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Polyurethane Nonionic Surfactants and Their Nanoparticles: Synthesis and Characterization of Their Structures

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FIVE NOVEL nonionic polyurethane surfactants were prepared by the reaction of polyethylene glycol with different molecular weight by toluene diisocyanate to obtain the polyurethane polymer, which was reacted by oleic acid to obtain the nonionic surfactants. The chemical structures of the prepared surfactants were determined using FTIR spectra and their molecular weights were determined using GPC analysis. Silver nanohybrids of the nonionic polyurethane surfactants were prepared via physical combination by chemically prepared silver nanoparticles. The silver nanohybrids were determined by UV, TEM, SEM, and DLS spectroscopy.

Keywords: Nonionic surfactant; Polyurethane, Nanohybrid.

Polyurethanes are playing an important role in many industries because of their widely ranging mechanical properties and their ability to be relatively easily machined and formed as plastics, foams and elastomers. In particular, urethane materials, such as foams and elastomers, have been found to be well suited for many applications. The production of polyurethane includes the reaction between isocyanate groups (diisocyanate) and hydroxyl groups (polyol) leading to urethane groups. The second reaction is the gas production by the reaction of isocyanate groups with water to form amine and carbon dioxide gas (chemical blowing agent) in the form of bubbles(1). The polyurethanes are three types: flexible foams when the used polyols molecular weights greater than 2500 g/mol.; semi-rigid foams used polyols with molecular weights of 2000-6000 g/mol.; while rigid foams used shorter chain polyols with molecular weights of 200 to 4000 g/mol(2). Water soluble polyurethanes are forming several polyurethane dispersions in aqueous medium. Polyurethane dispersions are polymer dispersions exhibit several advantages including the low volatility of organic solvent, non-toxic and non-flammability properties(3). For this reason, polyurethane dispersions gained thorough study and developed to more environmental, biodegradable and functional substrates(4). Among all types of polyurethane dispersions, nonionic polyurethanes are characterized by improved acid and alkali resistance and can be used in the synthesis of leather surfactant, dye dispersants and textile finishing agents (5). Organic fatty acids are renewable, environmentally friendly and biodegradable natural materials. The introduction of fatty acids, either pure acids or mixture of conventional fatty acids(6) into nonionic polyurethane polymeric chains increases their eco-friendly properties.

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Furthermore, the obtained compounds are provided more potential functions such as turning the polymer chains to more homogeneous by organic compounds. These features make nonionic polyurethanes more industrially striking raw material in the polyurethane industry. Nonionic polyurethane was synthesized directly by the reaction of polyurethane ingredients with Tung oil (7). Other types of nonionic polyurethane were prepared by functionalized compounds containing hydroxylated Tung oil from ester and/or by reaction at the double bond(8). Hydroxylated Tung oil is usually suitable for polyurethane foam. Moreover, the functionality of hydroxyl group is hard to control(3). Nonionic polyurethane surfactants had ideal dispersity, film-forming ability, environmental friendliness and stability (9-10).

Experimental Procedures

Materials

Toluene diisocyanate (TDI), polyethylene glycol with different molecular weights (MWt: 400, 600, 4000, 6000 and 10000 g/mol), toluene diisocyanate, oleic acid, silver nitrate and trisodium citrate were analytical grade chemicals supplied from Sigma Aldrich, Germany.

Synthesis

Synthesis of nonionic polyurethane polymers

Polyethylene glycols with different molecular weights (0.25 mol) were reacted individually by toluene diisocyanate (0.125 mol) in 500 ml one necked flask in 2-butanone (80 ml) as a solvent under reflux condition. The reaction temperature was gradually raised and fixed at 140 ^oC for 24 hr. Then the reaction mixture was cooled to room temperature and the solvent was stripped off under reduced pressure (0.3 atm.) at 40 ^oC for 24 hr(11). The obtained polyurethane was washed twice by ethanol and dried in warm oven for complete dryness. The obtained polyurethanes were designated as: PU4, PU6, PU40, PU60 and PU100 for PEG of 400, 600, 4000, 6000 and 10000 (g/mole). Molecular weight of the obtained polyurethanes were determined using HP 5890 gas chromatography provided with aflame ionization detector, and the average molecular weights of the different polyurethanes were 3900, 5300, 39970, 60240 and 100498 g/mole for PU4, PU6, PU40, PU60 and PU100.

Synthesis of nonionic polyurethane oleate derivatives

Nonionic polyurethane polymers (0.125 mole) (PU4, PU6, PU40, PU60 and PU100) and 0.125 mole of oleic acid (35.25 g) were charged separately in one neck flack equipped by Dean-Stark connection and Xylene (100 ml) was added as a solvent under heating condition (140 ^oC) until the water of reaction (4.5 ml) was obtained. Then the reaction mixture was allowed to cool and the solvent was removed under reduced pressure (0.3 atm.) at 70^oC(12). The obtained oleate esters of PU4, PU6, PU40, PU60 and PU100 were designated as PU4O, PU6O, PU40O, PU60O and PU100O. The chemical structures of the different products were determined using FTIR spectroscopy.

Preparation of the silver nanoparticles

The silver nanoparticles colloidal solution was prepared using the chemical reduction method of silver nitrate ($AgNO_3$) in bidistilled water using trisodium citrate (13). Briefly, 5 ml of trisodium citrate solution (1%) was added dropwise to

50 ml of $AgNO_3$ solution (1 mM) under heating and stirring conditions until the color is turned to pale yellow as an evident for the formation of silver nanoparticles (14).

Preparation of nonionic polyurethanes oleate-silver nanohybrids

The prepared silver nanoparticles solution (20 ml) was mixed with 5 ml saturated solution of the synthesized polyurethanes oleate (PU4O, PU6O, PU40O, PU60O and PU100O) in deionized water and stirred continuously for 1 hr. The polyurethane-silver nanohybrids solution was used for ultraviolet measurements and TEM image(15).

Analysis

FTIR spectra were recorded using Genesis Fourier transformer spectrophotometer FTIR™.

UV-Vis spectra were recorded at 200– 800 nm using a 3– 5 mm quartz holder using Specord S-600 spectrophotometer (Analytik Jena AG).

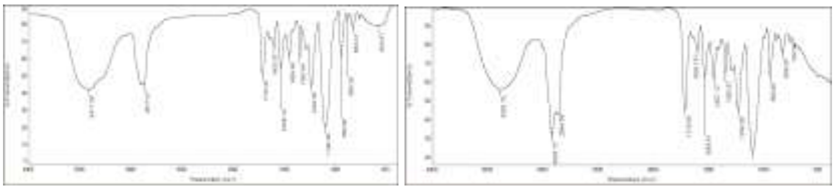
TEM spectroscopy was measured using JEM-(Jeol)-2000, Japan.

Dynamic light scattering (DLS) was measured using Malvern zetasizer nanoseries (Nano-ZS).

Results and Discussion

Structure of nonionic polyurethanes and nonionic polyurethane oleates

IR spectroscopy of the synthesized nonionic polyurethane (PU4) showed the following absorption bands: 3200-3700 cm^{-1} centered at 3396 cm^{-1} corresponds to stretching of O-H group; 2870 and 2923 cm^{-1} correspond to symmetric and asymmetric stretching of C-H groups of ethylene glycol units; 1460 cm^{-1} corresponds to C=C of aromatic ring of toluene diisocyanate moiety; 1353 cm^{-1} corresponds to stretching of C-N group and an absorption band appeared at 1106 cm^{-1} corresponds to stretching of C-O ether group (Fig. 1A). A weak absorption band appears at 2100 cm^{-1} corresponds to the C-N amide group of polyurethane segments. IR spectra of PU4O showed the appearance of two new absorption bands at 1734 cm^{-1} and 1647 cm^{-1} which are corresponding to the carbonyl group (C=O) of the formed esters and unsaturated bonds of the oleic acid moiety (C=C), respectively (Fig. 1B).



(A) **(B)**

Fig. 1. IR spectra of: A: nonionic polyurethane (PU4), B: nonionic polyurethane oleate (PU4O).

Structure of the nonionic polyurethanes nanohybrids

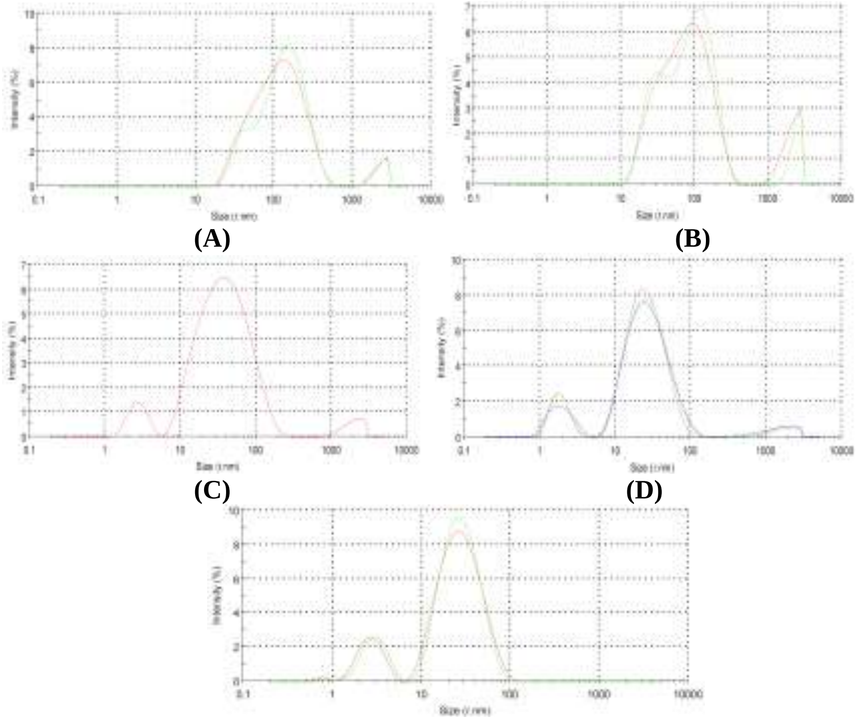
Dynamic light scattering of nonionic polyurethane oleates nanohybrids

The nonionic silver nanohybrids were characterized using dynamic light scattering (DLS). In general, the DLS analyses of the different nanohybrids presented bimodal distributions, (Fig. 2A-E). The distribution had a major peak at certain particle size diameter with area intensity % for each nanohybrid. PU4O = 143 nm (95% area intensity), PU6O = 119 nm (64% area intensity), PU40O = 47 nm (88.5% area intensity), PU60O = 31 nm (82.1% area intensity) and PU100O = 30 nm (83.4% area intensity), (Table 1). Size (including size distribution) and zeta potential are essential characteristic parameters for nanohybrids formation (16). Fig. 2A-E showed size distribution profiles of the silver nanohybrids of PU4O, PU6O, PU40O, PU60O and PU100O, respectively.

According to particle size distribution measurements (by number) (Fig. 3A-E), the particle size was 152 nm for PU4O, 61 nm for PU6O, 49 nm for PU40O, 32 nm for PU60O and 14 nm for PU100O silver nanohybrids. It is clear that the particle size range of the different nanohybrids mainly depends on the polyethylene glycol chains incorporated in the polyurethane nonionic derivatives(16). The nonionic polyethylene glycol chains are responsible for the protection of the formed nanoparticles. Increasing the polyethylene glycol chain length increases the interparticle distance between the formed silver nanoparticles. That prevents their coagulation and consequently decreases the diameter of the nanoparticles formed, (Table 1). The particle size of the different nanohybrids can be arranged in the following order: PU4O > PU6O > PU40O > PU60O > PU100O.

The polydispersity index (PDI) describes the particle sizes distribution of the formed nanohybrids. PDI more than unity indicates the scattering of formed nanohybrids diameter range with low intensity, while smaller PDI than unity indicates narrow range of nanohybrids diameter formed. It is clear that PDI of the synthesized nanohybrids is always lower than 1, indicating the narrow size and low scattering of the formed metal complex molecules. PDI increased by increasing the polyethylene glycol chain length with values ranged between 0.426 and 0.597 (Table 1). Increasing PDI values by increasing the polyethylene glycol chain length indicates the narrow size distribution of the formed nanoparticles.

Zeta potential is the net surface charge of the nanoparticles inside a solution. The liquid layer surrounding the nanoparticle exists as two parts; an inner region (Stern layer) where the ions are strongly bound, and an outer (diffuse) region where they are less firmly associated. Within the diffuse layer there is a notional boundary inside which the ions and particles form a stable entity(17). When nanoparticles move due to gravity, ions within the boundary move it. Those ions beyond the boundary stay with the bulk dispersant. The potential at the boundary surface is the zeta potential. The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system. If all the particles in the colloidal solutions have a large negative or positive zeta potential, they will tend to repel each other and there will be no tendency for the particles coagulation (18). On contrarily, if the particles have low zeta potential values, there will be no force to prevent the particles coagulation(19). The zeta potential values of the synthesized nonionic polyurethane nanohybrids (Table 1) are always in negative values and in the range of -20.6 to -27.28 mV. That showed the stability of the formed nanoparticles in their colloidal solutions, *i.e.*, the coagulation of the nanoparticles is rarely occurred. That was in a good agreement with the polydispersity index values and the particle size distribution measurements (by number).



(A) (B)

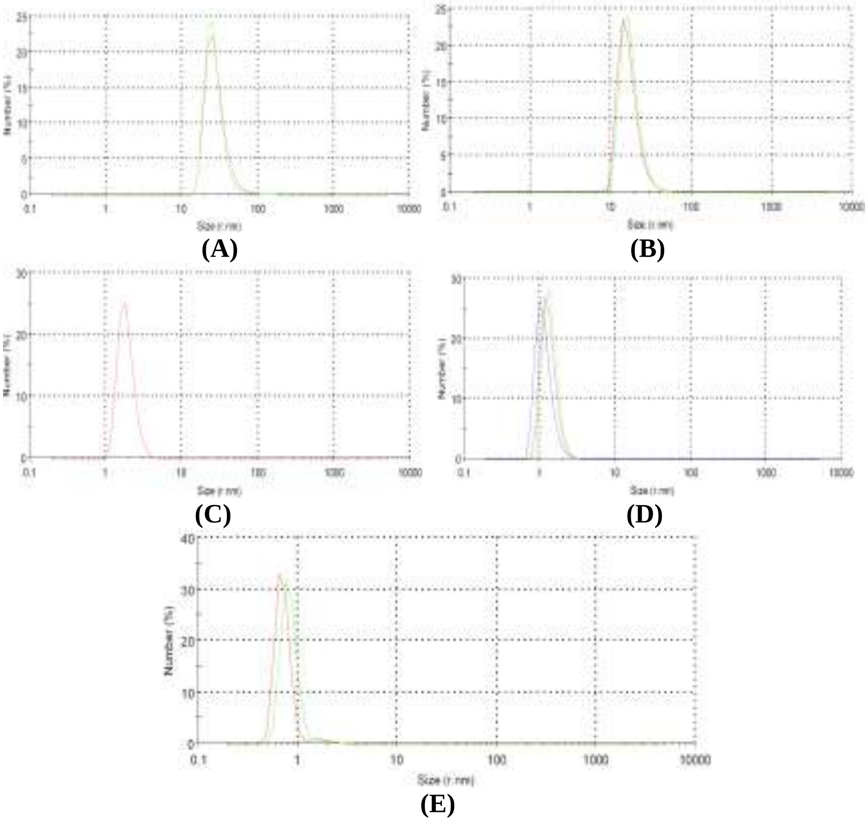
(C) (D)

(E)

Fig. 2. Particle size distribution profile by intensity for silver nanohybrids of: (A) PU4ON, (B) PU6ON, (C) PU40ON, (D) PU60ON and (E) PU100ON.

Transmission Electron Microscope (TEM)

The dimensions and morphology of the synthesized silver nanoparticles and the nanohybrids of the synthesized polyurethane (PU4, PU6, PU40, PU60, and PU100) were explored by using transmission electron microscope (TEM). TEM image of the synthesized silver nanoparticles by the reduction of $AgNO_3$ showed their spherical shapes and narrow diameters. That indicates the reduction procedures used in the synthesis of the silver nanoparticles produce uniform, spherical and mono-dispersed silver nanoparticles. Figure 4 (a-d) shows the nanohybrids of the different nonionic polyurethane oleate derivatives. It can be seen from TEM spectroscopy that the particles are non-uniform in shape and have a particle size distribution in various ranges depending on the polyethylene glycol chain length of each nonionic surfactant. It is obvious also that the diameter and shape of the silver nanoparticles did not change after formation of the different nanohybrids. Capping of silver nanoparticles by the different nonionic polyurethane oleate derivatives provides high protection of the silver nanoparticles. That can be monitored as no aggregation occurred for the silver nanoparticles. The diameter of the silver-nonionic polyurethane oleate derivatives nanohybrids was increased gradually by increasing the polyethylene glycol chain length. The fixing of the silver nanoparticles diameters was provided by interaction with the nonionic chains. While the aggregation prevention was provided by the electrostatic repulsion occurred between the capped nanoparticles. That is in a good agreement with the values of zeta potential obtained from DLS measurements (Table 1).



(A) **(B)**

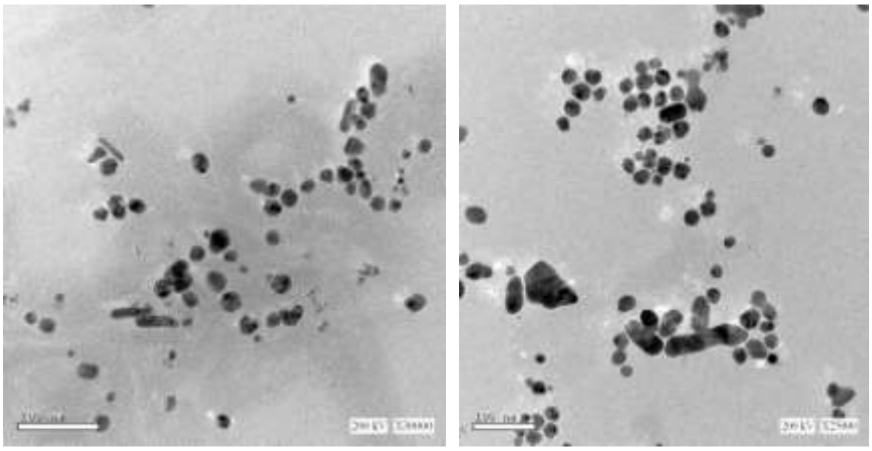
(C) **(D)**

(E)

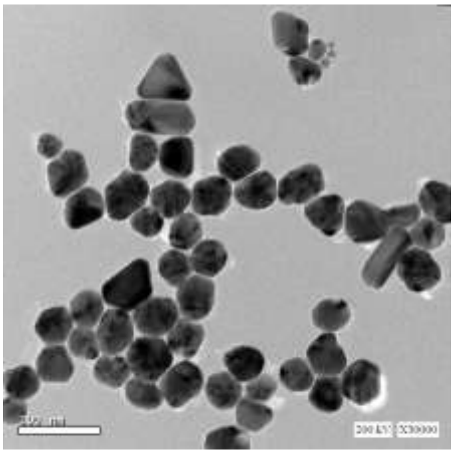
Fig. 3. Particle size distribution profile by number for silver nanohybrids of: (A) PU4ON, (B) PU6ON, (C) PU40ON, (D) PU60ON and (E) PU100ON.

TABLE 1. Particle size of the synthesized nanohybrids for different nonionic polyurethane surfactants.

Nonionic surfactant	Particle size by intensity		Particle size by number	Polydispersity index, PDI	Zeta potential, mV
	Diameter, nm	%	Diameter, nm		
PU4ON	143	95	152	0.426	-24.6
PU6ON	119	64	61	0.455	-24.5
PU40ON	47	88.5	49	0.489	-25.3
PU60ON	31	82.1	32	0.532	-20.6
PU100ON	30	83.4	14	0.597	-27.3



PU4ON PU6ON



PU100ON

Fig. 4. Transmission Electron Microscope Image (TEM) for silver nanohybrids of: (A) PU4ON, (B) PU6ON, (C) PU40ON.

UV-Vis spectroscopy

The stability of silver nanoparticles after addition of the nonionic polyurethane surfactants was determined by using UV spectroscopy. Figure 6 shows the UV-Vis spectroscopy of silver nanoparticles stabilized by PU4O, PU6O, PU40O, PU60O, and PU100O nonionic surfactants as stabilizing agent. The spectra of silver nanoparticles of the nonionic polyurethane surfactants have characteristic absorption bands in the range of 410-430 nm, which is due to the silver nanoparticles-surfactant plasmon absorption bands. The surface plasmon absorption band is due to the aggregation of silver nanoparticles in the surfactants solutions. The surface plasmon resonance absorption band of silver nanoparticles without addition of the synthesized surfactants is positioned at 415 nm. Silver nanoparticles in their colloidal dispersions are negatively charged as a result of the anions adsorbed on their surface. The loading of nonionic surfactant molecules on the silver nanoparticles protects these particles and prevent their aggregation during their collision in the solution (20).

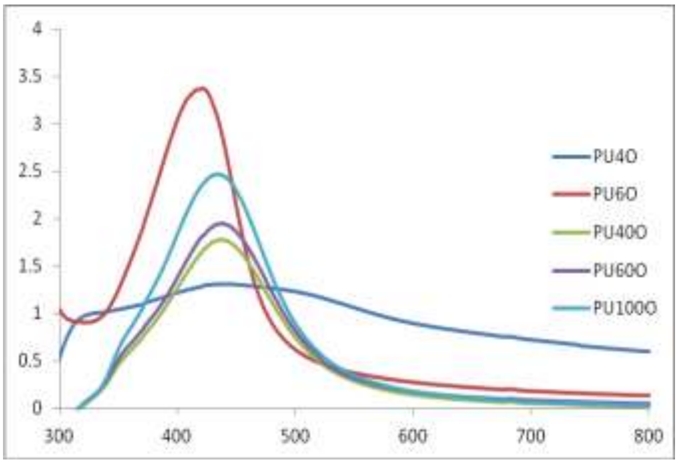


Fig. 6: UV-Vis spectroscopy of the synthesized nonionic polyurethane surfactants nanoparticles.

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مركبات البولى يوريثان ذات النشاط السطحي و جزيئاتها النانو. التخليق والتعرف علي تركيباتها البنائية

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أمكن تحضير خمسة من مركبات البولى يويثان غير الأيونية ذات النشاط السطحي من تفاعل البولي اثيلين جليكول مع كميات مختلفة من مركب الطولويندای أيزوسيانات ومفاعلة النواتج مع حمض الأولييك وتم تأييد تركيباتها البنائية بواسطة القياسات الطيفية والميكروسكوب الالكتروني، كما أمكن تحضير متراكباتها مع النانوفضة التي أمكن تحضيرها وتحديد مواصفاتها الطبيعية بالقياسات الطيفية والفيزيقية المختلفة.