



A New Route for Synthesis of Polyurethanevinyl Acetate Acrylate Emulsions as Binders for Pigment Printing of Cotton Fabrics

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HEREIN, two polyurethane oligomers were successfully synthesized using a prepolymer mixing process. The prepolymers were synthesized based on the step-growth addition polymerization of polypropylene glycol, Methylene diphenyl diisocyanate and 2-hydroxyethyl methacrylate or 2-hydroxyethyl acrylate. Isopropanol was functioned as the isocyanate blocking agent. Thereafter, different terpolymer emulsions were prepared by the emulsion graft copolymerization with the vinyl acetate monomer in presence of 2-ethylhexyl acrylate as a vinyl monomer. The chemical structures of the synthesized oligomeric monomers were probed by FTIR spectroscopy and found to vary with the content of acrylic monomer used in the oligomer synthesis phase (*i.e.* hydroxyethyl acrylate or hydroxyethyl methacrylate). The topography, thermal stability, and particle size of terpolymers were investigated by SEM, TGA, and zeta potential, respectively. The TGA results demonstrated marked enhancement in thermal stability of the synthesized terpolymers up to *ca.* 600°C, which was concurrent with enhanced surface homogeneity and film properties as evidenced by the SEM images. These terpolymers showed also property enhancement as binders for textile pigment printing in terms of rubbing resistance, color strength and fastness to washing when compared to the commercial binders. These judgments would provide a new competent synthesis route by introducing polyurethane acetate vinyl acrylate as the binder for use in pigment printing of cotton fabrics.

Keywords: Polyurethane acetate vinyl acrylate; Surface coating; Terpolymer; Textile binder; Vinyl monomer.

Introduction

The waterborne coating based on synthetic polymer latex is continued to be a most favored route in the coatings industry due to their minimal environmental impact, compared to solvent-borne technologies [1, 2], and the wide range of properties achievable through emulsion polymerization of vinyl monomers [3]. Currently, the waterborne coatings have substituted solvent-based coatings

for most industrial coating applications and have made significant inroads into some categories of industrial coatings as well as in textile industry. Numerous types of polymeric materials can be produced by the emulsion techniques including mass transfer and agitation, which provide eco-friendly synthesis processes. By adopting such technical procedures, the ability to control properties of the produced emulsion polymers

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will be accessible, that would be allowing the production of waterborne polymers by emulsion polymerization to expand progressively [4]. By now, the waterborne polymers have extensive products range which include synthetic rubbers, toughened plastics, paints, adhesives, paper coatings, floor polishes, sealants, cement/concrete additives, textile prints, and nonwoven tissues.

Especially, the homo-polymer from vinyl acetate emulsion was regarded from the first synthetic polymer latexes to be manufactured in a commercial scale [5]. From industrial side, the homo-polymers copolymers of vinyl acetate-based emulsions have a remarkable importance as well as scientific aspect. They represent about 28% of the total waterborne synthetic latexes [6].

Nevertheless, water-based acrylate polymer emulsions which offer reasonably good durability were also obtained by emulsion polymerization technique. They have been widely used as resins for aqueous coating applications [7]. Among them, polyurethane-acrylate (PUA) oligomers are a new class of polyurethane (PU) which produced by the reaction of polyols with diisocyanate and capped by acrylate. Nowadays, there have been growing demands for the modification of PUA by improving properties for multiple practices [8]. It was reported that aqueous polyurethane acrylate was synthesized for using as binders in pigment printing of cotton and polyester fabrics through the silk screen technique, and pigment fixation was achieved by the polymerization process of the binder using the thermo-fixation technique[9].

In this work, new monomers of acrylated/methacrylated polyurethanes were synthesized; and then were copolymerized with vinyl acetate and 2-ethyl hexyl acrylate monomers; afterwards the structure of the resultant copolymers and their morphologies were studied and discussed in detail. Thermal properties of the resultant copolymers were verified by TGA and MFFT techniques. In order to the application, the synthesized terpolymers were evaluated as waterborne binders for textile applications.

Experimental

Materials

Methylene diphenyl diisocyanate (ISONATE™ 50 OP) (DOW chemicals Co., UK), poly (propylene glycol) (Arcol PPG

1000) (Covestro Co., USA), Acrylates, i.e. 2-(hydroxyethyl methacrylate) (HEMA), hydroxyethyl acrylate (HEA), 2-ethylhexyl acrylate (EHA)) (ARKEMA Co., France), vinyl acetate monomer (VAM) (SOLVO Chem., India), EMULSOGEN EPA 073 and EMULSOGEN EPN 287 (CLARIANT Co., Germany), sodium bicarbonate (SISECAM Chemicals Co., Turkey), ADVANTAGE AM 1512 (Ashland Co., UK), potassium persulphate (SASOL Co., Italy), di-butyl amine (MERCK Co., USA), Bromophenol blue (LOBAL CHEMIE Co., India), and hydrochloric acid, isopropyl alcohol, sodium hydroxide, and toluene (El-Nasr pharmaceutical chemicals Co. Egypt). All chemicals and reagents were used as delivered without any further purification.

Synthesis of urethane methacrylate macro-monomer (UMAM)

UMAM was synthesized in four steps as follows. First, 190.5 g of polypropylene glycol (PPG1000) were charged to a 500 mL four-necked round glass equipped with a nitrogen gas inlet system; the system was then heated to 65°C. Second, 150 g of MDI 50 were added drop wise under continuous stirring for 2 h, to obtain 10 % isocyanate-terminated prepolymer as was confirmed by using a backtitration, and then the temperature decreased to 60°C. Third, 39 g of 2-hydroxyethyl methacrylate (HEMA) was added to the prepolymer in 5 min and after ward, 0.5 g of dissolved hydroquinone was also added in order to tolerate the presence of internal double bond in UMAM. Fourth, 36 g of isopropyl alcohol were added to the latter mixture and the final temperature was fixed at 60-65 °C for an additional one hour to attain complete consumption of the reactive NCO groups [10]. This was followed by the back-titration through the addition of an excess amount of isopropanol ranging from 0-0.1 mole to ensure the consumption of all isocyanate groups, as confirmed by the FTIR analysis. This reaction is presented in Scheme 1.

Synthesis of urethane acrylate macro-monomer (UAM)

The preparation of urethane acrylate monomer (UAM) was carried out through four-steps in which the first, second and fourth steps

were as described above. The third step process includes adding 33.5 g of hydroxyethyl acrylate (HEA) to the prepolymer, and simultaneously hydroquinone solution (0.5 g hydroquinone) was also added for the sake of retaining double bond (Scheme 2). The final product obtained was a clear liquid of the colorless urethane acrylate oligomer (UAM) [11]. The feed composition data is listed in Table 1.

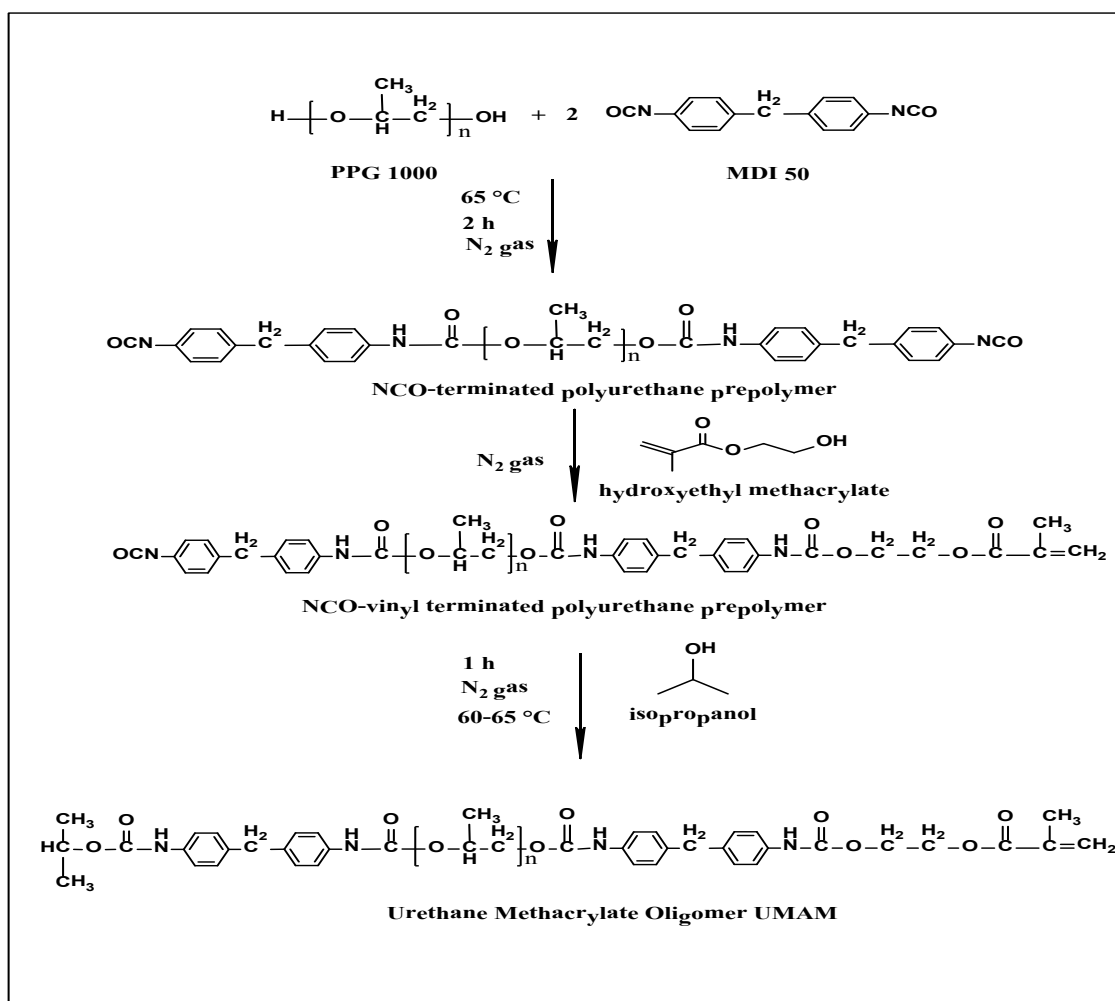
Synthesis of vinyl acetate polyurethane graft terpolymers using UMAM and UAM oligomers

In a typical semi-batch emulsion polymerization, 225 mL of demineralized water, 5 g of EMULSOGEN EPA 073 as an anionic emulsifier, 15 g of EMULSOGEN EBN 287 as a nonionic emulsifier, 0.5 g of sodium bicarbonate as a buffering agent and ADVANTAGE AM 1512 as anti-foaming agent were charged to a

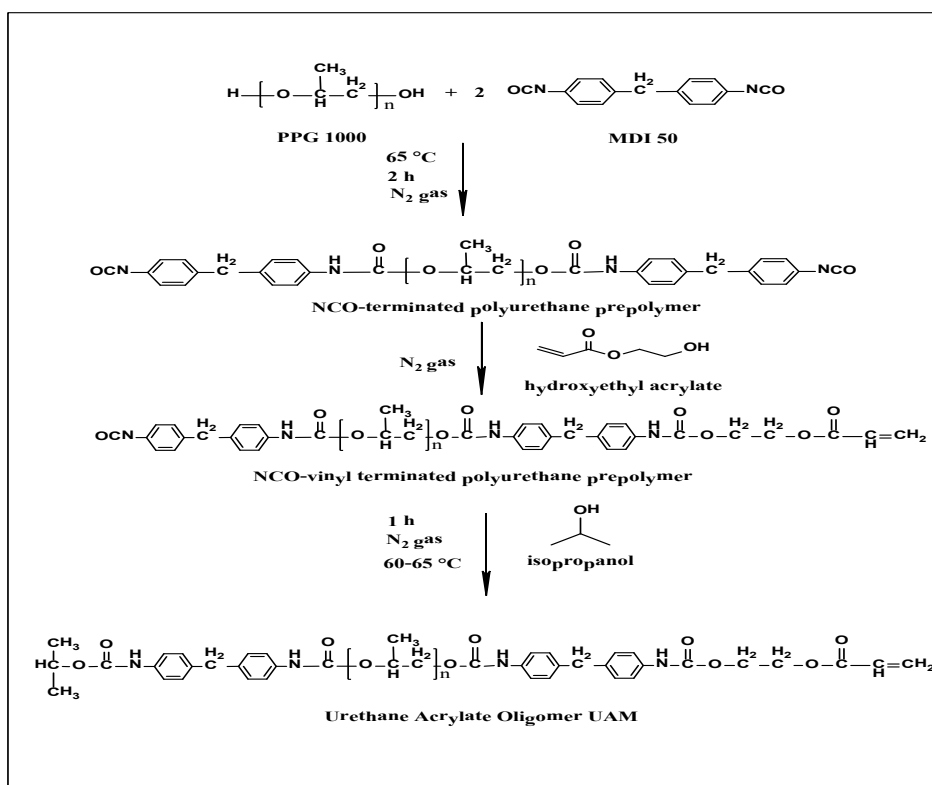
500 mL four-necked round-bottom flask. Mean while, 1 g of potassium persulfate ($K_2S_2O_8$) was dissolved in 25 mL water as the initiator solution (solution A). After ward, a monomer mixture was prepared by mixing 187.5 g of vinyl acetate, 50 g of 2-ethylhexyl acrylate (EHA) and 12.5 g of polyurethane oligomer (UMAM or UAM) (solution B). The polymerization process was carried out by continuous addition of solutions A and B to the preliminary ingredients at $82\pm 2^\circ\text{C}$ for 7 h with stirring at 180 rpm. The feed composition data is listed in Table 2, and the proposed chemical structures of UMAM and UAM terpolymers are presented in Fig. 1.

Determination of isocyanate group

The isocyanate group (NCO) content in the urethane intermediate and prepolymer was determined by back titration using the standard test method ASTM D2572 – 97 [12].



Scheme 1. Proposed synthesis protocol of the UMAM oligomer.



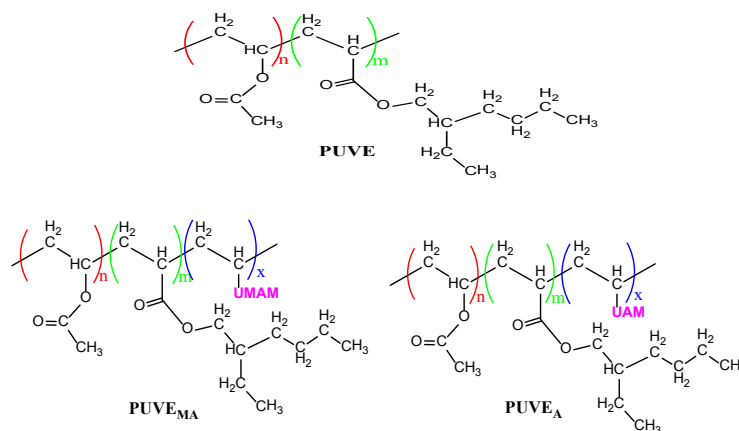
Scheme 2. Proposed scheme for synthesis of the UAM oligomer.

TABLE 1. Recipe for synthesis of polyurethane oligomers named UMAM and UAM.

Oligomer	MDI 50(g)	PPG 1000(g)	HEMA(g)	HEA(g)	Isopropyl alcohol(g)
UMAM	150	190.5	39	—	39
UAM	150	190.5	—	35	39

TABLE 2. Recipe for the semi-batch emulsion polymerization of the PUVE_{MA}, PUVE_A, PUVE polymers.

Exp. Code	Monomer mixture			
	VAM(g)	2-EHA(g)	UMAM(g)	UAM(g)
PUVE _{MA}	187.5	50	12.5	—
PUVE _A	187.5	50	—	12.5
PUVE	187.5	62.5	—	—

Fig. 1. Proposed chemical structures of the PUVE, PUVE_{MA}, and PUVE_A polymers.

Preparation of the polymeric films

The polymeric films grew with a dispersion of polymer solution onto leveled glass surfaces by the solution casting method. Samples were remained for drying at room temperature for 7 days, and then drying temperature was increased gradually to 60°C for 12 h. Films were casted by 90 µm applicators from the emulsions onto a glass surface (Dim. 7 cm × 2 cm) for obtaining dried films with ~25–30 µm thickness. The films were kept into the desiccator to remove moisture residues [13].

Physical properties of emulsion

Solids content, pH and viscosity of emulsions were determined by using a drying oven, a pH-meter (PL-700 PV), and a viscometer (Brook field RVDVE-II+Pro), respectively, according to the ISO 3251, ISO 976 and ISO 2555 standard methods [14].

Mechanical properties

The mechanical properties of the polyurethanes and its terpolymers were determined based on several factors such as type of soft and hard segments, interaction between hard and soft phases and crystallinity [15]. A high-speed mechanical shear agitator was applied to produce the shear between surfaces according to (ASTM D1417–16) for 15 min. The mass of coagulum produced was then determined by filtration and weighing [16].

Applications of polyurethane terpolymers in printing of polyester/cotton blend fabrics

Preparation of printing pastes

The pigment printing pastes were prepared according to the following recipe: Pigment 30 g, binder 150 g, thickener 40 g and distilled water 780 g in a total mass of 1000 g.

Printing and fixation techniques

In this type of printing, the thickener (40 g) was added to water (780 g) at a stirring rate of 750 rpm, and then pH adjusted to 7-8 for the purpose of obtaining maximum degree of viscosity. The binder (150 g) and pigment (30 g) were added to form a printing past; the homogenized printing pastes were applied to the fabrics using a flat screen technique. Then, the printed samples were thermo fixed at 150 -160°C for a period of 4 min [17].

Color strength measurements

The relative color strength of the prints, expressed as K/S value [18], of the colored samples was determined by measuring the reflection using

data color international model (SF 500, USA).

Fastness properties

Fastness to washing and rubbing were assessed according to the BS EN ISO 105 X12 and AATCC 8 standard methods as referred in Abdel-Halim et al. [19].

Instrumental characterization

FT-IR

The chemical composition of the synthesized terpolymers was analyzed using a FTIR spectrometer (Shimadzu FTIR- 8400 S, Kyoto, Japan). All spectra were recorded in the spectral range of 4000–400 cm⁻¹. A sample for executing FTIR spectroscopy was formed by applying a thin film on the top surface of a glass slide then drying [20].

Thermo-gravimetric analysis (TGA)

The weight loss and thermal stability of samples were determined by a thermo-gravimetric TGA (Shimadzu TGA-50, Japan). The experiment was adopted at a heating ramping rate of 10 °C/min and a nitrogen flow rate of 50 mL/min. The thermogram was recorded from room temperature up to 800°C [21].

Minimum film forming temperature (MFFT)

MFFT was determined accurately using BGD 451 tester from Biuged Laboratory Instruments Co. China, in accordance with ASTM D-2354 and ISO 2115 standard methods [22].

Scanning electron microscope (SEM)

SEM images of the dried polymer films were investigated by SEM (JEOL, JSM-6360LA, Japan) operating voltage at 10 kV.

Particle size of the prepared emulsions

Particle sizes of the copolymer lattices were measured by using Zeta-Sizer, Malvern Instruments Ltd., UK [23].

Results and Discussion

FTIR spectra

Figure 2 demonstrates the FTIR spectra of the UMAM and UAM oligomers compared to the PUVE, PUVE_{MA}, and PUVE_A terpolymers. As expected, the spectrum of UMAM was typically like that of UAM as due to no significant differences exists between both structures. In both the UMAM and UAM oligomers, the absorption bands at 3270 and 3500 cm⁻¹ correspond to NH stretching and hydrogen-bonded OH [24, 25], respectively. The broad peak at ~ 1560 cm⁻¹ is resulted from two peaks related to the C-N

and N-H stretching, while the broad band at $\sim 2900\text{ cm}^{-1}$ to $-\text{CH}_2$ stretching vibration [26]. The occurrence of C=O absorption at 1738 cm^{-1} along with that at 1130 cm^{-1} for C-O-C, ascertain the presence of PPG in both UMAM and UAM. The C=C vibrations were presented around 1560 , 868 and 748 cm^{-1} (UMAM) and 790 cm^{-1} (UAM) [27]. The absence of NCO vibration ($2270 - 2300\text{ cm}^{-1}$) might be taken as an evidence for the complete consumption of free isocyanate groups in the UMAM oligomer [28], emphasizing the successful synthesis of the UMAM and UAM oligomers.

The bands at 3270 and 3500 cm^{-1} are related to the -NH stretching in the spectra of UMAM oligomer and PUVE_{MA} terpolymer (Fig. 2) [29]. The stretching due to C=C in the FTIR spectra of UMAM and UAM macro monomers have shown to be disappeared in the spectra of PUVE_{MA} and PUVE_{A} polymers (Fig. 2); indicating that all monomers were completely converted into polymers. The UMAM sample exhibits a band at 1738 cm^{-1} as signed to C=O of methacrylate ester groups which was shifted to a higher frequency for PUVE_{MA} , i.e. 1790 cm^{-1} ; this may be due to hydrogen bonding between N-H groups and C=O group in the polymeric molecules [30].

Influence of polyurethane acrylate oligomers on minimum film forming temperature (MFFT) measurements

The MFFT of the vinyl acetate copolymer

lattices is very sensitive to the co-polymerized ester [31]; it increases with grafting of the harder UAM and UMAM oligomers to the vinyl acetate copolymerization system (Table 2). The PUVE_{MA} and PUVE_{A} terpolymers prepared from the UMAM and UAM oligomers show they have higher values of MFFT (20 and 17.5°C , respectively) as compared to the PUVE copolymer that had a MFFT of 10°C . This is consistent with a previous conclusion that reported the higher glass transition temperature of the HEMA-based polymer at 81°C than that of the HEA-based polymer at -25°C [32].

Thermal stability test by TGA

The TGA profiles of PUVE_{MA} , PUVE_{A} and PUVE are shown in Fig. 3 and the corresponding data are listed in Table 3. The weight loss at a temperature lower than 250°C was a result of the trapped volatile materials. There was a weight loss less than $5\text{ wt.}\%$ at temperatures about 200°C for PUVE_{MA} , PUVE_{A} and PUVE polymers; this might be due to the loss of humidity in cured films stored in the air. The thermal decomposition of cross-linked polyurethanes starts via significant two decomposition stages. The first decomposition stage occurs at $>220^\circ\text{C}$ as a means of degradation of polymer side chains; while both PUVE_{MA} and PUVE_{A} show delaying in the first degradation stage to 234 and 250°C , respectively (Table 3). The T_{onset} temperatures of the latter samples take place at 234 and 250°C , respectively, compared to that of PUVE at 220°C , signifying improved thermal stabilities of these samples.

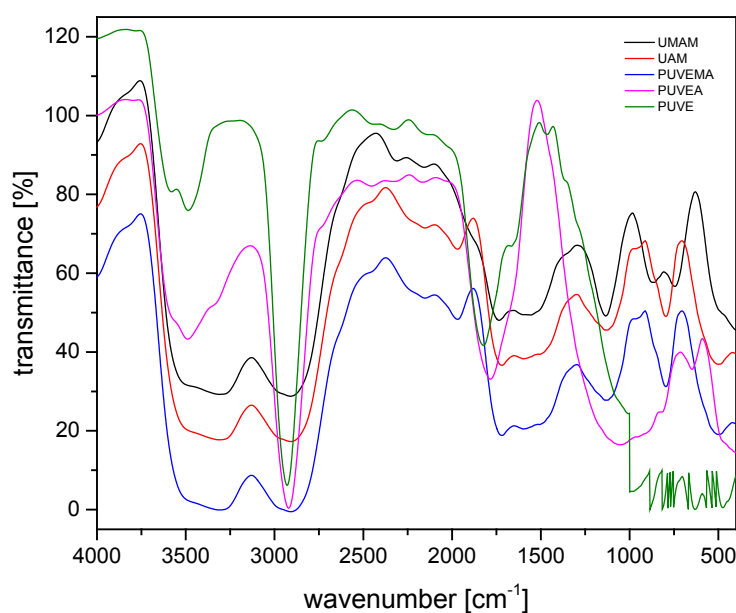


Fig. 2. FTIR spectra of the UMAM and UAM oligomers and the PUVE_{MA} , PUVE_{A} , and PUVE terpolymers.

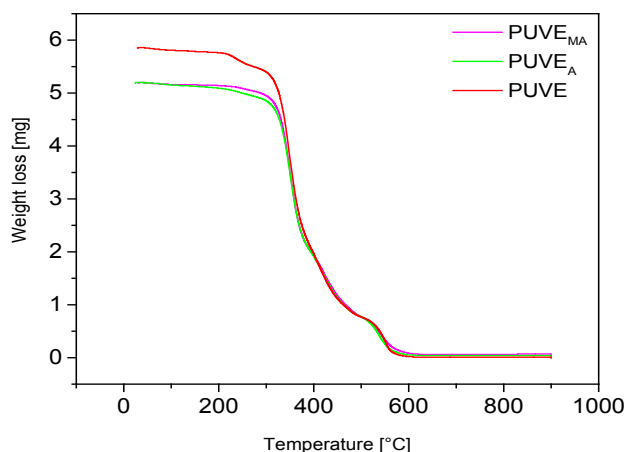


Fig. 3. TGA thermogram of the PUVE_{MA}, PUVE_A and PUVE terpolymers.

TABLE 3. TGA results of dried cured films.

	T _{onset} °C	1 st Decomposition stage °C, (Wt. loss %)	2 nd Decomposition stage °C, (Wt. loss %)
PUVE _A	250	250-472, (78.75)	472-617, (17.404)
PUVE _{MA}	234	234-518, (85.12)	518-619, (13.15)
PUVE	220	220-482, (83.573)	482-609, (14.205)

Interestingly, the PUVE_A and PUVE_{MA} films show an advanced thermal stability of the 1st decomposition stage in particular, compared to that of the PUVE film, where the former displayed a weight loss of 50% at 365°C, compared to 361°C of the PUVE film. The second decomposition stage arises at 360-460°C, owing to the decomposition of aromatic structure. The decomposition at temperature above 472°C indicates the complete thermal decomposition of the cured films. As shown in Table 3, the PUVE_{MA} and PUVE_A films show high thermal stability to 600°C, being a result of a high curing reaction of PUVE_{MA} and PUVE_A films, which would present the high cross-linked density films and better heat diffusion inhibition characteristics. Thus, PUVE_{MA} then PUVE_A show high thermal resistance decomposition, compared to PUVE due to their high cross linking density and curability.

Mechanical stability test

All prepared polymer lattices (PUVE_{MA}, PUVE_A and PUVE) show no changes in their viscosity when subjected to 750 rpm shear rate for 15 min, besides to no coagulation was observed, and hence high shear stability was achieved. The relation between the chemical structure of the PU-acrylate-g-vinyl acetate terpolymers (PUVE_{MA} and PUVE_A) and the resultant physical properties could be described by the mechanical characterization [33]. As reported in Table 4 (the averages of two runs were considered), the

films from PUVE_{MA} and PUVE_A terpolymer show a much high modulus of elasticity, compared to PUVE copolymer (20.33:50.08, 9.91:13.45 and 8.01:11.45 MPa, respectively) and tensile strength (4.24:7.86, 5.51:6.03 and 3.52:5.51 MPa, respectively). However, the new terpolymers reveal lower elongation at break than the PUVE copolymer (267.47:466.56, 450.74:637.4 and 470.13:640.2 %, respectively). Further, the PUVE_{MA} sample based on HEMA indicates a higher modulus of elasticity and tensile strength than PUVE_A terpolymer based on HEA. Alternatively, the lower modulus of elongation was observed with the PUVE_{MA} terpolymer than PUVE_A which maybe referred to the harder HEMA monomer in the UMAM oligomer compared with relevant HEA monomer in the UAM oligomer.

Morphology of polymeric films by SEM

The surface morphology of prepared polyvinyl acetate polymer due to the grafting of UMAM and UAM oligomers was investigated by SEM. It is clear from the images shown in Fig. 4, that there is an improvement in the surface morphology of polymer films prepared from the PUVE_{MA} (Fig. 4b) and PUVE_A (Fig. 4c) terpolymers with regard to smoothness and film defects, compared to the PUVE copolymer (Fig. 4a). The linear grafting of polyurethane UMAM and UAM oligomers might lead to the reduction in particle

size of the PUVE_{MA} and PUVE_{A} terpolymers on basis of the small particles were tightly packed together during the curing process [34]. As a result, the contact area between the polymer and the application substrate is increased. Therefore,

these terpolymers can be employed for pigment printing formulations, where enhanced rubbing fastness, high color strength, smooths and flexible prints are required and herein verified.

TABLE 4. Mechanical properties of dried cured films.

Polymer	Modulus of elasticity (MPa)	Tensile strength (MPa)	Elongation at break (%)
PUVE	9.73	4.52	555.17
PUVE_{A}	11.68	5.77	544.07
PUVE_{MA}	35.02	6.05	367.02

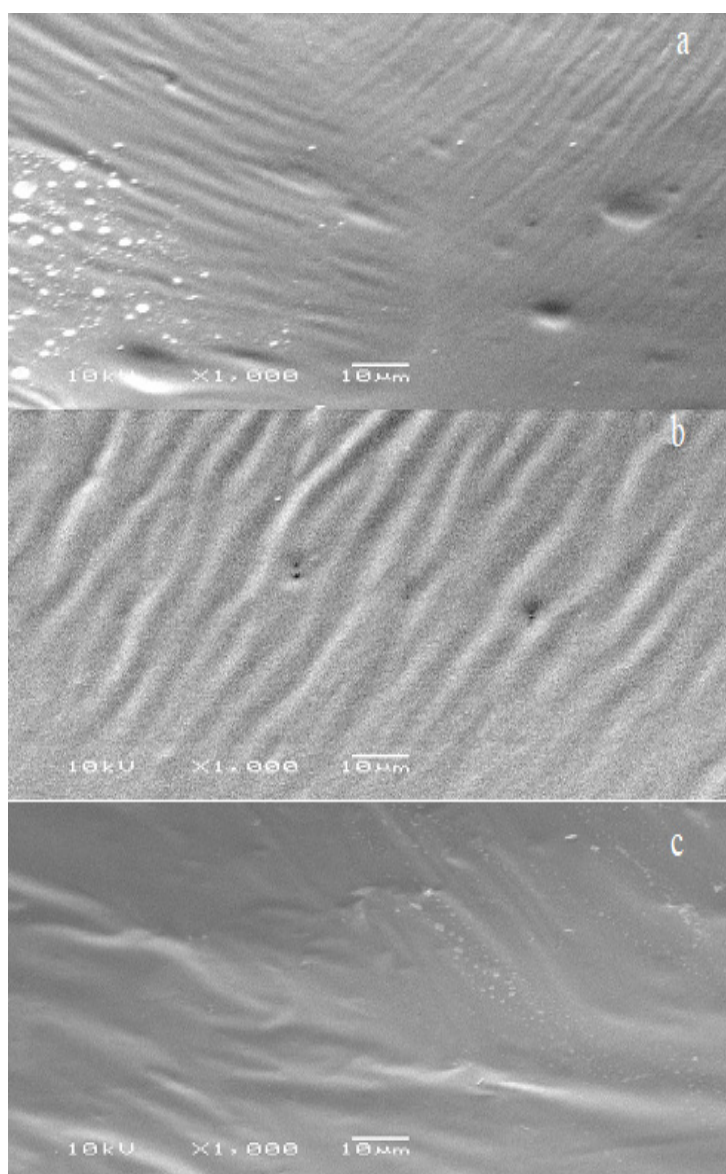


Fig. 4. SEM images of the PUVE (a), PUVE_{MA} (b) and PUVE_{A} (c) terpolymers.

Textile pigment printing applications

Table 5 shows the color strength and overall fastness properties of cotton-polyester blend fabrics that were first printed with the blue pigment printing pastes containing 15% of binder at 40% solid content and 3% PRINTOFIX BLUE T-P, then thermally cured at 150°C for 4 min. The results show that, both color strength and fastness features of the printed samples were found to depend on the type of used binder. The prepared binders gave fabric prints with much higher color strength, as compared to those obtained upon using the PUVE copolymer as a blank at the same preparation and curing conditions. The rubbing fastness for printed samples show improvements as compared to that printed with PUVE. The rubbing fastness varied from good to very good in case of using the synthesized terpolymers as binders and ranged from moderate to good in case of using

PUVE. This behavior may stem from the linear PU segments in the structures of the PUVE_{MA} and PUVE_A binders that lead to fixation of the pigment onto the surface of the fabrics and plasticization. Moreover, washing fastness properties were in the range of very good to excellent for fabric printed with applying the PUVE_{MA} and PUVE_A binders in the printed pastes. It was also shown that all the samples printed using PU-VAc binders acquired soft handle. The linear structure and particle sizes of the PUVE(a), PUVE_{MA}(b) and PUVE_A(c) emulsions (the average particle sizes are 750 nm, 500 nm, and 280 nm respectively as shown in Fig.5) of the latex may be the main reason for the performance improvements of binder latex, and the soft polymer compositions have been chosen to outfit the application in textile printing, which commonly require the soft handle for fabric printing.

TABLE 5. Applications of prepared polyurethane terpolymers in printing of polyester/cotton blend fabrics.

Oligomer code	Polymer code at 40% solid content	Color strength K/S (max. at 615 nm)	Washing fastness				Rubbing fastness		Handle
			St. ⁽¹⁾	St.** ⁽²⁾	St.*** ⁽³⁾	Alt. ⁽⁴⁾	Dry rubbing	Wet rubbing	
UMAM	PUVE _{MA}	14.23	4-5	4-5	4-5	4	4-5	3-4	Soft
UAM	PUVE _A	13.89	4-5	4-5	4-5	4	4	4	Soft
PUVE		13.35	4-5	4-5	4-5	4	4	3-4	Soft

⁽¹⁾St.*: staining on cotton, ⁽²⁾St.**: staining on wool, ⁽³⁾St.***: staining on polyester, ⁽⁴⁾Alt.: alternation

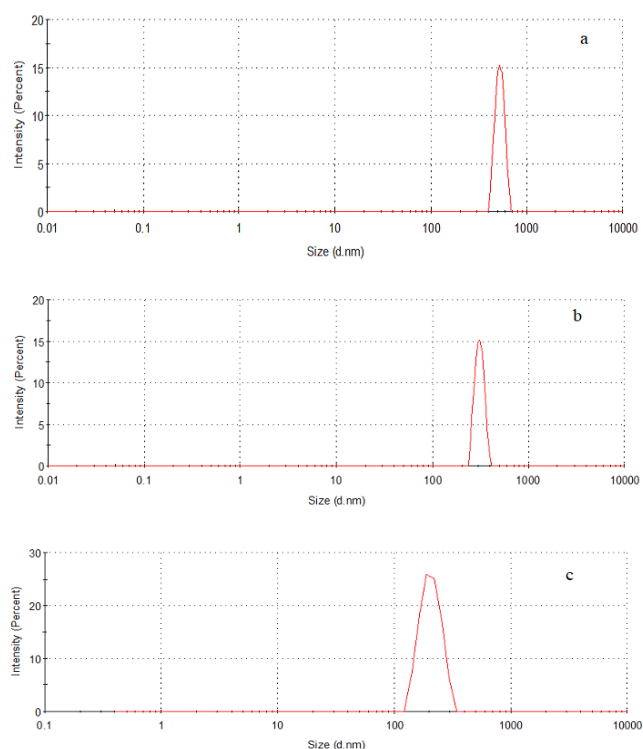


Fig. 5. Size distribution of the PUVE(a), PUVE_{MA}(b) and PUVE_A(c) emulsions.

Conclusions

Two polyurethane acrylate/methacrylate oligomers named UMAM and UAM were successfully prepared via NCO terminated urethane prepolymer, where the disappearance of C=C peaks in the FTIR spectra of all terpolymers were taken as an evidence for the complete grafting of the UMAM and UAM oligomeric monomers into the vinyl acetate copolymer backbone. Semi-continuous emulsion copolymerization of polyurethane-modified vinyl acetate emulsions initiated by $K_2S_2O_8$ was evaluated. Experimental conditions of oligomer type and vinyl ester type were varied and optimized. The following outcomes were attained:

- The presence of polyurethane moiety in vinyl acetate copolymer caused improvement in thermal stability as showed by the TGA data.
- The methacrylate based terpolymers showed lower thermal stability than acrylate-based terpolymers.
- SEM images showed that there were enhancements in the surface morphology of polymer films prepared from the $PUVE_{MA}$ and $PUVE_A$ terpolymers.
- There was a reduction in particle sizes due to grafting of the linear UAM and UMAM oligomers into the vinyl acetate copolymer structure that results in increasing the gloss values of the prepared coatings.
- The textile fabric prints were enhanced in terms of color strength, rubbing fastness, washing fastness and soft handle by using the $PUVE_{MA}$ and $PUVE_A$ terpolymers as water-based printing binders.

Competing Interests

The authors declare that they have no financial or competing interests.

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