Synthesis and Characterization of Aqueous Curcumin Polyurethane Dispersions Using Isophorone Diisocyanate: Efficiency Evaluation as Textile Finishes

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Abstract: This research is aimed at synthesizing some novel bio-based ecofriendly finishes for textile applications. A series of curcumin based aqueous polyurethane (PU) dispersions (CUR-WDPU-IPDI) was prepared using polyethylene glycol (PEG), isophorone diisocyanate (IPDI) and dimethylolpropanoic acid (DMPA) via conventional pre-polymer process. The dual functionality is incorporated by hindering the polyurethane pre-polymer with isocyanate (-NCO) groups and curcumin was utilized to extend the polymeric chain to achieve the CUR-WDPU-IPDI dispersion. Structural characteristics of the synthesized polymer were investigated by Fourier Transform Infrared (FT-IR) spectrophotometer. The performance of PU dispersions for increasing the color fastness properties (washing, rubbing and perspiration fastness) of plain weave fabrics (poly/cotton, dyed and printed) was studied. Furthermore, the mechanical strength (pilling, tearing and tensile strength) of the said fabric (dyed, printed and white) was also evaluated. Results clearly exhibited that the color fastness properties and mechanical strength of the dyed, printed and white fabrics were improved significantly after treating with the PU finishes. These synthesized curcumin-based water dispersible polyurethanes (CUR-WDPU-IPDI) finishing agents are greener products which are particularly derivatized from bio-resources. Owing to their biocompatibility, copious availability, less noxious, greener methodology and ecofriendly nature, these can be utilized as attractive ecofriendly alternatives for textile applications.

Keywords: Curcumin, Aqueous polyurethane dispersions, Textile finishes, Colorfastness, Mechanical strength

Introduction

Modification of textile surfaces, offers a brilliant approach to incorporate advanced and varied functional properties like; hydrophobicity, hydrophilicity, biocompatibility, selfdecontamination, and antibacterial activity to textile goods without affecting its comfort and mechanical strength [1-6]. But this surface modification technique frequently involves several chemical events which could be hazardous to human health, utilize a bulk amount of water and energy due to which the product costs and impacts on environment are usually increased [7,8].

Traditionally the formaldehyde-based finishing agents were used to impart some functional properties to textiles, but these are associated with so many risks and also toxic for humans: these can cause coughing, teary eyes, headache, irritate mucous membranes [9-11] and also trigger problems in breathing [12]. Furthermore, the textiles finished with formaldehyde-based finishing agents could cause eczema and allergic reactions to skin [13-17]. Therefore many researchers have given much attention to develop formaldehyde free finishes [18-21] and ecofriendly surface modification procedures that can be adapted excluding hazardous textile chemicals [22-24]. The textile diligence prefers to carry out

array of the finishing procedures in one step or at least lessening the number of required steps to reduce the expenditures of manufacturing. As a result, multifunctional textiles offer additional features to textiles finishing merely in a one step. Moreover, lately the needs for textiles with great specifications and exceptional performances are constantly multiplying [25-27].

By reviewing previous literature, it is well documented that water dispersible polyurethanes (WDPU) are the most rapidly emerging and dynamic categories of polyurethane chemistry. Several researchers have investigated the structure and composition of WDPU [28-30] and progressed WDPU's utilization via structure/surface modifications and hybridization or combination with other materials. WDPU's have been extensively consumed in various textile applications [31-33] due to its superior molecular structure, good quality softness, effective abrasive resistance, excellent permeability for finishing textiles and exhibit outstanding adhesion to textiles [33]. Moreover, the dye fixing agents formulated by WDPU might significantly enhance the washing fastness, rubbing fastness and soaping fastness of dyed textiles for reactive, direct and acid dyes [34].

A wide-ranging WDPU has been reported, principally based on binary colloidal system in which the stabilizing group that contains PU particles thoroughly dispersed in water medium instead of organic solvent [35-37]. Structural

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modifications by incorporating hydrophilic groups into the hydrophobic polyurethane backbone, results the formation of WDPU [38] after that polymeric chain is extended followed by the drop wise addition of distilled water to disperse and emulsify the hydrophilic WDPU prepolymer [39]. A formation of stable WDPU emulsion is carried out by the insertion of hydrophilic centers, for example cationic, anionic or non-ionic groups into the polyurethane backbone. Diisocyanates, polyols, chain extenders, neutralizing agents and water are the raw materials for WDPU and these has been broadly utilized as coatings for various materials [40] due to the numerous structural features and devoid of detrimental effects on environment results in several useful and fascinating properties [41] for example: low temperature flexibility, zero or less volatile organic concentrations, pH stability, excellent solvent, water and weathering resistance, advantageous mechanical and chemical properties [42].

Keeping in view the rapid improvement of hygienic living standard, many researches have focused on the development of environmental friendly processes that produce unhazardous multifunctional textiles. For example, propolis [43], cyclodextrin [44], collagen [45,46], chitosan [47-50] and alginate [24,51] are the suitable alternative agents and open up an innovative opportunity for multifunctional finishing of textile materials.

Curcumin is the biologically active, hydrophobic, low molecular weight poly-phenolic molecule which is extracted from the roots of *Curcuma longa* plant. 1,7-bis(4-hydroxy-3methoxy phenyl)-1,6-heptadiene-3,5-dione is the active compound that imparts numerous pharmacological effects. This poly-phenolic compound displays outstanding antibacterial [52], anti-fungal [53], anti-oxidant [54], antiinflammatory [55], anti-coagulant [56] and anti-tumor activities. Curcumin bioavailability and pharmaceutical role is severely restricted due to its very low solubility in aqueous medium, degradation at alkaline pH, inadequate tissue absorption and rapid systemic elimination. Curcumin is utilized as a native therapeutic and anti-infectious agent for injuries. Traditionally it is also used as a dying or coloring agent in textile.

More recently, water dispersible polyurethanes (WDPUs) have gaining popularity. The latter are biodegradable nontoxic polyurethanes which are typically synthesized using aliphatic diisocyanate, hydrolytically degradable polyester diol, and various chain extenders by solution polymerization or bulk polymerization [45]. The preparation procedures for WDPUs has received increasing attention owing to the continuous reduction in costs and its control of volatile organic compound emissions, thus, being more eco-friendly and greener approach. To obtain bio-based WDPUs textile finishes with good physical, biocompatible and biodegradable properties, a new method for the preparation of nontoxic WDPUs was designed using isophorone diisocyanate (IPDI), polyethylene glycol (PEG), and curcumin (CUR), without any other

organic reagents involved in the synthetic process. In this research work we used curcumin as naturally bioactive agent in water dispersible polyurethane to synthesize bio-functional textile finishes. The insertion of functional biopolymer into the WDPUs backbone as chain extender has turned out to be the center interest of too many researchers [45,57,58]. Polyurethane and chitosan are previously utilized for encapsulation of curcumin in numerous medical applications [46]. The insertion of curcumin into the backbone of WDPU is not only being nontoxic but it is also advantageous to impart the multifunctional properties to the finished textiles. It is the pioneer step that curcumin is introduced for the extension of polymeric chain of water dispersible polyurethane. In this research project curcumin-based water dispersible polyurethane is synthesized using polyethylene glycol (PEG), isophrone diisocyanate (IPDI), dimethylolpropanoic acid (DMPA), dibutyltindilurate (DBTDL), triethyl amine (TEA) and curcumin (CUR). The intention to design this research project is to develop and open up a new avenue for the preparation of bio-based finishing material for textile applications. The structural and textile efficiency evaluation of curcumin-based water dispersible polyurethanes was done to evaluate the effects of curcumin molar quantity on final WDPU properties.

Experimental

Reagents and Chemicals

Polyethylene glycol (PEG) (Mn=600 g/mole) (99 % Merk Chemical Co., USA). Isophorone diisocyanate (IPDI, 99.9 %), dibutyltindilaurate (DBTDL, 99.9 %), curcumin (99 %) and dimethylolpropanoic acid (DMPA, 99.9 %) were bought from Sigma Aldrich Chemical Co., USA. Triethyl amine (TEA, 99 %), methyl ethyl ketone (MEK, 99 %), acetone (99 %) and acetic acid (99 %) were procured from Merk Chemicals. NP-6 (HLB=10) and WN (HLB=14) were generously provided by Textile Chemical Industry, Pakistan. All the reagents utilized during this whole research project were consumed as received but DMPA and PEG were dried in oven for 4 hours at 60 °C before usage to remove air and water vapors. Anhydrous CaSO₄ was used to dry MEK.

Textile Specifications

Mill desized, scoured and bleached plain weaved polyester/cotton (white, dyed and printed) blended fabrics were delivered by Kamal Textile Mills Ltd., Khurrianwala, Faisalabad, Pakistan. Before the treatment with CUR-WDPU-IPDI finishes all the textile samples were washed with detergent for 30 minutes at 100 °C. After washing, the fabric samples were rinsed and air dried at room temperature. During all the fabric treatment processes, the pH of the tested fabric samples was maintained at about 6.5-7.5. Specifications related to fabric are given in Table 1.

Synthesis of Curcumin Based Aqueous Polyurethane Dispersions

Synthesis of the said PU dispersions was carried out by a suggested procedure [59] by which PU pre-polymer, terminated with NCO at both ends, was formed in a round bottom glass reactor equipped with a nitrogen inlet, a reflux condenser, a mechanical stirrer, a thermometer and a temperature regulator. Firstly 1.0 mole of polyethyleneglycol (PEG) and 0.8 mole of DMPA were poured into the reactor, then allowing the reaction at 80 °C for 30 minutes. After that DBTDL (1-2 drops) was added using micro syringe and isophorone diisocyanates (IPDI) (2 mol) was added under vigorous stirring. At this moment the reaction mixture was allowed to react for further 2 hours maintaining temperature at about 70-80 °C to get hydrophilic PU-prepolymer with NCO terminals. The FTIR spectrum of the NCO-end capped PU-prepolymer was acquired to check the progression of

prepolymer formation. The isocyanate content into the PUprepolymer terminated with NCO was continuously analyzed after some intervals of time and reaction was stopped when determined value (9.2 %) was close to the theoretical value (9.29 %). TEA (triethyl amine, 0.9 mol) was added into the reaction mixture to neutralize carboxylic (-COOH) groups that exist in polymeric chain and the reaction was further carried out for 45 minutes at 55 °C and to ensure the complete neutralization of the carboxylic (-COOH) groups, the amount of triethyl mine (TEA) was kept in slight excess to that of DMPA [60]. Methyl ethyl ketone (MEK) was also added batch wise in a small amount into reaction mixture to decrease the viscosity of reaction mixture. Formation of neutralized PU-prepolymer with NCO terminals was confirmed by FTIR analysis. After that, the chain of neutralized NCO end capped PU-prepolymer was extended by the addition of estimated amount of curcumin dissolved



Figure 1. A schematic illustration for the synthesis of curcumin based aqueous polyurethane dispersions.

in appropriate amount of MEK into the reaction mixture and stirred for next 30 minutes. Afterwards, the determined volume of deionized water was added drop wise into the reactor with the help of dropping funnel under vigorous stirring which was continued for next 2 hours at room temperature. A stable CUR-WDPU-IPDI dispersion with almost 35 % solid content was formed. The Schematic illustration of synthesis of curcumin based aqueous polyurethane dispersions (CUR-WDPU-IPDI) has been presented in Figure 1. A total of 5 samples of the curcumin water dispersible polyurethanes using isophorone diisocyanates (IPDI) were prepared by proceeding the exhaustive synthetic route mentioned above. The detailed formulation and sample code designation of all these samples is given Table 2.

Molecular Structure Characterization

In order to validate the incorporation of curcumin into the WDPU structure, spectral analysis of the prepared finishes were achieved in ATR mode by a Bruker-IFS 48 FTIR spectrometer (Ettlingen, Germany). All the FTIR spectral analysis of the series CUR-WDPU-IPDI were recorded in 400-4000 cm⁻¹ wavelength region.

Finish Application

To prepare 2 % or 4 % solutions of the CUR-WDPU-IPDI polymeric dispersion, two emulsifiers WN (HLB=14) and NP-6 (HLB=10) were used, both of these were dissolved in 1000 m/ distilled water followed by the addition of 20 g or 40 g of synthesized dispersion under vigorous stirring for 5 minutes. The tested fabric samples were immersed in dispersion solution of 2 % or 4 % concentrations. After some minutes, the immersed fabric swatches were squeezed

between two stainless steel rollers, the padding speed was kept 3 m/min and padding pressure was adjusted to allow a pickup of 75 % (pad-dry-cure method). The textile swatches were dried and cured in an electric oven at 150 °C for 1 min.

Performance Evaluation of Finished Textiles

In daily usage and maintenance of textiles, particularly sportswear, textile goods are constantly exposed to stretching, bending, shearing, twisting and compression. It is necessary to assess the textile goods for predictable lowermost level of comfort and strength properties. Performance of treated P/C fabric samples (white, dyed and printed) was assessed by applying standard test methods and before testing, all the finished textiles were conditioned at standard atmospheric circumstances.

Textile Assets Evaluation

The colorfastness to washing (shade change and staining), colorfastness to rubbing (dry and wet) and perspiration (acidic and alkaline) of the tested dyed and printed fabrics after treatment with curcumin WDPU's were assessed using standard assessment system. The washing and rubbing fastness performances of the tested fabrics were evaluated as per standard textile test procedures such as ISO-105 C06 C25 and ISO 105-12 respectively. The fastness to perspiration was evaluated by ISO 105 E04. The mechanical performance testing such as pilling, tear and tensile strengths of tested plain weaved poly/cotton fabrics samples (Table 1) after being finished with different dilutions of CUR-WDPU-IPDI emulsion were assessed using standard test procedures ISO-129455-2, ASTMD-1424, ASTM-D5034, respectively. The tear and tensile strength of fabric from both warp-wise and

Table 1. Quality, processed applications and specifications of tested fabrics

Sr. no.	Quality	Construction/count	Blend ratio cotton/ polyester	GSM (g/m ²)	PPI ^a	EPI ^b	Processed application
01	Plain weave poly cotton	(40×40/96×76)	44/56	106	76	96	Dyed with reactive dyes
02	Plain weave poly cotton	(40×40/96×76)	44/56	111	76	96	Printed with pigment dyes
03	Plain weave poly cotton	(40×40/96×76)	44/56	108	76	96	White

^aPPI: picks per inch: number of weft threads per inch of woven fabric and ^bEPI: ends per inch: number of warp threads per inch of woven fabric.

Table 2. Formulation of curcumin based WDPU dispersion

Sample code	IPDI ^a (moles)	PEG ^b (moles)	DMPA ^c (moles)	TEA ^d (moles)	Curcumin (moles)
CUR-WDPU-01	2.0	1	0.8	0.9	0.01
CUR-WDPU-02	2.0	1	0.8	0.9	0.02
CUR-WDPU-03	2.0	1	0.8	0.9	0.03
CUR-WDPU-04	2.0	1	0.8	0.9	0.04
CUR-WDPU-05	2.0	1	0.8	0.9	0.05

^aIsophrone diisocyanates, ^bployethylene glycol, ^cdimethylolpropionic acid, ^dtriethyl amine.

weft-wise direction was assessed.

Results and Discussion

Molecular Characterization

FTIR spectra of all the monomers, prepolymers and final curcumin/WDPU based on IPDI emulsion (CUR-WDPU-IPDI) are presented in Figures 2 and 3. The assignments of prominent signals, appeared due to the principal functional groups of monomers, were exhaustively conferred elsewhere in our previous reported work [57]. PEG, DMPA and IPDI were reacted in a flask in the presence of a catalyst DBTDL which leads to the formation of PU pre-polymer with NCO terminals. FTIR spectrum of NCO end capped PU prepolymer (Figure 2d) displayed a broad band at 3323.35 cm⁻¹ which is attributed to -NH stretching [45], other significant peaks have been observed at; 1699.29 cm⁻¹ entitled to -C=O stretching: peaks seemed at 2889.37 cm⁻¹ and 2962.66 cm⁻¹ are attributable to -CH symmetric and asymmetric stretching's of -CH₂ group. The NCO end capped PU pre-polymer was further allowed to react with triethyl amine that leads to the



Figure 2. FTIR spectra; (a) PEG, (b) DMPA, (c) IPDI, (d) NCO terminated PU prepolymer, (e) TEA, (f) neutralized NCO terminated PU prepolymer, (g) curcumin, and (h) final CUR-WDPU-01.

formation of neutralized NCO terminated PU prepolymer. The FTIR spectrum of this neutralized PU pre-polymer with NCO terminals (Figure 2f) showed a prominent broad band at 3323.35 cm⁻¹ attributed to -NH stretching. The asymmetric stretching of -CH₂ group was detected at 2960.73 cm⁻¹ and symmetric stretching at 2881.65 cm⁻¹, sharp signals at 1697.36 cm^{-1} and 1529.55 cm^{-1} were assigned to the -C=O and -C=C stretching respectively. From the FTIR spectrum of neutralized polyurethane prepolymer with NCO terminals, it was observed that the signal associated to isocyanate (-NCO) group has been disappeared. Afterwards neutralized NCO terminated PU prepolymer extended with curcumin which resulted in the formation of proposed curcumin-based water dispersible polyurethane (CUR-WPU). FTIR spectrum of curcumin presented in Figure 2g showed a prominent band at 3515 cm⁻¹ associated to the phenolic -OH stretching vibrations, sharp absorption signals appeared at 1627 cm⁻¹ and 1602 cm⁻¹ because of enol-carbonyl stretching vibrations. Stretching vibrations of benzene ring appeared at 1600- 1400 cm^{-1} , where 1597 cm⁻¹ for -C=O, 1508 cm⁻¹ assigned to -C=C vibrations and 1426 cm⁻¹ for olefinic -CH bending vibration [61-63] and absorbance peaks at 1274 cm⁻¹, 1197 cm⁻¹,



Figure 3. FTIR spectra; (a) CUR-WDPU-01, (b) CUR-WDPU-02, (c) CUR-WDPU-03, (d) CUR-WDPU-04, and (e) CUR-WDPU-05.

1153 cm⁻¹ and 1024 cm⁻¹ related to -C=O stretching vibration [46,64,65]. FTIR spectrum of CUR-WDPU-1 (Figure 2h) showed a typical broad band of -NH stretching vibration at 3365.78 cm⁻¹, -CH symmetric and asymmetric stretching vibrations of -CH₂ groups were seemed at 2927.94 cm⁻¹. The absorption peaks at 1685.79 cm⁻¹ and 1548.84 cm⁻¹ were correlated to -C=O stretching and -NH deformations. The peaks at 1454.33 cm⁻¹, 1409.96 cm⁻¹, and 1323.17 cm⁻¹ were attributed to CH₂ bending vibration, -CH₂ bending vibration, and -CH₂ wagging, respectively. C-O-C stretching has been observed at 1041.56-1244.09 cm⁻¹. On extending the neutralized PU prepolymer with different proportions of curcumin, the FTIR spectral series of CUR-WDPU 01 to CUR-WDPU-05 presented in Figure 3(a-e) all the five spectra have shown the identical peaks of -NH stretching vibration, -CH symmetric and asymmetric stretching vibrations of CH₂ groups, hydrogen bonded -C=O stretching, -NH bending and C-O-C vibrations of curcumin-ether-type absorption.

Appearance of CUR-WDPU-IPDI Dispersion and Solid Contents

The Synthesized CUR-WDPU-IPDI dispersions, physically observed by eye have same in appearance, texture and consistency (Figure 4). Solid contents of the prepared series of CUR-WDPU-01 to CUR-WDPU-05 emulsions range from 35.60 % to 39.89 %. The gradual enhancement in the dry weight contents may be due to the continuing rise in the molar amount of curcumin. The appearance was approximately identical in all the synthesized emulsions, i.e., milky yellow, and the diluted solution of all the emulsions was light yellowish in color. This yellow color was due to curcumin which is a yellow colored bioactive compound, incorporated into the WDPU backbone as a chain extender. Tackiness is another considerable aspect of the coated material. To observe the tackiness, each one of the synthesized samples was tack-free. The consequences associated to the stability of the CUR-WDPU-01 to CUR-WDPU-05 emulsions shows that stability of all the emulsions was approximately the same, i.e., greater than one year.

Colorfastness Properties of CUR-WDPU-IPDI

In this study we evaluated the effect of curcumin based water dispersible polyurethanes on to the color fastness properties of poly/cotton textiles. This is the novel work conducted for the first time on curcumin till to date that the incorporation of curcumin into water dispersible polyurethane as antibacterial textile finishes. Literature reviewed on curcumin, reported the use of curcumin as a native dyeing agent for cotton, silk and wool. Here we introduce curcumin based water dispersible polyurethanes as antibacterial textile finishes. To study the colorfastness effects of synthesized CUR-WDPU finishes on to poly/cotton textiles, the dyed and printed fabric swatches were treated with 2 % and 4 %



Figure 4. Appearance of CUR-WDPU-IPDI dispersion.

diluted solutions of CUR-WDPU finishes. The diluted solution of CUR-WDPUs was yellow in color due to curcumin which is a yellow colored bioactive compound introduced into the polymeric chain of PU for extension.

Colorfastness to Washing

The prepared 2 % and 4 % dilutions of CUR-WDPU-IPDI polymeric dispersions were applied on the dyed and printed tested fabric swatches and the findings of washing fastness (staining and shade change) have been displayed in Table 3. The outcomes presented in Table 3 revealed that the treatment of CUR-WDPUs have markedly improved the color fastness to washing of all the CUR-WDPU-IPDI treated fabric samples. The untreated poly/cotton dved fabric has shown staining rating 3/4 while shade change rating is of 3. On the other hand the untreated poly/cotton printed sample has shown staining and shade change rating 3 and 3 respectively. However, the treated poly/cotton dyed fabric swatches have shown stain rating in the range of 4 to 4/5 and shade change rating in the range of 3/4 to 4. Whereas the treated printed fabric swatches have shown stain rating and shade change rating in the range of 3/4 to 4. From the outcomes shown in Table 3 we clearly disclose that every fabric swatch treated with emulsion enhanced resistance against staining and shade change. The sample CUR-WDPU-02 and CUR-WDPU-03 of the dyed fabric shows better washing fastness as compared to other, it may be due to the good penetration and adhesion of CUR-WDPU finish to fabric. Overall results presented that printed fabric does not show as much improvement in washing fastness as compared to dyed fabric. It might be due to less contact of emulsion with fabric cellulose due to printing paste on the printed fabric.

Colorfastness to Rubbing (Crock Fastness)

The findings of rubbing fastness (dry and wet) have been exhibited in Table 4. According to the outcomes, the untreated dyed fabric sample has shown dry and wet rubbing

	Strength of applied solution										
Comula codo		Dyed (40×4	40/96×76)		Printed (40×40/96×76)						
Sample code	20 g/l		40 g/l		20 g/l		40 g/l				
	Staining	Shade change	Staining	Shade change	Staining	Shade change	Staining	Shade change			
CUR-WDPU-01	4	4	3/4	3/4	4	3/4	3/4	3/4			
CUR-WDPU-02	4/5	3/4	4	4	4	3/4	4	3/4			
CUR-WDPU-03	4/5	4	3/4	4	3/4	3/4	4	4			
CUR-WDPU-04	4	4	3/4	3/4	3	4	3/4	4			
CUR-WDPU-05	4	4	4	3/4	4	3/4	4	4			
Untreated sample	Staining		Shade change		Staining		Shade change				
Std.	3/4		3		3		3				

 Table 3. Colorfastness to washing assessment of tested poly/cotton fabrics

rating of 3/4 and 3, respectively. While the untreated printed fabric sample has shown dry and wet rubbing rating 3 and 2/3, respectively. Dyed fabric swatches treated with 2 % and 4 % of the CUR-WDPUs show dry rubbing rating in the range of 3/4 to 4 and wet rubbing rating in the range of 2/3 to 3. All the printed fabric swatches treated with 2 % and 4 % of the synthesized products CUR-WDPU-01 to CUR-WDPU-05 show dry rubbing rating in the range of 3/4 to 4 and wet rubbing rating in the range of 3/4 to 4 and wet rubbing rating in the range of 3/4 to 4 and wet rubbing rating in the range of 3/4 to 4 and wet rubbing rating in the range of 3/4 to 4 and wet rubbing rating in the range of 2/3 to 3. The performance of curcumin based WDPU emulsions have shown better crock fastness as compared to untreated one, improvement in color fastness to rubbing due to the molecular interaction between CUR-WDPU and cellulose of fabric has been observed.

Colorfastness to Perspiration

The untreated dyed fabric swatches have shown acidic and alkaline rating 4 and 4 respectively and the untreated printed fabric swatches have shown acidic and alkaline rating 3/4 and 3/4, respectively. All the dyed treated fabric swatches have shown acidic rating in the range of 4 to 4/5, alkaline rating in the range of 4 to 4/5. All the printed treated fabric

swatches have shown acidic rating in the range of 4 to 4/5, alkaline rating in the range of 3/3 to 4. From the results, presented in Table 5 it is concluded that all the fabric samples treated with 2 % of CUR-WDPUs emulsion solution display certain improved resistance to perspiration. It might be because of the good penetration of emulsion into the fabric and better compatibility between fabric and CUR-WDPU. But as compared to lower concentrations, the higher concentration solutions showed less improvement in perspiration fastness. Perspiration alkaline rating (3 to 3/4) is decreased with 4 % solution of CUR-WDPU emulsions.

Pilling Characterization

By increasing the curcumin concentration, there is continual increase in the pilling rating. The dyed, printed and white polyester/cotton blended textiles were treated with synthesized CUR-WDPU-IPDI finishing samples and assessed the performance of treated fabrics to upgrade the pilling rating. The consequences (Table 6) showed that there is a prominent effect of CUR-WDPU finishes to upgrade the pilling rating of the treated poly/cotton fabric swatches. All the treated dyed and printed fabric swatches attained the

Table 4. Color fastness to rubbing evaluation rating of dyed and	I printed fabrics after treatment with CUR-WDPU-IPDI series
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		Strength of solution applied								
Somula codo		Dyed (40×	40/96×76)		Printed (40×40/96×76)					
Sample code	20	20 g/l 40		0 g/l 2		gv	40 g/l			
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet		
CUR-WDPU-01	4	3	4	3	4	3	3/4	3		
CUR-WDPU-02	3/4	3	4	3	4	3	4	2/3		
CUR-WDPU-03	4	3	3/4	2/3	4	2/3	4	2/3		
CUR-WDPU-04	4	3	3/4	2/3	3/4	2/3	3/4	2/3		
CUR-WDPU-05	4	2/3	3/4	2/3	3/4	2/3	3/4	2/3		
Untreated sample	D	Dry		Wet		Dry		Wet		
Std.	3	/4	2	/3		3	2	/3		

	Such Sur of Solution upplied										
Comula codo		Dyed (40×	40/96×76)		Printed (40×40/96×76)						
Sample code	20 g/l (2 %)		40 g/l (4 %)		20 g/l (2 %)		40 g/l (4 %)				
	Acidic	Alkaline	Acidic	Alkaline	Acidic	Alkaline	Acidic	Alkaline			
CUR-WDPU-01	4	4	4	3/4	4	4	4	3			
CUR-WDPU-02	4	4	4	3	4/5	4	4	3			
CUR-WDPU-03	4	4	4	3/4	4	4	3/4	3/4			
CUR-WDPU-04	4/5	4	4	3/4	4/5	4	3/4	3/4			
CUR-WDPU-05	4/5	4	4	3	4/5	4	4	3			
Untreated sample	Acidic 4		Alkaline		Acidic		Alkaline				
Std.			4		3/4		3/4				

Strength of solution applied

Table 5. Color fastness to perspiration appraisal ratings of dyed and printed fabrics after treatment with CUR-WDPU-IPDI series

highest pilling rating as compared to untreated fabric swatches. While the bleached white poly/cotton fabric has not attained the highest pilling rating of 5. All white treated fabric swatches have shown progressive pilling trend of 3/4 to 4. These CUR-WDPU-IPDI finishes have efficiently fixed or stabilized the loose fibers within the threads and attained no pilling. Superior emulsion stability assumed for outstanding pilling resistance performance of treated textiles. Finishes played an exciting function to control the interlocking of protruded loose fibers by fixing them inside the yarns to decrease the formation of pills which leads to enhance the quality of textile.

Tear Strength

In the present research work, 2 % and 4 % of CUR-WDPU-IPDI finishes were applied on the white, dyed and printed poly/cotton textiles. Findings of tearing strength of dyed, printed and white treated fabrics have been presented in Figures 5, 6 and 7 respectively. Results showed a great enhancement in warp and weft tearing strength of all samples of poly-cotton fabric specimens treated with CUR-WDPU-01 to CUR-WDPU-05. Dyed fabric treated with CUR-WDPU-01 sample showed highest tearing strength in warp ways direction 33 % with 2 % of CUR-WDPU-01 and

32 % with 4 % of CUR-WDPU-01 among all the dyed fabric. While in weft ways the highest tearing strength was 49.4 % with 2 % of CUR-WDPU-04 and the highest tearing strength among all the dyed fabric swatches treated with 4 % of CUR-WDPU-03 was 50.5 %. Printed fabric treated with 2% of CUR-WDPU-01 sample showed 34.7% highest tearing strength in warp ways and 22.6% in weft ways direction among all the treated printed fabric swatches. Whereas printed fabric specimen treated with 4 % of CUR-WDPU-01 exhibits the highest tearing strength in warp ways was 22.6 % and 16.5 % in weft ways. White fabric treated with 2 % of CUR-WDPU-05 showed 63 % and with 4 % of CUR-WDPU-01 sample showed 58.5 % highest tearing strength in warp ways direction among all the white fabric. While the white fabric specimen treated with 2 % of CUR-WDPU-02 showed highest tearing strength in weft ways of 62.9 % and white fabric specimen treated with 4 % of CUR-WDPU-01 showed highest tearing strength 45.2 % in weft ways. It was observed that the white fabric treated with 2 % and 4 % of the diluted solution of CUR-WDPUs showed a great enhancement in the tearing strength in both directions (warp and weft ways) as compared to treated dyed and printed fabrics. Furthermore, it was also observed that textile swatches treated with solutions having lower concentration

Table 6. Pilling evaluation rating of dyed, printed and white fabrics after treatment with series CUR-WDPU-IPDI

	Strength of solution applied								
Sample code	Dyed (40×4	40/96×76)	Printed (40	×40/96×76)	White (40×40/96×76)				
-	20 g/l	40 g/l	20 g/l	40 g/l	20 g/l	40 g/l			
CUR-WDPU-01	4/5	4/5	4/5	4	4	3/4			
CUR-WDPU-02	4/5	4/5	5	4/5	3/4	4			
CUR-WDPU-03	4	4/5	5	4/5	4	4			
CUR-WDPU-04	5	4/5	4/5	4/5	3/4	4			
CUR-WDPU-05	4/5	4/5	4/5	4	4	4			
Untreated sample	Dy	Dyed		Printed		White			
Std.	3/4		4		3				







Figure 5. Graphical representation of tear data of dyed fabric treated with (a) 2 % emulsion and (b) 4 % emulsion.



Figure 6. Graphical representation of tear data of printed textiles treated with (a) 2 % emulsion and (b) 4 % emulsion.



Figure 7. Graphical representation of tear data of white textiles treated with (a) 2 % emulsion and (b) 4 % emulsion.

of finishes showed more upgraded results. It is because of excellent disperse-ability and penetrating ability of finishes into the fabrics and good adhesion properties. The lower concentrations of finishes improved the strength of treated fabrics, whereas the increase in the concentration of finishes leads to decrease the asset of treated fabric and softness of fabric was decreased due to the higher concentration of emulsion. Deposition of the emulsion ingredient on to the fabric surface causes the enhancement in toughness of treated fabric.

Tensile Strength

The recorded results of the tensile strength of treated dyed, printed and white poly/cotton fabric swatches are displayed in Figures 8, 9 and 10 respectively. The 2% and 4% of WDPU emulsions were applied on the described textiles. Treated dyed fabric showed small increase in the tensile strength in warp ways direction with 2 % of finish sample CUR-WDPU-01 and the other samples, i.e. CUR-WDPU-02, CUR-WDPU-03, CUR-WDPU-04 and CUR-WDPU-05 showed slight decrease in the tensile strength in warp ways, while in weft ways with 2 % of finish only CUR-WDPU-04 and CUR-WDPU-05 showed slight increase. Dyed fabric swatches treated with 4 % of diluted solution of CUR-WDPU-03 showed little improvement in warp ways direction and the other samples treated with CUR-WDPU-01, CUR-WDPU-02, CUR-WDPU-04 and CUR-WDPU-05 finish exhibited slight decrease in the tensile strength in warp ways. Whereas, treated dyed fabric with 4 % of finish

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Figure 8. Graphical representation of tensile data of dyed textiles treated with (a) 2 % emulsion and (b) 4 % emulsion.



----- Printed fabric (2%) IPDI Tensile(wp) Printed fabric (2%) IPDI Tensile(wft)

Figure 9. Graphical representation of tensile data of printed textiles treated with (a) 2 % emulsion and (b) 4 % emulsion.

samples CUR-WDPU-01, CUR-WDPU-03, CUR-WDPU-04 and CUR-WDPU-05 showed slight increase in the tensile strength in weft ways direction. Printed fabric samples treated with 2 % of finish dilutions CUR-WDPU-02, CUR-WDPU-04 and CUR-WDPU-05 showed slight increase in the tensile strength in warp ways directions. While in weft ways the printed fabric samples treated with 2 % of CUR-



4

CUR-WDPU-IPDI series

5

7

600

0

Tensile strength

White fabric (4%) IPDI Tensile(wp) - White fabric (4%) IPDI Tensile(wft)

3



Figure 10. Graphical representation of tensile data of white textiles treated with (a) 2 % emulsion and (b) 4 % emulsion.

WDPU-01, CUR-WDPU-02, CUR-WDPU-03 finish showed slight increase in the tensile strength and samples CUR-WDPU-05 showed no effect, CUR-WDPU-04 presented negligible decrease in weft ways tensile strength. Printed fabric swatches treated with 4 % of dilutions of CUR-WDPU-01, CUR-WDPU-02 and CUR-WDPU-03 showed small increase in warp ways, CUR-WDPU-03, CUR-WDPU-04 and CUR-WDPU-05 showed slight improvement in weft ways tensile strength. CUR-WDPU-02 present no effect on to the tensile strength. White fabric samples treated with 2 % of finish dilutions CUR-WDPU-02, CUR-WDPU-03, CUR-WDPU-04 and CUR-WDPU-05 showed slight increase in the tensile strength in warp ways directions, while in weft ways the white fabric samples treated with 2 % of CUR-WDPU-01, CUR-WDPU-03, CUR-WDPU-04 and CUR-WDPU-05 finish showed slight increase. White fabric swatches treated with 4 % of dilutions of CUR-WDPU-01, CUR-WDPU-02, CUR-WDPU-03, CUR-WDPU-04 and CUR-WDPU-05 showed small increase in warp ways. CUR-WDPU-01 and CUR-WDPU-05 showed slight improvement in weft ways tensile strength. Results revealed that significant improvement in the warp and weft tensile strength of most of the fabric samples after treated with different dilution of CUR-WDPU emulsions was observed.

Conclusion

The incorporation of natural molecules into water dispersible polyurethanes (WDPUs) is an advanced and innovative technique to develop bio-based finishing materials for various textile applications. A series of curcumin based

WDPUs with varying mole ratios of curcumin were synthesized using polyethylene glycol (PEG), isophorone diisocyanate (IPDI) and dimehylolpropanoic acid (DMPA) via conventional pre-polymer process. The dual functionality is incorporated by guarding the polyurethane pre-polymer with isocyanate (-NCO) groups and curcumin was utilized to extend the polymeric chain to prepare water dispersible polyurethanes. Structural characteristics of these polyurethanes (CUR-WDPUs) were studied through Fourier Transform Infrared (FTIR) spectrophotometer. Appearance of characteristic peaks associated to keto-enol, primary or secondary amide and aromatic ring confirmed the successful insertion of CUR into the polymeric chain of WDPU. It was found that emulsions having lower contents of curcumin exhibited outstanding miscibility with polyurethane which leads to improve the stability of emulsion. The effects of CUR-WDPU-IPDI finishes on the color fastness of dyed and printed poly/cotton textiles were also assessed and the results revealed that the washing fastness (staining, shade change), rubbing fastness (dry, wet) and perspiration fastness (acidic, alkaline) were improved significantly after using CUR-WDPU-IPDI. Furthermore, the mechanical testing (pilling, tear and tensile strength) of CUR-WDPU-IPDI treated dyed, printed and white textile swatches were evaluated. The outcomes displayed that mechanical strength and pilling performance of the treated fabric swatches were also enhanced after finishing with CUR-WDPU-IPDI. Future investigations of dispersions will deal with the biological and antimicrobial activities for medical textile purposes. This whole research project is a pioneer step towards the synthesis of ecofriendly biomaterials that could probably be employed for perspective textile applications.

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Conflict of Interest

The authors declare no conflict of interest in this study.

References

- 1. S. Afzal, W. A. Daoud, and S. J. Langford, *J. Mater. Chem. A*, **2**, 18005 (2014).
- 2. M. Gouda, J. Ind. Text., 41, 222 (2012).
- 3. A. Hou and G. Sun, *Carbohydr. Polym.*, **95**, 768 (2013).
- 4. T. Nikolic, M. Kostic, J. Praskalo, B. Pejic, Z. Petronijevic, and P. Skundric, *Carbohydr. Polym.*, **82**, 976 (2010).
- 5. J. Zhuo and G. Sun, *ACS Appl. Mater. Interfaces*, **5**, 10830 (2013).
- R. Dastjerdi, M. Montazer, and S. Shahsavan, *Colloids Surf. A: Physicochem. Eng. Asp.*, 345, 202 (2009).

- 7. T. Harifi and M. Montazer, *Carbohydr. Polym.*, **88**, 1125 (2012).
- 8. J. Zhuo and G. Sun, Carbohydr. Polym., 112, 158 (2014).
- 9. M. Krzyzanowski, J. J. Quackenboss, and M. D. Lebowitz, *Environ. Res.*, **52**, 117 (1990).
- K. A. Daily, L. P. Hanrahan, M. A. Woodbury, and M. S. Kanarek, *Arch. Environ. Health: An Inter. J.*, 36, 277 (1981).
- 11. K.-H. Kim, S. A. Jahan, and J.-T. Lee, *J. Environ. Sci. Health C*, **29**, 277 (2011).
- 12. G. McGwin Jr, J. Lienert, and J. I. Kennedy, Jr., *Environ. Health Perspect.*, **118**, 313 (2010).
- J. F. Fowler Jr, S. M. Skinner, and D. V. Belsito, J. Am. Acad. Dermatol., 27, 962 (1992).
- 14. D. S. Brookstein, Dermatologic Clinics, 27, 309 (2009).
- 15. J. F. Fowler, Curr. Probl. Dermatol., 31, 156 (2003).
- 16. H. C. Reich and E. M. Warshaw, Dermatitis, 21, 65 (2010).
- 17. H. Bai, I. Tam, and J. Yu, Dermatitis, 31, 53 (2020).
- K. J. Yoon, J. H. Woo, and Y. S. Seo, *Fiber. Polym.*, 4, 182 (2003).
- 19. H.-M. Choi and Y. M. Kim, Fiber. Polym., 2, 190 (2001).
- 20. Y. H. Yu, E. S. Lee, and E. S. Bang, *Fiber. Polym.*, **9**, 715 (2008).
- A. Castellano, C. Colleoni, G. Iacono, A. Mezzi, M. R. Plutino, G. Malucelli, and G. Rosace, *Polym. Degrad. Stab.*, 162, 148 (2019).
- A. El-Shafei, M. ElShemy, and A. Abou-Okeil, *Carbohydr. Polym.*, 118, 83 (2015).
- 23. N. Ibrahim, A. El-Gamal, M. Gouda, and F. Mahrous, *Carbohydr. Polym.*, 82, 1205 (2010).
- 24. M. Shahid and F. Mohammad, *Ind. Eng. Chem. Res.*, **52**, 5245 (2013).
- 25. N. Ibrahim, R. Refaie, and A. Ahmed, *J. Ind. Text.*, **40**, 65 (2010).
- 26. L. Ammayappan, J. J. Moses, K. A. Senthil, and J. K. Lam, *J. Nat. Fibers*, **8**, 272 (2011).
- 27. L. Ammayappan, J. J. Moses, K. A. Senthil, A. Raja, and L. K. Jimmy, *Text. Color. Finish.*, **23**, 1 (2011).
- D. K. Chattopadhyay and K. Raju, *Prog. Polym. Sci.*, **32**, 352 (2007).
- X. Jiang, J. Li, M. Ding, H. Tan, Q. Ling, Y. Zhong, and Q. Fu, *Eur. Polym. J.*, 43, 1838 (2007).
- H. Sardon, L. Irusta, M. J. Fernández-Berridi, M. Lansalot, and E. Bourgeat-Lami, *Polymer*, 51, 5051 (2010).
- Z. Dai, F. Shi, B. Zhang, M. Li, and Z. Zhang, *Appl. Surf. Sci.*, 257, 6980 (2011).
- 32. Z. Gao, J. Peng, T. Zhong, J. Sun, X. Wang, and C. Yue, *Carbohydr. Polym.*, **87**, 2068 (2012).
- J. Zhang, X. Y. Zhang, J. B. Dai, and W. H. Li, *Chin. Chem. Lett.*, **21**, 143 (2010).
- H. H. Wang and C. T. Gen, J. Appl. Polym. Sci., 84, 797 (2002).
- G. N. Chen and K. N. Chen, J. Appl. Polym. Sci., 63, 1609 (1997).
- 36. M. C. Delpech and F. M. Coutinho, Polym. Test., 19, 939

(2000).

- 37. S.-H. Son, H.-J. Lee, and J.-H. Kim, *Colloids Surf. A: Physicochem. Eng. Asp.*, **133**, 295 (1998).
- 38. G. A. Anderle, S. L. Lenhard, A. V. Lubnin, G. E. Snow, and K. Tamareselvy, *U.S. Patent*, 6576702 (2003).
- C. Fang, X. Zhou, Q. Yu, S. Liu, D. Guo, R. Yu, and J. Hu, Prog. Org. Coat., 77, 61 (2014).
- 40. S. A. Madbouly and J. U. Otaigbe, *Prog. Polym. Sci.*, **34**, 1283 (2009).
- 41. D. B. Otts and M. W. Urban, Polymer, 46, 2699 (2005).
- 42. P. Russo, D. Acierno, G. Marletta, and G. L. Destri, *Eur. Polym. J.*, **49**, 3155 (2013).
- S. Sharaf, A. Higazy, and A. Hebeish, *Int. J. Biol. Macromol.*, 59, 408 (2013).
- A. Martin, N. Tabary, L. Leclercq, J. Junthip, S. Degoutin, F. Aubert-Viard, F. Cazaux, J. Lyskawa, L. Janus, and M. Bria, *Carbohydr. Polym.*, 93, 718 (2013).
- K. M. Zia, S. Anjum, M. Zuber, M. Mujahid, and T. Jamil, *Int. J. Biol. Macromol.*, 66, 26 (2014).
- A. Anitha, S. Maya, N. Deepa, K. Chennazhi, S. Nair, H. Tamura, and R. Jayakumar, *Carbohydr. Polym.*, 83, 452 (2011).
- 47. Y. Xu, C. Huang, and X. Wang, *Carbohydr. Polym.*, **92**, 982 (2013).
- 48. F. Ferrero, C. Tonetti, and M. Periolatto, *Carbohydr. Polym.*, **110**, 367 (2014).
- 49. H. Gaffer, M. Gouda, and E. Abdel-Latif, *J. Ind. Text.*, **42**, 392 (2013).
- J. He, F. Wang, Y. Wu, Y. Huang, and H. Zhang, *Cellulose*, 18, 1651 (2011).
- D. Mihailović, Z. Šaponjić, M. Radoičić, T. Radetić, P. Jovančić, J. Nedeljković, and M. Radetić, *Carbohydr: Polym.*, **79**, 526 (2010).
- 52. E. Rouhollahi, S. Z. Moghadamtousi, M. Paydar, M.

Fadaeinasab, M. Zahedifard, M. Hajrezaie, O. A. A. Hamdi, C. Y. Looi, M. A. Abdulla, and K. Awang, *BMC Complementary and Alternative Medicine*, **15**, 1 (2015).

- O. A. K. Khalil, O. M. M. de Faria Oliveira, J. C. R. Vellosa, A. U. de Quadros, L. M. Dalposso, T. K. Karam, R. M. Mainardes, and N. M. Khalil, *Food Chem.*, 133, 1001 (2012).
- 54. T. Ak and İ. Gülçin, Chem. Biol. Interact., 174, 27 (2008).
- 55. P. Basnet and N. Skalko-Basnet, *Molecules*, **16**, 4567 (2011).
- G. Yakub, A. Toncheva, N. Manolova, I. Rashkov, D. Danchev, and V. Kussovski, *J. Appl. Polym. Sci.*, 133, 42940 (2016).
- N. Arshad, K. M. Zia, F. Jabeen, M. N. Anjum, N. Akram, and M. Zuber, *Int. J. Biol. Macromol.*, **111**, 485 (2018).
- F. Zia, K. M. Zia, M. Zuber, S. Rehman, S. Tabasum, and S. Sultana, *Int. J. Biol. Macromol.*, 92, 1074 (2016).
- C. Y. Bai, X. Y. Zhang, J. B. Dai, and C. Y. Zhang, *Prog. Org. Coat.*, **59**, 331 (2007).
- J. Y. Jang, Y. K. Jhon, I. W. Cheong, and J. H. Kim, *Colloids Surf. A: Physicochem. Eng. Asp.*, **196**, 135 (2002).
- K. K. Chereddy, R. Coco, P. B. Memvanga, B. Ucakar, A. des Rieux, G. Vandermeulen, and V. Préat, *J. Controlled Release*, **171**, 208 (2013).
- 62. M. M. Yallapu, M. Jaggi, and S. C. Chauhan, *Colloids and Surfaces B: Biointerfaces*, **79**, 113 (2010).
- P. Wang, W. Hu, and W. Su, Anal. Chim. Acta, 615, 54 (2008).
- 64. C.-C. Su, J.-S. Yang, S.-Y. Lin, H.-F. Lu, S.-S. Lin, Y.-H. Chang, W.-W. Huang, Y.-C. Li, S.-J. Chang, and J.-G. Chung, *In Vivo*, **22**, 63 (2008).
- 65. H. Souguir, F. Salaün, P. Douillet, I. Vroman, and S. Chatterjee, *Chem. Eng. J.*, **221**, 133 (2013).