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Synthesis, characterization and efficiency evaluation of chitosan-polyurethane based textile finishes

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ABSTRACT

A series of polyurethane dispersions were synthesized through two step polymerization technique. A PU prepolymer with NCO termini was prepared using isophorone diisocyanate (IPDI), poly caprolactone diols (CAPA of mol. wt. 1000) and DMPA (3:1:1), and PU prepolymer chain was extended with different mole ratios of low molecular weight chitosan and finally aqueous emulsion was prepared by adding suitable volume of water. The proposed structure of chitosan based PU dispersions was confirmed through FTIR spectroscopy. The prepared aqueous $CS_{(LMW)}$-CPUIs emulsions were applied onto the different quality plain weave poly-cotton dyed and printed fabric pieces using pad-dry-cure procedures. The physical properties such as air permeability, stiffness and crease recovery angle (CRA), pilling resistance, tear and tensile strength of the treated and untreated fabric samples were also evaluated. The results revealed that the incorporation of chitosan has pronounced effect on the properties of treated fabrics. This research could be extended in future for performance evaluation of pure cotton and woolen fabrics.

1. Introduction

Polyurethanes are the unique materials in their properties and applications as they can be tailored for any specific application by right choice of constituent monomers. They can be easily personalized by using various aliphatic and aromatic diisocyanates [1] and α, ω-alkane diols as chain extenders to synthesis materials with desired functionalities and properties [2,3]. Chemical, mechanical and morphological properties of PUs provide the basis for their wide range applications [4,5].

Preparation and characterization of waterborne polyurethane emulsions [6,7], effects of diisocyanate monomer structure on properties of PU composites based on blocked polyisocyanate [8] and investigations of blended polyurethane and natural rubber [9,10] have been reported by a large number of researchers. The uniqueness of polyurethanes reflected in their properties can be ascribed to the definite micro-level construction of linear polyurethanes based on soft-segments and hard-segments [11].

In recent years aqueous polyurethane emulsions, a category of multipurpose materials, have gained much consideration for academic research and shares a wide array of industrial applications as paints, coatings and adhesives primarily due to the facts that these are eco-friendly materials. Water dispersible PU surpasses conventional isocyanate and/or solvent containing PU in performance and also for being cost-effective products due to replacement of costly organic solvents with water [12–14]. Binary colloidal system of aqueous polyurethanes serves as a continuous emulsion medium for PU particles [13]. The basic building components of water dispersible PUs include aromatic or (cyclo) aliphatic diisocyanate, long–chain polyester, polyether or polycarbonate polyol, low molecular weight bis–hydroxyl carboxylic acid, diamine and/or glycol as chain extenders and a neutralizing base. Generally an NCO caped prepolymer having segmented structure is synthesizes by reacting a long-chain linear polyol, di hydroxy carboxylic acid and a low-molecular-weight glycol with an excess amount of diisocyanate. In this polymer, diisocyanate, glycol and di hydroxyl carboxylic acid constitutes the hard segments and soft segments are created by long-chain polyol units. The base neutralizes the pendant —COOH groups forming water dispersible prepolymer with salt group. The unique properties of aqueous polyurethane

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emulsions can be attributed to micro-phase separation between the discordant hard and soft segment structures [15].

By default, conventional polyurethanes, having hydrophobic diisocyanates, do not dissolve in water, but these can be converted to water dispersible materials by incorporation of nonionic and/or ionic hydrophilic groups in the polymer chains [16]. Based on these functional groups, PU emulsions can be categorized into cationic, anionic and nonionic emulsion. Cationic emulsion include emulsions containing N-methyl diethanol amine and poly(tetramethylene adipate diol) while anionic ones are poly(tetramethylene glycol) (PTMG), poly(propylene glycol) (PPG), poly(ethylene glycol) (PEG) and dimthylolpropanoicacid (DMPA). Nonionic emulsions have hydrophilic groups such as polyethylene oxide comprising the soft segments of Pus.These groups are incorporated in the polymer backbone during synthetic process [17,18]. Aqueous polyurethanes have widely been employed in dyeing and finishing investigations of synthetic fibers for their antistatic finishing, anti-soiling and hydrophilic finishing [19–22]. The augmented awareness of general public about transmission of cross infections and ailment generated by microorganisms has led people to show careful consideration in choice of antimicrobial materials in many applications like the preparation of protective garments for people working in medical field, microbiological labs, sportswear, undergarments and others health care stuffs [23].

Chitosan is derived from most plentiful natural polysaccharide chitin which occurs in exoskeletons of crabs and shrimps like crustaceans [24]. Proven and well documented properties of chitosan include total biodegradability, biocompatibility with plants and animal tissues, antimicrobial & antifungal activity, non-toxicity and tissue regenerative effects, besides hydrogel, film and fiber formation properties [25]. These properties make chitosan most prospective material for many fields as wastewater treatment, dentifrices, cosmetics, pulp and paper, agriculture, food, biomedical and textile fields [26–28], in fabrics engineering for hygiene and health-care products, such as bandages, medical sutures, gauze and artificial implants [29]. In the field of textile, comprehensive investigations for prospective applications of chitosan have been done which show that chitosan has potential to be used as dye fixing agent, in pigment printing of cellulosic fabric as thickener and binder, as well as it improves the fastness properties of dyed fabrics [30–32]. Improvement in properties of cotton fabric through synthesized nano-chitosan [33], ecofriendly antimicrobial finishing of textiles using natural bioactive agents including chitosan [34] and application of low-molecular-weight chitosan in durable press finishing of cotton [35] has also been reported.

Application of polyurethane acrylate copolymers on cellulosic fabric followed by evaluation of antimicrobial and pilling improvement [36], investigation of physicochemical properties of cellulosic fiber modified with polyurethane acrylate copolymers [37] and study of performance behavior of cellulosic fabrics modified by application of polyurethane acrylate copolymer [38] has been well documented. Chitosan-based elastomeric polyurethane emulsions have also been synthesized and their characterization by FTIR, ^{1}HNMR, and ^{13}C NMR spectroscopy and TGA has also been investigated and reported in literature [39]. Synthesis and surface modification of polyurethanes with chitosan for antibacterial properties [40], synthesis of waterborne PU extended with chitosan and application to acrylic fabrics as antibacterial finish [41] is also well documented. Considering all above documented literature about aqueous polyurethane emulsions and chitosan, this project was designed to accomplish the properties of both water dispersible PU and chitosan in a single polymeric material to improve the performance of textiles. In this study the synthesis and effect of "low molecular weight chitosan based polyurethane emulsion" on the properties of the dyed and printed polyester/cotton fabrics has been investigated. A series of low molecular weight chitosan based polyurethane ($CS_{(LMW)}$-CPUIs) emulsions was synthesized by reacting isophorone diisocyanate (IPDI) and poly (ε-caprolectone) diol (CAPA), dimethoxy propionic acid (DMPA) and chain extension was achieved by reaction with different amounts of chitosan of reduced molecular weight through oxidation with hydrogen peroxide. These finishes were applied onto the different quality of plain weave poly-cotton dyed and printed fabrics. Various tests were performed in order to determine the performance behavior of the prepared materials.

2. Experimental

2.1. Materials

2.1.1. Chemicals

All chemicals used for synthesis of CS_{LMW}-PUs were of analytical grade. Isophorone diisocyanate (IPDI) (100%), dimethylol propionic acid (DMP), triethyl amine (TEA), dimethyl sulfoxide (DMSO), low molecular weight chitosan (mol wt 50 000 g/mol) and dibutyltin dilaurate (DBTDL) catalyst (95%) were procured from Sigma Aldrich Chemicals Co, USA. 1,4-butanediol (BDO) and methyl ethyl ketone (MEK) were purchased from Merck Chemicals (Darmstadt, Germany). Poly(ε-caprolactone) diol (CAPA 2100A, molecular weight 1000) was generously provided by Perstorp Polyols (Solvay Chemicals, Inc. Toledo, OH).

CAPA and DMPA were dried at 60 °C for 4 h in oven before use for the removal of water vapors and air to ensure that these may not interfere with isocyanate reaction. BDO was also heated at 60 °C for 2 h to dry it. Anhydrous $CaSO_4$ was used to dry MEK. IPDI and other chemicals used in this study were used as received.

2.1.2. Polyester-Cotton (PC) fabric substrates

Mill desized and scoured dyed and printed poly cotton, 1 × 1 plain weaved fabrics (48/52 and 55/45 polyester cotton blend ratio respectively) were provided by Sadaqat Textile Mills Ltd., Khurrianwala, Faisalabad, Pakistan. Fabric specifications are depicted in Table 1. The fabrics were washed in laboratory before application of $CS_{(LMW)}$-CPUI finishes at 100 °C for 30 min with detergent. After washing, the fabrics were rinsed thoroughly with hot water and cold water successively and were air dried at ambient temperature.

2.2. Synthesis of low molecular weight chitosan based polyurethanes ($CS_{(LMW)}$-CPUIs)

Polyurethane pre-polymers were synthesized and extended with low molecular weight chitosan following the recommended procedure [42].

Table 1
Specification of fabric used.

Fabrics	Blend Ratio P:C	Construction	Count Warp: Weft	GSM (g/m^2)	EPI[a]	PPI[b]
Dyed	48:52	1 × 1 plain weave	30:30	132	127	59
Printed	55:45	1 × 1 plain weave	30:30	106	82	51

[a] Ends per inch; is the number of warp threads per inch of woven fabric.
[b] Picks per inch; is the number of weft threads per inch of woven fabric.