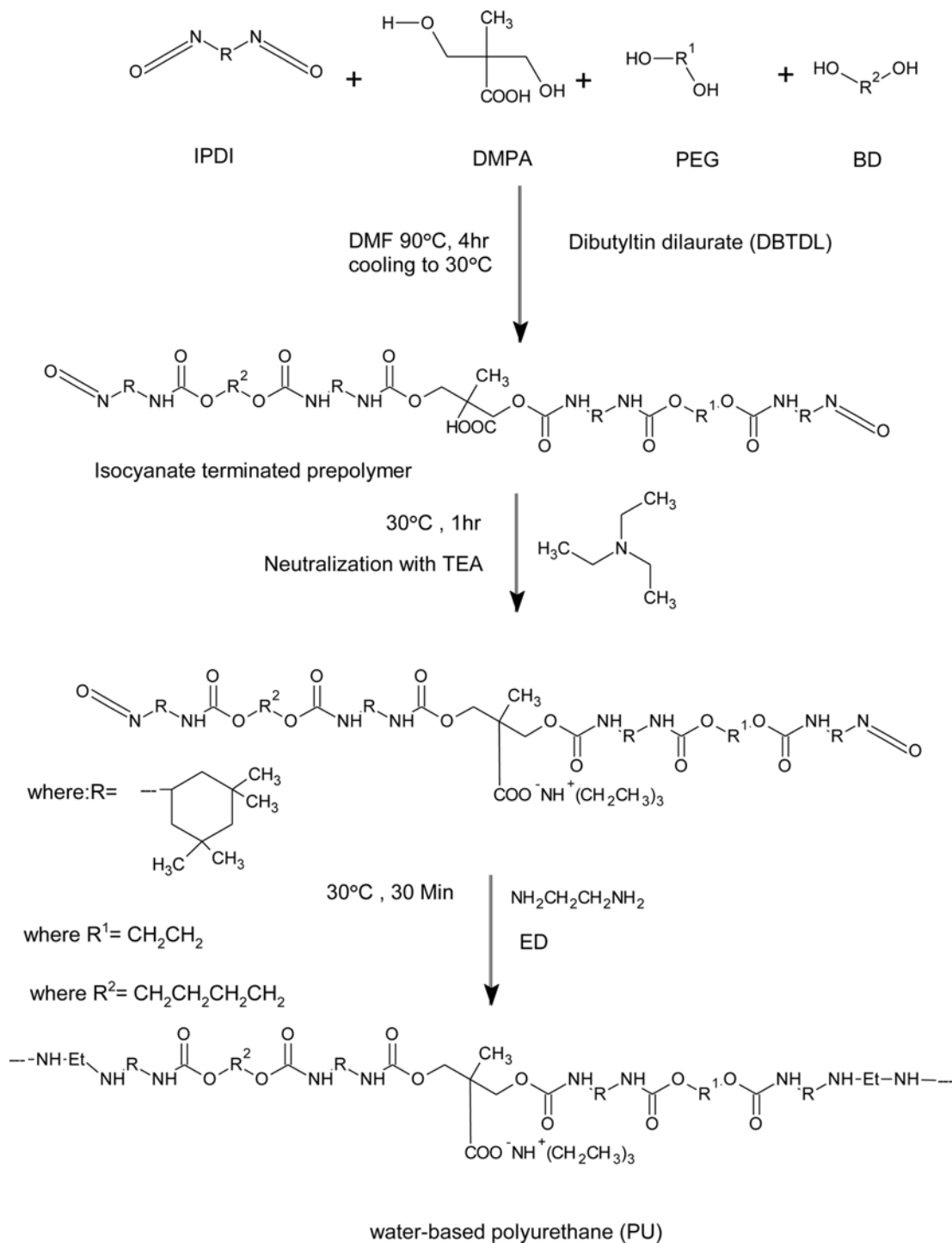
After coating processes the performance properties of leather were evaluated. Nanoparticle, dispersing agent and water were pre-mixed and sonicated for 30 min and it was added to the coating mixture formulation i.e., with water, polyurethane resin binder. The final mixture was sonicated for 30 min. Cow crust leather from Egyptian origin with thickness of 1.6/1.8 mm was taken for evaluation.

Modification of Binder Resin Leather Coating Agent with SiO_2

The binder resin leather coating agent is modified by mixing with the SiO_2 sol. A fixed quantity of polyurethane binder resin was weighted and the SiO_2 sol 5 % of polyurethane latex (based on TEOS) was added into a three-necked reactor, stirred for 30 min at a definite temperature. Then, the mixture was disposed into a supersonic wave cell disruption machine for a period of time.

Instrumentation and Characterization

The fourier transform infrared (FTIR) spectra were taken with a Nexus 670 spectroscopy (Nicolet, United States) over the range of $400\text{-}4000\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} ; the KBr disk technique was applied. Gel-permeation chromatography (GPC) was used to investigate the molecular weight of the prepared copolymers, the instrument was from Knauer-Berlin, with a RI detector in combination with a PL-GEL 5 mm mixed C column, $300\times 7.5\text{ mm}$ (Polymer Laboratories, UK) using a flow rate of 1 ml/min and THF as eluent and calibration was performed with linear polystyrene (PS) standards. The particle size distribution was measured by dynamic light scattering (DLS, Zetasizer Nano ZS, Malvern Instr., UK) in accordance with ISO 22412, average particles diameters and particle size distribution were determined from the intensity-weighted size distributions.



Scheme 1. Preparation of polyurethane binder (PU).

Transmission electron microscopy (TEM) were obtained using instrument of JEM-100CXII TEM (Japan) at 120 KV, the hybrid concentrations specimens were prepared by dropping the specimen solution (polyurethane binders+ SiO₂) on carbon coated copper grid to form a very thin hybrid film (S160-3 Plano GmbH). Water vapour permeability

(WVP) or water vapour transmission rate (WVTR) is a measure of the passage of water vapor through the material. WVTR of leather coated with PU modified with silicon oxide nanoparticles was carried out on the Herfeld's appliance (according to DIN 5333 and ASTM-E96) [28]. It is the mass of water vapor transmitted through unit area in

Table 1. Preparation of water-based polyurethanes binder

Sample	PEG (ml)	DMPA (g)	IPDI (ml)	BD (ml)	ED (ml)	Physical properties
PUB1	2.66	1.34	8.38	1.78	0.67	Insoluble
PUB2	2.66	1.34	6.3	-	0.67	Insoluble
PUB3	2.66	1.34	6.31	0.89	0.67	Insoluble
PUB4	2.66	1.34	6.3	0.89	1.0	Insoluble
PUB5	2.66	1.34	4.2	-	0.67	Partially soluble
PUB6	1.33	0.81	6.3	0.85	0.67	Partially soluble
PUB7	1.33	0.81	6.3	1.69	0.67	Partially soluble
PUB8	1.33	1.34	9.4	1.78	0.67	Completely soluble

With 0.14 ml TEA.

unit time under specified conditions of temperature and humidity. ASTM-E96 is one of the most widely used breathability measurement method (the cup/Gravimetric method). Although the standard method suggests range of testing conditions such as temperature, relative humidity and air flow velocity, results reported in practice do not always conform to these suggest ions. Herfeld's device consists of a glass container with a metal top cover which contains a circular hole of diameter 60 mm. 50 ml of water is poured into the glass vessel (water method). The studied material pattern is placed (face up) on the cover of the vessel of circular diameter of 55 mm and the lid is closed and tightened. The device is placed in a desiccator with 97 % of sulphuric acid. The weight of the apparatus with the specimen and the water is determined at the beginning and after the given time interval of 24, 48 and 72 h. Water vapour permeability or transmission (WVTR) is determined according to equation:

$$WVP = [m_0 - (m_1 + m_2 + m_3) / 3] / tA = G / tA = (G/t)A$$

G : weight change (g)

m_0 : mass of the device with water and specimen at the beginning (g)

m_1 : mass of the device with water and a test tube after 24 h (g)

m_2 : mass of the device with water and a test tube after 48 h (g)

m_3 : mass of the device with water and a test tube after 72 h (g)

t : time (h)

G/t : slope of the straight line (g/h)

A : test area (cup mouth area) (m^2)

WVP: rate of water vapor permeability or transmission ($g/h m^2$) or ($mg/h cm^2$)

Scanning electron microscopy (SEM) images of the leather samples ($1 cm^2$) were subjected to sputter coating with gold ions which acted as a conducting medium during scanning, and observed using a Philips Quantan 250 electron microscope. Energy-dispersive X-ray spectroscopy (EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample, its characterization

capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray emission spectrum. Determination of mechanical properties by dumbbell shaped specimens were used for the measurement of the tensile strength and elongation at break (%), these tests were carried out using a Zwick/ Roell (Z010) according to ASTM D 412 and tear strength according to ASTM D624. The average value for each test was taken for three samples to confirm the results. Thermal gravimetric analysis (TGA) was studied with a Perkin Elmer thermogravimetric analyzer (rate= $10^\circ C/min$) from room temperature to $600^\circ C$.

Results and Discussion

Characterization of Water-based Polyurethane (PU)

Molecular Weight Determination by Gel Permeation Chromatography (GPC)

The molecular weight characteristics, particle size and the appearance of PU showed in Table 2. The number average molecular weight (Mn) of PU and weight average molecular

Table 2. Molecular characteristics and appearance of PU

Name	Mn (g/mol)	Mw (g/mol)	Particle size (nm)	Appearance
PU	850	1730	50	Liquid, completely soluble

Table 3. Relation between particle size distribution and addition of silicon nanoparticles

Sample	Diameter size (nm)
PU	50.2
PU/1 % Si	57.3
PU/2 % Si	124.8
PU/3 % Si	130.6
PU/4 % Si	140.9
PU/5 % Si	163.8

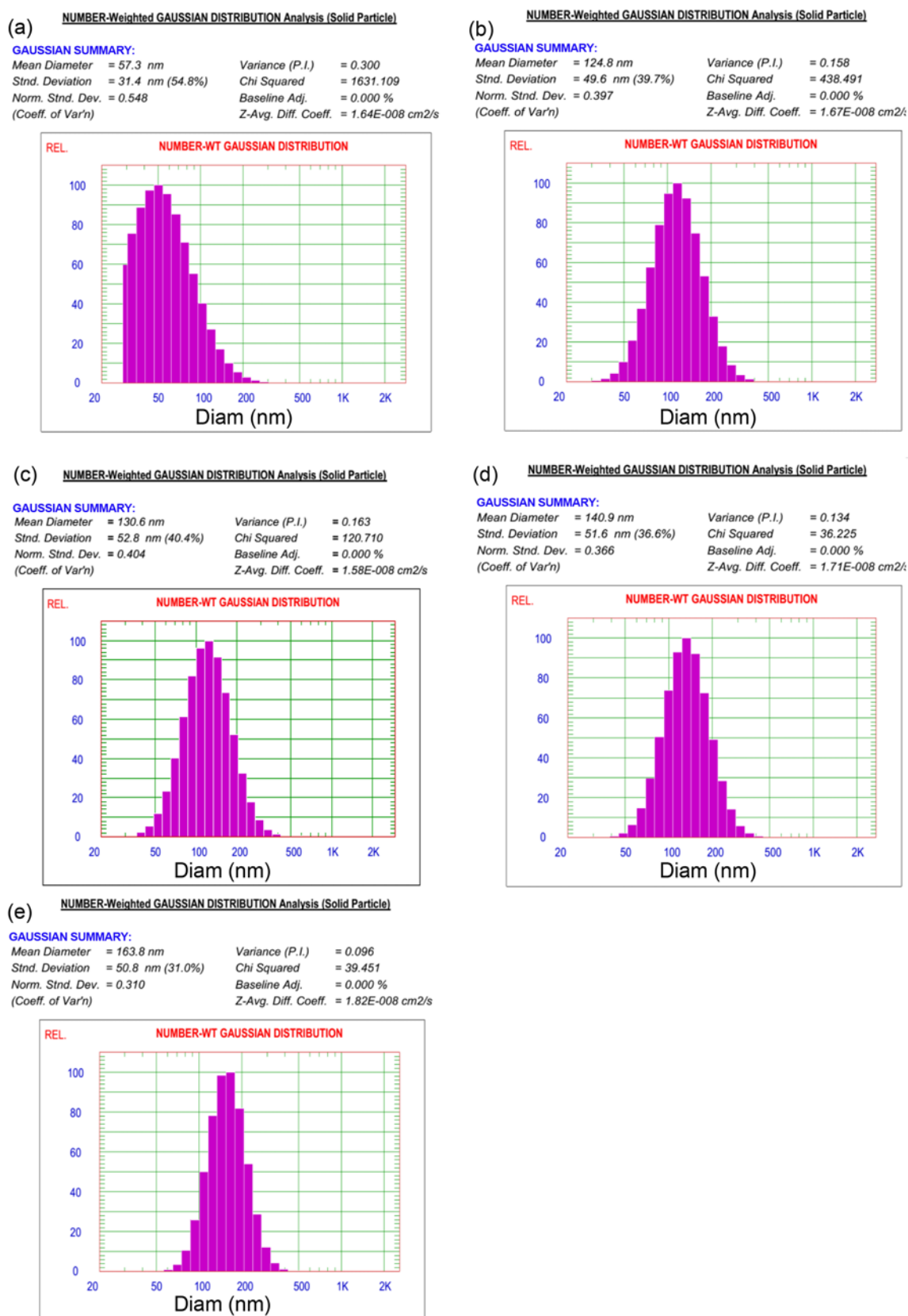


Figure 1. DLS images of colloidal particle size of PU with (a) 1 %, (b) 2 %, (c) 3 %, (d) 4 %, and (e) 5 % silicon dioxide nanoparticles.

weight (Mw) were calculated by GPC as follow.

Dynamic Light Scattering (DLS) of PU and Silicon Dioxide Nanoparticles

The crosslinking waterborne polyurethane (PU) formed dispersal of 26 % solid content and pH value about 8. Table 3 displays the particle size distribution of the water-based polyurethane crosslinked by IPDI and effect of increasing SiO₂ during the synthesis process. The crosslinking waterborne polyurethane shows fine particle size, as SiO₂ increase and the number of colloidal particles size increased. These obtained results shown in Figure 1(a-e).

FTIR Spectra of the SiO₂, Prepared PU and Leather Coated with PU Modified with SiO₂

FTIR spectroscopy is a great technique to analyze chemistry of water-based polyurethane films. The assignments of IR bands of the aqueous polyurethane are offered in Table 4 and Figure 2. The crosslinking reaction of polyurethane dispersion shows increasing in the intensity urea band with respect to C=O of urethane and urea groups at 1704 cm⁻¹. The IPDI and EDA produced increasing in the intensity band of NH

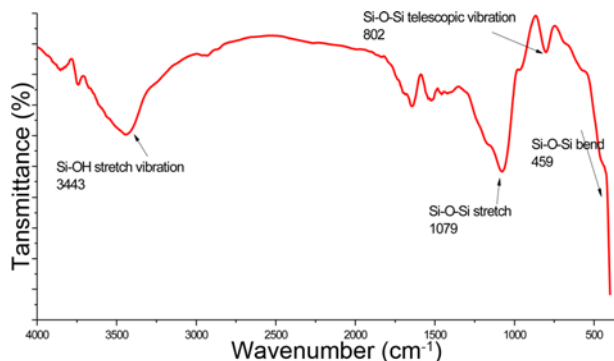


Figure 2. FTIR spectra of SiO₂.

Table 4. FTIR spectra for SiO₂, PU and leather coated with PU/SiO₂

Assignment	Peak wavenumber (cm ⁻¹)		
	SiO ₂	PU	Leather/PU/SiO ₂
NH stretching	-	3480	3500
Si-OH, OH stretch of water	3443	3375	3370
CH ₂ asymmetrical stretching	-	2948	2925
CH ₂ symmetrical stretching	-	2867	2857
C=O stretch coupled with COO-	-	1704	1662
NH bend coupled C-N stretching	-	1554	1574
CH ₂ bending	-	1462	1410
CH ₃ bend, C-N, CH ₂ wagging of proline	-	1384	1339
NH bending	-	1244	1239
C-O-C, Si-O-Si stretching	1078	1127, 1045	1107
bending vibration of Si-OH, -C-C- stretching	968	953	952
Si-O-Si telescopic vibration -C-C-, CH out of plane	802	773	814
Si-O-Si bending vibration, CH out of plane, skeletal stretching	452	646	765, 675, 418

stretching at 3480 cm⁻¹ and broadening band at about 3375 cm⁻¹ created from the hydrogen bond of OH group which doesn't contribute in the reaction. An increase in relative intensity of CH stretching band at 2948 cm⁻¹, 2888 cm⁻¹ st CH₂, CH₃, CH

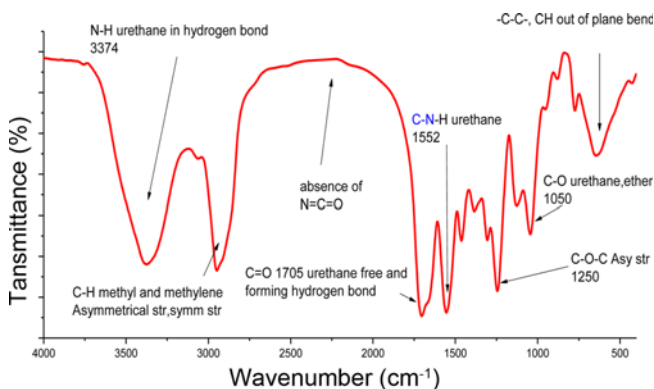


Figure 3. FTIR spectra of PU.

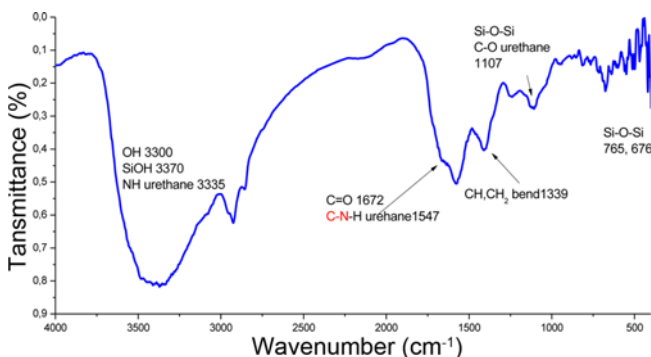


Figure 4. FTIR spectra of leather coated with PU modified with 3 % SiO₂.

and stretching C-N and N-H band at 1554 cm^{-1} and 1384 cm^{-1} . Moreover, the FTIR spectrum shows the appearances C-O-C stretching bands at 1127 , 1045 , 953 and 773 cm^{-1} of the macroglycol. It is clear from the Figures 3, 4, that no absorption band was detected at around $2100\text{--}2270\text{ cm}^{-1}$ which related to absence of $\text{N}=\text{C}=\text{O}$ group, indicating that the whole amount of each IPDI were completely reacted and consumed through the reactions. Therefore, these confirm the addition reaction and formation of the water-based polyurethane of PU polymers.

Figures 4 display the changes between the structures of SiO_2 , polyurethane binder and leather coated by PU modified with SiO_2 . It shows abroad overlapping band at 3480 cm^{-1} related to the absorption peak of O-H, N-H stretch and Si-OH related to spectra of SiO_2 appear at 3443 cm^{-1} which still exists in the curve of leather/PU/ SiO_2 . A strong expanding absorption peak at 1078 cm^{-1} related to Si-O-Si vibration and weaker absorption peak for the bending vibration of Si-OH at 968 cm^{-1} . Because of the hydrolysis and condensation of Si-OH, bond Si-O-Si formed. The stretching vibration of the bond Si-O-Si appears at 814 cm^{-1} while the bending vibration of Si-O-Si appears at 445 cm^{-1} . The results of SiO_2 were in

agreement with the literature [26].

Transmission Electron Microscope (TEM) of SiO_2 and PU Modified with SiO_2

The TEM images of the pure (SiO_2) and the water-based polyurethane with different amount of SiO_2 (1, 3, 5 %) are provided in Figures 5. Figure 5(a) shows pure SiO_2 particles distributed in the solution without any aggregation or agglomeration. This indicates the dispersion of SiO_2 is very good with a uniform spherical particles prepared by the sol-gel process. The SiO_2 domains formed by the sol-gel process are in range of 10-60 nm. Figure 5(b-d) shows the TEM pictures obtained for the modified polyurethane binder / SiO_2 . The SiO_2 domains are embedded in the polymeric matrix on nano-metric scale. The SiO_2 particles are the core covered by a layer of polyurethane, and these particles containing polymer shell layer. This connection may be due to the presence of both hydroxyl groups on leather surface and amide group of the polyurethane.

By increasing SiO_2 content from 1-5 % the particle size increase reaching to 250 nm, in the same time the particles is stabilized and don't form aggregation because the formation of a strongly interconnected hybrid organic-inorganic network.

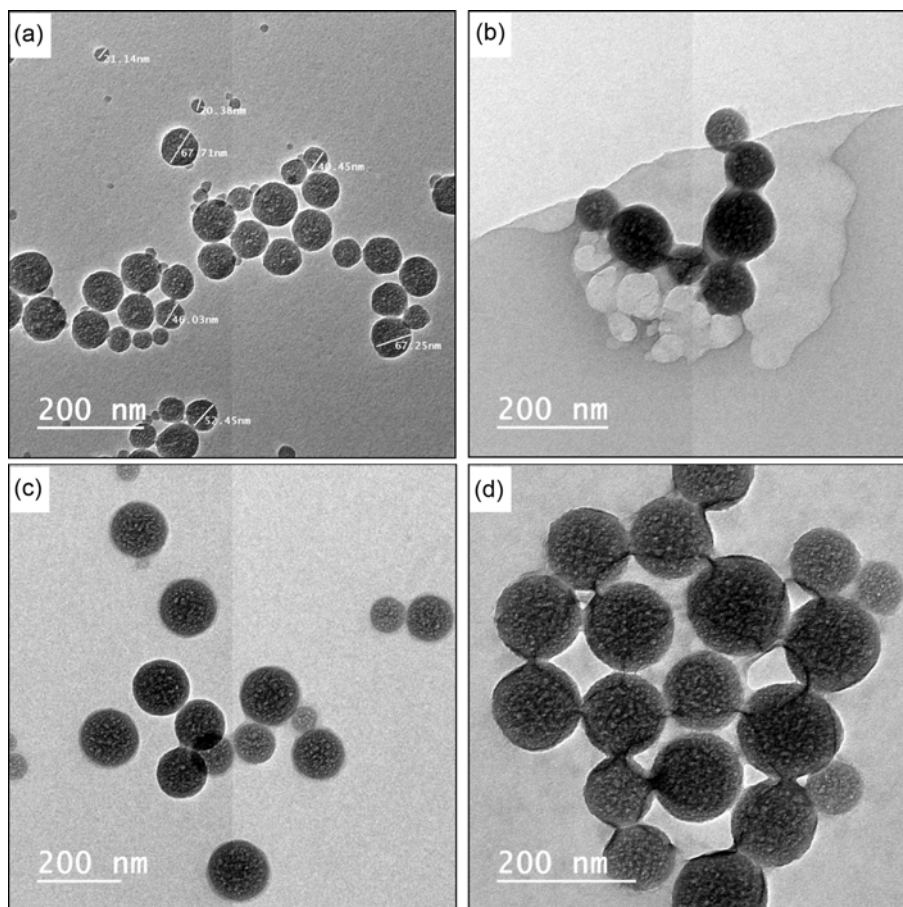


Figure 5. TEM image of (a) SiO_2 (5-70), PU binder modified with (b) 1 % (50-116 nm), (c) 3 % (55-120 nm), and (d) 5 % (90-250 nm) SiO_2 .

Table 5. Effects of different SiO₂ concentration and PU binder mix. on water vapor permeability of coated leather

Leather samples coated with different amount of silicon dioxide	Water vapor permeability (mg/10 cm ² 72 h) ^a	Thickness (mm) ^b
Blank	0.2867	2.30
0 %	0.3652	2.55
1 %	0.3805	2.55
2 %	0.3882	2.50
3 %	0.3925	2.55
4 %	0.3907	2.45
5 %	0.3889	2.50

^aMean±SD (0.002-0.008), n=3, ^bMean±SD (0.08-0.11), n=5 average value of 5 times measured from different area in leather surface.

Evaluation of the Coated Leather with Polyurethane WVP of Coated Leather with PU and Leather Coated with PU Modified with SiO₂

Water vapor permeability of the leather is a mixture of the process that water transfers via the holes and water vapor moves through the hydrophilic groups of collagen. Table 5 shows that, WVP of the leather finished by polyurethane/SiO₂ is more than that of the leather finished by polyurethane only. The water vapor barrier properties of leather can be enhanced by using polymer nanocomposites, which include two-phase system of a polymeric matrix and dispersed inorganic nanoparticles. However, there is a limiting factor as dispersion of the nanoparticles in the polymer matrix [26,29,30]. The presence of SiO₂ increases the hydrophilic groups, which improve and quickens the spreading of water

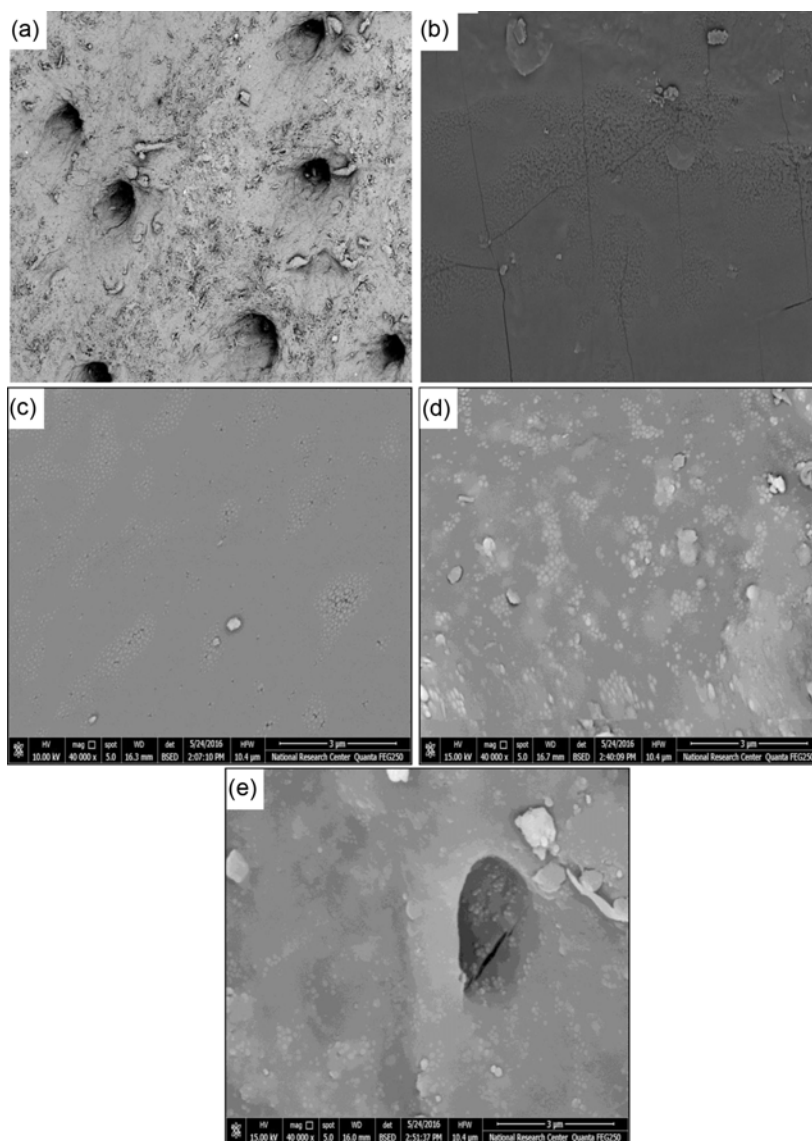


Figure 6. SEM images of (a) the grain surface of uncoated leather ($\times 600$) (b) the grain surface of leather coated with polyurethane (c) the grain surface of leather coated with polyurethane modified with 1 %, (d) 3 %, and (e) 5 % SiO₂ ($\times 40000$).

vapor molecular. Also, the presence of SiO₂ particles growths and increases the interspaces holes of leather coating during the film formed period with polyurethane modified by SiO₂, thus helping to improve WVP of finished leather.

Scanning Electron Microscope of Leather Coated with PU and Leather Coated with PU Modified with SiO₂

SEM is a valuable technique for evaluation the effects of various treatments onto the leather surface, used to measure the penetration of the polyurethane by the leather surface and onto the hierarchy of the structure. SEM of leather with polyurethane binder and leather with PU modified with SiO₂ carried out to show the effect of the prepared polyurethane and different concentration of SiO₂ on the grain and fiber bundles as a binder in finishing leather.

Figures 6 present SEM images for uncoated leather, leather coated with PU and leather coated with PU binder modified with different mole ratios (1, 3, 5 %) SiO₂. The SiO₂ impregnated leathers showed SiO₂ nano-spheres along collagen fibers with increasing amount of SiO₂ content. Figure 6(a) shows the presence of uncoated grain of crust leather composed of interwoven collagen fibers and hair holes follicles even at low magnification. Alternatively, the leather coated with polyurethane sample shown in Figure 6(b-e), the pores filled with the prepared copolymers and these confirm the coating process.

The SEM morphology of the PU modified with SiO₂ fractures is shown in Figures 6(c-e) which displays a continual matrix with uniform distributing nanometer part, as the amount of SiO₂ increases, bigger size particles detected. As soon as the SiO₂ reaches to 3 %, the average particle size of SiO₂ in the matrix reaches to 70-140 nm with uniform distribution. While at 5 % SiO₂, although the SiO₂ still presents mostly uniformly and distributed in polymer continuous matrix, the average particle size increases to larger gathered particles reaching to 250 nm Figure 6(e).

Energy-dispersive X-ray Spectroscopy (EDX) of Leather Coated with PU Binder Modified with SiO₂

Figure 7 and Table 6 showed the EDX results of leather coated with polyurethane binder modified with 3 % SiO₂ nanoparticles which confirmed the presence of Si and oxygen elements due to SiO₂ nanoparticles in addition to the presence of principal elements as Cr, Na and C that present in leather as a result of salting and tanning process.

Mechanical Properties of Leather Coated with PU and Leather Coated with PU Modified with SiO₂

The mechanical properties of leather coated with PU and leather coated with polyurethane binder modified with SiO₂ were investigated. Tensile strength, elongation at break (%) and tear strength were studied and the results are presented in Table 7.

It is noticeable; that coating agents covered the pores of hair follicles hide parts, resulting in more strength for leather fibers. Tensile, tear strength and elongation at break % tests

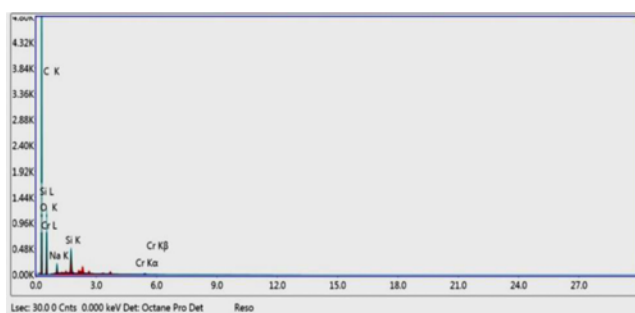


Figure 7. EDX peaks of PU binder modified with 3 % SiO₂ nanoparticles.

Table 6. Elemental analysis of leather/PU/SiO₂ nanoparticles

Element	Weight (%)	Atomic (%)
C	66.2	73.23
O	29.93	24.85
Na	1.52	0.88
Si	1.98	0.94
Cr	0.36	0.09

were performed to determine whether the application of SiO₂ emulsions nanocomposites could modify the mechanical properties of leathers by affecting on their quality and agreement with some standard requirements for certain types of leather.

Table 7 shows that different amounts of SiO₂ effects significantly on the mechanical properties of the PU films. Tensile, tear strength and elongation at break % increase with increasing of SiO₂ percent up to 3 %. This means that, only a certain quantity of SiO₂ (3 %) can improve the mechanical properties. However, excessive amount of SiO₂ more than 3 % cause irregular uniform dispersion of nanoparticles, deformity of microstructure of composite materials leading to reduction of the mechanical properties of the polyurethane films. As a whole, using 3 % of SiO₂, the properties of modified water-based polyurethane films gave better results and improved than others. From the obtained results of 3 % SiO₂, the tensile strength increases from 12.4 to 17.1 MPa, tear strength increased from 293 to 397 N/cm and the elongation at break % also increases significantly by 30 %.

Thermal Gravimetric Analysis (TGA) of Leather Coated with PU and Leather Coated with PU Modified with Different Amounts of SiO₂

Thermo-gravimetric analyses of leather, polyurethane, leather coated with PU and leather coated with PU modified with different amounts of (SiO₂) were presented in Figure 8. The thermo-gravimetric curve of uncoated leather Figure 8(a) show two-step degradation, however leather coated with polyurethane showed three-step degradation, with an initial weight loss of about 10-12 % at 100 °C because of the

Table 7. Mechanical properties of leather coated with PU and leather coated with PU modified with different percents of SiO₂

Coated leather samples with SiO ₂ (%)	Tensile strength (MPa) ^a	Increase of tensile strength (%)	Tear strength (N/cm) ^b	Increase of tear strength (%)	elongation at break (%) ^c	Increase of elongation at break (%)
Blank	10.4	-	262.8	-	40	-
0 %	12.4	0.0	293	0.0	51	0.0
1 %	15.1	21.77	350	19.45	67	31.37
2 %	15.9	28.22	387	32.08	72	41.17
3 %	17.1	37.80	397	35.49	81	58.82
4 %	16.5	33.06	366	24.9	75	47.05
5 %	14.3	15.32	330	12.62	69	35.29

^aMean±SD (0.5-0.9 MPa), n=3, ^bMean±SD (20-30 N/cm), n=3, and ^cMean±SD (5-7 %), n=3.

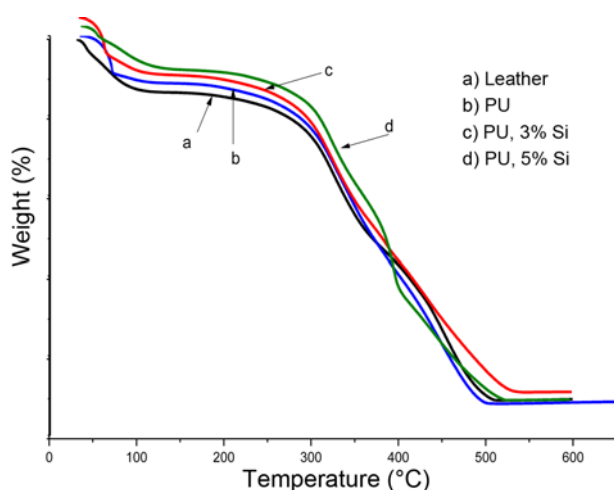


Figure 8. TGA images of (a) uncoated leather (b) PU, leather coated with PU binder modified with (c) 3 %, and (d) 5% SiO₂.

release of moisture included in the leather fibers. After this process, the leather fiber was approximately stable up to 304 °C, at which gradual decomposition began to occur. Figure 8(b) shows The TGA curve of polyurethane which exhibits three distinctive weight loss stages, from 42 °C to approximately 800 °C. The 1st stage, in temperature range of 50-290 °C, effects from the evaporation of water and loss of oligomer and byproducts existing in the PU. The 2nd stage, about 304 °C is primarily the decomposition of the hard segment, involves the dissociation of urethane to the original polyethylene glycol and diisocyanate, which then form primary amines, alkenes and carbon dioxide. The 3rd stage, about 350 °C related to the decomposition of the soft segment of polyurethane.

The TGA curves in Figure 8(b) show that, the decomposition temperature of the leather coated with polyurethane is higher than uncoated crust leather. This may be due to the incorporation of the polyurethane into leather which increases the thermal stability of the collagen/polyurethane leather over that of the uncoated blank leather. This improvement in thermal stability recognized to the crosslinking between

polymer and collagen. Which can be illustrated by brought about multiple weak hydrogen bonding between the various carbonyl groups (C=O) of the polyurethane and the uncountable hydrogen atoms of (NH) peptide groups in the leather, which support the linkages between the polyurethanes and grain of corium in the leather. These obtained results indicate that, polyurethane filling up and fix the interwoven collagen fibers and hair holes follicles of leather fibers.

The thermo-gravimetric curve of leather/polyurethane/silicon dioxide (3, 5 %) show three-step degradation Figures 8(c,d), obviously with leather coated with polyurethane/5 % SiO₂ suggest, an initial weight loss of about 9-10 % at 100 °C due to the release of moisture included in the leather fibers. After this process, the leather fiber was approximately stable up to 291-295 °C, at which gradual decomposition began to take place. The second degradation at 323 °C, there was a loss of nearly 46-66 wt % that resulted from the burning of organic hydrocarbon chains of the leather and the hard segment of polyurethanes. It involves the evaporation of (CO, CO₂), and the dissociation of urethane to the polyethylene glycol and diisocyanate, which then form a primary amines, alkenes and carbon dioxide. The third degradation at 440-501 °C included the degradation of the soft segment of polyurethane and a release amount of silicon dioxide.

The incorporation of different percents of SiO₂ didn't improve the first degradation temperature; however enhance the second degradation temperature. The TGA results were shown in Figures 8(c,d), the second degradation of polyurethane/SiO₂ occurred at about 438 °C and the third degradation at 501 °C. This indicates that silicon dioxide nanoparticles interact with the soft segment in polyurethane structure which limits the segmental movement of PU with SiO₂, leading to the increase in the thermal stability [29,30].

Conclusion

The aim of this article is, preparation of water-based polyurethane and its modification with different ratios of silicon dioxide nanoparticles (SiO₂) then application onto

leather surface and evaluation of these leather samples through visual, physical, chemical and mechanical analysis.

Dynamic light scattering (DLS) of PU and SiO₂ showed that as SiO₂ increase the number of colloidal particles size increased. FTIR spectra of leather coated with PU modified with SiO₂ nanoparticles showed the presence of leather functional group of and PU modified with SiO₂ which prove the presence of PU and SiO₂ onto leather surface. TEM of SiO₂ and the polyurethane modified with SiO₂ showed an increase of SiO₂ content from (1-5 %) the particle size increase from (50-250) nm. WVP of leather coated with PU modified with SiO₂ nanoparticles showed that the presence of SiO₂ particles increases the interspaces of the polyurethane leather coating matrix so improving WVP of finished leather. SEM leather coated with PU modified with SiO₂ showed that when the amount of SiO₂ nanoparticles increases, there is uniform nanoparticles accumulated can be observed. When the SiO₂ reaches to 3 % the particle size is about (70-140) nm. EDX of leather coated with PU modified with SiO₂ nanoparticles confirmed the presence of Si and oxygen elements and the formation of SiO₂ nanoparticles. Mechanical properties of leather coated with PU modified with SiO₂ nanoparticles showed that tensile strength; tear strength and elongation at break % increase with increase (SiO₂) concentration until 3 % nano-SiO₂. TGA of leather coated with PU modified with SiO₂ nanoparticles showed an improvement of thermal stability of coated leather. This study succeeded in preparation of ecofriendly water-based polyurethane binders modified with silicon dioxide nanoparticles materials for using in leather finishing.

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