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Antimicrobial and pilling evaluation of the modified cellulosic fabrics using polyurethane acrylate copolymers

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ABSTRACT

Polyurethane acrylate copolymers (PACs) were synthesized by three step synthesis process via emulsion polymerization using toluene-2,4-diisocyanate, hydroxy terminated poly (caprolactone) diol (PCL), 2-hydroxyethylacrylate (HEA) and butyl acrylate (BuA). The proposed structure of the synthesized polyurethane acrylate copolymer (PAC) was confirmed using Fourier transform infrared (FTIR) spectrophotometer. The pilling characteristic and antimicrobial activities of the plain weave poly-cotton grey, white, printed and dyed fabric swatches after application of PAC were evaluated. The results revealed that by increasing the molecular weight of PCL in the synthesized PAC samples, the antimicrobial activities increased and this behavior was interpreted in term of increasing hydrophilic character. An increase in pilling ratings of the treated samples has been observed by increasing the molecular weight of the polycaprolactone diols in the synthesized PAC samples.

1. Introduction

Polyurethane elastomers (PUEs) are possibly the most versatile classes of polymers as they can be molded, injected, extruded and recycled [1]. Molecular characterization and morphological studies of PUEs have been reported [2,3]. The effect of the diisocyanate structure [2] and chain extender (CE) length using α,ω-alkane diols on the crystallinity, surface morphology [3] and thermo-mechanical properties [4] of PUEs have also been investigated and well documented. Extensive work on structural characterization, crystalline patterns, and thermal properties of chitin-based polyurethane elastomers (PUEs) have been comprehensively reported elsewhere [5–8]. Few reports have been found on the structural characterization of chitin-based polyurethane with their shape memory characteristics [9,10]. Surface morphology of starch [11], cellulose [12], and chitin–humic acid [13] has also been investigated and well documented. XRD studies and surface characteristics of UV-irradiated, non-irradiated chitin-based polyurethane elastomers and chitin based PU bio-nanocomposites [14–19], and structural, surface and thermo-mechanical characteristics of UV-irradiated polyurethane elastomers extended with α,ω-alkane diols have been comprehensively presented elsewhere [20–22]. The physicochemical properties including colorfastness and surface properties of treated finished fabrics using polyvinyl alcohol [23,24], polyurethane acrylate copolymers [25] have also been reported. Modifications of cellulosic fibers to enhance their dye-ability and their after-treatment affects using UV-irradiation have also been filed [26,27]. Regarding textile applications of the materials many reports on amino silicone based softener are also available [28,29].

Waterborne polyurethanes (WPUs) have potential array of commercial applications involving coatings, adhesives and paints, since they are non-hazardous, nonflammable and do not pollute the air due to no or little volatile organic compounds [30]. Preparation and properties of urethane/acrylate composite by emulsion polymerization technique, and comparative study between core–shell and physicochemical properties of interpenetrating network (IPN) structure of polyurethane/polyacrylate composite emulsions have been well documented [31,32]. Latex IPNs based on polyurethane, polyacrylate and epoxy resin have also been reported elsewhere [33]. Particle formation, film properties, and application of waterborne polyurethane/poly(n-butyl acrylate-styrene) hybrid emulsions [34], comparison of hybrid and blend systems in waterborne polyurethane/acrylate and self-assembly of graft polyurethanes having both PCL blocks and soft poly(n-BuA) segments have been reported [35,36]. Literature regarding synthesis and properties of poly(acrylates-co-urethane) adhesives and hyperbranched polyurethane acrylate used for UV curing coatings is also a part of some studies [37,38]. The professional literature and scientific writings have reported possible applications of

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Table 1
Specification of fabrics with quality (construction/count and blend ratio) and type of processing done on the fabrics.

S. no.	Quality	Construction/count	Blend ratio cotton/polyester	Type of processing of fabrics
01	Plain weave poly cotton	(60 × 60/20 × 20)	49/51	White
02	Plain weave poly cotton	(60 × 60/22 × 22)	52/48	Grey (unbleached)
03	Plain weave poly cotton	(76 × 68/30 × 30)	51/49	Dyed with reactive dyes
04	Plain weave poly cotton	(100 × 80/40 × 40)	52/48	Pigment printed

waterborne polyurethanes [39]. Acrylic (AC) emulsions and polyurethane (PU) aqueous dispersions have been extensively used in coating applications. It is worth mentioning that acrylic finishes exhibit the lack of film forming properties and PU on the other hand represents the high cost, low pH stability, limited outdoor durability [40]. To achieve all the required properties in a single polymeric material, the molecular engineering is required. Polyurethanes (PUs) can present better mechanical stability, good solvent and chemical resistance, excellent biocompatibility [41–43] and toughness against loading [25]. Acrylic (AC) component on the other hand shows high outdoor resistance, pigment ability, and lower cost [44]. So, blending of properties of AC & PU definitely will help to get such a polymer with required properties. Great efforts have been dedicated to combine the polyurethanes with acrylic polymers to increase the performance-to-cost ratio of the coatings [45]. There are only a limited number of reports about the preparation and application of eco-friendly binders for textile finishing purposes [25]. Polyurethane acrylate oligomers have gained more and more attention and speedy development. Considering excellent outdoor resistance of acrylic and versatile biocompatibility of polyurethanes the present project is designed to synthesize polyurethane acrylate copolymers with polycaprolactone diols of various molecular weights. The effect of molecular weight of PCL incorporated in PU based finish on the properties of the treated and untreated fabrics has been studied and discussed.

2. Experimental

2.1. Materials

2.1.1. Chemicals

Toluene diisocyanate (TDI), butyl acrylate (BuA), 2-hydroxy ethyl acrylate (HEA) were purchased from Sigma Chemical Co. (St. Louis, MO, USA). Polycaprolactone diol CAPA 2047A (molecular weight 400), CAPA 2077A (molecular weight 750), CAPA 2100A (molecular weight 1000), CAPA 2125A (molecular weight 1250), CAPA 2161 (molecular weight 1600), CAPA 2200A (molecular weight 2000), CAPA 2302A (molecular weight 3000), CAPA 2403A (molecular weight 4000) were kindly gifted by Perstorp Polyols (Solvay Chemicals, Inc. Toledo, OH). Potassium persulphate (KPS), sodium thiosulphate ($Na_2S_2O_3$), polyoxyethylene glycol octylphenol ethers, Na_2CO_3, polyvinyl alcohol (PVA), Montane 80 (HLB = 4.3) and Montanox 80 (HLB = 15) were purchased from Merck Chemicals (Darmstadt, Germany). The polyol and acrylates used in this study were dried at 80 °C in vacuo for 24 h before use to ensure the removal of all air bubbles and water vapors that may otherwise interfere with the isocyanate reactions. The molecular weight of used polyol was confirmed by following the procedure reported in ASTM D-4274C [46]. TDI and all of the other materials were used as received. All of the reagents used in this study were of analytical grade.

2.1.2. Polycotton fabric – a substrate

Mill desized, un-scoured, un-bleached grey fabrics and desized, scoured, bleached, white, printed and dyed poly cotton, plain weaved fabrics (with almost 50/50 cotton/polyester blend ratio) was supplied by Sadaqat Textiles Mills Ltd., Khurrianwala, Faisalabad, Pakistan. The characteristics i.e., quality of the fabrics, construction, count, blend ratio, etc., are presented in Table 1. Before application of the polyurethane acrylates copolymer, the fabric was further decontaminated in the laboratory by washing at 100 °C for 60 min using a solution containing 2 g/L, Na_2CO_3 and 1 g/L, polyoxyethylene glycol octylphenol ethers: C_8H_{17}–(C_6H_4)–(O–C_2H_4)$_{1-25}$–OH: (Triton X-100) a nonionic surfactant (BASF). The fabric was then washed several times with hot water then with cold water and finally dried at ambient conditions.

2.2. Synthesis of polyurethane acrylate copolymers

Polyurethane acrylate copolymers have been synthesized by following three step syntheses. In first step, the synthesis of isocyanate (NCO) terminated polyurethane (PU) prepolymer was carried out according to the recommended procedure [3]. For this purpose 2 moles of hydroxyl terminated poly caprolactone diols (polyol) was reacted with 3 moles of toluene-2,4-diisocyanate (TDI) in order to get isocyanate (NCO) terminated polyurethane (PU) prepolymer (Fig. 1a). A Fourier transform infrared (FTIR) spectrum of the PU prepolymer was obtained to confirm the progress of reaction (Fig. 2). In the second step NCO terminated PU prepolymer was reacted with 2-hydrxy ethyl acrylates to get vinyl terminated PU prepolymer which was finally copolymerized with butyl acrylates. The detailed procedure regarding preparation of NCO terminated PU

Table 2
Sample code designation and different formulation of polyurethane copolymer varying molecular weight of polycapralactone diols.

Sample code	CAPA[a] (MW)	CAPA trade name	TDI[b]	CAPA[c]	HEA[d]	VT-PU[e]	BuAC[f]
PAC-1	400	2074A	3	2	2	10%	90%
PAC-2	750	2077A	3	2	2	10%	90%
PAC-3	1000	2100A	3	2	2	10%	90%
PAC-4	1250	2125A	3	2	2	10%	90%
PAC-5	1600	2161A	3	2	2	10%	90%
PAC-6	2000	2200A	3	2	2	10%	90%
PAC-7	4000	2403A	3	2	2	10%	90%

[a] Different molecular weights of polycaprolactone diol.
[b] Toluene-2,4-diisocyanate (mole ratio).
[c] Polycaprolactone diol (mole ratio).
[d] 2-Hydroxyethylacrylate (mole ratio).
[e] Vinyl terminated polyurethane prepolymer blend (%).
[f] Butyl acrylate blend (%).