

Synthesis and Characterization of Aqueous Chitosan-polyurethanes Dispersion for Textile Applications with Multipurpose Performance Profile

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Abstract: As the use of high performance textiles has grown, the need for chemical finishes to provide the fabric properties required in the special applications has grown accordingly. In this project, a series of water dispersible polyurethanes dispersion (CS-PU) with multipurpose performance profile was developed using isophorone diisocyanate (IPDI), polyethylene glycol (PEG), 2,2-dimethylol propionic acid (DMPA) and chitosan (CS) for textile applications. In two step synthesis process, NCO functional PU prepolymers prepared by reacting IPDI, PEG, and DMPA were extended with varying molar quantities of chitosan followed by structural characterization through FTIR. The prepared CS-PU dispersions were applied onto the dyed and printed poly-cotton blend fabrics. The performance behavior of the treated fabric in terms of crease recovery, tear strength, tensile strength, and antibacterial properties was evaluated by applying standard test methods. These investigations show that the CS-PU dispersions can be applied as antibacterial textile finishes with significant improvement in the physical and mechanical properties of poly-cotton fabrics.

Keywords: Chitosan, Polyurethanes, Crease recovery angle, Tear strength, Tensile strength, Antibacterial properties

Introduction

Chemical finishing of fibers and/or fabrics has always been an essential part of textile wet processing, but in recent years the demand of high tech textile products has amplified the interest and usage of chemical finishes. A number of chemical finishes are now being used to change textile materials into technical textiles with special properties [1]. Adaptable polyurethane dispersions as textile finishes have been developed which stand out for their performance profile. A chemical modification of cotton was achieved with shape memory polyurethanes through shape-memory finishing leading to high washing fastness and durable anti-creasing of the treated cotton has been reported [2]. To develop biocompatible as well as biodegradable polyurethanes for many industrial applications, chitin and starch have been integrated into PU structure [3-6]. Chemical modification of PU structure has also been achieved by incorporation of chitosan [7-9]. The chitosan based water born polyurethane (WPU) film membranes show better antimicrobial activity against *E. coli* than *Staphylococcus aureus* in comparison to pure WPUs [10]. Being a valuable antibacterial agent, chitosan has been extensively employed in antimicrobial finishing of cotton and many other textile finishes [11]. Antibacterial, wound healing and moisture retention properties of chitosan have made it a popular material to be used in finishing of textile materials. Chitosan application significantly improves the antibacterial activity, dye ability and soil release properties of cotton and incorporates substantial anti-static effect of polyester. The durable press and antibacterial

effects of chitosan crosslinked to cotton through hydroxyl groups using dimethylol, dihydroxy-ethylene urea (DMDHEU), citric acid, 1,2,3,4-butane tetra carboxylic acid (BTCA) and glutaric dialdehyde have also been documented [12,13]. Treatment of cotton fabrics with chitosan with good antibacterial properties, improved dye coverage of neps on fabric surfaces in cotton dyeing and application of chitosan in pigment printing as binder and thickener [11,14-16], contribution of chitosan in enzyme treatments of wool [17], as antibacterial mordant in eco-friendly cotton printing with natural dyes [18], as antibacterial finish as well as a mordant in wool printing with natural dyes [19] has also been reported in literature. Investigations of chitosan-grafted PET (C-PET) and quaternized-chitosan-grafted PET (QC-PET) prepared by grafting of poly(ethylene terephthalate) (PET) with chitosan and quaternized chitosan have revealed 75-86 % growth inhibition of microbes [20]. The antibacterial effect of chitosan has also been confirmed by many other researchers [21-26]. Innovative dressings for wounds have been prepared by chitosan coated alginate filaments [27]. Chitosan-based elastomeric polyurethane dispersions have also been synthesized and their characterization by FTIR, ¹HNMR, and ¹³C NMR spectroscopy and TGA has also been investigated and reported in literature [28]. Synthesis and surface modification of polyurethanes with chitosan for antibacterial properties [29], synthesis of waterborne PU extended with chitosan and application to acrylic fabrics as antibacterial finish [30] is also well documented.

The new finishes providing high values addition to textiles fabric are really treasured by much more demanding consumers markets. The textile industry is frequently endeavoring for innovative and eco-friendly finishes and finishing techniques

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to meet the customers' expectation for the improved qualities of products. For textile products in which requirement for soothe and security at work place dominates, alternative bio-based finishing materials and techniques are required to be pursued. Multifunctional finish is a contemporary and appealing term in wet processing of textile industry that makes it possible to achieve various functional properties in single finish application simultaneously claiming the labor, time, energy and money savings and increased production. The fabric materials are treated with particular chemical finishes to improve the functional properties like better wrinkle recovery with lesser loss of tensile and tear strength, less bending rigidity, superior whiteness retention and improved soil release features. The multifunctional, water borne chitosan based polyurethane dispersion, combining the ample beneficial properties of polyurethane and chitosan, could be potential solution to consumers' demand to achieve fabric strength, comfort as well as antimicrobial security in one finish. Keeping in view all these factors, a series of six aqueous chitosan based polyurethane dispersions was designed, synthesized, characterized, applied on poly-cotton blend fabrics and fabric performance was evaluated in terms of CRA, tear & tensile strength and antimicrobial properties following the standard test methods.

Experimental

Materials

All chemicals used in this project for synthesis of CS-PU were of analytical grade. Isophorone diisocyanate (IPDI) (100 %), polyethylene glycol (PEG) (M=6000), dimethylol propionic acid (DMP), triethyl amine (TEA), chitosan (M=50,000), dimethyl sulfoxide (DMSO) and tributyltin dilaurate (DBTDL) catalyst (95 %) were procured from Sigma Aldrich Chemicals Co, USA. Methyl ethyl ketone (MEK) and 1,4-butanediol (BDO) were purchased from Merck Chemicals (Darmstadt, Germany). Before use, PEG and DMPA were dried at 60 °C for 4 hours in oven to avoid the interference of water vapors and air with isocyanate reaction. BDO was also dried at 60 °C for 2 hours. Anhydrous CaSO₄ was used for drying of MEK. Other chemicals used in this project were used as received.

Table 1. Specification of poly-cotton fabrics

Fabrics	Blend ratio P:C	Quality	Fabric construction EPI ^a ×PPI ^b /Count (warp:weft)	GSM (g/m ²)
Dyed	48:52	1×1 plain weave	127×59/30:30	132
Printed	55:45	1×1 plain weave	82×51/30:30	106

EPI^a: ends per inch; it is the number of warp threads per inch of woven fabric and PPI^b: picks per inch; it is the number of weft threads per inch of woven fabric.

Polyester-Cotton (P/C) Fabric Substrates

Mill desized and scoured, 1×1 plain weaved dyed (127×59/30:30) and printed (82×51/30:30) poly cotton fabrics (48/52 and 55/45 polyester cotton blend ratio respectively) were generously provided by Sadaqat Textile Mills Ltd., Khurrianwala, Faisalabad, Pakistan. Fabric specifications are presented in Table 1. Before applying the CS-PU dispersion, the poly-cotton fabrics were washed with detergent in laboratory at 100 °C for 30 minutes followed by sequential rinsing with hot and cold water. The washed fabrics were air dried at ambient temperature.

Synthesis of Chitosan Based Polyurethane Dispersions (CS-PU)

Water dispersible chitosan based polyurethanes were made by conventional two-step process to prepare the CS-PU dispersions [30,31]. In synthesis of CS-PU, DMPA was incorporated into PU chains which act as internal emulsifier to prepare stable dispersions. Mole ratios of IPDI, PEG and DMPA (3:1:1) were kept constant throughout the synthesis, but chain extension of pre-PU was carried out by reacting different molar quantities of chitosan and BDO (CS+BDO=1 mole). The detailed synthetic procedure was as follows:

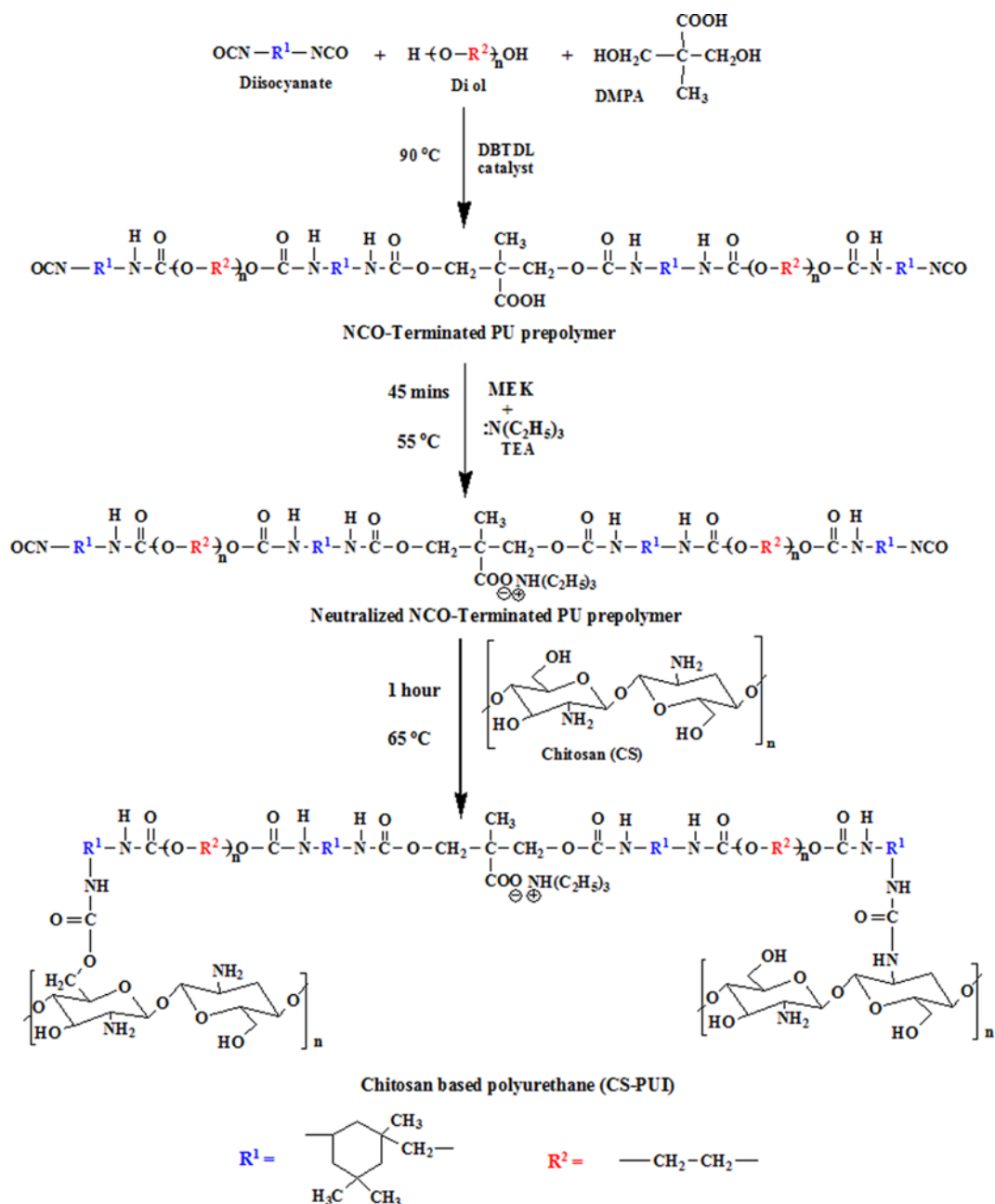
For synthesis of -NCO functional PU prepolymer, PEG (1 mol) and DMPA (1 mol) were charged into a four necked round bottomed glass flask equipped with reflux water condenser, mechanical stirrer, dropping funnel and nitrogen (N₂) inlet/outlet, fitted in heating oil bath along with thermometer. The reaction flask was heated at 60 °C in nitrogen environment till melting of PEG and DMPA and then IPDI (3 mol) was dropwise poured into the reaction with constant stirring. Few drops of DBTDL catalyst were also transferred into reaction medium and polymerization was carried out for 2 hours at 80 °C to get NCO-terminated hydrophilic PU prepolymer. A suitable volume of methyl ethyl ketone (MEK) was added to reduce the viscosity of the prepolymer and the temperature of diluted prepolymer was reduced to 55 °C. Then TEA (1.1 mole) was added to neutralize the carboxylic groups (-COOH) present in DMPA and reaction mixture was continuously stirred for 45 minutes maintaining the temperature at 55 °C. Neutralization of PU prepolymer was followed by chain extension step. At this stage, temperature was increased to 65-70 °C and chain extender (chitosan powder dissolved in suitable volume of DMSO and BDO) was slowly dropped into prepolymer with vigorous stirring to avoid the gel formation. Chain extension step was performed for 4-8 hours till completion of reaction. Then at final stage, calculated volume of distilled water was poured into CS extended PU polymer and was continuously stirred for another 30 minutes at 35 °C for the formation of uniform dispersion. Following this procedure, a series of CS-PU dispersions was synthesized by varying the molar quantities of chitosan and BDO.

Sample code designations, molar quantities of chitosan

Table 2. Sample code designations, molar quantities of chitosan used for chain extension and physical properties of CS-PU dispersions

Sample code	CS (moles)	BDO (moles)	Dispersion stability	Dispersion appearance	Solid contents (%)
CS-PU ₁	0.05	0.95	≅ 8 months	Translucent White	26.31
CS-PU ₂	0.1	0.9	≅ 8 months	Translucent White	26.34
CS-PU ₃	0.2	0.8	≅ 8 months	Translucent White	26.42
CS-PU ₄	0.3	0.7	≅ 8 months	Translucent White	26.50
CS-PU ₅	0.5	0.5	≅ 7 months	Translucent slightly yellow	26.65
CS-PU ₆	0.0	1.0	≅ 10 months	Transparent White	26.30

CS: chitosan, BDO: 1-4, butane diol, and CS-PU: chitosan-polyurethane.

**Figure 1.** Synthesis of CS-PU dispersion with varying chitosan content.

and BDO used for chain extension and physical properties of CS-PU dispersions are presented in Table 2 and summary of sequential steps of synthesis are shown in Figure 1.

Molecular Characterization

Fourier transform infrared (FTIR) spectroscopy was used for molecular characterization of the monomers, prepolymer and final CS-PU to confirm the proposed structure. FTIR measurements were executed in the transmission mode on Shimadzu Fourier Transform Infra-red (FT-IR) spectrophotometer.

Application of CS-PU Dispersions on Poly-cotton Blend Fabrics

The 10 % and 20 % solutions of CS-PU dispersions were applied to the dyed and printed P/C fabrics by pad-dry-cure method. After finishing of fabric samples with CS-PU dispersions in a padder, drying and curing was carried out at 80 °C for 3 minutes and at 140 °C for 5 minutes successively. The samples were washed after curing before carrying out the further analysis. The color of the treated and untreated dyed fabrics was slightly changed as checked using the DATACOLOR, Spectra-Flash 600; however there is no change in the treated and untreated printed fabrics due to pigmentation process. The CS-PU coated fabrics has shown very non-significant changes in shades after washing than the untreated/uncoated fabrics due to formation of CS-PU network on the surface of the fabrics.

Performance Evaluation of Finished Fabric Samples

Since fabrics are exposed to bending, twisting, stretching, shearing as well as compression in routine use, it is essential to evaluate the fabric for expected lowest level of strength and comfort properties of fabric. Similarly, Clothing and textile materials are not only the carriers of microorganisms such as pathogenic bacteria, odor generating bacteria, mold and fungi, but also good media for the growth of the microorganisms. Antimicrobial finishing of textiles is effective to control microorganisms, to reduce the odor produced by sweating, to reduce the risk of cross infections in hospitals, to control the risk of spread and infections following the injuries and to control the corrosion of natural fiber based fabrics' surfaces by mildew [32].

Crease recovery angle, tear strength, tensile strength and antibacterial properties of dyed and printed poly-cotton blend fabrics finished with CS-PU dispersions were investigated using standard test methods. All samples were conditioned in standard atmospheric conditions before testing.

Crease Recovery Angle (CRA)

Crease recovery angle values in warp & weft directions of finished and unfinished dyed & printed fabric samples were measured on lab scale crease recovery tester following ASTM D 1295 standard method [33].

Tear Strength

Tear strength of treated and untreated P/C fabric samples was evaluated by standard ASTM D1424/ISO 13937-1 method [34].

Tensile Strength

Tensile strength of treated and untreated P/C fabric samples was evaluated by standard ISO 13934-1 method [35].

Antimicrobial Activity

The antibacterial activity of prepared CS-PU dispersions was evaluated by agar diffusion method [36]. Pathogenic bacterial strains used for the evaluation of antibacterial activity of treated and untreated fabric samples were *Staphylococcus aureus* (gram positive bacteria) and *Escherichia coli* (gram negative bacteria) and inhibition zone formed around the treated and untreated fabric samples were measured in millimeters (mm).

Physical Properties

Dispersion appearance, stability and solid contents were examined according to standard procedures and are presented in Table 2.

Results and Discussion

Molecular Characterization by Fourier Transform Infrared (FT-IR) Spectroscopy

FTIR spectra of the monomeric polyethylene glycol diol (PEG), DMPA, isophorone diisocyanate (IPDI), PU prepolymer with NCO terminals, chitosan chain extender and final chitosan based polyurethane product (CS-PU₅) are shown in Figure 2. FTIR spectra of six CS-PU₅ are collectively displayed in Figure 3.

An important broad peak in FTIR spectrum of PEG (Figure 2(a)) at 3433.29 cm⁻¹ is assigned to stretching vibrations of -OH group of macro diol. A main characteristic intense peak corresponding to stretching vibrations of ether C-O-C group in PEG molecules appears at 1101.35 cm⁻¹. Other prominent peaks in spectrum of PEG are designated as: 2861.55 cm⁻¹ (symmetric C-H stretching vibrations of -CH₂); and 1463.97 cm⁻¹ (combined band of C-H and O-H bending vibration).

A narrow peak at 3560.59 cm⁻¹ in spectrum of DMPA (Figure 2(b)) is assignable to O-H stretching vibration of CH₂OH groups, an intense band at 3361.93 cm⁻¹ is assigned to O-H stretching vibrations of carboxylic acid (COOH) functional group present in structure of DMPA molecule. A broad band at 2588.47 cm⁻¹ is assigned to O-H stretchings of hydrogen bonded -OH group. A C=O stretching peak of COOH is present at 1691.57 cm⁻¹. Other significant bands are; 1460.11 cm⁻¹ (C-H bending vibrations of CH₂), 1037.70 cm⁻¹ (C-O stretchings of primary alcohol) and peaks at 1139.93 cm⁻¹ and 1305.81 cm⁻¹ are assignable to alcoholic and carboxylic C-O stretching vibrations [37].

The FTIR spectrum of IPDI (Figure 2(c)) presented a very

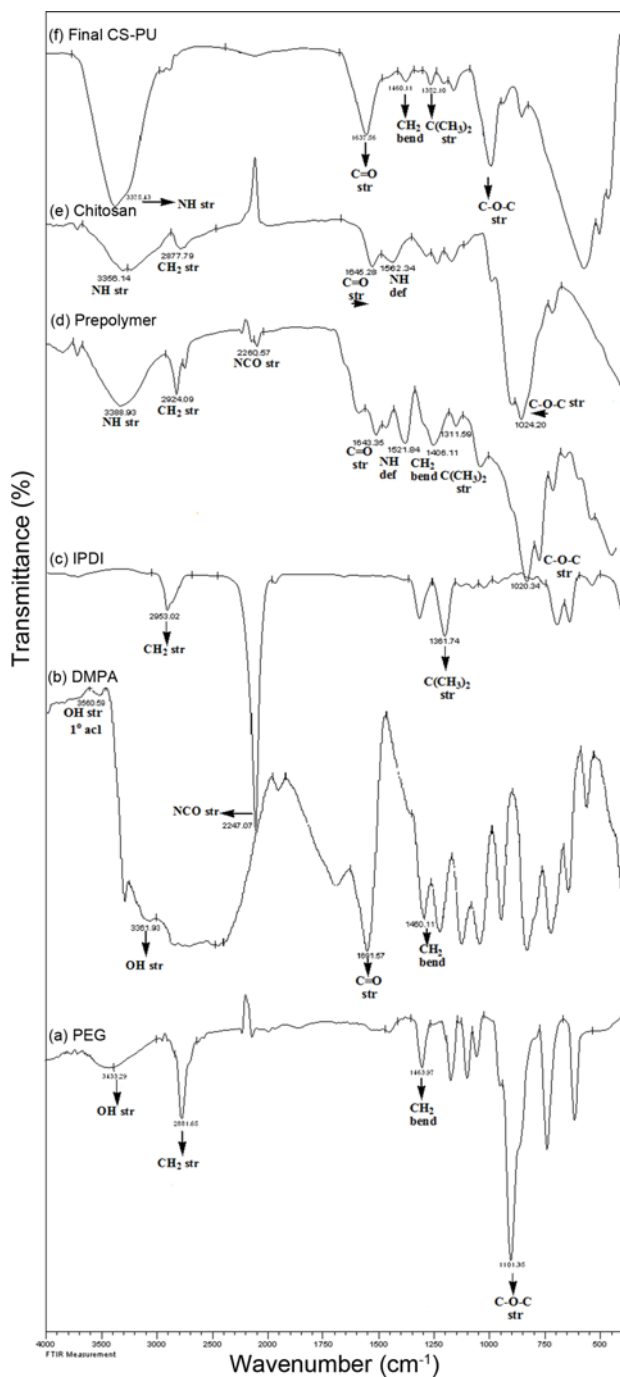


Figure 2. FTIR spectra of (a) polyethylene glycol (PEG), (b) dimethylol propionic acid (DMPA), (c) isophorone diisocyanate (IPDI), (d) PU prepolymer, (e) chitosan (CS), and (f) final chitosan based polyurethane (CS-PU).

sharp and strong peak at 2247.08 cm^{-1} that can be assigned to -N=C=O stretching vibrations of isocyanate group of IPDI [38]. Assignment of other peaks displayed in IPDI spectrum is: 2953.02 cm^{-1} corresponding to C-H asymmetric stretching vibrations of CH_3 group, 1463.96 cm^{-1} arising

from C-H bending vibrations and a strong peak at 1361.74 cm^{-1} is attributed to C-C stretchings of the $\text{-C(CH}_3)_2$ group present in isophorone diisocyanate structure.

The FTIR spectrum of PU prepolymer with -NCO terminals (Figure 2(d)) displayed a noticeable emergent peak at 3327.21 cm^{-1} which is designated as NH stretching band [39]. This peak is evidence of formation of urethane bond in prepolymer by reaction of PEG, DMPA and IPDI. An important peak in spectrum of PUI prepolymer at 2262.50 cm^{-1} is allocated to -NCO (isocyanate) group. The presence of -NCO peak at 2262.50 cm^{-1} confirms that this intermediate species is -NCO terminated pre-PU. Intensity of this peak is appreciably less than the -NCO stretching peak at 2247.08 cm^{-1} in spectrum of IPDI (Figure 2(c)) because of its reaction with hydroxyl (-OH) group of polyol [40]. Disappearance of a stretching bands of -OH group of PEG and DMPA at 3433.29 cm^{-1} and 3560.59 cm^{-1} respectively, decrease in intensity of absorption peak at 2262.50 cm^{-1} attributed to -NCO stretching vibrations of IPDI and appearance of a peak in spectrum of prepolymer at 3327.21 cm^{-1} depicting -NH stretching vibrations of urethane bond are strongly supporting evidences for the completion of prepolymer formation step presented in Figure 1. A prominent peak at 1643.36 cm^{-1} because of C=O stretchings of urethane linkage (-NHCOO-) also confirmed the formation of urethane bond between diols and diisocyanate monomers. A C-H asymmetric stretchings band and C-H bending vibrational band are visible at 2924.09 cm^{-1} and 1406.11 cm^{-1} . Another small band present at 1311.59 cm^{-1} corresponds to $\text{-C(CH}_3)_2$ group of IPDI. A C-O stretching band at 1020.34 cm^{-1} is also present in spectrum of PU prepolymer.

At next step, extension of PUI prepolymer chain having -NCO terminals was achieved by reacting with chitosan following the established and well documented procedure [30].

A number of common peaks allocated to functional groups of chitosan are exhibited in FTIR spectrum of chitosan (Figure 2(e)). The FT-IR spectrum of chitosan displayed a noticeable broad peak at 3356.15 cm^{-1} that can be assigned to combined N-H stretching vibrations of -NH_2 group and O-H stretchings of hydroxyl group. A small band of free O-H stretchings is also visible above 3600 cm^{-1} in spectrum of chitosan that is attributed to hydroxyl (O-H) group present as CH_2OH group. Another band at 1562.34 cm^{-1} is due NH deformations that manifests the presence of hydrogen bonded amino group in structure of chitosan. A characteristic absorption peak of chitosan, at 1315.45 cm^{-1} was assigned to C-N stretchings of amine I & amine II C-N bond [41-43]. The others peaks which are shown in spectrum are allocated as: a characteristic band of C-H symmetric stretching vibrations of CH_2 group at 2877.79 cm^{-1} , C=O stretchings of amide (-NHCOCH_3) at 1645.3 cm^{-1} , another band at 1375 cm^{-1} corresponding to -CH symmetrical deformation mode, and ring and bridge C-O-C stretching vibrations of chitosan

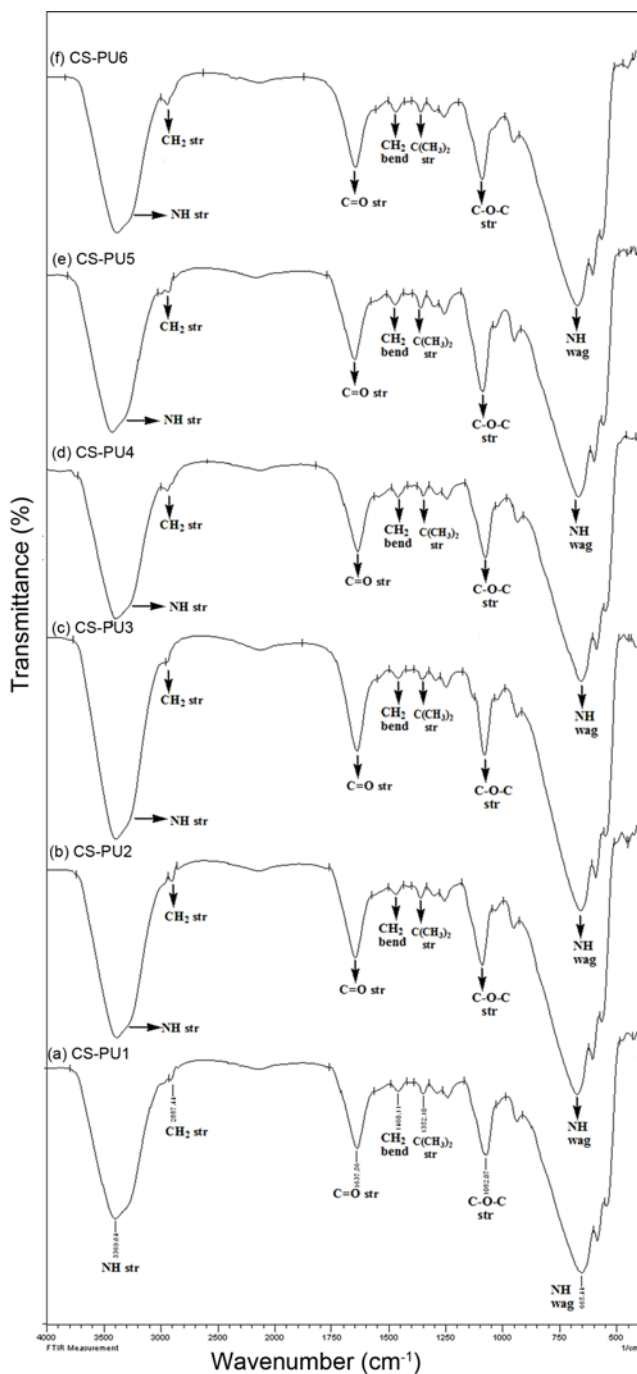


Figure 3. FTIR spectra of (a) CS-PU1, (b) CS-PU2, (c) CS-PU3, (d) CS-PU4, (e) CS-PU5, and (f) CS-PU6.

appear at 1024.20 cm^{-1} [44-46]. The intensity of absorption band at 1024.20 cm^{-1} due to stretching vibrations C-O-C group in chitosan is much less than the C-O-C band of PEG. A noticeable peak corresponding to the saccharide structure is also shown approximately at 894.97 cm^{-1} in FTIR spectrum of chitosan [43].

The FTIR spectrum of final CS-PU after extension of

-NCO capped PU prepolymer with chitosan is shown in Figure 2(f). The FTIR is widely used to study the synthesis process of pre-PU and final polyurethane by monitoring the attenuation of -NCO band at $2200\text{--}2300\text{ cm}^{-1}$. As shown in Figure 2(f), the disappearance of -NCO band at 2260.57 cm^{-1} after chain extension reaction can be attributed to the additional polymerization that consumed all the -NCO groups of pre-PU to form the final CS-PU. Simultaneous increase in the strength of the peaks at 3375.43 cm^{-1} designated as -NH stretching vibrations and at 1637.56 cm^{-1} ascribed to the C=O stretching vibrations of urethane linkage indicates the formation of CS-PU [47]. The bands at 1460.11 cm^{-1} , 1352.10 cm^{-1} and 1082.07 cm^{-1} are attributed to CH₂ bending, stretching vibrations of -C(CH₃)₂ group present in IPDI and C-O-C stretching vibrations.

In FTIR spectra of six CS-PU (Figure 3) stretching vibrational bands attributed to -NH group are present in the range of 3375.43 cm^{-1} to 3367.71 cm^{-1} . The symmetric and asymmetric stretching peaks of C-H bond of -CH₂- group are present in the range of $2887.44\text{--}2969.01\text{ cm}^{-1}$. No peak is present in the range of $2200\text{--}2300\text{ cm}^{-1}$ indicating the complete utilization of -NCO group of pre-PU in chain extension step of polymerization reaction. Clear band present around $1639.49\text{--}1637.56\text{ cm}^{-1}$ corresponding to stretching vibrations of -C=O (carbonyl) bond of urethane (-NHCOO-) group is also present in all spectra. Relating to the characteristic C=O stretching and N-H stretching peaks, the formation of -NHCOO- (urethane) group was confirmed in final product [48]. Absorption peaks around $1462.04\text{--}1458.18\text{ cm}^{-1}$ correspond to -CH₂ bending vibrations. The band in the range of 1354.03 cm^{-1} to 1352.10 cm^{-1} indicates the C-C stretchings of -C(CH₃)₂ group in IPDI. Spectral data of all the Cs-PU shows absorption at 1082.07 cm^{-1} that verifies the symmetric stretchings of C-O-C and N-COO groups in the final polymer product (CS-PU).

Crease Recovery Angle (CRA)

Creases or wrinkles mean undesirable random residual distortive bends that arise during use and impart unpleasant appearance to fabric. Bending and folding of all apparels occurs during wear and laundry [49,50]. Cellulosic chains in cotton fibers are held together by inter-chain hydrogen bonding between cellulosic hydroxyl groups in crystalline regions of fibers where cellulose molecules are closely packed. Under sufficient stress applied on fibers, slippage of cellulosic chains occurs leading to breaking of old hydrogen bonds and formation of new hydrogen bonds at new places which causes wrinkling of fabrics.

Crease recovery angles of dyed and printed poly-cotton fabric samples before and after finishing with CS-PU were measured and are presented in Table 3. The results show a gradual increase in the CRA values for finished dyed and printed poly-cotton fabric samples with the increase in chitosan content in dispersions when compared with untreated

samples. CRA values are even higher for samples treated with 20 % solution of PUA finishes as compared to the samples treated with 10 % solution of PUA dispersions. Maximum increase in CRA for dyed and printed poly-cotton fabric is achieved through treatment with PUA₅. CRA value of fabric sample finished with PUA₁ is slightly higher than fabric treated with PUA₆ (control). The CS-PU bonding to fibers of poly-cotton substrate through intermolecular dipole-dipole attractions, van der waals forces and hydrogen bonding [51] and formation of two dimensional network structure through hydrogen bonding and occasional ether bridging of chitosan [52,53] has improved the crease recovery angle of the finished poly-cotton substrate fabrics. Increase in chitosan content increase formation of two dimensional network structure and gluing effect of CS-PU also keeps the fiber held together and reduces the crease formation by preventing the slippage of fibers under applied stress. It can be concluded that CRA is increased with increasing the concentration of chitosan in to the final polyurethane. The application of CS-PU dispersion onto the fabrics results in cross-linking onto the surface of the fabrics. This network structure require maximum amount of energy to break these bonds. These bonds keep the cellulose

molecules in to their respective position. Thus it resists the breakage and slippage of the cellulose molecules. It results in increase in the crease recovery angle.

Tear Strength

Tearing strength is a very vital characteristic of a finished textile material as it provides a rational assessment of fabric serviceability and a fabric is considered an inferior material if its tear strength is low. Tear strength is described as the progressive rupture of the fabric in terms of sequential yarn breakage, thread by thread or in groups, along a line through the textile material [54,55]. Under tensile load, the applied load is shared by all yarns aligned in the direction of applied load whereas in case of tearing load, stress is shared by only one, two or few yarns [54]. Important factor that affect the tear strength of fabric include fiber, geometry yarn and fabric geometry, fiber relaxation and intra-fiber frictional characteristics in combination with the nature of fabric's mechanical and chemical finishing treatments. In tightly constructed fabrics, the fibers have restricted movement and hence low tear strength. On the other hand, in loosely constructed fabrics the fibers can easily move and cluster together, so fabric will have high tear strength [54]. The use

Table 3. Properties of poly-cotton fabric samples before and after treatment with CS-PU

Test performed	Sample code	Dyed fabric				Printed fabric			
		10 %		20 %		10 %		20 %	
		Warp ^a	Weft ^a	Warp ^a	Weft ^a	Warp ^a	Weft ^a	Warp ^a	Weft ^a
Crease recovery angle (degree)	PUA ₁	105±0.09	94±0.08	106±0.07	95±0.08	121±0.06	110±0.04	123±0.08	111±0.04
	PUA ₂	107±0.06	96±0.07	108±0.07	97±0.08	123±0.04	111±0.05	125±0.05	112±0.03
	PUA ₃	110±0.06	98±0.10	111±0.08	99±0.05	127±0.04	113±0.05	128±0.06	115±0.07
	PUA ₄	112±0.08	100±0.04	114±0.05	102±0.06	129±0.06	116±0.05	132±0.03	117±0.03
	PUA ₅	116±0.05	104±0.06	118±0.07	106±0.09	133±0.8	119±0.07	136±0.08	122±0.05
	PUA ₆	104±0.08	93±0.08	105±0.09	94±0.07	119±0.05	108±0.08	121±0.04	110±0.05
	UF	100±0.07	90±0.08			116±0.04	105±0.02		
Tear strength (N)	PUA ₁	7.71±0.04	3.94±0.03	7.46±0.04	3.70±0.06	14.88±0.05	8.65±0.02	14.47±0.04	8.26±0.03
	PUA ₂	7.57±0.04	3.81±0.03	7.33±0.01	3.61±0.02	14.69±0.02	8.40±0.04	14.24±0.05	8.05±0.02
	PUA ₃	7.44±0.01	3.67±0.04	7.20±0.01	3.47±0.04	14.49±0.03	8.26±0.04	14.07±0.05	7.86±0.02
	PUA ₄	7.28±0.03	3.53±0.02	7.06±0.02	3.34±0.04	14.17±0.04	7.96±0.06	13.78±0.02	7.58±0.03
	PUA ₅	7.03±0.01	3.30±0.03	6.81±0.03	3.10±0.03	13.72±0.04	7.52±0.03	13.33±0.04	7.17±0.03
	PUA ₆	7.98±0.05	4.05±0.01	7.81±0.02	3.86±0.04	15.52±0.05	9.26±0.06	15.04±0.06	8.80±0.04
	UF	8.24±0.03	4.31±0.03			16.08±0.07	9.81±0.05		
Tensile strength (N)	PUA ₁	704.53±0.08	371.73±0.06	720.40±0.04	378.81±0.05	654.46±0.08	412.42±0.07	661.50±0.08	415.94±0.04
	PUA ₂	713.01±0.06	374.11±0.06	724.82±0.07	380.02±0.05	657.61±0.08	416.56±0.07	664.42±0.07	420.03±0.07
	PUA ₃	721.58±0.03	378.99±0.04	731.12±0.07	385.72±0.05	667.75±0.07	420.70±0.06	671.87±0.06	423.40±0.08
	PUA ₄	730.09±0.05	382.98±0.08	746.81±0.05	391.42±0.03	679.11±0.09	426.85±0.09	683.87±0.05	429.79±0.07
	PUA ₅	754.46±0.03	397.18±0.04	767.54±0.04	403.09±0.04	691.61±0.07	437.03±0.08	701.41±0.09	441.30±0.08
	PUA ₆	702.82±0.06	370.02±0.03	709.14±0.04	372.18±0.03	651.36±0.09	410.51±0.10	658.08±0.09	413.21±0.09
	UF*	694.31±0.06	364.76±0.06			644.00±0.10	405.68±0.08		

^aEach value is expressed as mean±standard error (S.E.) (n=5) and UF* =untreated fabric.

of urethane prepolymers and diisocyanates for durable press finishing of cotton, polyester and poly-cotton blends had shown that blends demonstrated improved dimensional stability and rigidity owing to cross linking hydrogen bonding [56].

To evaluate the outcome of CS-PU treatment on dyed and printed poly-cotton fabric strength, tear strength of unfinished and finished fabric samples was determined and the results are presented in Table 3. Results show that the tearing strength of the dyed as well as printed poly-cotton fabric specimens treated with PUAs has decreases with increase in chitosan content in the dispersions. Control PUA₆ dispersion when applied to dyed and printed poly-cotton fabrics in 10 % and 20 % solution, tear strength of poly-cotton fabrics was decreased. Dyed fabric showed 3.2 % warp-ways and 6.0 % weft-ways decrease in tear strength with 10 % PUA₆ and 5.2 % warp-ways and 10.4 % weft-ways decrease in tear strength with 20 % PUA₆ dispersion application respectively. In case of printed fabric sample, 10 % PUA₆ has decreased 3.5 % warp-ways and 5.6 % weft-ways tear strength, 20 % solution of PUA₆ dispersion has decreased 6.5% warp-ways and 10.3 % weft-ways tear strength in comparison to unfinished fabric. Tear strength showed inverse relation with chitosan concentration in finishes. Increase in chitosan quantity in the PU dispersions resulted in the decreased tear strength of treated fabrics pieces. Tear strength (warp+weft) values of the dyed fabric samples finished with 10 % PUA₁, PUA₂, PUA₃, PUA₄ and PUA₅ solutions are 11.65, 11.38 and 11.11, 10.81 and 10.33 N respectively i.e.; 7.2 %, 9.3 %, 11.5 %, 13.9 % and 17.7 % less than the unfinished dyed poly-cotton fabric. Printed poly-cotton fabric pieces treated with 10 % PUA₁, PUA₂, PUA₃, PUA₄ and PUA₅ dispersion solutions displayed 25.53, 23.09, 22.75, 22.13 and 21.24 N tear strength i.e.; 9.1 %, 10.8 %, 12.1 %, 14.5 % and 17.9 % less than the unfinished printed fabric. Tear strength of all the dyed and printed fabric pieces was further decreased with 20 % solution application of all the PUA dispersions with 21.0 % and 20.8 % maximum decrease in tear strength in case of PUA₅ dispersion application.

Highly polar polyurethane chains of CS-PU dispersions bond to fibers of poly-cotton textile material through hydrogen bonding, intermolecular dipole-dipole attractions and van der waals forces [53] that causes the substrate to stiffen with restricted movement of fibers. A negative aspect regarding increased stiffness is the corresponding loss of tear strength reason being the immobilization of the fibers so that these cannot slide freely under tearing loads. In contrast yarns that are mobile enough to slide freely under pressure will group up, such as in flexible and elastic fabrics, and these grouped fibers can better tolerate the applied load resulting in better tear strength. In stiffer fabrics, each fiber beside the tear line independently tolerates the whole impact of the tearing force, therefore, it requires less force to start and propagate the tear [54,57]. Increase in chitosan con-

centration leads to more bonding of finish molecules with the fibers adding to the restricted fiber movements under stress. The restricted movements of the fibers under tearing load results in low tear strength of treated fabrics.

Tensile Strength

Tensile strength is the ability of a material to endure the stretching pressures intending to elongate that material. In short, the tensile strength tends to resist the applied tension (being pulled apart) and is measured in terms of maximum load borne by material, under stretching load applied to pull it apart, before breaking. In case of textile substrates, it is the strength displayed by a natural or synthetic fiber, yarn or fabric to withstand breaking under stretching pressure. Numerically, it is newton (or pound) force of resistance shown by fabric before breaking on tensile testing machine. Under tensile load, the applied load is shared by all yarns aligned in the direction of applied load [54].

Tensile strength of the untreated and treated, dyed and printed poly-cotton fabrics was evaluated by BS EN ISO 13934-1 standard test method and results are presented in Table 3. Application of CS-PU(PUA) finishes, comparing with untreated fabric, has increased the tensile strength of both the treated dyed and printed fabric samples. Tensile strength (warp+weft) of the dyed fabrics treated with 10 % PUA₆ dispersion was 1.23 % warp-ways and 1.44 % weft-ways higher than untreated dyed fabric. Similarly, tensile strength of dyed fabric was 2.14 % and 2.03 % respectively improved with 20 % solution of PUA₆ dispersion. Tensile strength (warp+weft) of dyed poly-cotton fabric pieces treated with 10 % solution of PUA₁, PUA₂, PUA₃, PUA₄ and PUA₅ is 1.62 %, 2.65 %, 3.92 %, 5.10 % and 8.74 % respectively better than untreated fabric; and 0.32 %, 1.33 %, 2.58 %, 3.75 % and 7.34 % respectively better than poly-cotton fabric treated with control (PUA₆) finish. At 20 % finish application, tensile strength (warp+weft) of dyed fabric samples is 3.79 %, 4.32 %, 5.45 %, 7.47 % and 10.53 % better than untreated sample. Whereas dyed poly-cotton fabric pieces treated with 20 % solution of PUA₁, PUA₂, PUA₃, PUA₄ and PUA₅ have displayed 1.65 %, 2.18 %, 3.28 %, 5.26 % and 8.25 % respectively better strength to tensile load than poly-cotton fabric treated with control (PUA₆) finish. Comparing poly-cotton samples treated with 10 % and 20 % dispersion solutions, the samples treated with 20 % solutions of each dispersion have shown better tensile strength values.

On printed poly-cotton fabric strips, all the PUAs have also shown improved tensile strength than untreated printed poly-cotton fabric. Tensile strength (warp+weft) of the printed fabrics treated with 10 % PUA₆ dispersion was 1.14 % warp-ways and 1.19 % weft-ways higher than untreated dyed fabric. Similarly, tensile strength of dyed fabric was 2.19 % and 1.86 % respectively improved with 20 % solution of PUA₆ dispersion. At 10 % applied concentration, PUA₁,

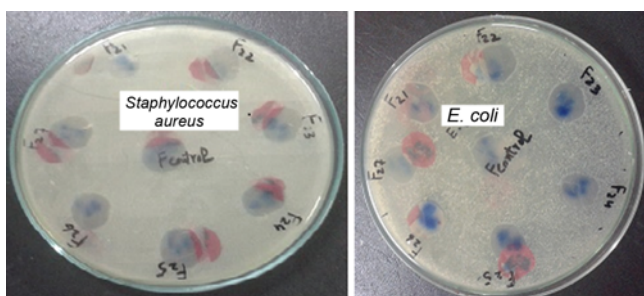


Figure 4. Photographs showing antibacterial evaluation of dyed and printed poly-cotton fabric samples treated with CS-PU by disc diffusion method.

negative) type bacteria offered by self-stratifying antimicrobial polyurethane coatings has been reported by researchers [65]. Untreated dyed and printed poly-cotton fabrics showed no antimicrobial activity. All the dyed and printed fabrics treated with polyurethane dispersions synthesized from IPDI, PEG, and extended with different molar quantities of chitosan (CS-PU) have shown antimicrobial activity and effectiveness of dispersion against both strains of bacteria was enhanced with the increasing concentration of chitosan. It is worth to mention that the chitosan is bio-macromolecules and amino functionality on C-2 position of chitosan is responsible for biocompatibility. On the other hand polyurethane itself is biocompatible material due to presence of carbamate linkages (R-NHCO-OR') in the PU structure. This carbamate linkages is very similar to peptide linkages (-CO-NH-) present in protein, analogues to this polyurethane show biocompatible character and hence show antibacterial property. It can be observed that the antibacterial activity is shown by both dyed and printed fabrics treated with 10 % CS-PU dispersions and 20 % CS-PU dispersions. No bacterial growth was observed above, under and in close vicinity of the treated poly-cotton fabric pieces. This is in accordance with our claim that PUAs are non-leaching antibacterial materials and antimicrobial mechanism of PUAs is contact killing.

Antibacterial activity is even better in fabrics treated with CS-PU dispersions containing 0.4 and 0.5 molar chitosan which can be explained in terms of increased number of $-NH_2$ groups with increased amount of chitosan. Comparing the dyed and printed treated fabric samples, the inhibition activity is similar. It can be hypothesized that the amino groups of polycationic chitosan on the surfaces attract the negatively charged microbial cells, disrupt the integrity of the cell membrane leading to cell rupture causing leakage of intracellular electrolytes like potassium ions (K^+) and other low-molecular weight proteinaceous constituents like nucleic acids, proteins, glucose and lactate dehydrogenase enzymes [66-70] and through complexation between amino ($-NH_2$) groups in chitosan molecules and trace metal ions essential

for bacterial growth present outside the bacterial cells [71]. Since the surfaces of poly-cotton fabrics treated with chitosan based CS-PU dispersions containing $\frac{3}{4}NH_2$ groups were found lethal on contact to both gram-positive and Gram-negative bacteria, it can be claimed that these CS-PU dispersions can be applied with an aim to guard the skin of wearer and the textile fabric surface itself from the attack and growth of pathogenic bacteria.

Conclusion

Keeping in view the demand for multifunctional finishing of textiles to achieve various functional properties in single finish application, these chitosan based polyurethane dispersions were designed for textile finishing to improve the antibacterial property and crease recovery of fabrics in one bath without compromising the fabric strength. For this purpose, isophorone diisocyanate (IPDI) and polyethylene glycol (PEG) based PU prepolymers, synthesized through bulk polymerization process, were extended with different molar quantities of chitosan (molecular weight: 50,000) and aqueous dispersions were prepared by addition of calculated volume of water. The Fourier Transform Infrared (FT-IR) spectroscopy was used for molecular characterization of the monomers, prepolymers and final CS-PU. The dyed and printed, plain weave polyester-cotton blend fabrics were finished with 10 % and 20 % solutions of all these CS-PU dispersions by pad-dry-cure method followed by the evaluation of CRA, tear strength, tensile strength and antibacterial properties of these finished poly-cotton fabrics by standard test procedures. The results revealed that chitosan based polyurethane dispersions improve the crease recovery of the blend fabrics with the simultaneous increase in the tensile strength of the fabrics. However, tear strength of the fabrics was decreased which can be explained on the basis of increased crosslinking of polyurethane chains with the fibers through hydrogen bonding which stiffens the fabrics thus reducing the fiber mobility and ultimately strength under tearing load. These improved properties can be interpreted on the basis of better penetration of finish into the inert-fiber spaces thus covering the protruding fibers with sufficient inter-fiber crosslinks for better crease recovery and fabric strength. Tensile strength also depends upon inter-chain cross-linking which increases with increase in the chitosan content in CS-PU dispersions and hence better tensile strength is incorporated to the poly-cotton fabrics. It was observed that all the chitosan based polyurethane dispersion are contact active antibacterial materials and all dispersion offer good and lasting protection from pathogenic bacteria. On the basis of the results obtained in these investigations, it can be claimed that chitosan based polyurethane dispersions can be prepared and applied for multifunctional finishing of textile materials along with antibacterial properties.

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