Ultrasound Assisted Synthesis and Characterization of Polyurethane for Coating Applications

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Abstract

Objectives: Exceptional reaction conditions can be generated by ultrasonic irradiation via acoustic cavitation, which allows for the synthesis of new materials with unusual properties. Inspired by the importance of this efficient and environmentally friendly synthetic route, waterborne polyurethane copolymer with pendant carboxylate in the hard segment is prepared. In this current attempt, 2,2-bis(hydroxymethyl)-propionic acid was used to incorporate ionic groups into polyurethane polymer. **Methods/Analysis:** Factors affecting the sonochemical polymerization such acoustic power, type of solvent, using of catalyst, and monomers molar ratio were studied. The prepared waterborne polyurethanes were investigated by FTIR and GPC. Furthermore, in the construction of surfaces, the influence of the application of prepared waterborne polyurethane on the interaction of polyester fabrics with methylene blue as cationic dyes was assessed. For that purpose, color strength and fastness tests were carried out to prove the effectiveness of surface modification. **Findings:** The results indicated that the one-shot sonochemical polymerization by ultrasound at 100 W was more effective in N,N-dimethyl formamide (DMF) than thermally assisted polyurethane polymerization. **Novelty/Improvement:** The rate of sonochemical polymerization is much faster than thermal polymerization. Improvement in the printability of PET fabrics treated with the prepared polyurethanes.

Keywords: Isophorone diisocyanate, Polyurethane Copolymer, Sonochemical Polymerization, Surface Modification, Ultrasound

1. Introduction

The use of high-intensity ultrasound energy provide a facile, multipurpose synthetic tool to generate novel materials with unusual properties. In recent years, ultrasound irradiation has been proven as an effective method for the synthesis of polymers and composites[1,2]. These include polymerization of styrene[3-5], acrylonitrile, acrylamide and acrylic acid[6]. Regarding to the traditional energy sources, ultrasonic irradiation offers rather uncommon reaction conditions (mainly enormously high temperatures and pressures in liquids for short periods) that cannot be reached by other methods. In addition, it provides some control over the molecular weight, tacticity and polydispersity[7]. Moreover, Ultrasound irradiation method is now recognized as a viable environmentally benign alternatives[8-10].

Generally, the sonochemical effects is regarded to the hot spots formed during acoustic cavitation (i.e., the formation, growth, and implosive collapse of bubbles in liquids), a process that dramatically concentrates the low-energy density of a sound field[11]. A considerate of the parameters affecting acoustic cavitation will permit one to design the experimental conditions that can maximize its effect[12]. Factors that could affect the sonochemical reactions are: the minimum energy required to induce cavitation (cavitation threshold), the ultrasonic frequency and power, the medium in which the chemical reaction is occurring. Also, external factors such as temperature and pressure can the sonochemical reaction[13].

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Polyurethanes (PUs) are unique polymeric materials which utilized in a variety of industrial parts, building materials, adhesives, and coatings, their production was defined approximately 80 years ago[14-18]. PUs are block copolymers consisting of soft segments and hard segments. The most common method of preparing poly-urethane (–NH–COO–) is the step-growth reaction of a diisocyanate and a polyol by thermal energy. Typically, polyurethane synthesis proceeds through two popular synthetic strategies. One method of preparation includes the addition of all the components at the same time which known as one-shot method[14,19]. Alternatively, the prepolymer or two-shot, method requires the synthesis of oligomer with isocyanate functionality (end-capping) first, and then adding the chain extender in a following step[20]. Tailor-made properties can be obtained from well-designed combinations of monomeric materials.

Waterborne polyurethanes (WPUs), or waterborne polyurethane dispersions (PUDs) represent an industrially established class of ion-containing polyurethanes[21,22]. As it is known for its simply valid eco-friendly safe aqueous medium, WPUs function as outstanding coatings and adhesives, providing the properties of a segmented poly-urethane in variety of industries.

To best of our knowledge, there are rare studies dealing with the use of ultrasonic irradiation in the preparation of waterborne polyurethanes (WPUs) by one-shot synthetic strategy. Therefore, the aim of the present work is the synthesis of carboxylate-containing segmented polyurethane copolymers with high molecular weight and at a very short time using the ultrasound irradiation. Furthermore, we propose that the incorporation of car-boxylate-containing segmented polyurethane copolymers on the poly(ethylene terephthalate) (PET) fabric surfaces radically alters many important properties such as color-ation[23,24] and adhesion.

2. Experimental

2.1 Materials

Polyethylene Glycol 600 (PEG 600; Mn= 600, Merck) was dried at 80 °C under vacuum for three h before used. Isophorone diisocyanate (IPDI, Fluka), Dibutyltindilaurate (DBTDL, Sigma-Aldrich) and 2,2-bis(hydroxymethyl)-propionic acid (DMPA, Sigma-Aldrich). DMF (N, N-dimethyl formamide) and butanone

of analytical grade were used as polymerization media. Carboxymethyl cellulose sodium salt (CMC, Aldrich), methylene blue dye, urea, citric acid, Ammonium sul-phate solution. All other chemicals are of laboratory grades and were used without further purification.

Polyester plain weave fabric (100%) of 165 g/m^2 sup-plied by private sector Co., Cairo, Egypt. It was washed with a solution containing 0.5 g/L non-ionic detergent and 1 g/L sodium carbonate at temperature 70 °C for one h, and then thoroughly rinsed, and air dried at room tem-perature.

2.2 Preparation of Waterborne Polyurethane.

PEG, DMPA and 10 ml solvent (DMF or butanone) were initially mixed in a four-necked flask equipped with an ultrasonic horn, thermometer, reflux condenser and nitrogen inlet. IPDI and DBTDL as a catalyst were added gradually through a separating funnel, which replaced with a reflux condenser after complete addition. After complete addition of the IPDI, the polymerization reac-tion was started using ultrasonic irradiation produced by Hielcher Ultrasonic device (100W, 30 kHz), equipped with titanium horn (MS7, Ø=7mm and the length=80mm). During the polymerization, cooling water was circulated to decrease reaction system temperature, and constant N$_2$ purging rate was kept.

A similar polymerization reaction was performed thermally instead of the ultrasonic irradiation, in which the ultrasonic horn was substituted with a mechani-cal stirrer and the reaction was carried out at 80°C for fourh[18]. The change in the amount of NCO group dur-ing the polymerization reaction was determined with the standard dibutylamine back-titration method (ASTM D1638).

Ultrasonic power, polymerization media, initiator and molar ratio that may affect the polymerization reaction were studied, and the parameters for the preparation of PU are shown in **Table 1**.

2.3 Surface Modification of Polyester Fabrics

An aqueous emulsion of the prepared polyurethane was obtained by adding water (30 °C) to the mixture. Since the water addition rate is a critical parameter to obtain a stable emulsion, water was fed for 10 min with a

Table 1. Polymerization parameters for waterborne PU preparation

Designation	IPDI (mole)	PEG (mole)	DMPA (mole)	DBTDL (%)	Solvent	Acoustic power (W)
PU1	2	1	1	0.1	DMF	**100**
PU2	2	1	1	0.1	DMF	**80**
PU3	2	1	1	0.1	DMF	**50**
PU4*	2	1	1	0.1	DMF	**Thermally prepared**
PU5	2	2	**0**	0.1	DMF	100
PU6	2	1	1	0.1	**Butanone**	100
PU7	2	1	1	**0**	DMF	100
PU8	**2.5**	1	1	0.1	DMF	100
PU9	**3**	1	1	0.1	DMF	100
PU10	**4**	1	1	0.1	DMF	100

*PU4 thermally prepared (80 °C for 4 h).

pump at a constant flow rate. The resulting product was a PU emulsion with a solid content of about 30%.

To modify PET fabric surfaces, the aforementioned PU emulsions were applied to the fabrics using conventional flat screen printing method. Fixation of the PU was made by drying at room temperature followed by thermofixation at 150 °C for 5 min.

2.4 Printing of Polyester Fabrics

The printing paste was prepared according to the recipe shown in **Table 2**. The thickener (CMC) was soaked in a small amount of water and kept overnight at room temperature. The dye is pasted with the dye solvent, acetic acid and mixed with urea. Onto the paste, hot water (80–90 °C) is poured to produce a solution, which is sieved and stirred into the thickener. Finally, the total mass of the whole paste was then adjusted to 1kg by the addition of other auxiliaries and water (**Table 2**).

Table 2. Printing paste composition

Constituent	Weight (g)
Thickener	100
citric acid	5
Urea	50
Ammonium sulphate solution (1:2)	60
methylene blue dye	20
Thickener	100
Water	765
Total	1000

The aforementioned printing pastes were applied to unmodified and modified polyester fabrics using the flat-screen printing technique. The printed samples were then air dried followed by steaming at 108 °C for 30 min. The printed samples were then washed with water containing (2g/L nonionic detergent) at 60 °C for 30 min to remove the thickener and unfixed dye, then rinsed in water several times and finally air dried.

2.5 Characterizations

2.5.1 Infrared Spectroscopy (FTIR)

The chemical structure of the polyurethanes was analyzed in a JASCO 6100 infrared spectrophotometer, provided with Fourier transform analysis (FTIR). The scanning range was 400-4000 cm^{-1}. It worth noting that, the FTIR analysis of the prepared polyurethane samples was conducted before addition of water in the final preparation step.

2.5.2 Molecular Weight Distribution of PU

The molecular weight and molecular weight distributions of the polyurethane polymer were obtained by Agilent Gel Permeation Chromatography (GPC), using a Waters peristaltic pump HPLC (flow rate of DMF 1 ml/min), and a Waters 410 refraction index detector.

2.5.3 *Colour Strength of Printed Fabric*

The efficiency of different surface modifications has been compared regarding K/S absorption spectra. The colour strength of the printed polyester fabrics was measured using a recording filter Spectrophotometer Hunter Lab (The Colour Management Company, USA). The colour value expressed as K/S of the printed samples was determined by applying the Kubelka-Munk[25] equation.

$$K/S = \frac{(1-R)^2}{2R} - \frac{(1-R_o)^2}{2R_o}$$

Where: R: is the decimal fraction of the reflectance of the dyed substrate.

R$_o$: is the decimal fraction of the reflectance of the undyed substrate

S: is the scattering coefficient

K: is the absorption coefficient

2.5.4 *Fastness Properties*

Fastness properties of the dyed samples were measured according to ISO standard test methods; washing fastness (ISO 105-C02, 1989), rubbing fastness (ISO 105-X12, 1987).

3. Results and Discussion

One aim of this work is to optimize the reaction conditions for ultrasonically initiated polymerization of polyurethane to attain high molecular weight as well as high polymerization rate. To achieve this goal, different parameters were investigated namely acoustic power, type of solvent, using of catalyst, and monomers molar ratio. Also, the prepared PUs with the optimum condition were compared to PU obtained by the conventional thermal method. Finally, the prepared PUs were used to enhance coloration behavior of the PET fabric towards cationic dyes.

3.1 Ultrasonically or Thermally Assisted Polyurethane Polymerization

A major factor affecting the polymerization in the sono-chemical polymerization, is the ultrasound intensity. It is difficult to determine the ultrasound intensity quantitatively. However, the relationship between the power output and ultrasonic intensity is directly proportional, i.e., with increasing the power output, the ultrasound intensity is increased. Therefore, we will take the power
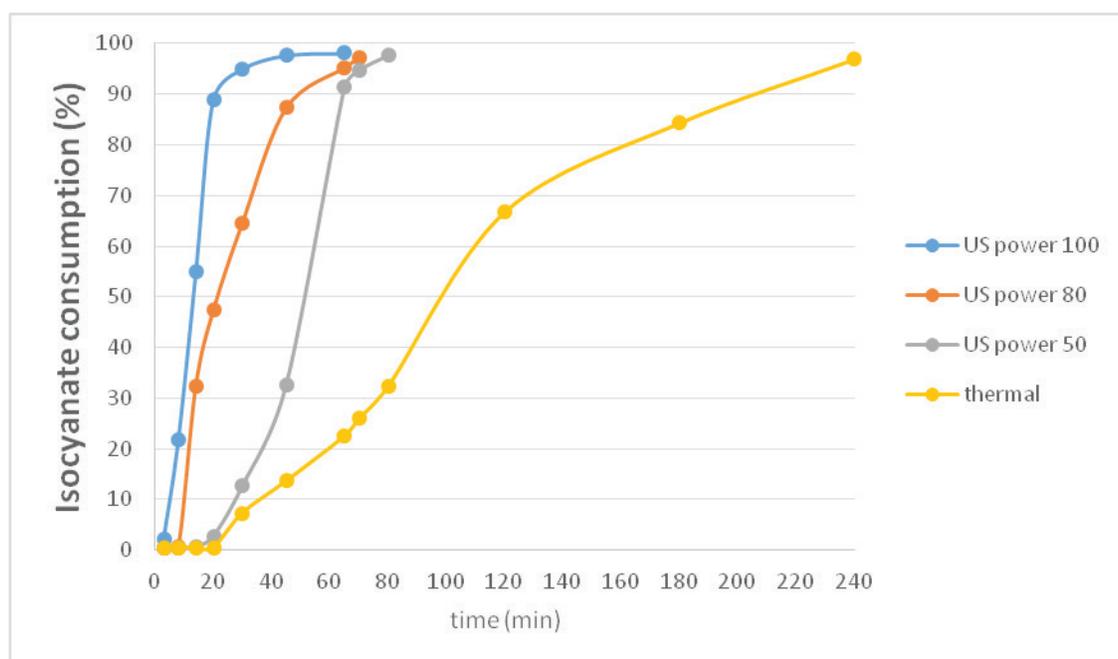
Figure 1. The effect of acoustic power and thermal polymerization on the NCO group consumption.
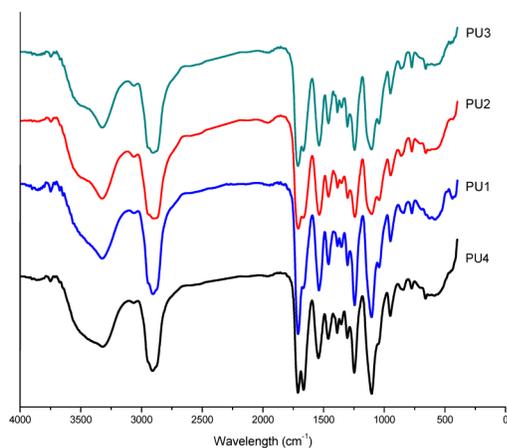
Figure 2. FTIR spectrum of the synthesized polyurethane (PU1, PU2, PU3 and PU4).

Table 3. FTIR Characteristic bands assigned to the prepared polyurethanes

Characteristic groups	Wavenumber (cm^{-1})
N-H stretching of urethane	3319
CH$_2$ symmetric and asymmetric	2909
CO (ester and urethane)	1710-1665
C-N-H urethane	1540
C-O-C of polyethylene glycol	1246
C-O urethane and ether groups	1104

output as a relative description of ultrasound intensity to get a better explanation of our results[26].

The NCO group consumption was monitored to investigate the efficiency of the polymerization reaction of polyurethane at different acoustic powers or thermally (**Figure 1**).

Generally, sonochemical polymerization of polyurethane at different acoustic powers (50, 80 or 100W) shows nearly the same polymerization rate plateau in comparison with that obtained by thermal polymerization. It is also observed that, regardless to the applied acoustic power, the rate of sonochemical polymerization is much faster than thermal polymerization. The effect of ultrasonic irradiation on this polymerization reaction could be explained by the hot spot theory[1,2,27]. Although there are many different explanations for the effect of ultrasound on the polymerization, it is well established that the extreme conditions lead to the creation of free radicals, mechanical shocks, high shear gradients as a result of the bubble collapse, and a very fast and efficient

mixing in multiphase systems. The aforementioned ultrasonic effects could explain why the ultrasonically-assisted polymerization is almost completed after 20 min at 100W while it needs four hours for maximum consumption of the NCO groups using thermal polymerization.

The prepared polyurethanes were characterized by FTIR and GPC. **Figure 2** shows FTIR spectroscopic analyses of the prepared PU1, PU2, PU3 and PU4. The related characteristic peaks of functional groups in the four polymers were listed in **Table 3**.

It is worth mentioning that, the variation of the ultrasonic power doesn't affect the FTIR spectrum of the prepared polyurethane, while the thermally prepared polyurethane shows an additional band at 1665 cm^{-1}. This variation could be explained as follow; the magnitude of the frequency shifts in the region of (1700-1600 cm^{-1}) is usually used as an indication of the participation of the urethane or carboxylic carbonyl group in the hydrogen-bonding formation. Previous works have stated that the band at 1725 cm^{-1} is ascribed to the urethane carbonyl groups (stretching) while the urethane carbonyl stretching at around 1710 cm^{-1} is attributed to hydrogen bonding in the disordered sections[28,29]. The urethane carbonyl stretching around at 1710 cm^{-1} is attributed to the urethane carbonyl presence in the soft phase. The absorption band around 1695 cm^{-1} is due to the stretching of the stronger hydrogen bonds in crystalline regions. The band is centered near 1665 cm^{-1} is apportioned to the stretching of hydrogen-bonded carboxylic carbonyl groups, which come from the 2,2-bis (hydroxymethyl)-propionic acid.

The molecular weight study for the number average molecular weights (Mn) and weight average molecular weights (Mw), also the molecular weight distribution (Mw/Mn) for each polymer sample examined, and are given in **Table 4**. The molecular weight values for the obtained ultrasonically initiated polyurethane are large in magnitude compared to that prepared thermally, also increasing the ultrasonic irradiation power causes noticeable increases in the polymer molecular weight. We can

Table 4. Polymer Molecular Weight Data

Designation	Mn (X10³)	Mw(X10³)	Mw/Mn
PU1	36.5	152	4.1
PU2	29.4	120	4.1
PU3	25.4	82.4	3.2
PU4	25.0	74.7	2.9

conclude that the larger intensities are leading to a superior ultrasonic energy entering the system and therefore, an increase in the number of cavitation bubbles and therefore, higher sonochemical effect. As well as the increase in ultrasound intensity, will lead to an increase in acoustic pressure, which results in an increase in the maximum radius of the cavitation bubbles and thus an increase of collapse time[30], and therefore, favoring further polymerization reaction.

3.2 Effect of Solvent

Solvent plays an important role in sonochemical reaction; therefore, the polymerization reaction of polyurethane was conducted in the presence of two different solvents (DMF or butanone), keeping in mind the other reaction variables such as sonication power remained constant. **Figure 3** shows the % consumption in NCO groups during the sonochemical polymerization reaction in the presence DMF or butanone as a solvent. It is obvious that 30 min was required to attain 93% NCO consumption using DMF as solvent while 70 min was required to attain similar conversion using butanone as a solvent. The FTIR spectrum of the prepared polyurethane in the presence of butanone solvent (**Figure 4**) shows a band at 2266 cm^{-1}, which chosen as an indication for the presence NCO group. The GPC data also shows lower polymer molecular weight values (Mn= 25.7X10^3 and Mw= 101
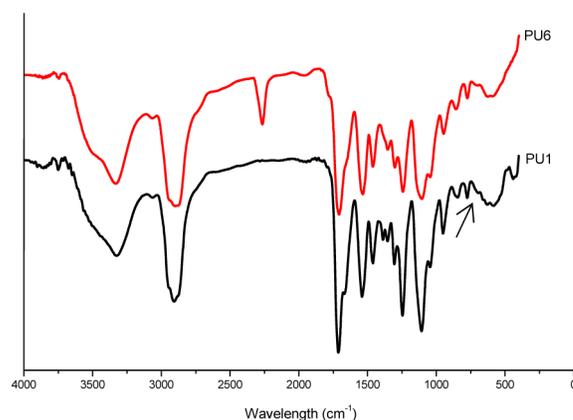
Figure 4. FTIR spectrum of the synthesized polyurethane in the presence of DMF or butanone as solvents (sonication power 100W, sonication time 30 min).

X10^3) in the case of butanone solvent in comparison of those obtained in DMF as a solvent. Thus, it has been convincingly shown that the DMF represents a favorable medium for the sonochemical preparation of polyurethane compared with butanone. That could be explained on the basis of the vapor pressure of the two solvents (DMF is 0.5 kp$_a$ and butanone is 10.5 kp$_a$), which affects the highest temperature generated by the collapse of cavitation bubbles as well as the highest pressure generated
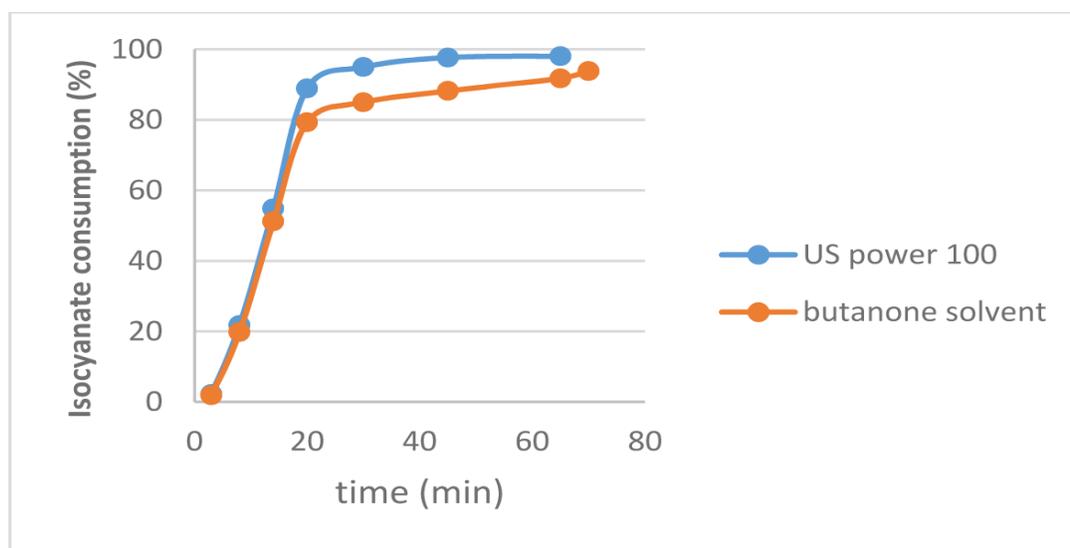
Figure 3. Effect of solvent on the consumption of NCO groups.

by the collapse of cavitation bubbles as shown from the following acoustic equations.

$$T_{max} = \frac{T_b P_m (\gamma - 1)}{P_v} \qquad \textit{Equation 1}$$

$$P_{max} = P_v \left[\left[\frac{T_b P_m (\gamma - 1)}{P_v} \right] \right]^{\frac{\gamma}{(\gamma - 1)}} \qquad \textit{Equation 2}$$

Where T_{max} is the maximum temperature produced by the collapse of cavitation bubbles.

P_{max} is the maximum pressure produced by collapse of cavitation bubbles.

P_m is the atmosphere pressure.

γ is the ratio of specific heat capacities of solvent vapor.

P_v is the vapor pressure of the solvent at the reaction medium temperature T_b[26].

So, higher vapor pressure leads to more vapor enters the cavitation bubble while it has been formed and therefore, the bubble collapse is cushioned and less violent i.e. weak sonochemical reaction[31-33].

3.3 Effect of Catalyst

Figure 5 represents the % consumption of NCO group in the absence and presence of DBTDL catalyst. The data show, maximum consumption of NCO group (91%) could be attained after 80 min in the absence of the catalyst.

Investigations on the role of the Sn catalysis throughout the reaction revealed that the reaction continues by scission of the Sn–OR bond then by a coordination reaction on the catalyst[34]. Promotion of these active species is one effect that the sonochemical enhancement might occur; additionally, the formation of unusual coordination species[35]. Another possibility for the superior action of the catalyst in the presence of the ultrasonic irradiation is the improved distribution of the catalysts through the system due to the efficient microscopic mixing enabled by ultrasonic energy. Also, regarding the chemical investigation of the prepared polyurethane, the FTIR spectrums (not presented) of the prepared polyurethane in the presence and absence of the catalyst doesn't show any significant different. Moreover, the GPC data also shows lower polymer molecular weight values (Mn= 20.7X10³ and Mw= 88 X10³) in the absence of the catalyst. It is worth noting that, the sonochemical formation of polyurethane in the absence of the catalyst could be attributed to the severe conditions of temperature and shear generated around collapsing cavitation bubbles, which leading to breakdown as well as free radicals formation of the monomer.

3.4 Effect of Molar Ratio

The sonochemical synthesis of the polyurethane at a variable molar ratio of PEG, DMPA and IPDI was studied. The % consumption of the NCO groups through the sono-
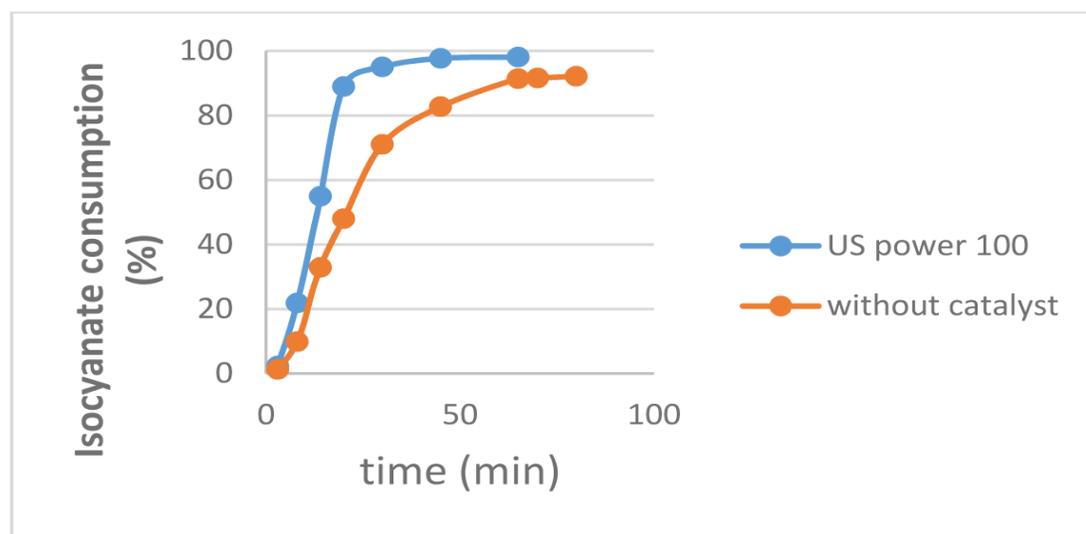
Figure 4. The effect of DBTDL catalyst on the % consumption of NCO group. (Ultrasonic power 100W).
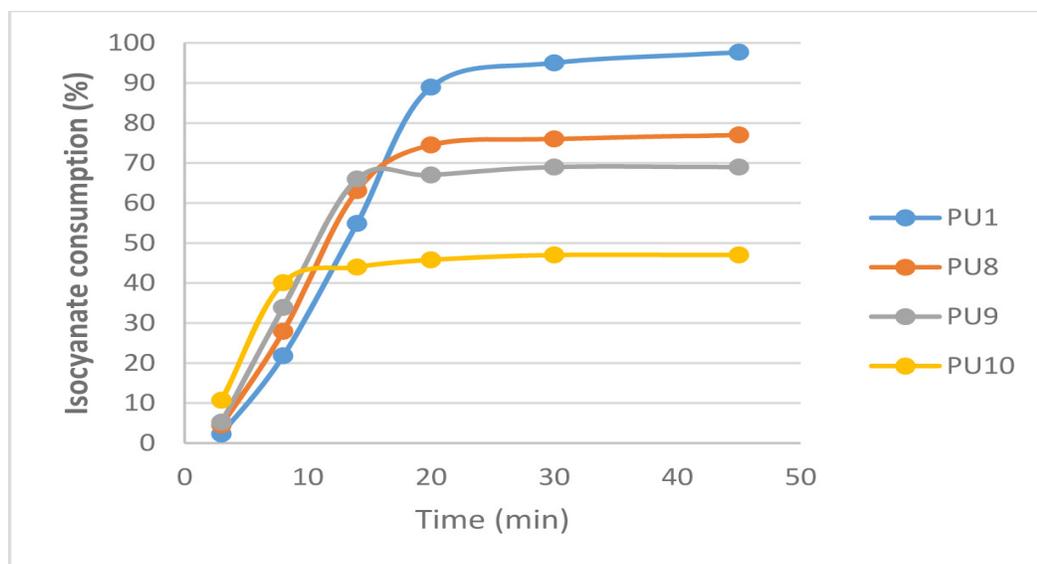
Figure 6. The effect of molar ratio of PEG, DMPA and IPDI on the % consumption of NCO group. (Ultrasonic power 100W).

chemical polymerization reaction (**Figure 6**) show that as the molar ratio of IPDI increases the % consumption of the NCO groups was initially increase, which indicates that the excess IPDI accelerate the rate of sonochemical polymerization.

Comparing the FTIR spectrum of the prepared poly-urethanes (PU1, PU8, PU9 and PU10), an intense peak at 2265 cm^{-1} was observed in the case of PU8, PU9 and PU10. This peak, which is specific to the NCO group, was taken as evidence for the presence of the isocyanate groups at the end of the polymer chains[18].

3.5 Applications of the Prepared Polyurethane in Printing of Polyester Fabrics

Peering in mind printing is a kind of fabrics surface mod-ification, consequently it's expected to give good results upon printing of PET fabrics post-treated with anionic polyurethane comparing to that untreated. **Table 5** shows the fastness properties and the colour strength (K/S) of the printed PET fabrics. The high (K/S) values show the great affinity of the dyes to the treated fabrics. Data obtained from **Table 5** could be summarized as follow:

- Comparing the K/S value of the untreated PET fab-rics to those treated with PU1, PU2, PU3 or PU4. The improvement in the printability could be attributed to

Table 5. Fastness properties of the printed PET fabrics pretreated with PU

Type of polyurethane used in treatment of PET fabrics	K/S	Washing fastness		Rubbing fastness	
		Alt.	St. wool	Dry	Wet
Untreated PET fabric	0	--	--	--	--
PU1	3.7	3	3	2-3	2
PU2	2.9	3	3	2-3	2
PU3	1.2	2	3	2-3	2
PU4	1.1	3	2-3	2-3	2
PU5	0.3	2	3	2-3	2
PU8	8.13	3-4	4	3-4	3
PU9	9.74	4-5	4	4	4
PU10	11.95	4-5	5	4-5	4

Alt. = Alteration, St. = Staining

the occurrence of the carboxylic groups in the polymer chains, which attract and fix the positively charged dye molecule to the fabric surface. That verdict is confirmed by the K/S value (0.3) obtained by using PU5 (doesn't contain DMPA i.e. absence of the carboxylic groups).

- The prepared polyurethane molecular weights is an important factor in the fixation of the polymer layer

on the fabric surface, and therefore, good printability also good fastness properties.

- The excellent printability obtained upon using PU8; PU9 or PU10 could be explained on the basis of the presence of NCO groups at the end of the polymer chains. Those NCO groups can undergo further chain extension in the presence of the water molecules during the steaming process[36]. The chain extension results in the formation of higher molecular weight, which is enough to assure permanent fixation of the polymer on the fabric surface.

4. Conclusion

The sonochemical polymerization of polyurethane at different acoustic powers shows nearly the same polymerization rate plateau as well as the FTIR spectrum in comparison with that obtained by thermal polymerization, also regardless to the applied acoustic power, the rate of sonochemical polymerization is much faster than thermal polymerization.

The molecular weight values of the polyurethane that obtained by ultrasonic initiation are directly proportional to the ultrasonic irradiation power and all are higher in comparison to that synthetized thermally. Also, the excess IPDI accelerate the rate of sonochemical polymerization, and the DMF represents a favorable medium for the sonochemical preparation of polyurethane compared with butanone; and that could be explained on the basis of the vapor pressure of the two solvents.

Improvement in the printability of PET fabrics treated with the prepared polyurethanes (PU8, PU9 or PU10) could be attributed to the presence of the carboxylic groups in the polymer chains, which attract and fix the positively charged dye molecule to the fabric surface. The prepared polyurethane molecular weight's is an important factor in the fixation of the polymer layer on the fabric surface, and therefore, good printability also good fastness properties.

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