



Developing a New Class of UV-curable Polyurethane Acrylate Resins for Coating Applications

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POLYESTER (PET) fabrics that containing nitrogen can be considered as a potential material for multipurpose applications. For this purpose, primary attention is given to introduce nitrogen-containing functional group onto the surface of PET fabrics using synthesized UV-curable polyurethane acrylate built-in amine. Moreover, the effect of incorporation the amino groups on the printing behavior of polyester fabric was evaluated. Polyurethane acrylate built-in amine resins were prepared either by one-shot sonochemical polymerization or by using conventional thermal synthesis procedure. Then, UV-curable coatings were prepared by mixing the prepared polyurethane acrylate built-in amine resin with the main components of UV curable coatings such as monomer as a diluent and 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone as photo-initiator. The prepared built-in amine photopolymers were characterized by ($^1\text{H-NMR}$), (FTIR), and (GPC). The morphology of the cured coating was also examined by using scanning electron microscopy (SEM). In addition, fastness properties of the printed fabrics and color strength were carried out to assess the effectiveness of the incorporation of the nitrogen groups on the stability of the coating layer. The results showed that, the IR Spectra of vinyl terminated PU polymers has a characteristic peak of N-H stretching at 3326 cm^{-1} accredited to the formation of urethane bond. It was also found that treatment of PET fabric with polyurethane acrylates resin containing built-in amine results in an increase in the affinity to acid dyes. The current work opens up a novel opportunity to develop nitrogen-containing PET fabrics.

Keywords: Coatings, Photocurable resin, Photopolymerization, Polyester, Textile printing.

Introduction

The market of photocured materials such as acrylic resins would grow at a rapid pace and reached approximately US\$ 4.94 billion in the year 2012 [1-4]. The use of UV curable resins in coating application is growing as a result of the stringent environmental standards imposed by many countries. However, restrictions of the application of UV curable resin such as polyurethane acrylates could be attributed to the “tacky” or under-cured surface which resulted from oxygen air that inhibits radical induced polymerizations [5]. Thus, in case of oxygen inhibition, curing needs longer exposure time and results in partial loss of the surface and other physical properties of air-cured coatings.

Molecular oxygen is known to inhibit free radical polymerizations due to its reaction with the initiator, and the radicals of the growing polymer to form the peroxy radicals [6, 7]. The peroxy radicals inhibit the polymerization reaction and more stable, and thus, the oxygen basically terminates or consumes radicals [1, 8]. The presence of oxygen is leading to the development in the induction time, since the polymerization cannot continue until the propagation reaction participates with the inhibition reaction.

Therefore many scientific papers trying to overcome of oxygen inhibition reaction have been published in the coating industry [9, 10]. Several techniques have been used for the

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application of high-intensity irradiation sources in order to increase the rate of initiation. As a result of enhancing the construction of primary radicals, it becomes much superior to their consumption by oxygen [9, 11-13]. Another alternate is to polymerize the samples in the presence of inert atmosphere [9], where the oxygen is removed from the reaction [14-16]. However, higher expenses for extra equipment and inert gas stream could be overcome by high speed curing and reduced photo-initiator addition. There are also several methods that include the application of two photo-initiators, whose absorption properties in accordance the emission bands of the mercury lamp [17, 18], the inhibitory effect of oxygen can be decreased by the addition of molecules, for instance adding amines and thiols to the polymerization systems is recognized to decrease the oxygen harmful effects [19-21] or utilization of wax additives [22, 23].

However, the aforementioned methods increase the production cost or drawbacks in the products. For example, excess concentrations of photo-initiator will decline light penetration to the bulk of the coating layer, leading to non-homogeneous and/or low conversion, which may result to the inferior of adhesion properties. Many amines are characterized by having low ionization potentials, such property enables this amine to participate in a plethora of photoinduced electron transfer reactions [24], which can react with peroxy radicals and produce new reactive radical capable of propagating the polymerization process.

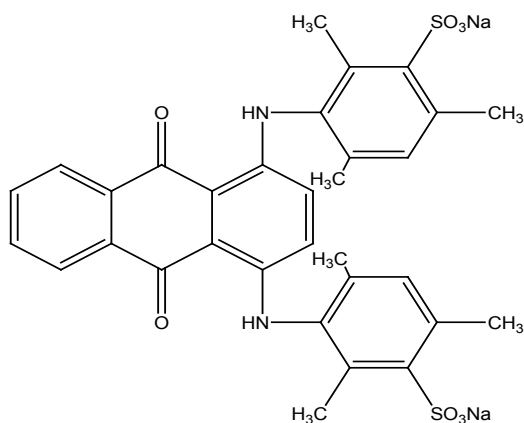
In this study, we propose a two different procedures namely one-shot sonochemical

polymerization or by using conventional thermally synthesis procedure to develop new class of polyurethane acrylates with built-in amine co-initiators, which can reduce tacky problems and enhance substantively of coated surfaces towards anionic dyes such as acid dyes i.e., modifying polyurethane acrylate backbone with hydrogen donor group as anti-oxygen inhibition strategy. Also, the present research work demonstrates the comparisons between sonochemical and thermal polymerization systems to synthesis polyurethane acrylates with built-in amine co-initiators.

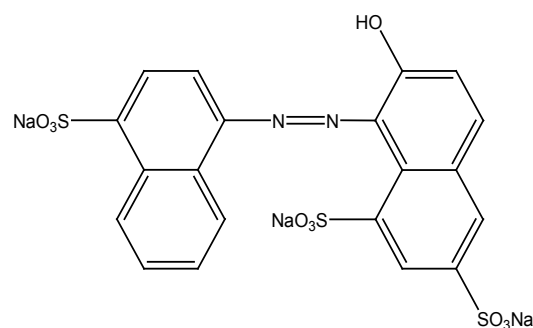
Experimental

Materials

Polyester plain weave fabric (100%) of 165 g/m² (supplied by private sector Co., Cairo, Egypt) was treated with a solution containing 0.5 g/L non-ionic detergent Tissocyl CSB (Zschimmer and Schwarz, Burgstädt, Germany) and 1 g/L sodium carbonate at temperature 70 °C for 1 h, and then thoroughly rinsed and air dried at room temperature. Two commercial acid dyes (Fig. 1) were used in this study kindly supplied from Bruno Ludewig GmbH (Emsbüren, Germany). Polyethylene Glycol 600 (PEG; Mn= 600, Across) was dried at 80 °C under vacuum for three hours before used. Isophorone diisocyanate (IPDI, Sigma-Aldrich), Dibutyltindilaurate (DBTDL, Sigma-Aldrich), 2-hydroxyethyl acrylate (HEA, Fluka), and Diethanolamine (DEA, Riedel-de Haen) were used as polymerization media. Hydroquinone (SRLchem) was used as an inhibitor agent of acrylate. 2-Hydroxy-4'- (2-hydroxyethoxy) -2-methylpropiophenone (Aldrich) was used as photo-initiator for acrylates group. Butanone of analytical grade was used as polymerization media.



C.I. Acid Blue 80



C.I. Acid Red 18

Fig. 1. The chemical structures of used dyes.

Methods

Synthesis of polyurethane Acrylates.

Conventional heating synthetic route

For preparation polyurethane acrylate, PEG and 10 ml solvent (butanone) were initially mixed in a four-necked flask equipped with a thermometer, reflux condenser and nitrogen inlet attached on the mechanical stirrer. IPDI and DBTDL as a catalyst were added gradually through a separating funnel at 40-45 °C for 30 min, which replaced with a reflux condenser after complete addition. After complete addition of the IPDI, the polymerization reaction was started using mechanical stirrer at 50 °C for 60 min. HEA and inhibitor (hydroquinone) were added to the system gradually through a separating funnel and left the polymerizations for 3 hours. During the polymerization, the reaction temperature was kept constant at 80 °C and under constant N₂ purging. More solvent was added to the polymerization process, till the total amount of solvent (butanone) in polymerization reaction was 35 ml.

In case of polyurethane acrylate preparation with build in amine, a similar polymerization reaction was performed but the amine was added before HEA where acrylate was added as capping for the polyurethane build in amine. The obtained polymers were kept in a dry and dark place. The molar ratio that may affect the polymerization reaction were studied, and the parameters for the preparation of polyurethane acrylate are shown in Table 1.

Sonochemical Synthetic route

The preparation of polyurethane acrylate resins sonochemically was performed in details as follows: PEG and 10 mL solvent (butanone) were initially mixed in a four-necked flask equipped with an ultrasonic horn, nitrogen inlet, reflux condenser, and thermometer. The polymerization reaction was initiated via using ultrasonic irradiation produced by Hielscher Ultrasonic device (100 W, 30 kHz), attached with titanium horn (MS7, Ø=7 mm, and the length=80 mm). During the polymerization, a constant rate of N₂ purging and water-cooling circulation to decrease the reaction temperature of the system were both used. IPDI and DBTDL as a catalyst were both added gradually (30 min) through a separating funnel, which replaced with a reflux condenser. After complete addition, we observed that the reaction temperature was raised to 90 °C, then the system was cooled down to 40 °C before adding HEA and inhibitor (hydroquinone) during 10 min and change the ultrasonic parameter to 50% power with 0.5 cycles. The reaction was finished after 60 min of adding HEA. In case of polyurethane acrylate with build in amine, amine was added first before acrylate (HEA). After 30 min, HEA and hydroquinone were added and the obtained polymer was kept in a dry and dark place. The polymerization parameters were summarized in Table 1.

TABLE 1. Codes and molar ratio composition of different polyurethane resins prepared either by the sonochemical or conventional heating synthetic route.

Sample code	Molar ratio of monomers				Preparation Method
	IPDI	glycol	HEA	DEA	
PU-1	2	1	---	---	Conventional route
PUA-2	2	1	2	---	
PUA-3	2	1	2	1	
PU-4	2	1	---	---	Ultrasonic route
PUA-5	2	1	2	---	
PUA-6	2	1	2	1	

UV curing of polyurethane acrylate resins

Various UV-cured coatings have been formulated using PUA-2, PUA-3, PUA-5 and PUA-6, and a reactive diluent. The UV cured PUAs films were formed by casting the formulation with 2 wt % free radical type photo-

initiator (2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone) onto polyester fabrics. Film formation was carried out at room temperature. The solvent was then allowed to evaporate at temperature 25°C and 80°C in an oven. Then it was exposed to medium pressure

under a mercury lamp (UV 125 W). Properties of cured films were tested and compared after 48h.

Printing procedure of polyester fabrics

The printing pastes were prepared according to the following recipe:

Acid dye	1 g
Guar gum	1.5 g
Urea	10 g
Ludigol	0.5 g
Water	87 g
Total	100 g

The aforementioned printing pastes were applied to unmodified and modified polyester fabrics by using a conventional flat screen-printing method. After printing, the printed samples were dried followed by steaming at 100 °C for 20 min. The fabrics were then soaped using 3 g/L of non-ionic detergent (Tissocyl CSB) at 60 °C for 15 min, rinsed thoroughly with hot water, then cold water in order to remove the unfixed dyes and finally air dried.

Color strength measurements

The PET fabrics printed under different conditions of treatments were individually tested for their color strength. The color strength (K/S) values of the printed fabrics were instrumentally determined from reflectance measurements with the Kubelka–Munk Equation [25, 26] as shown in equation (1).

$$\frac{K}{S} = \frac{(1-\beta)^2}{2\beta} \quad (1)$$

Where β is the degree of remission = $R/100$. Reflectance (R) obtained from software calculation is expressed as a percent value. (S) is the scattering coefficient and (K) is the absorption coefficient of the printed fabrics. This K/S value is a parameter commonly used to demonstrate how deep the material color is of given textile fabrics. The higher the K/S value is, the deeper the color is [27]. We can use the increase of the K/S value as a characteristic of the binding dye molecules onto PET surfaces modified with polyurethane acrylates either with or without built-in amine [28, 29]. The colorimetric measurement by reflectance was carried out in ACS imaging system CS-5 Chroma Sensor colorimeter (standard illuminant D65; 10° standard observer). The reflectance of

the printed fabrics was measured in the range of 400–700 nm. In the process, the unprinted fabrics were used as a reference.

Color fastness properties

The color fastness properties of the printed fabrics to washing and crocking were assessed by DIN EN 20105-C01:1992 and DIN EN ISO 105-X12:2002, respectively.

Characterization

Infrared Spectroscopy (FTIR)

The infrared spectra for the prepared polymeric resins were measured to analyze its chemical structure. The polyurethanes were conducted to infrared Spectrometer (JASCO FTIR 6100, made in Japan), attached with a detector of deuterated triglycine sulfate (TGS). The transmission spectra (T%) were collected in the scanning range of 4000–400 cm^{-1} using a resolution of 4 cm^{-1} with 1 cm^{-1} interval scanning and scanning speed of 2 mm/sec.

Gel Permeation Chromatography (GPC)

The average number molecular weights (Mn), the average molecular weights (Mw) and the molecular weight distribution (Mw/Mn) were all measured for the prepared polymer by using Agilent Gel Permeation Chromatography (GPC). The measurements were performed using water peristaltic pump HPLC (flow rate of DMF 1 mL/min) and water 410 refraction index detector.

Rheological behavior

The rheological properties of the polyurethane acrylates were determined by using an AR2000 Rheometer (TA Instruments, New Castle, DE) at a constant temperature (25°C). For each solution, average values were obtained from at least three measurements.

Scanning electron microscopy & EDAX

The morphological structure of photocurable polyurethane acrylate films was investigated with scanning electron microscopy. All samples were mounted on aluminum stubs, and sputter coated with gold in a 150 Å sputter (coated Edwards) and examined by Quanta FEG 250. Electron Probe Microanalysis (Japan) equipped with Energy-Dispersive X-ray facility (EDAX), magnification range 35–10,000, accelerating voltage 20 kV.

NMR

All prepared samples were examined by Proton NMR spectroscopy was performed with a Varian Gemini 400 MHz instrument. The tests were carried out at Microanalytical Center, Faculty of Science, Cairo University, Egypt.

Mechanical properties

Tensile strength (kg) and elongation at break (%) of UV cured films of the prepared resins were measured using Instron Series 2701 Pneumatic Grip Control, Assembled in the USA. Dual clamps and 40-mm samples with 10 mm width and 1 mm thickness were used. The tests were carried out at Clothing and Knitting Department, Textile Research Division, National Research Center, Egypt.

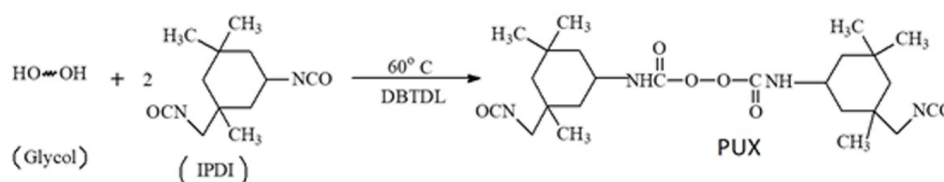
Results and Discussion*Synthesis of UV-curable polyurethane acrylates resins with built-in amine*

UV-curable polyurethane acrylates resins were synthesized via shorter reaction time ultrasonic synthetic route compared to conventional heating two-step synthesis process in case of polyurethane

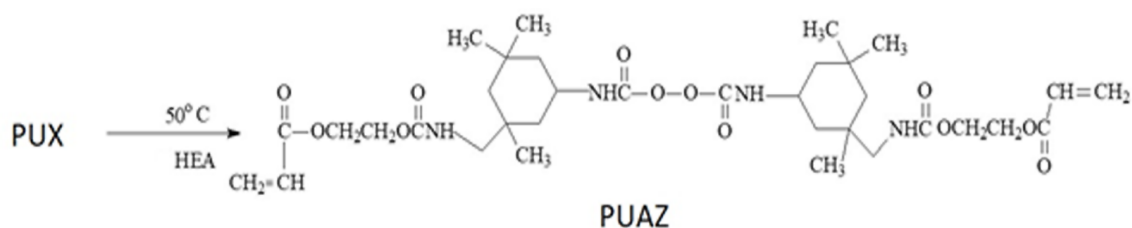
acrylates, or three-step synthesis process in case of synthesis built-in amine counterpart. These resins were synthesized by the reaction of Isophorone diisocyanate (IPDI), polyethylene glycol (PEG), 2-hydroxyethyl acrylate (HEA), and diethanolamine (DEA) in the presence of dibutyltin dilaurate (DBTDL). The free radical inhibitor was applied to avoid free-radical initiated polymerization via acrylic groups. The reactants stoichiometry of each synthetic route is mentioned in Table 1.

The UV-curable polyurethane acrylate resins were prepared according to the schematic outline as shown in Scheme 1 & 2.

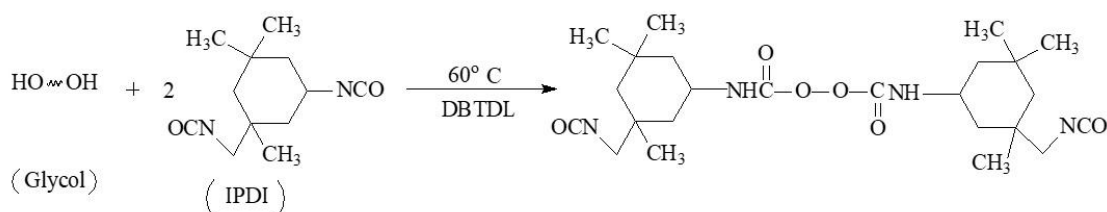
The UV-curable polyurethane acrylate built-in amine resins were prepared according to the schematic outline as shown in Scheme 3-5.

Step 1: Synthesis of isocyanate (NCO) terminated polyurethane (PUX) pre-polymer

Scheme 1. PUX = PU-1, PU-4

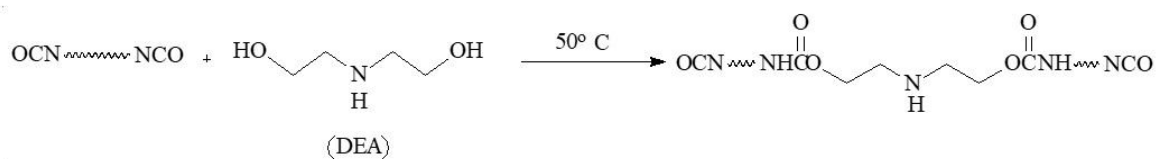
Step 2: Reaction of isocyanate (NCO) terminated polyurethane (PUX) with HEA

Scheme 2. PUAZ = PUA-2, PUA-5

Step1: Synthesis of isocyanate (NCO) terminated polyurethane (PUX) prepolymer

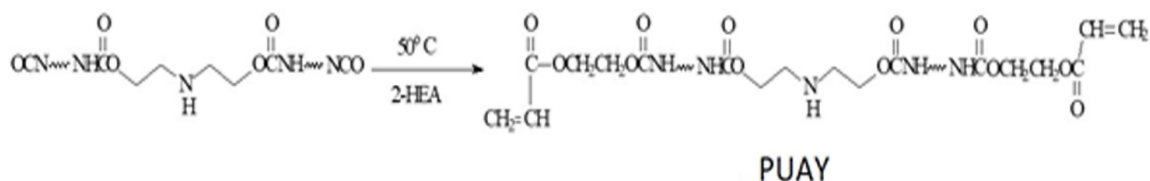
Scheme 3

Step 2: Synthesis of built-in amine polyurethane pre-polymer



Scheme 4

Step 3: Reaction of built-in amine polyurethane prepolymer with HEA



Scheme 5. PUAY = PUA-3, PUA-6

FTIR spectrum analysis of the polyurethane acrylate resins

Fourier-transform infrared (FTIR) spectral study of prepared polymers provides useful information about their structural features as it gives the idea about the nature of functional groups and the skeletal structure of the polymers. In suitable cases, the IR spectral study proved a useful understanding in the course of a polymerization reaction. PU-1, PUA-2, PUA-3, PU-4, PUA-5, and PUA-6 have been well considered by FT-IR spectroscopy as shown in Fig. 2-6 and the summary of their characteristic absorption peaks is represented in Table 2.

In the two-steps reaction process, the peaks assignment of the important functional group of synthesis isocyanate (NCO) terminated polyurethane (PU-1) and (PU-4) are presented and interpreted in Fig. 2, respectively. It was observed that there is no significant difference between sonochemical and conventional heating in the first step.

Figure 1 shows the FT-IR spectrum of the formation of isocyanate terminated polyurethane pre-polymer. It can be obviously detected from the spectrum that the NH groups appeared at 3328 cm^{-1} . Another peaks detected in the FT-IR graph of polyurethane prepolymer were allocated at 2930 cm^{-1} (the C-H symmetric stretching of

$-\text{CH}_2$); 2877 cm^{-1} (the C-H asymmetric stretching of $-\text{CH}_2$ groups); 2240 cm^{-1} (N=C=O group); 1112 cm^{-1} ($-\text{C}=\text{O}$ stretching band of the soft segment). The PU prepolymer has shown some characteristic absorption peaks, were assigned at 1535 cm^{-1} , 1495 cm^{-1} for ($-\text{N}-\text{H}$ and $-\text{C}-\text{N}$, bending and stretching bands), 1720 cm^{-1} (CO stretching band) and 3328 cm^{-1} (N-H stretching).

Figures 3 and 4 show the IR Spectra of vinyl terminated PU polymers namely the PUA-2 and PU-5 respectively. It is obviously detected from the FT-IR spectrum of vinyl terminated PU prepolymers that the isocyanate ($-\text{N}=\text{C}=\text{O}$) peak at 2240 cm^{-1} has been vanished, which indicates a complete consumption of the $-\text{N}=\text{C}=\text{O}$ contents during the reaction with 2-hydroxyethyl acrylate to form vinyl terminated PU prepolymer. In addition, FT-IR graph of polyurethane with terminated vinyl groups show N-H stretching peak at 3334 cm^{-1} , which could be regarded to the formation of urethane linkage in the polyurethane prepolymer. The $-\text{C}-\text{H}$ stretching of the CH_2 group was detected at 2879 cm^{-1} (asymmetric $-\text{C}-\text{H}$) and 2944 cm^{-1} (symmetric $-\text{C}-\text{H}$). The FT-IR graph demonstrations sharp peaks at 1718 cm^{-1} and 1641 cm^{-1} which could be assigned for the $-\text{C}=\text{O}$ stretching and $\text{C}=\text{C}$ stretching of the prepared polymer, respectively. 1193 cm^{-1} assigned to $-\text{C}-\text{O}$, $-\text{C}-\text{C}$ stretching.

In the three-steps reaction process, the peaks assignment of the important functional group of synthesis built-in amine polyurethane terminated with vinyl groups (PUA-3 and PUA-6) are presented and interpreted in Fig. 5 and Fig. 6 respectively. It is clearly observed in the FT-IR spectrum of the formation of built-in amine groups between isocyanate ($\text{N}=\text{C}=\text{O}$) terminated polyurethane C-O, C-C stretching at 1193 cm^{-1} has been disappeared indicating the formation of the built-in amine group. After that capping the

product with HEA, FTIR graph of polyurethane containing vinyl terminated groups show a distinct peak of N-H stretching at 3326 cm^{-1} ascribed for the generation of urethane linkage in the polyurethane prepolymer. The C-H stretching of the methylene group was detected at 2900 cm^{-1} . The FT-IR graph shows sharp peaks at 1712 cm^{-1} and 1635 cm^{-1} , which are ascribed to the C=O stretching and C=C stretching of the prepared polyurethane.

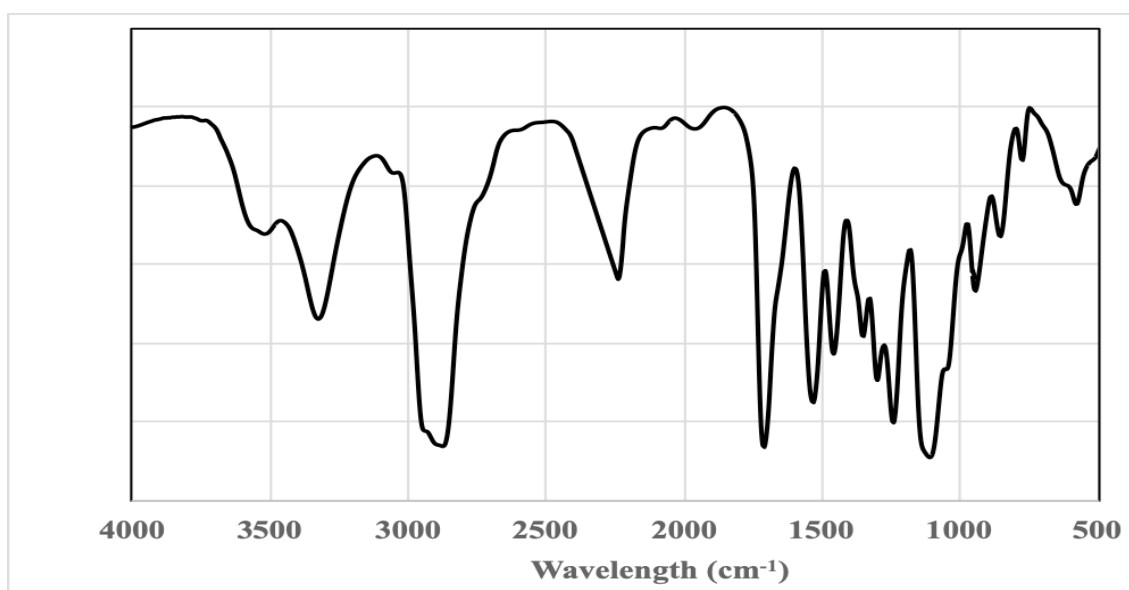


Fig. 2. IR spectrum of Polyurethane (PU-1 & PU-4).

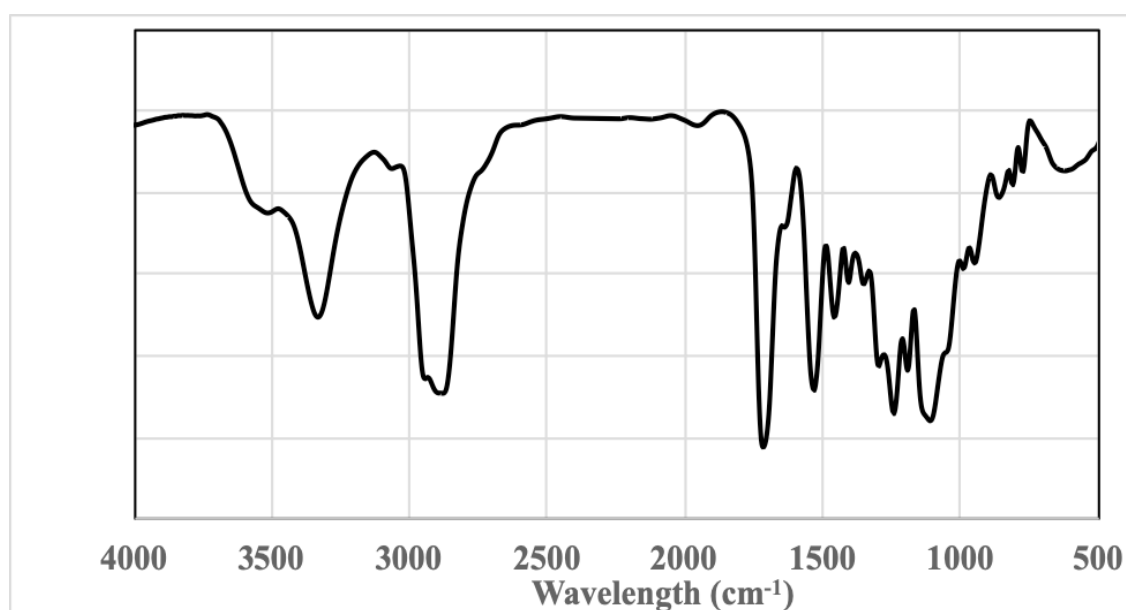


Fig. 3. IR spectrum of Polyurethane Acrylate (PUA-2)

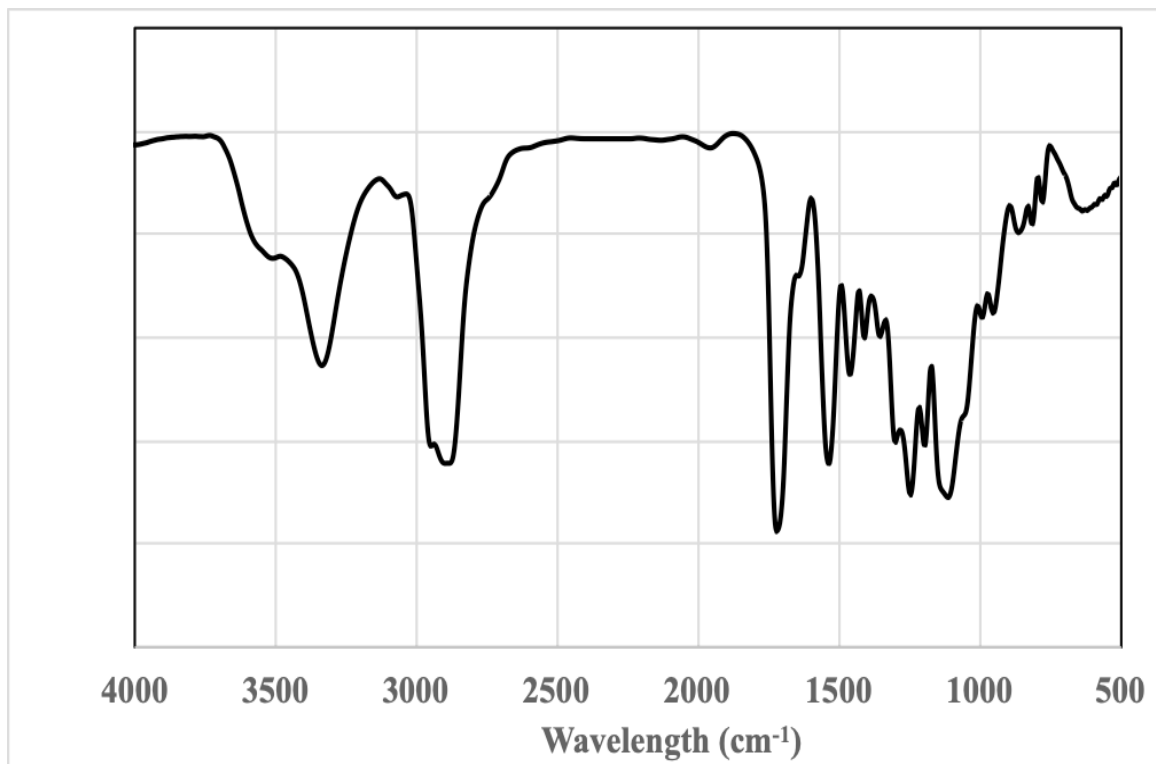


Fig. 4. IR spectrum of Polyurethane Acrylate (PUA-5).

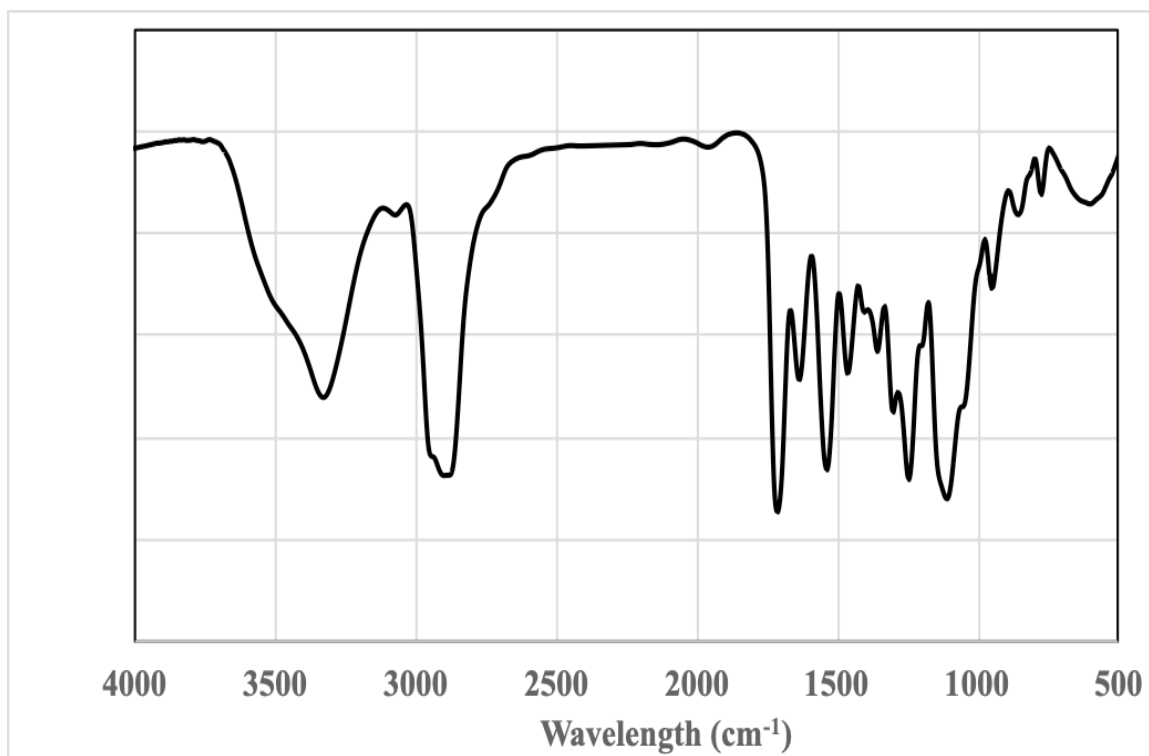


Fig. 5. IR spectrum of Polyurethane Acrylate (PUA-3).

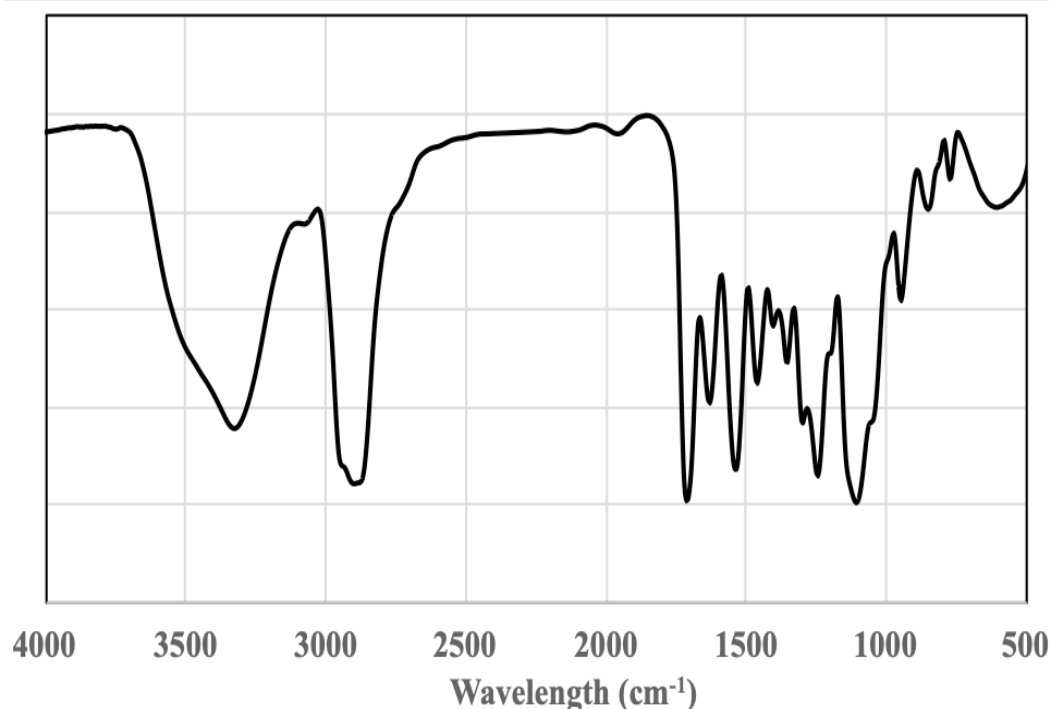


Fig. 6. IR spectrum of Polyurethane Acrylate (PUA-6).

TABLE 2. FTIR peaks and its chemical composition for polyurethane acrylate resins.

PU-4 & PU-1		PUA-2 & PUA-5		PUA-3 & PUA-6	
Absorption peak (cm ⁻¹)	Functional groups	Absorption peak	Functional groups	Absorption peak	Functional groups
3328	-NH	3334	-NH	3326	-NH
2930	-CH	2944, 2879	-CH	2900	-CH
2240	-NCO	2240	-NCO	1712	-C=O
1720	C=O	1718	-C=O	1635	C=C
1535	-N-H	1641	C=C	--	--
1495	-C-N	1193	-C-O	--	--
1112	C-O	--	--	--	--

The extensiveness of the polymerization could be guaranteed by the disappearance or appearance of some distinguished peaks. In the present work, the FT-IR graph of isocyanate (N=C=O) peak at 2240 cm⁻¹ was vanished and a new peak was detected at 3334 cm⁻¹, which may belong to the N-H

¹H NMR characterization of the polyurethane acrylate resins

Spectroscopic characterization of polyurethane acrylates resins with and without built-in amine has been carried out using ¹H-NMR. Fig. 7

shows the ¹H-NMR spectrum of the synthesized polyurethane PU-4 peaks at 7.00 and 7.2 ppm due to the urethane protons of (-NHCOO-).

While three characteristic peaks at 5.9, 6.1, and 6.3 ppm are clearly observed in Fig. 8, which demonstrate the presence of acrylic groups (-CH₂=CH-COO-) in the molecular structure of PUA-2 and PUA-5. The peaks 7 and 7.2 ppm are given to the urethane groups (-NHCOO-), demonstrating that the structure of -NH- is formed due to the reaction between -N=C=O of the IPDI with hydroxyl groups.

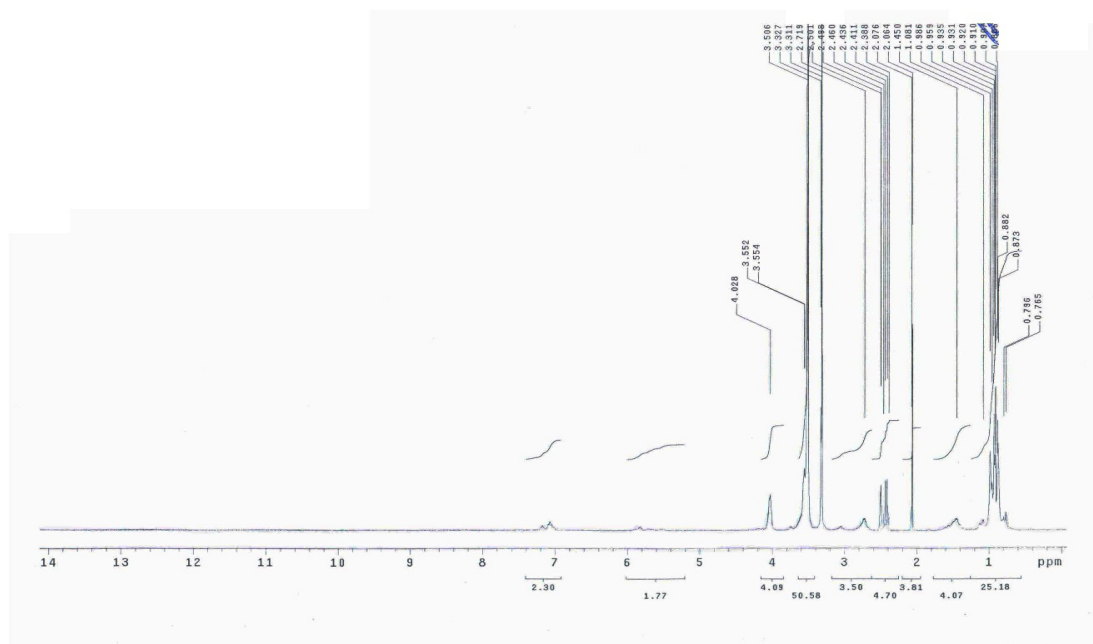


Fig. 7. NMR chart of PU-4.

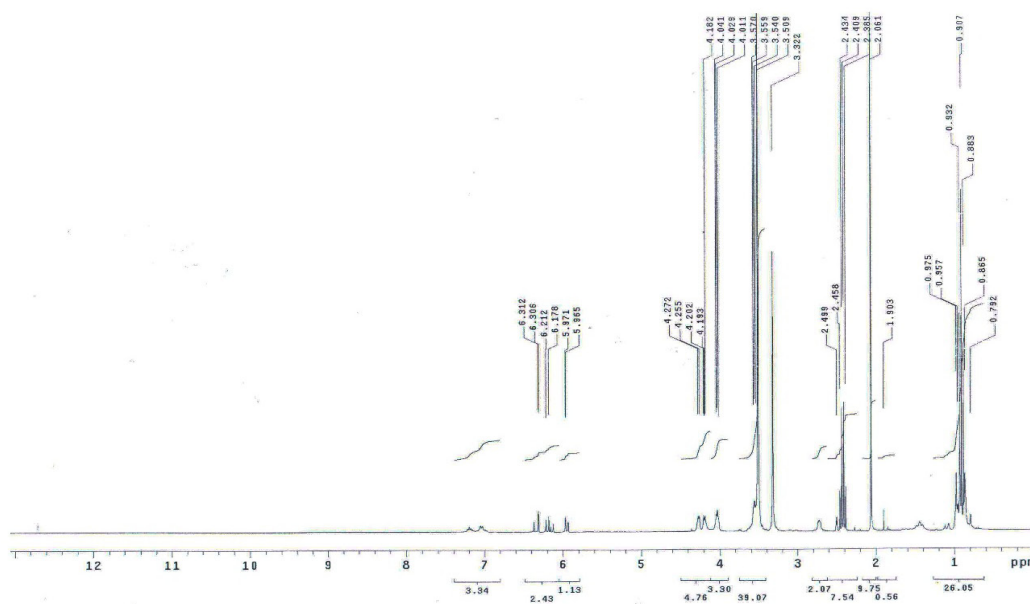


Fig. 8. NMR chart of PUA-2 and PUA-5.

In Fig. 9 the peaks at 2.8 and 3.8 ppm δ are due to the methylene proton (CH_2 (b)– CH_2 (c)) of the long alkyl side chain formerly existing in diethanolamine and peak at 4.8–5.0 ppm is characteristic to the $-\text{NH}$ (a) group in diethanolamine Scheme 6. These peaks prove the formation of built-in amine in the molecular structure of PUA-3 and PUA-6.

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Three characteristics peaks at 5.9, 6.1, and 6.3 ppm are clearly observed in Fig. 9, which verify the presence of acrylic groups ($-\text{CH}_2=\text{CH}-\text{COO}-$) in the chemical composition of PUA-3 and PUA-6. Also, the characteristic peaks are summarized in Table 3.

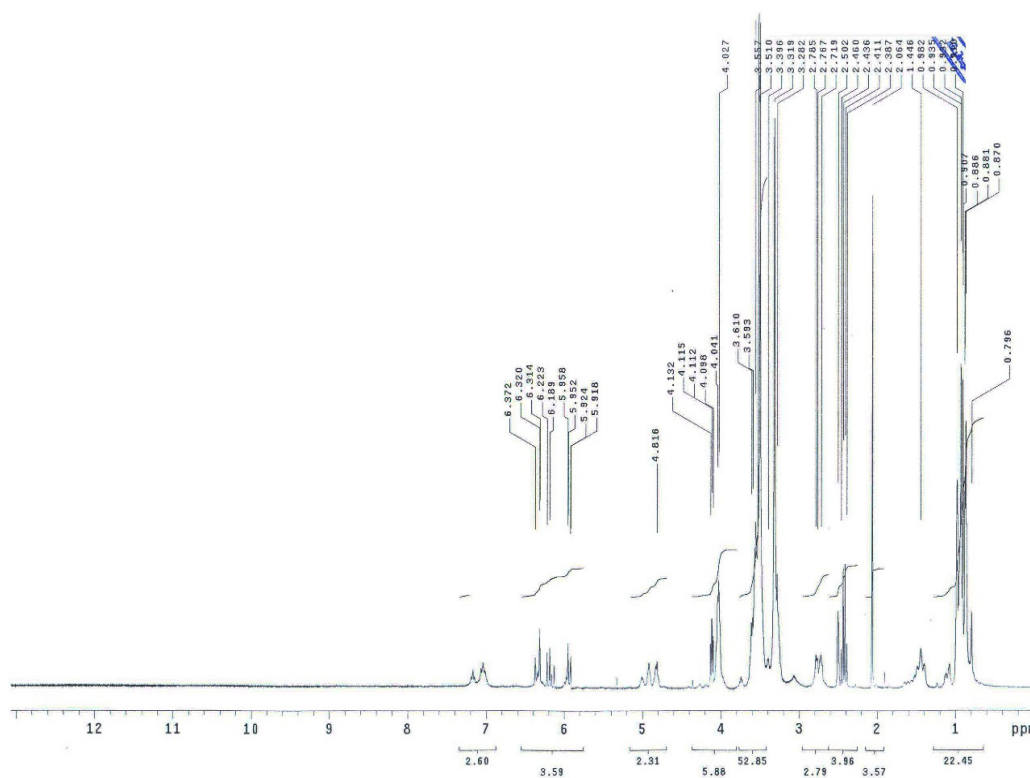
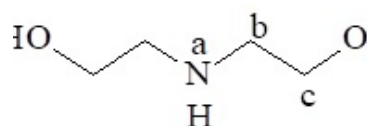


Fig. 9. NMR chart of PUA-3 and PUA-6.



Scheme 6.

TABLE 3. ^1H -NMR spectral data of polyurethane acrylates resins.

^1H NMR single peak (ppm)	PU-1 and PU-4	PUA-2 and PUA-5	PUA-3 and PUA-6
7-7.2	—NHCOO—	—NHCOO—	—NHCOO—
5.9-6.3	--	$\text{CH}_2=\text{CH}-\text{COO}-$	$\text{CH}_2=\text{CH}-\text{COO}-$
4.8-5.0	--	--	-NH
2.8-3.8	--	--	$-\text{CH}_2$

Molecular Weight Determination

Gel permeation chromatography can determine several important parameters such as (M_n), (M_w) and (M_w/M_n). The results of GPC analysis comprising average number molecular mass (M_n), average molecular mass (M_w), and polydispersity (M_w/M_n) were presented in Table 4.

The GPC data in Table 4 showed that all the prepared polyurethane-acrylate possess a higher molecular weight than those of polyurethane alone. For instance, in sonochemical synthetic route, the (M_w) and (M_n) were both dramatically increased from 5000 and 1980 for polyurethane (PU-4) to 156200 and 2800 for polyurethane-acrylate (PUA-5), respectively. On the other hand M_w and M_n increased to 4200 and 21800 respectively for polyurethane acrylate built-in amine (PUA-6). Also, the PUA-5 has a polydispersity of 5.6, indicating that the molecular weight distribution of the PUA-5 is wide. These results indicate that there is some degree of oligomerization taking place under the sonochemical reaction conditions employed.

Rheology characterization

The variation in the rheological behaviors is an essential factor in determination of the processability and cured films properties. Viscosity of synthesized resins is related to the dynamic extension and segment density, which depends on intermolecular chain entanglement and the volume of a molecule. Fig. 10 shows the viscosity profiles of polyurethane acrylate resins PUA-5 and PUA-6 versus share rate.

Also, Fig 10 shows that, the viscosity of PUA-5 and PUA-6 resins decrease severely as the shear rate rises (1 to 5), also decreases steadily from 5 to 50. As the shear rate increases, the physical crosslinks are broken down, therefore a remarkable decrease in viscosity. This suggests that PUA-5 and PUA-6 exhibit shear thinning or pseudo-plastic behavior. Figure 10 shows that, the rate of PUA-6 viscosity is higher than those of PUA-5 resin implying less entanglement in case of built-in amine resin.

UV-curing of polyurethane acrylate resins on polyester fabrics

Regarding to the processing techniques of thermosetting polymers, the curing process is proposed in which the polyfunctional reactive groups in the oligomer or the polymer are modified into a cross-linked macromolecular three-dimensional structure. Scheme 7 describes the main processing steps for the production of UV-curable polyurethane acrylate films with and free of the built-in amine group.

In order to study the potential of polyurethane acrylate resins after synthesis of built-in amine resin for their utility in UV-cure coatings, a number of UV-cure coatings formulas at Table 5 were formed and their characterizations were studied.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray analysis (EDX)

SEM was used to full characterize the surface morphology of the UV-cured films. Fig. 11a, b and c illustrates the SEM images corresponding to the morphology of UV cured films of polyurethane UVPU-4, polyurethane acrylate resins UVPUA-2 and UVPUA-5 respectively.

TABLE 4. Molecular weight data of sonochemically prepared polyurethane-acrylate resins.

Sample code	M_n ($\times 10^3$) (g mol^{-1})	M_w ($\times 10^3$) (g mol^{-1})	M_w/M_n
PU-4	1.98	5.00	2.5
PUA-5	2.80	15.62	5.6
PUA-6	4.20	21.80	5.19

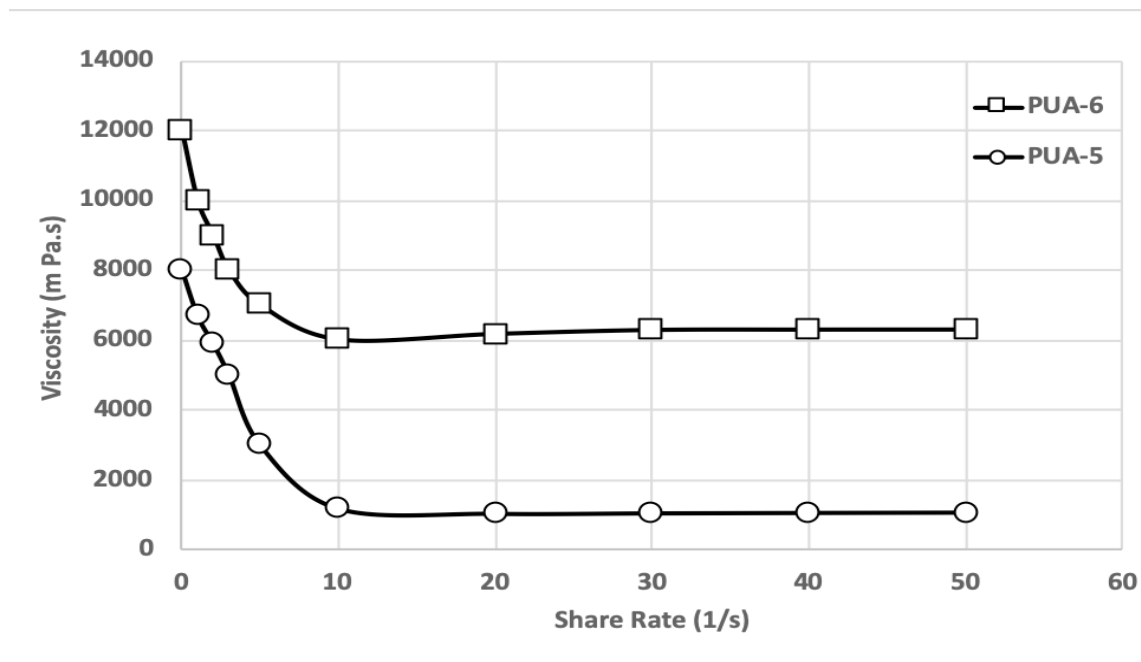
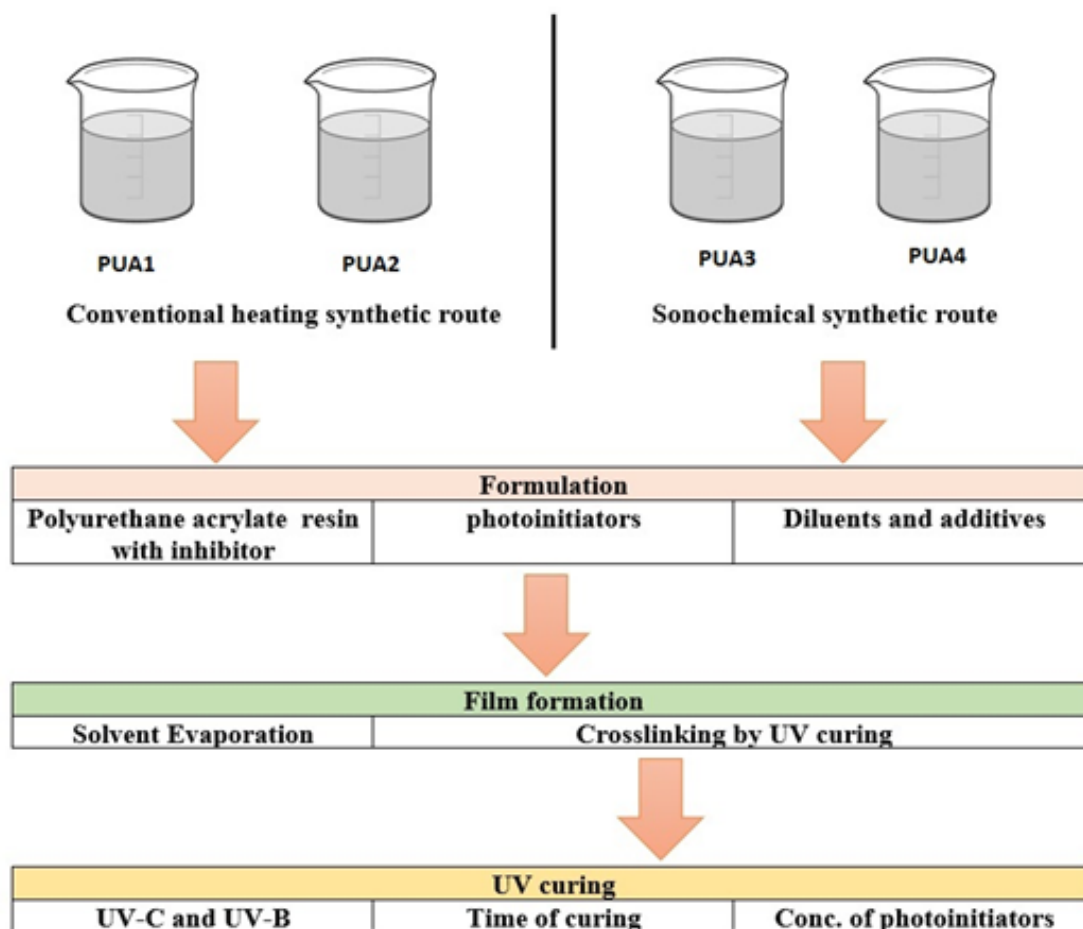


Fig. 10. Rheological curve behavior of PUA-5 and PUA-6.



Scheme 7.

TABLE 5. Composition of UV-curable of polyurethane resins

UVPUA-2	UVPUA-3	UVPUA-5	UVPUA-6	UVPU-4
Polyurethane acrylates resin	Polyurethane acrylates built-in amine resin	Polyurethane acrylates resin	Polyurethane acrylates built-in amine resin	Polyurethane resin
photoinitiator				
Reactive diluent				

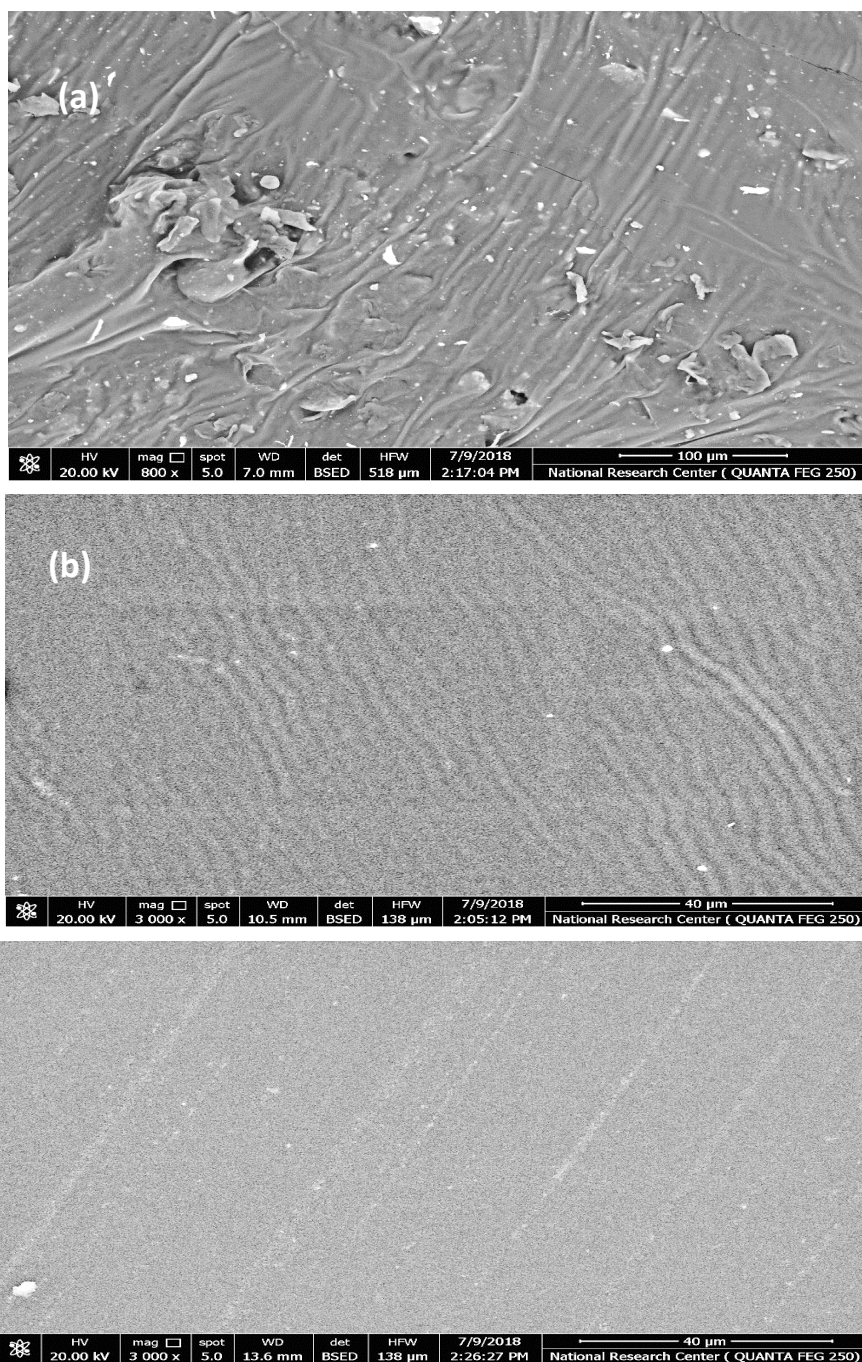


Fig. 11. SEM images of UV-cured films, (a) UVPU-4; (b) UVPUA-2 and (c) UVPUA-5. Cured film composition: prepolymer/reactive diluent = 50/50 (wt %); photo-initiator 2 wt %.

Cured films composition: prepolymer/reactive diluent = 50/50 (wt %); photoinitiator 2 wt %.

The UVPU-4 (Fig. 11a) possesses an irregular and rough surface structure due to the rubbery character of PU-4, which can be produced by incomplete UV curing even after a long time. We can understand this surface morphology a result of the absence of acrylate group in the molecular structure of UVPU-4, which may lead to crosslinking and complete curing. On the other hand, UVPUA-2 and UVPUA-5 (Fig. 11b and c) have a less irregular surface and exhibits continuous phase morphology in comparison with that of UVPU-4. The overall net effect of UV curing on polyurethane acrylate resins has been known to depend on the concentration of the terminal-CH=CH₂ group.

The surface morphology of UVPUA-6 was investigated as shown in Fig. 12. It was found that the UV cured film morphology depends on the viscosity of the resin and in turn the type of applied UV zone. Fig. 13 shows the relationship between UV light penetration depth and UV light wavelength, as the UV wavelength decrease its effect is limited to the film surface and vice versa. For this reason, as the viscosity increase, it is

useful to apply UV light with higher wavelength to obtain through cure. Also, there is another hypothesis that is built-in amine may be plasticized UV curable and reduce the strength of UV curable film. Then, show some surface irregularities as in Fig 12.

To further elucidate the nature of UV cured film surface, the elemental composition was measured by energy dispersive X-ray spectroscopy (EDX). In comparison with UVPU-4, UVPUA-2, UVPUA-5 and UVPUA-6, it was found that UVPUA-6 has the highest carbon contents (Fig 14), this may result from the existence of extra four carbons of diethanolamine in the molecular structure of polyurethane acrylate resin built-in amine UVPUA-6.

Mechanical properties

The mechanical properties for UVPUA films were listed in Table 6. Which show the influence of formation built-in amine in polyurethane acrylates resin on its elasticity by measuring Young Modulus (YM). Young's modulus can be used to predict the elongation or compression of UV cured films when exposed to force, YM evaluated from stress-strain curves.

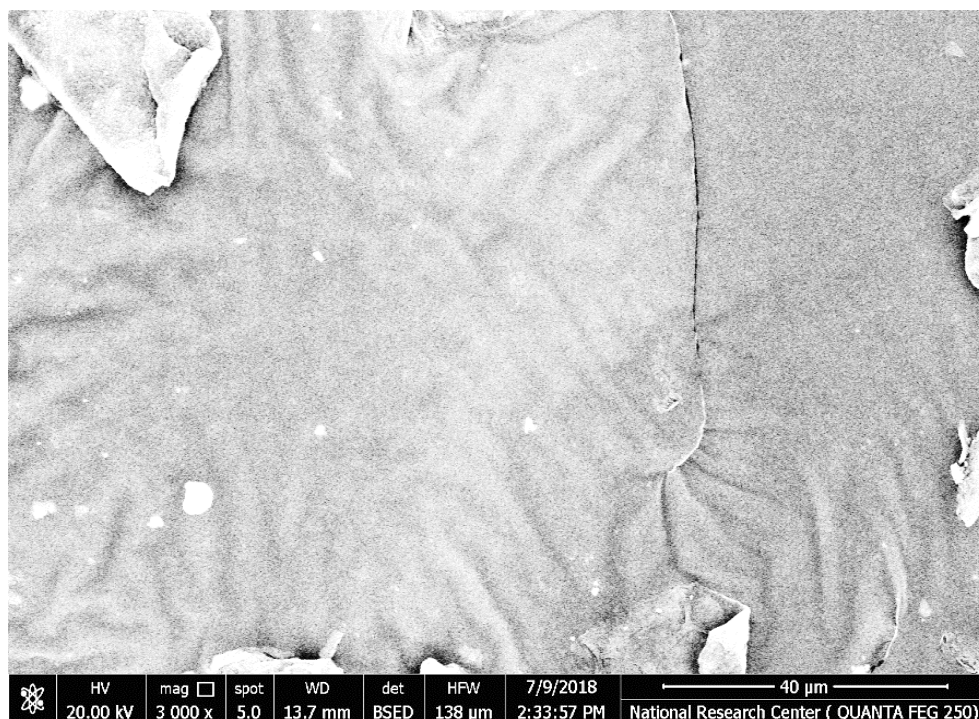


Fig. 12. SEM image of UVPUA-6 cured film.

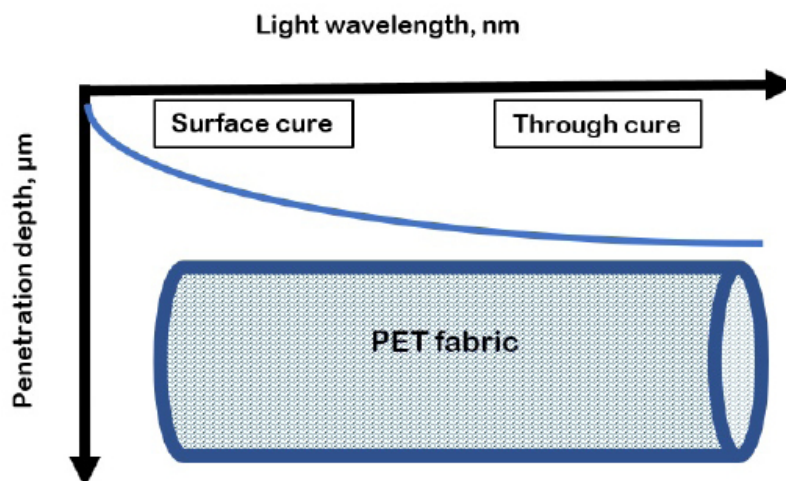


Fig. 13. The relation between light wavelength and penetration depth during the curing process of polyurethane acrylate resins on PET fabric surface.

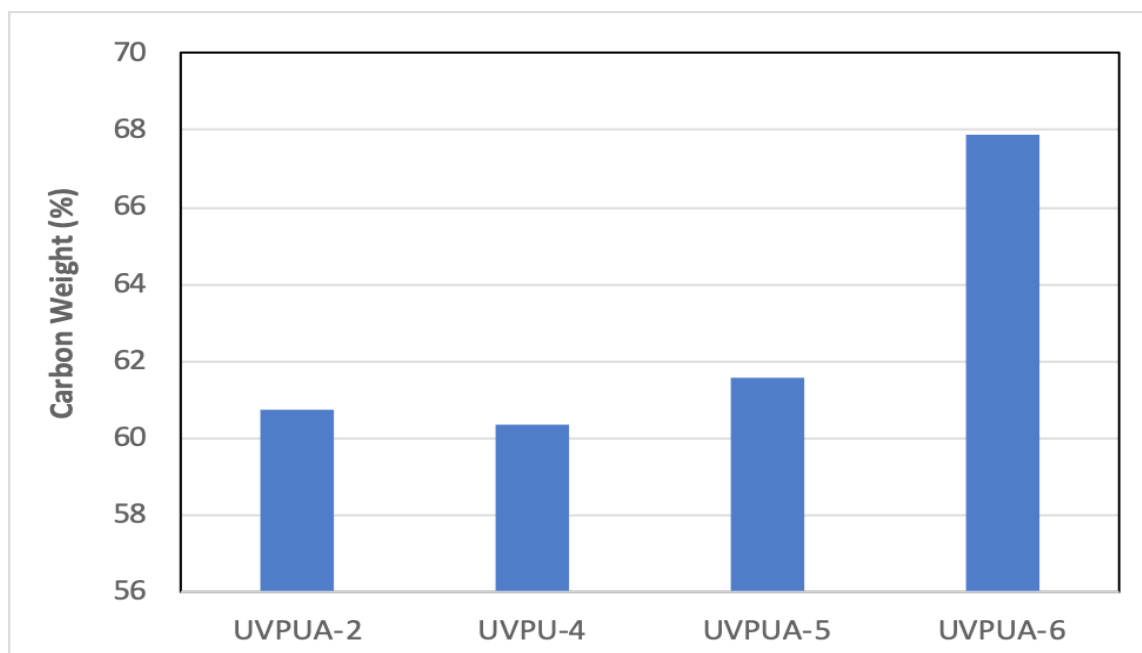


Fig. 14. The carbon weight (%) of different UV curable polyurethane films.

TABLE 6. The effect of chemical composition on the mechanical properties.

Sample code	Strain at max. Load (%)	Stress at max. load (KgF/mm ²)	Young Modulus (KgF/mm ²)
UVPUA-2	27.167	0.354	1.565
UVPUA-3	109.000	0.014	0.017
UVPUA-5	22.667	0.099	0.496
UVPUA-6	107.569	0.013	0.015

It is clearly observed that the elastic modulus of the UV curable polyurethane acrylate resins decreased with the introduction of amine group regardless of the applied synthetic approach. This result may be attributed to crosslinking density formed during UV curing. For this reason, UVPUA-2 and UVPUA-5 have high crosslinking density, on contrast UVPUA-3 and UVPUA-6 have high viscosity as shown on rheology characterization, which prevents through cure and formation low density crosslinking films.

Printing behavior

The color strength (K/S) for the untreated polyester fabric (PET), PUA-3 and treated PET fabrics with PUA-6 printed with C.I. acid blue 80 and C.I. acid red 18 dyes was represented in Fig. 15. Obviously, it can be observed that, the K/S values of treated fabrics were enhanced for two dyes used in comparison with the unmodified printed fabrics. It was expected that polyurethane acrylates built-in amine layer contains free amino groups. This improvement in K/S values of modified PET fabrics with polyurethane acrylates built-in amine is related with the presence of amino groups into the fiber building matrix which affords a high substantivity to acid dyes via corresponding electrostatic attractions. The coloration of untreated polyester fabric with acid dyes class

is not possible, since unmodified polyester fabric does not include amino groups in their building matrix, which is essential for the dye-fiber interaction.

Fabrics are exposed to regular washing and rubbing during their custom. Hence, the color fastness of printed treated fabrics were evaluated to evaluate the tendency of wash down and cross staining between the adjacent fabrics. Optically assessment of all samples was contacted using the gray scale. The gray scale value 5 indicates no shade change (no stain on the adjacent fabric), whereas gray scale value 1 indicates a severe shade change (staining). Table 7 shows the evaluations of diverse color fastness of the printed fabrics with the aforementioned acid dyes. The results are ranging from very good (4–5) to moderate (2–3) change in color for staining of adjacent fabrics. The resistance toward abrasion was also evaluated, and it found to be moderate (2–3).

It is worth noting that, the color fastness evaluations for the untreated PET are not given since there is no interaction between PET surfaces and acid dyes. Though, the discoveries obviously determine that the molecules of acid dyes were reserved on the matrix of polyurethane acrylates built-in amine.

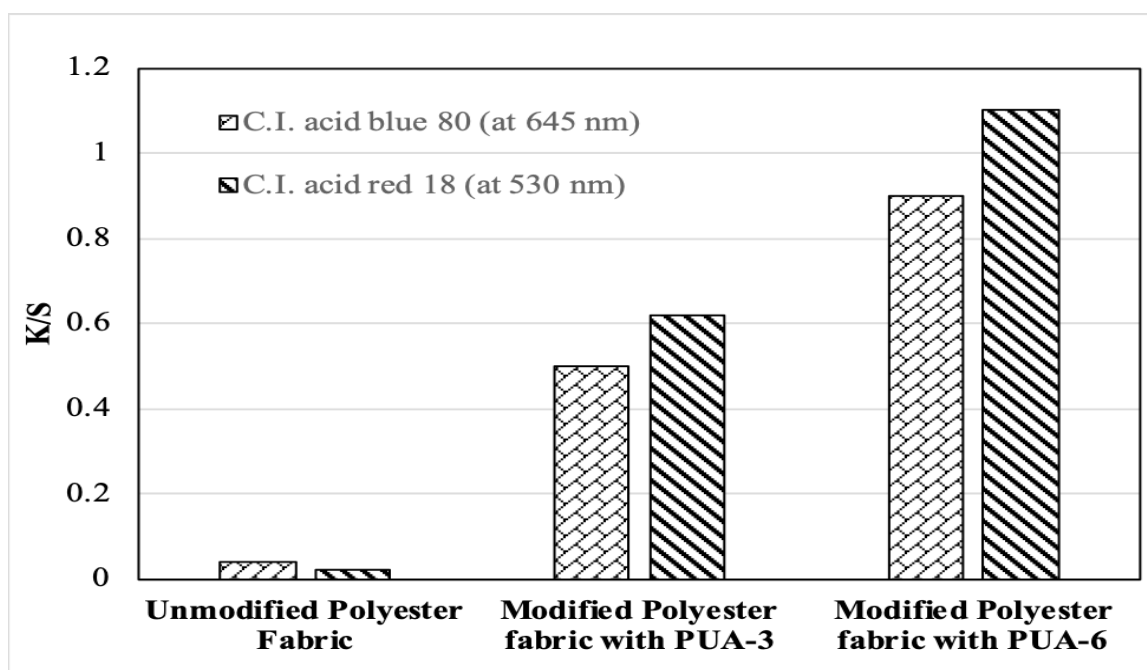


Fig. 15. Color strength (K/S) of untreated PET and PET fabrics treated with PUA-3 (conventionally prepared polyurethane acrylates built-in amine) and PUA-6 (sonochemically prepared polyurethane acrylates built-in amine) printed fabrics.

TABLE 7. Color fastness properties of polyurethane acrylates built-in amine treated PET fabrics modified with PUA-3 and PUA-6.

Dye	Washing fastness			Rubbing fastness	
	Staining on		alteration	Dry	wet
	cotton	wool			
C.I. acid Red 18	4-5	4-5	2-3	2-3	2-3
C.I. acid Blue 80	4-5	4	2-3	3	2-3

Conclusions

In the current work, several UV-curable polyurethane acrylates resins with different molecular structures were synthesized and the effects of the synthetic approach on their chemical and physical properties were investigated. The function groups of -NHCOO, -NCO and content of unsaturated double bonds (-CH=CH₂) were confirmed by FT-IR and ¹H-NMR. The combination of acrylate groups was confirmed by ¹H-NMR due to the appearance of the peaks at 5.9, 6.1, and 6.4 ppm. The sonochemical process produces low viscosity product UVPUA-5 with a very high degree of acrylation under mild reaction conditions hence offer systems with significantly reduced environmental impact. The results indicated that the synthetic resin possess excellent UV curing performance when (-CH=CH₂) existed in the molecular structure. On the other hand, this performance decreased in the case of polyurethane acrylate resins containing amine group as built-in amine due to increasing the viscosity and low efficient through cure process by using UV lamp from UV Zone-C with the tested thickness. The UV-cured film properties of suggested UV curing composition were studied. The effect of formation built-in amine group on thermal and mechanical properties of cured films was examined. The results exposed that polyurethane acrylates resin containing built-in amine possessed medium photopolymerization efficiency under UV curing system and UV curing composition. However, treatment of PET fabric with polyurethane acrylates resin containing built-in amine results in an enhancement of the printability of PET with acid dyes via complementary electrostatic attractions at neutral printing condition. This word can be considered as an important step toward substrate independent coloration of polyester.

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تطوير نوع جديد من راتنجات البولي يوريثين اكريليت المتصلبه بالاشعه فوق البنفسجية لاستخدامها في تطبيقات الطلاء

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يمكن اعتبار أقمشة البوليستر المحتوية على النيتروجين ركيزة اساسيه للتطبيقات متعددة الاستخدامات. يهدف هذا البحث الي إدخال مجموعة وظيفية محتوية على النيتروجين على سطح أقمشة البوليستر باستخدام متراكب محضر من البولي يوريثين اكريليت المتصلب بالاشعه فوق البنفسجيه والغني بمجموعات الامين. تم تحضير راتنجات البولي يوريثين اكريليت المضمنة بمجموعات الامين إما عن طريق بلمره باستخدام الموجات فوق الصوتيه أو باستخدام التحضير الحراري التقليدي. بعد ذلك ، تم تحضير الراتنجات القابلة للتصلب عن الأشعة فوق البنفسجية عن طريق مزج راتينج أمين مدمج من البولي يوريثين أكريليت مع المكونات الرئيسية لمثل هذه التركيبات مثل مخفف وبادئ التفاعل الضوئي. تمت دراسته خصائص البوليمرات الضوئية المحضرة باستخدام الرنين المغناطيسي النووي (NMR)، والأشعة تحت الحمراء (FTIR)، والفصل الكروماتوغرافي (GPC). كما تم فحص خصائص السطح للراتنج المتصلب باستخدام المجهر الماسح الإلكتروني. بالإضافة إلى ذلك، أجريت اختبارات قياس قوة الثبات للأقمشة المطبوعة وقوة اللون لتقييم مدي فاعليه دمج المجموعات المحتوية على النيتروجين وكذلك ثبات طبقة الطلاء. وقد اظهرت نتائج الأشعه تحت الحمراء لبوليمرات البولي يوريثين المحضر والمحتوي اطرافه علي مجموعات فينيل ضهور مجموعه N-H عند الطول الموجي 3326 سم⁻¹ ويعزى ذلك إلى تكوين رابطة اليوريثين. وقد اوضحت النتائج كذلك أن معالجة اقمشه البوليستر باستخدام راتنجات البولي يوريثان المحتوية على مجموعات أمين مدمجة تؤدي إلى زيادة القابليه للصبغة بالأصباغ الحمضية. يفتح البحث الحالي فرصة جديدة لتطوير أقمشة البوليستر المحتوية على النيتروجين والقابله للصبغة بالأصباغ الحمضية والتي لديها القدره علي استخدامها في التطبيقات الصناعية المختلفة.