

Structural variation in soft segment of waterborne polyurethane acrylate nanoemulsions

Misbah Sultan,¹ Atif Islam,² Nafisa Gull,² Haq Nawaz Bhatti,³ Yusra Safa⁴

¹Institute of Chemistry, University of the Punjab, Lahore, Pakistan

²Department of Polymer Engineering and Technology, University of the Punjab, Lahore, Pakistan

³Department of Chemistry and Biochemistry, University of Agriculture, Faisalabad, Pakistan

⁴Department of Chemistry, Lahore College for Women University, Lahore, Pakistan

Correspondence to: M. Sultan (E-mail: misbah_sultan@yahoo.com)

ABSTRACT: High solid content waterborne polyurethane acrylate (WPUA) nanoemulsions are prepared as textile finishes. Two structurally different soft segments, that is, polyether and polyester are used with isophorone diisocyanate, 2-hydroxyethyl methacrylate, and butyl acrylate. Structural variations are investigated in features of nanoemulsions and their coatings. Physical properties of nanoemulsions, such as average particle size, stability, solid content, and viscosity, are investigated. Nanoemulsions with high solid content, that is, 40–47% are produced without any internal emulsifier. Average nanoparticle size, that is, <100 nm is confirmed by dynamic light scattering and atomic force microscopy (AFM). Fourier transform infrared spectroscopy proved synthesis of proposed WPUA products. Synergistic effect of polyurethane and acrylate is observed in chemical and water resistance of WPUA. Differential scanning calorimetry (DSC) and thermogravimetric analysis indicate stable uniformly cross-linked network of WPUA. Application of nanoemulsions on 100% cotton fabric shows a significant improvement in tear strength, which is more pronounced for polyester-based WPUA. Scanning electron microscope images of treated fabric samples show good adhesion of nanoemulsions on cotton surface. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41706.

KEYWORDS: applications; coatings; polyurethanes

Received 24 June 2014; accepted 31 October 2014

DOI: 10.1002/app.41706

INTRODUCTION

A great shift in coating technology was observed with constraint on volatile organic compounds. In this shifting era, waterborne polyurethane (PU) has significantly replaced solventborne systems. These materials are used extensively in commercial products, for example, coatings, adhesives, finishing agents, leather, paper, and fibers surface treatment agents. WPU has been commercially available since 1960s. Now, these are an accelerating area of research and development due to their proficient characteristics, increasing concern of environmental hazards and respective legislations. Researchers are continuously adding innovative literature of WPU to scientific writings. Above 1000 patents have been issued for WPU, but still there is an open prospect for research and product development due to wide variety of structural options and end uses.^{1–11}

Conventional PUs are hard to disperse in aqueous medium. Thus, usually, internal dispersing agents, for example, dimethylpropanoic acid and dimethylbutanoic acid are incorporated in the backbone of polymer. Furthermore, commercially avail-

able WPU are mainly composed of linear structural units.^{2,5,6,10,12,13} This structural linearity and enhanced hydrophilicity due to internal dispersing agent have encouraging effect on dispersion of PU in water. Unfortunately, some performance properties of WPU, for example, chemical, solvent, and water resistance are abandoned due to these structural aspects. To improve such limitations of WPU, a possible structural modification is acrylate inclusion.^{1,6,10,14}

Incorporation of acrylate into WPU is normally possible by three ways, that is, (a) physical mixing or blending; (b) hybrid emulsion polymerization where emulsion polymerization of acrylate monomer is carried out in the presence of already prepared WPU dispersion; (c) copolymerization of acrylate with PU. First two methods are just physical mixing of two components which may involve some secondary interactions. However, third method results in the development of permanent covalent linkages between acrylate and PU. Such type of waterborne polyurethane acrylate (WPUA) emulsions are expected to provide the advantages of both components, such as excellent weather resistance, affinity to pigments, lower cost, better mechanical

stability, excellent adhesion, abrasion resistance, solvent, and chemical resistance.^{7,12,15} However, long drying time, transportation costs, storage costs, and shelf-life are associated issues of WPU. These issues can be addressed with high solid content and smaller particle size which makes their applications more efficient with longer shelf-life, reduction in cost, time, and energy loads.^{1,8,12} As reported previously, WPU systems have normally <40% solid content.^{3,5,6,16–18} Few reports are available on high solid content, but their particle size was larger than nanoscale, which would abandon the shelf-life of products.^{8,19,20}

In this study, high solid content WPUA nanoemulsions were prepared by copolymerization approach. Particular intention was to use these nanoemulsions as textile-finishing agents to improve the quality of cotton fabric. Incorporation of internal emulsifier was avoided to get better water and chemical resistance of product. Also, by copolymerization, a cross-linked structure was proposed to enhance thermal stability, water, and chemical resistance. Two structurally different soft segments of equal molecular weight were used, that is, polycaprolactone diol (PCL) and polyethylene glycol (PEG) in this designing. In addition, concentration of PU and acrylate was assorted progressively. Effect of these structural variations was studied in terms of emulsion properties, for example, particle size, viscosity, solid contents, etc., thermal stability, water and chemical resistance, and performance as textile-finishing agent.

EXPERIMENTAL

Materials

1-Isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane or isophorone diisocyanate (IPDI), poly(ethyleneglycol) (PEG) ($M_w = 1000$ g/mole), polycaprolactone macrodiol (PCL, CAPA2100) ($M_w = 1000$ g/mole), 2-hydroxyethyl methacrylate (2-HEMA), butyl acrylate (BA), polyvinyl alcohol (PVA, 87–89% hydrolyzed), sorbitonmonolaureate ($C_{18}H_{34}O_6$) were provided by Sigma Aldrich Chemicals Co., USA. Ammonium persulfate (APS), sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$), sodium carbonate (Na_2CO_3), sodium salt of alkyl aryl polyglycol ether sulfate and dibutyltindilaurate (DBTDL) were of analytical grade and purchased from local market. The plain stripe (Satin stripe = 1 cm), white and 100% cotton, with 5/1 weave was supplied by local textiles Mills in Faisalabad, Pakistan. It was dyed royal blue by the cooperation of National Textile University, Faisalabad.

Synthesis of WPUA Copolymer Nanoemulsions

For the synthesis of WPUA copolymers, three-step synthesis processes were opted. The proposed route for this reaction is given in Figure 1. Basic formulation and general procedure for synthesis of WPUA copolymers have been well documented previously.²¹ Sample codes and compositions are given in Table I. Briefly, stoichiometric amounts of polyol (2 moles) and IPDI (3 moles) were charged into a 500-mL five-necked round bottom glass reactor equipped with a mechanical stirrer, a thermometer, a reflux condenser, heating oil bath, and a nitrogen gas inlet system. Two drops of catalyst, that is, DBTDL were also added to glass reactor. Temperature of the oil bath was increased up to 60°C. This mixture of polyol and isocyanate was stirred contin-

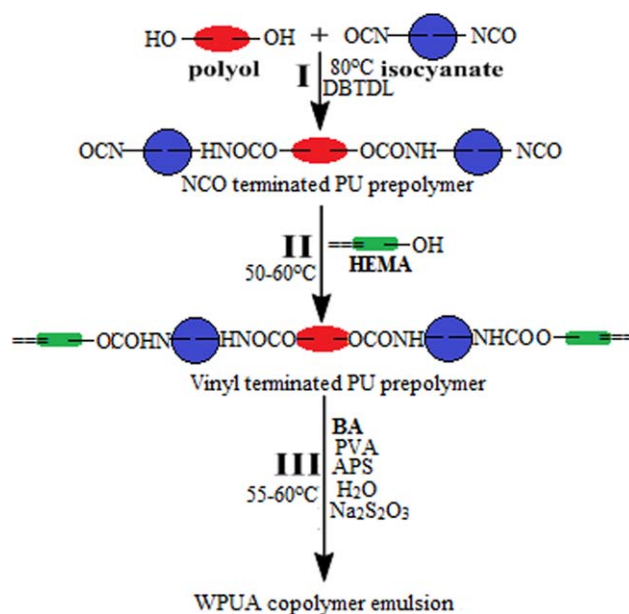


Figure 1. Stepwise reaction scheme for the synthesis of WPUA copolymer emulsions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

uously under the blanket of nitrogen gas, and the reactor temperature was increased steadily from 60°C to 80°C. After ≈ 2.0 h, –NCO terminated PU prepolymer was obtained as confirmed by Fourier transform infrared spectroscopy (FTIR). Then, the temperature of reaction vessel was decreased gradually from 80°C to 60°C (Figure 1).

As shown in Figure 1, the stoichiometric amount of 2-HEMA (2 moles) was added slowly to PU prepolymer at lower temperature approximately. 50–60°C. Vinyl-terminated PU prepolymers or resins were obtained after 1 h as a viscous and transparent material.

The copolymerization of vinyl terminated PU resin with BA was carried out through emulsion polymerization process in an aqueous medium (Figure 1). Deionized water and emulsifier (12% w/w) was charged to the reactor initially. A small amount of low molecular weight, partially hydrolyzed PVA (3% w/v) was also used as protective colloid. APS (0.02 g) and $Na_2S_2O_3$ (0.02 g) were used as initiator. Calculated amount of BA and vinyl terminated PU resin was slowly fed to the reactor. This copolymerization was completed in almost 3.5 h with continuous stirring at 55°C to 60°C. Nanoemulsions obtained at the end of reaction were saved for further investigations.

Measurements

For molecular characterization of synthesized WPUA copolymers and to verify the path of synthesis, FTIR spectra were collected for all of the monomers and at every stage of synthesis process by Bruker Equinox 55, spectrophotometer, Germany.⁵ The scanning region was 4000 cm^{-1} to 500 cm^{-1} . Before analysis, all emulsion samples were dried in an oven at 90°C. Then, these dried samples were analyzed by applying on KBr/NaCl.

Particle size, particle size distribution (PSD), and polydispersity index (PDI) of WPUA copolymer emulsions were measured

Table I. Physical and Thermal Properties of WPUA Nanoemulsions

Code	PU/BA (%)	Average particle size (nm)	PDI ^a	Stability	App. ^b	Solid content (%)	Viscosity (mPas)	DSC (°C)					TGA (°C)	
								T _{gs} ^d	T _c ^e	T _m ^f	T _{5%} ^g	T _{10%} ^h	T _{max.} ⁱ	T _{90%} ^j
PUA1	10 : 90	58.0	0.21	Stable	T ^c	47.3	98.2	16.5	148	237	240	295	440	559
PUA2	20 : 80	56.6	0.14	Stable	T	44.0	57.6							
PUA3	30 : 70	48.0	0.11	Stable	T	41.0	36.2							
PUA4	10 : 90	63.0	0.21	Stable	T	46.44	71.4	18	149	226	236	295	405	534
PUA5	20 : 80	60.0	0.18	Stable	T	46.0	64.2							
PUA6	30 : 70	50.0	0.28	Stable	T	41.62	45.9							

^a Polydispersity index.^b Physical appearance of emulsion^c Translucent.^d glass transition temperature of soft segment^e crystallization temperature^f melting temperature^g temperature for 5% degradation of sample^h temperature for 10% degradation of sampleⁱ temperature for maximum rate of degradation^j temperature for 90% degradation.

using SEMA Tech Laboratory, SEM 633 dynamic light scattering apparatus, France. In this light scattering apparatus, helium–neon laser was the source of light with wavelength 632.8 nm. The average frequency of light was 363.62 KHz. Appearance and shelf stability of emulsion samples were assessed with naked eye by placing all samples undisturbed at ambient conditions for a time period of 6–12 months.

Viscosity of WPUA emulsions was measured by Brookfield DV-II + Pro viscometer using UL adapter spindle. The average temperature and shear rate were 25°C and 20 rpm, respectively. Solid contents of WPUA emulsions were calculated according to standard method, that is, ISO 124:1997. It was recorded by placing a weighed amount of emulsions in an oven at 90°C. These samples were weighed after regular time intervals till a constant weight was achieved. The dry weight contents were calculated according to following formula:

$$\% \text{ dry weight} = (W_b/W_a) \times 100$$

where “W_a” is weight of sample before drying and “W_b” is weight after drying.

Chemical and water resistance was evaluated according to ASTM D 1647-89. Glass panels coated with WPUA were dried for 72 h at room temperature. Honey wax was used to cover

the periphery of panels. For chemical resistance, dried panels were placed in 3% (w/w) solutions of H₂SO₄ and NaOH and any changes in the appearance of coatings were monitored for 3 days. For water resistance, coated panels were placed in a beaker containing deionized water at room temperature, immersing the ends that were uppermost during drying. Dipped panels were removed from water after 18 h, wiped carefully and placed at room temperature to monitor any change, that is, rupture or partial peeling of coatings.

For the application of nanoemulsions in textiles, 100% cotton fabric samples were cleaned in the laboratory by placing at 100°C for 1 h in a solution of Na₂CO₃ (2 gL⁻¹) and sorbiton monolaureate (1 gL⁻¹). Then, washing was carried out with hot water, and finally, samples were dried at ambient conditions. On the basis of solid content, 5% w/v dilutions of synthesized WPUA emulsions were prepared. These dilute emulsions were coated on dried fabric samples by dip-coating technique. Coated fabric samples were dried at 100°C for 4 min in vacuum oven and placed at ambient temperature (25–20°C) for 24 h. Tear strength of these coated fabrics was evaluated according standard test method, BS EN ISO 13937-2. Results were calculated in a relative manner, that is, % improvement with the help of following formula.

$$\frac{\text{Force required to tear treated fabric} - \text{Force required to tear untreated fabric}}{\text{Force required to tear untreated fabric}} \times 100$$

Coating thickness was measured by difference of with and without treatment fabric samples by a digital textile thickness tester. An average of three readings was recorded.

Thermal history of oven-dried WPUA copolymers was studied using differential scanning calorimeter (DSC) NETSCH DSC 200 F3 Germany. Dried copolymers of few milligrams were

placed in standard aluminum pans with pierced lid. The DSC analysis was carried out for temperature range –60°C–250°C with heating rate of 10°C/min. Thermogravimetric analysis (TGA) of synthesized samples was carried out by TGA-PL, England available at Iran Polymer and Petrochemical Institute, Tehran. TGA was performed in platinum pan with a neutral

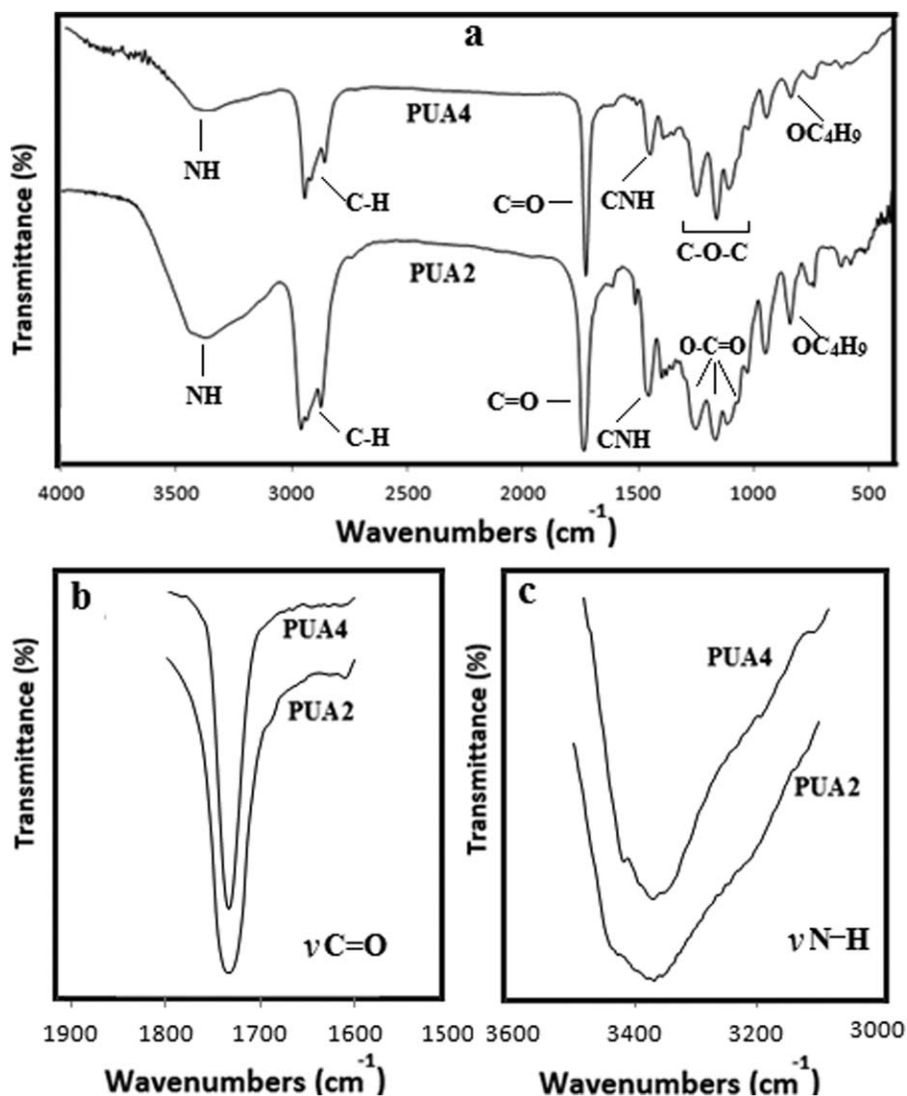


Figure 2. FTIR spectra of representative samples, that is, PUA2 and PUA4; complete spectra (a), selected spectral regions (b) and (c).

environment under the flow rate of 50 mL/min of nitrogen gas. Temperature scan was carried out from ambient temperature, that is, 25°C–600°C with the ramp of 10°C/min.

The morphological characterization of WPUA copolymers was carried out by atomic force microscopy (AFM), DME Denmark, equipped with an E 95–200 scanner and controller dual scope C-26. The noncontact mode silicone tip (height 10–15 micron and curvature 10 nm) was used and resonance frequency was 285 KHz. To minimize the possible contamination of the sample surface by ambient air, samples were freshly prepared just before the AFM experiments. For sample preparation, nanoemulsions were diluted with deionized water up to 1 : 10 ratio and coated on a mica substrate.

To study the interaction of nanoemulsion coatings with cotton surface, scanning electron microscope (SEM), Quanta 250 FEG was used to capture microscopic images of fabric samples.

RESULTS AND DISCUSSION

FTIR Characterization of WPUA Copolymers

Synthesis of WPUA copolymers was carried out in three steps as shown in Figure 1. At first step, IPDI was reacted with PCL or PEG resulting in –NCO-terminated PU prepolymer. End capping of –NCO-terminated prepolymer was performed in next step with 2-HEMA. In this way, vinyl-terminated PU prepolymer was obtained, which was copolymerized with BA during last step. FTIR spectra of all of the monomers, intermediates, and final copolymers were recorded as given in another similar study published elsewhere.²¹ However, comprehensively FTIR spectra of representative samples of series, that is, PUA2 and PUA4 are displayed in Figure 2(a). Both FTIR spectra exhibited characteristic peaks of N–H stretching vibration at 3450–3208 cm^{-1} (free and H-bonded –NH); asymmetric and symmetric stretching vibration of aliphatic –CH at 2958 cm^{-1} and 2872 cm^{-1} , respectively; stretching vibration of –C=O due to urethane and acrylates at 1734 cm^{-1} ; –CNH

bending vibration at 1454 cm^{-1} ; stretching vibration of $-\text{OC}_4\text{H}_9$ (ester linkage of BA) at 841 cm^{-1} .^{2,3,22} Broad $-\text{NH}$ peaks indicated enhanced phase mixing in WPUA structures. The $-\text{NH}$ peak of PUA2 is broader than PUA4, it might be due to an extensive chance of H bonding in polyester-based copolymer. On lower side of spectrum of PUA2, three consecutive peaks at 1102 cm^{-1} , 1163 cm^{-1} , and 1238 cm^{-1} presented stretching vibration of ester linkage in soft segment. While in spectrum of PUA4 asymmetric and symmetric vibration of ether (C–O–C) groups of soft segment can be seen at 1243 cm^{-1} and 1108 cm^{-1} .⁸ Disappearance of peaks for $-\text{NCO}$ of IPDI, $-\text{OH}$ of soft segments, C=C of acrylates and appearance of peaks for $-\text{NH}$, $-\text{C}=\text{O}$, $-\text{CNH}$, $-\text{OC}_4\text{H}_9$ are strong evidences for the synthesis of WPUA copolymers through proposed route.^{2,3,23}

Microphase separation between hard and soft segment is an important structural characteristic of PU. This structural aspect is more evident in PU elastomers where diisocyanates with chain extenders develop independent hard regions in matrix of soft segments. However, in current study of PU-based coatings phase mixing was observed entirely. Generally, C=O and N-H stretching peaks are considerable areas in microphase structure of PU. Selected spectral regions of C=O and N-H stretching are given in Figure 2(b,c), respectively. To cover the whole C=O and N-H stretching areas, spectral regions were plotted from $1800\text{--}1600\text{ cm}^{-1}$ and $3500\text{--}3100\text{ cm}^{-1}$, respectively. Both WPUA copolymers showed just one smooth peak at $1740\text{--}1730\text{ cm}^{-1}$. Also, a broad peak for N–H stretching was observed at around 3390 cm^{-1} in both segments. The absence of any shoulder or side peaks subtracted the possibility of phase separation.²⁴ Furthermore, both C=O and N-H peaks are relatively broader for PUA2 indicating more enhanced phase mixing in polyester-based soft segment. These results are in agreement with observations recorded by thermal analysis of copolymers.

Physical Properties of WPUA Copolymer Nanoemulsions

Sample composition and physical properties of nanoemulsion, that is, average particle size, PDI, stability, appearance, solid content, and viscosity of synthesized WPUA copolymer emulsions are given in Table I. These emulsion properties are important parameters in deciding the commercial value and end use of products. These parameters not only affect the processability of coatings, but also the properties of cured films. Average particle sizes mentioned in Table I are in quite nanoscale range, that is, $<100\text{ nm}$ with smaller PDI. The particle size of final copolymer depends upon several factors such as hydrophilicity of monomers, molecular weight of prepolymer, and flexibility of main chain.²⁵ It is important to mention that the particle size has a direct effect on the stability of emulsions which determines their safe storage period. The emulsions with larger particle sizes ($>1000\text{ nm}$) are generally unstable, while with the smaller particle sizes ($<200\text{ nm}$) are considered to be storage-stable. Also, such nanoemulsions have high surface energy that plays driving role in film formation.^{10,26} According to the data presented in Table I, particle sizes of PUA1, PUA2, and PUA3 are smaller as compared to the next three nanoemulsions. This small difference in sizes can be correlated with chemical structure of two different soft segments. The polyester polyol, that is, PCL has more polar structure due to polar carbonyl groups in

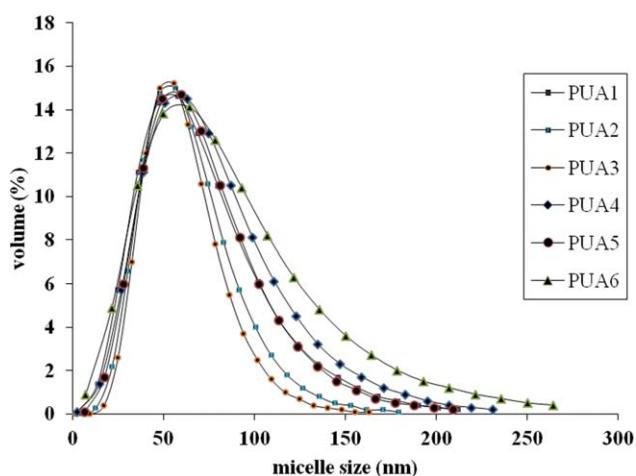


Figure 3. PSD of WPUA copolymer emulsions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ester linkages, while polyether-based soft segment lack this polarity. Ultimately, the nature of PU prepolymer based on PCL was more rigid, generating smaller particles, while on the other hand PU prepolymers based on comparatively less polar and flexible PEG soft segment generated slightly larger particles. These findings are in accordance with previous reports in literature.^{27,28} A decrease in particle size was observed with a decrease in BA content. When BA content was decreased from 90–70%, probability of copolymerization was decreased resulting in smaller particle size along with lesser acrylate swell. PSD curves are given in Figure 3. These PSD curves were smooth and unimodal, depicting fairly stable nanoemulsions without any probability of secondary coalescence. Nonunimodal PSD curves lead toward instability of emulsions as proved in previous reports.¹⁸ Samples were saved in air-tight bottles, no coagulation or sedimentation was appeared in all nanoemulsions during observation period, predicting their safe storage life. The appearance of nanoemulsions was translucent, which confirmed their nanoparticle sizes.

One of the main objectives of this study was to improve solid content of WPU with nanoparticle size. This objective was achieved successfully as solid content of nanoemulsions was $>40\%$ for all samples as presented in Table I. These results are encouraging as compared to the previous commercial and academic research informations.^{5,10,14,16,18} A decrease in solid content was recorded with decrease in BA content. This trend of solid content is in direct relation with average particle sizes of nanoemulsions. With decrease in BA content, probability of copolymerization was decreased. Consequently, amount of copolymer produced was decreased giving lower solid content in the prepared nanoemulsions. Viscosity of nanoemulsions was quite low, that is, $<100\text{ mPas}$ as shown in Table I. Since high solid content gives high solid volume fraction, viscosity of the synthesized WPUA samples is agreed with their solid content and particle sizes.¹⁸ A similar trend was observed for viscosity as for solid content and average particle size, that is, decrease in viscosity with decrease in BA content.¹⁴ Hence, stable nanoemulsions with high solid content and low viscosity were prepared without any internal emulsifying agent.

Table II. Sample, Chemical Resistance, Water Resistance, and % Improvement in Tear Strength of Treated Fabric

Sample	Chemical resistance		Water resistance	Improvement in tear strength (%)
	H ₂ SO ₄	NaOH		
PUA1	EX	VG	EX	37.59
PUA2	EX	VG	EX	57.44
PUA3	EX	VG	EX	81.35
PUA4	EX	VG	EX	56.84
PUA5	EX	VG	EX	54.81
PUA6	EX	VG	EX	19.85

EX= excellent.
VG =very good.

Chemical and Water Resistance of WPUA Copolymers

A main target of acrylate incorporation into WPU structure was to improve the chemical and water resistance. So chemical and water resistance of prepared WPUA nanoemulsions was evaluated according to standard test methods. From the data given in Table II, it can be revealed that all the coatings of nanoemulsions had shown excellent water and acid resistance. Samples were carefully observed everyday during testing period of 3 days. Coated nanoemulsions were in the form of transparent films, without any rupture or removal. A slight haziness was experienced for films placed in alkaline media, that is, 3% NaOH solution. It was disappeared just after the removal of films from alkaline environment. It is a matter of fact that urethane links are more prone to basic pH. However, these encouraging results could be due to exceptional performance of acrylates in an alkaline medium. Overall improvement in chemical and water resistance could be attributed to synergistic combination of acrylates and PU in a cross-linked network of WPUA nanoemulsions.^{21,29}

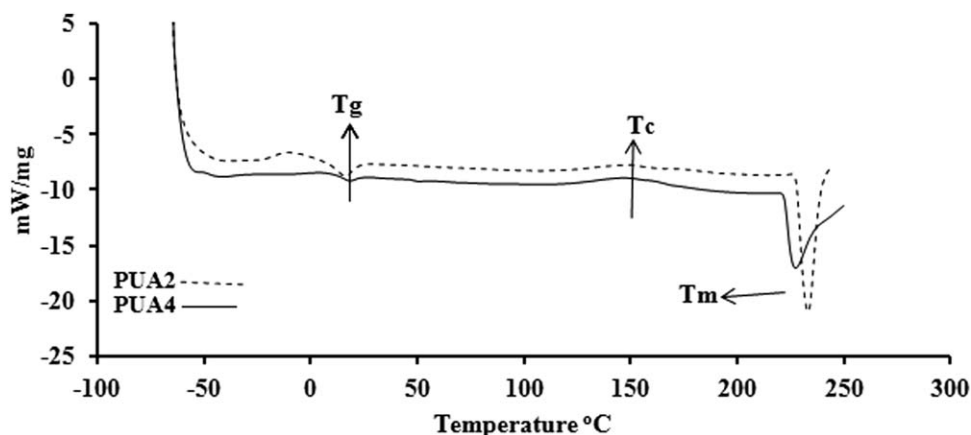
Improvement in Tear Strength of Coated Fabrics

WPU flexible coatings are used commercially in textiles and clothing as surface finishes. Tear strength is one of the important fabric utility parameter that decides their quality and end

application.^{30,31} In this study, synthesized WPUA nanoemulsions were applied on 100% cotton fabrics and improvement in tear strength is given in Table II. An average thickness of WPUA coatings on fabric was $0.9 \mu\text{m} \pm 03$. Results showed a significant improvement, that is, 19.85–81.35% in tear strength of treated fabrics. Cotton is 99% cellulose in nature. Anhydro- β -cellobiose is the repeating unit in cellulose long chains. Three hydroxyl groups ($-\text{OH}$), one primary and two secondary, in each repeating cellobiose unit of cellulose are chemically reactive. These hydroxyl groups may interact with polar $-\text{NH}$ and $\text{C}=\text{O}$ groups of WPUA nanoemulsions through polar interactions and hydrogen bonding resulting in enhancement in tear strength of fabric. Tear strength of fabrics treated with polyester-based WPUA was superior comparatively; it may ascribed to more polar interaction of PCL with cotton surface. Improvement in tear strength of polyester-based nanoemulsions was observed in following order $\text{PUA1} < \text{PUA2} < \text{PUA3}$. Actually, this is an increase in tear strength of treated fabrics with an increase in PCL-based PU content. This inclination can be justified on the basis of an increase in polar content as PU/BA ratio raised from 10 : 90 to 30 : 70. Increase in PU concentration was an increase in soft segment content, that is, PCL in these samples. In this way, the presence of more polar ester groups leads toward more polar interactions of nanoemulsions with cotton surface, hence improved tear strength.

In case of polyether-based nanoemulsions, that is, PUA4, PUA5, and PUA6 tear strength has also improved with respect to untreated fabric. However, there was no considerable difference in tear strength with an increase in PU content. Although particle size of nanoemulsions was decreased with an increase in PU content. It may be explained as hydrophilic soft segment, that is, PEG content was increased; WPUA nanoemulsions became more smooth with smaller particle size in aqueous medium, but substantivity on substrate was decreased. So it can be inferred that by increasing polyether-based soft segment tear strength of fabric was improved, but the role of PU content was minimized.

SEM images of fabric samples were recorded to understand the interaction of WPUA copolymer nanoemulsions with cotton [Figure 8(a,b)]. These images were captured at the same time

**Figure 4.** DSC thermograms (10°C/min.) of PUA2 and PUA4.

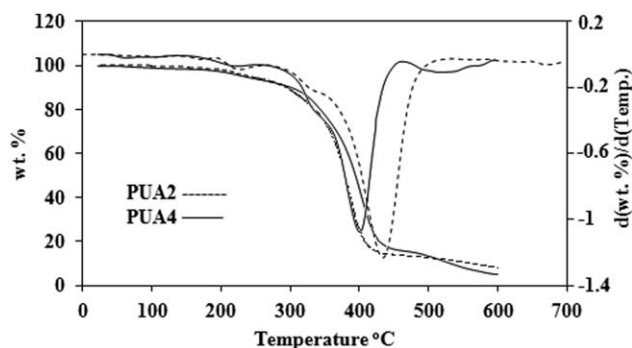


Figure 5. TGA and DTG curves (10°C/min.) of PUA2 and PUA4.

with equal magnification, that is, 1000 \times . A clear difference in microappearance can be observed in these images. In Figure 8(b), threads of fabric are coated with copolymer coating. Copolymer is properly adhered to the threads as well as between the threads to establish close interactions with cotton.

Thermal Analysis of WPUA Copolymers

Thermal behavior and stability of representative samples of series, that is, PUA2 and PUA4 were studied by TGA and DSC. Dried films of nanoemulsions were used for thermal investigation. In DSC thermograms, as given in Figure 4 and Table I,

both samples showed single glass transition temperatures (T_g), crystallization temperature (T_c), and a prominent endotherm of melting temperature (T_m). The presence of single T_g rejected any possibility of phase separation in structure at molecular level.¹⁵ Such an enhanced phase mixing resulted from extensively cross-linked structure of PU and acrylates in WPUA copolymers. T_g of PUA2 and PUA4 was around 0°C and 5°C, respectively. These glass transition temperatures are higher than pure PCL and PEG, but this difference can be justified by bonding and cross-linking of these soft segments in PUA structures.¹⁸ Both WPUA copolymers showed exothermal transitions (T_c) near 150°C, which might be associated with heat directed crystallization of copolymeric chains at molecular level. Both copolymers showed an endotherm at higher temperature related to melting of hard segment domains. A more intense endotherm of PUA2 was observed at relatively higher temperature, that is, 237°C. It might be ascribed to probability of more regular packing of hard segment in cross-linked polymer network of PUA2, due to expanded availability of polar interactions.

To evaluate the thermal stability of synthesized samples, TGA and respective DTG curves are shown in Figure 5. Also, $T_{5\%}$, $T_{10\%}$, T_{max} , and $T_{90\%}$ are given in Table I. In general, thermal stability of PUA copolymers has improved as compared to

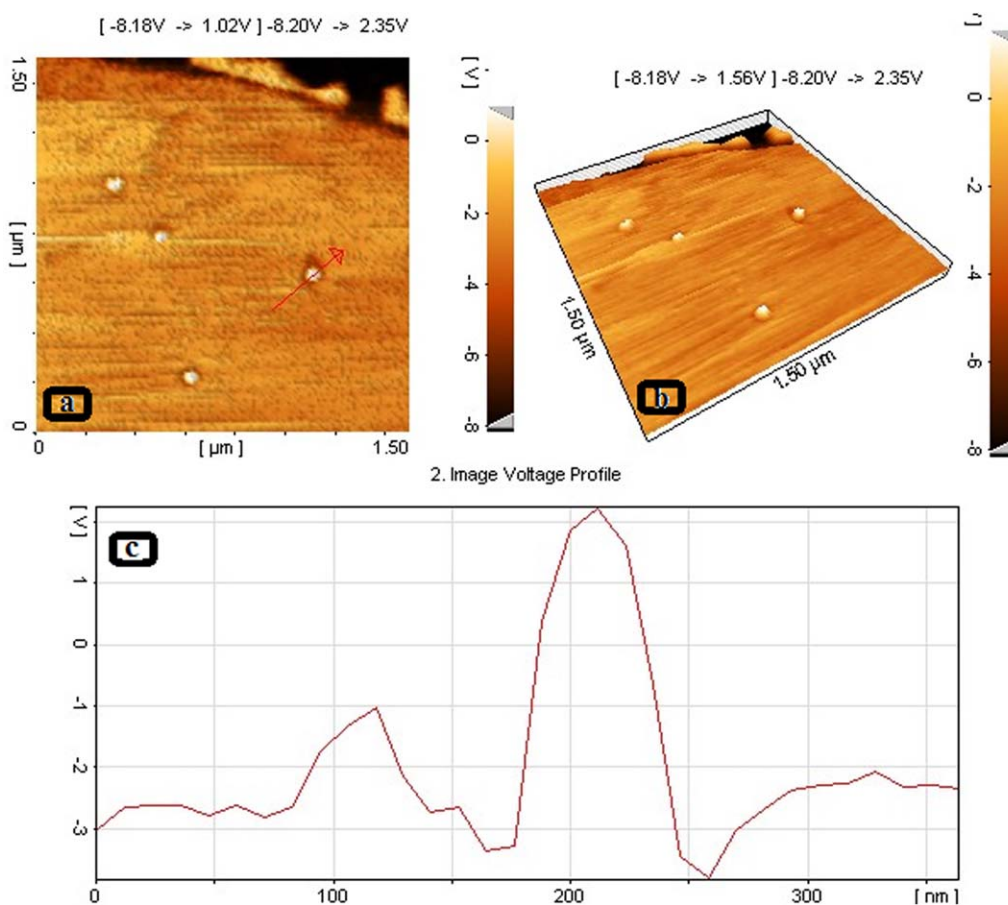


Figure 6. AFM images of PUA2, (a): two-dimensional image; (b): three-dimensional image; (c): image voltage profile. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

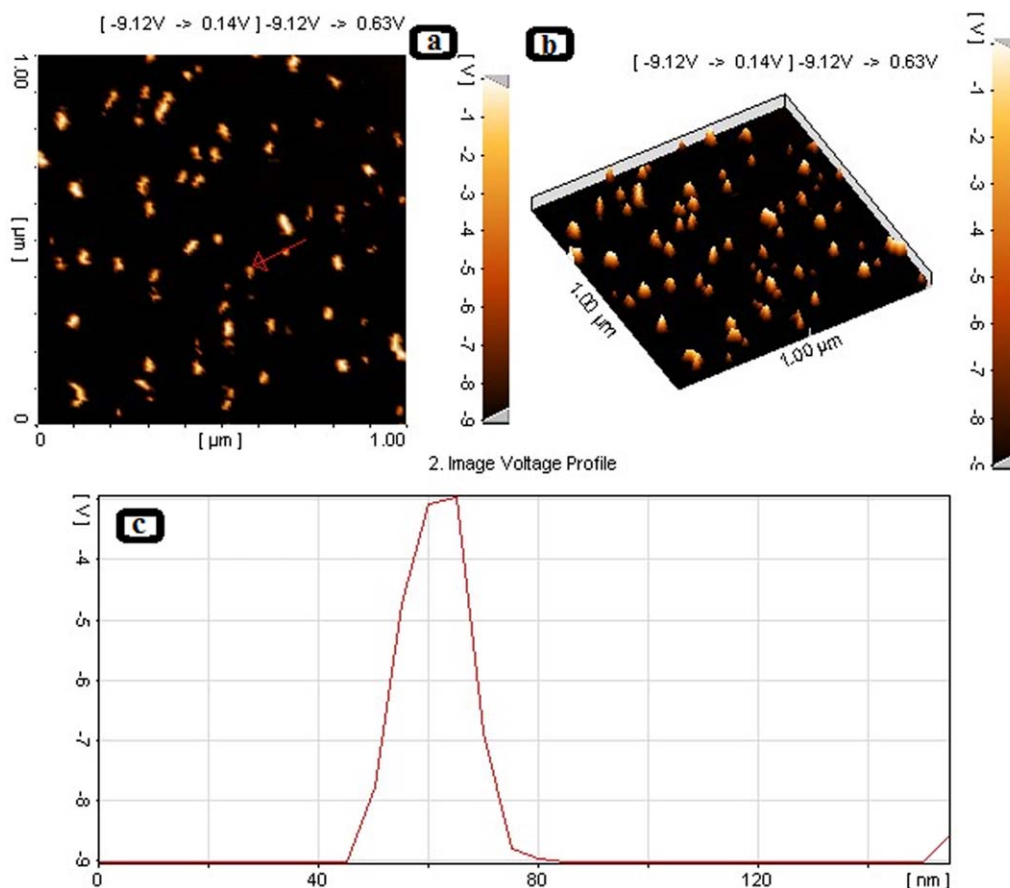


Figure 7. AFM images of PUA4, (a): two-dimensional image; (b): three-dimensional image; (c): image voltage profile. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reported literature.^{22,32} It can be accredited to stable cross-linked copolymer network of PU and acrylates.¹⁴ In TGA and DTG curves, it is clear that both copolymers exhibited just one-stage decomposition with single T_{max} . It might be attributed to the more uniform phase structure of cross-linked copolymers due to cross-linking reactions during

copolymerization.^{22,33} Since hard segment is more vulnerable to thermal degradation, it was decomposed at 320–330°C. Then, soft segments were started to decompose in both copolymers with maximum rate of degradation recorded after 400°C. If thermal curves and tabulated data are observed carefully, it can be concluded that PUA2 was more stable

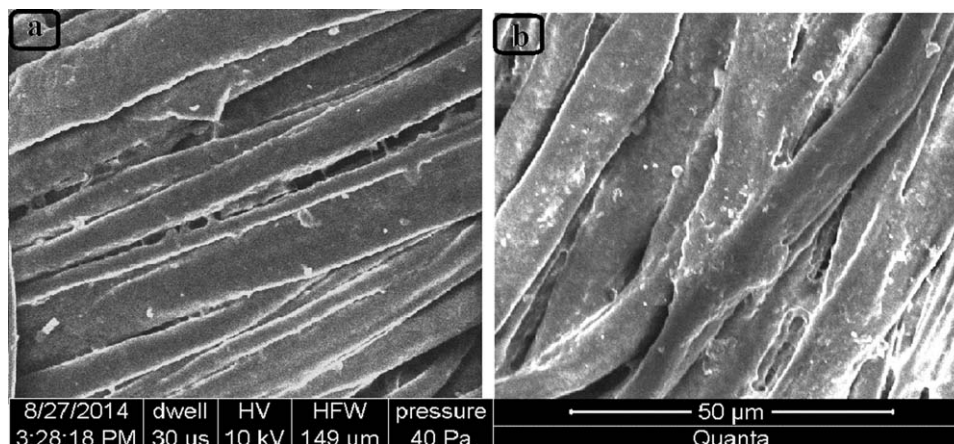


Figure 8. SEM images of fabric sample without (a) and with treatment (b) of WPUA nanoemulsions [magnification 1000×].

than PUA4, also supported by DSC results. $T_{5\%}$, T_{\max} , and $T_{90\%}$ of PUA2 were at relatively higher temperatures than PUA4. It could be possible due to higher chance of strong secondary forces between polar urethane and acrylate groups in PCL-based polymer backbone.³⁴

Thermal analysis of WPUA copolymers by DSC and TGA was also exploited to trace the purity of end products. Exclusion of glass transition temperatures of pure monomers and the absence of any unanticipated transition temperature in DSC thermograms was a strong evidence for the purity of copolymers. Also, no unexpected degradation pattern was observed in TGA of final products.

Morphology of WPUA Copolymers by AFM

The two-dimensional, three-dimensional AFM images and image voltage profiles of representative samples of the series, that is, PUA2 and PUA4 are given in Figures 6 and 7, respectively. The PUA2 [Figure 6(a,b,c)] has shown relatively smooth morphology of emulsion particles as compared to PUA4 [Figure 7(a,b,c)]. It can be attributed to polar and miscible soft segment of PUA2, that is, PCL. However, both copolymers have shown particle size in nanoscale (50–200 nm) as observable in the image voltage profiles. These particle sizes were supportive for the stability of synthesized emulsions.

CONCLUSIONS

Series of eco-friendly WPUA nanoemulsions were prepared by copolymerization approach. Effect of structural variation in soft segment of PU and varying concentrations of BA used for copolymerization was investigated. A cross-linked network of WPUA copolymers was obtained by primary linkages of PU and acrylates. Also, strong secondary interactions were developed between PU and acrylates as confirmed by FTIR and DSC. Average particle size of WPUA emulsions was in nanoscale range <100 nm. It was slightly smaller for polyester-based WPUA due to relatively more polar soft segment. PSD curves for nanoemulsions were smooth and unimodal. High solid content, that is, >40% was achieved without internal emulsifier. Average particle size, solid content, and viscosity were decreased with decreasing content of BA. It may be due to decrease in the chance of copolymerization with decrease in BA content. Chemical and water resistance indicated stability of WPUA due to synergistic effect of PU and cross-linked acrylates. Tear strength of cotton fabric was improved appreciably by the application of WPUA nanoemulsions, especially when soft segment was polyester. It could be due to extensive polar interactions between PCL-based WPUA and cotton surface. Thermal stability of WPUA was substantial, degradation started after 240°C. PCL-based WPUA was more stable with higher T_{\max} . Tgs obtained in DSC results proposed an application of WPUA as phase-changing materials with suitable structural amendments. SEM images showed good adhesion of nanoemulsion coatings on cotton. Briefly, stable, unimodal nanoemulsions with high solid content were prepared, and

polyester-based WPUA has shown relatively better performance properties.

ACKNOWLEDGMENTS

Financial support of Higher Education Commission (HEC), Government of Pakistan is highly appreciated and acknowledged for the conduct of this work.

REFERENCES

1. Lee, T. J.; Kwon, S. H.; Kim, B. K. *Prog. Org. Coat.* **2014**, *77*, 1111.
2. Guo, Y. H.; Miao, J. J.; Teng, H.; Huang, L. J.; Z. *Prog. Org. Coat.* **2014**, *77*, 988.
3. Rahman, M. M.; Lee, I.; Chun, H.-H.; Kim, H. D.; Park, H. *J. Appl. Polym. Sci.* **2014**, *131*, 33905.
4. Li, Y.; Noordover, B. A. J.; Benthem, R. A. T. M. v.; Koning, C. E. *ACS Sus. Chem. Eng.* **2014**, *2*, 788.
5. Li, J.; Zheng, W.; Zeng, W.; Zhang, D.; Peng, X. *Appl. Surf. Sci.* **2014**, *307*, 255.
6. Wu, Z.; Wang, H.; Tian, X.; Xue, M.; Ding, X.; Ye, X.; Cui, Z. *Polymer* **2014**, *55*, 187e194.
7. Luo, Q.; Shen, Y.; Li, P.; Wang, C.; Zhao, Z. *J. Appl. Polym. Sci.* **2014**, *131*, 40970.
8. Peng, S.; Jin, Y.; Sun, T.; Qi, R.; Fan, B.; Cheng, X. *J. Appl. Polym. Sci.* **2014**, *131*, 40420.
9. Fua, C.; Zheng, Z.; Yang, Z.; Chen, Y.; Shen, L. *Prog. Org. Coat.* **2014**, *77*, 53.
10. Kim, B. K. *Colloid. Polym. Sci.* **274**, 599, **1996**.
11. Bai, C.; Zhang, X.; Dai, J.; Wang, J. *J. Coat. Technol. Res.* **2008**, *5*, 251.
12. Howarth, G. A. *Surf. Coat. Int.* **2003**, *86*, 91.
13. Kim, B. S.; Park, S. H.; Kim, B. K. *Colloid. Polym. Sci.* **2006**, *284*, 1067.
14. Lee, H. T.; Wang, C. C. *J. Polym. Res.* **2005**, *12*, 271.
15. Šebenik, U.; Golob, J.; Krajnc, M. *Polym. Int.* **2003**, *52*, 740.
16. Wu, G. M.; Kong, Z. W.; Chen, J.; Huo, S. P.; Liu, G. F. *Prog. Org. Coat.* **2014**, *77*, 315.
17. Wu, G. M.; Chen, J.; Huo, S. P.; Liu, G. F.; Kong, Z. W. *Carbohydr. Polym.* **2014**, *105*, 207.
18. Fang, C.; Zhou, X.; Yu, Q.; Liu, S.; Guo, D.; Yu, R.; Hu, J. *Prog. Org. Coat.* **2014**, *77*, 61.
19. Li, Q.-A.; Sun, D. C. *J. Appl. Polym. Sci.* **2007**, *105*, 2516.
20. Jung, D. H.; Kim, E. Y.; Kang, Y. S.; Kim, B. K. *Colloids. Surf. A: Physicochem. Eng. Asp.* **2010**, *370*, 58.
21. Sultan, M.; Bhatti, H. N.; Zuber, M.; Barikani, M. *Korean J. Chem. Eng.* **2013**, *30*, 488.
22. Wang, X.; Hu, Y.; Song, L.; Xing, W.; Lu, H.; Lv, P.; Jie, G. *Surf. Coat. Technol.* **2010**, *205*, 1864.
23. Xu, G.; Shi, W. *Prog. Org. Coat.* **2005**, *52*, 110.
24. Kojio, K.; Nakashima, S.; Furukawa, M. *Polymer* **2007**, *48*, 997.

25. Kim, B. K.; Lee, J. C. *J. Appl. Polym. Sci.* **1995**, *58*, 1117.
26. Asif, A.; Huang, C.; Shi, W. *Colloid. Polym. Sci.* **2004**, *283*, 200.
27. Sebenik, U.; Krajnc, M. *Colloids. Surf. A: Physicochem. Eng. Asp.* **2004**, *233*, 51.
28. Lee, Y.; Lee, J.; Kim, B. *Polymer* **1994**, *35*, 1095.
29. Athawale, V. D.; Kulkarni, M. A. *Prog. Org. Coat.* **2009**, *65*, 392.
30. Witkowska, B.; Frydrych, I. *Fib. Text. East. Eur.* **2004**, *12*, 42.
31. Wang, C. B.; Cooper, S. L. *Macromolecules* **1983**, *16*, 775.
32. Mishra, R. S.; Mishra, A. K.; Raju, K. V. S. N. *Eur. Polym. J.* **2009**, *45*, 960.
33. Chai, S. L.; Jin, M. M.; Tan, H. M. *Eur. Polym. J.* **2008**, *44*, 3306.
34. Deka, H.; Karak, N. *Prog. Org. Coat.* **2009**, *66*, 192.