



Performance behavior of modified cellulosic fabrics using polyurethane acrylate copolymer



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ARTICLE INFO

Article history:

Received 3 February 2014

Received in revised form 2 March 2014

Accepted 8 March 2014

Available online 21 March 2014

Keywords:

Cellulose

PU acrylate

FT-IR

Pilling

Tear strength

ABSTRACT

The surface of the cellulosic fabrics was modified using self-prepared emulsions of polyurethane acrylate copolymers (PUACs). PUACs were prepared by varying the molecular weight of polycaprolactone diol (PCL). The PCL was reacted with isophorone diisocyanate (IPDI) and chain was extended with 2-hydroxy ethyl acrylate (HEA) to form vinyl terminated polyurethane (VTPU) prepolymer. The VTPU was further copolymerized through free radical polymerization with butyl acrylate in different proportions. The FT-IR spectra of monomers, prepolymers and copolymers assured the formation of proposed PUACs structure. The various concentrations of prepared PUACs were applied onto the different fabric samples using dip-padding techniques. The results revealed that the application of polyurethane butyl acrylate copolymer showed a pronounced effect on the tear strength and pilling resistance of the treated fabrics.

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1. Introduction

Historically, polyacrylates (PAC) have found extensive uses as adhesives, coatings, and sealants [1]. They generally display low glass transition temperature (T_g) which makes them convenient to handle, process, and use in diversified environment. Furthermore, the large and diverse range of available monomers allows the physical properties of the resultant polymeric material to be tailored. However, a common drawback of these polymers is that their flexible backbones impart limited thermal stability and mechanical strength. Thus, a number of techniques have been developed to enhance their properties by crosslinking the polymer chains [2]. Polyurethanes (PUs) are a distinctive class of polymers, because they have a wide range of applications due to their properties which can be voluntarily adapted by the variation of their components [3]. Molecular characterization and morphological studies of PUEs have been reported by many researchers [4,5]. The effect of the diisocyanate structure [4] and chain extender (CE) length using α,ω -alkane diols on the crystallinity, surface morphology [6] and thermo-mechanical properties [7] of PUEs have also been investigated and well documented. Many research articles on the synthesis and characterization of chitin based PU and extensive

work on structural characterization, crystalline patterns, and thermal properties of chitin-based polyurethane elastomers (PUEs) have been comprehensively reported [8–10]. In vitro biocompatibility and cytotoxicity of chitin/1,4-butane diol blend based PUEs have also been reported in the literature [11,12]. Few reports have been found on the structural characterization of chitin-based PUEs and their shape memory characteristics [13,14]. XRD analysis and surface characteristics of UV-irradiated and non-irradiated chitin/alkane diols based PUEs have also been presented [15–17]. The microstructure of a PU block itself is generally known to be composed of different phases, i.e., it is based on domains which have been built of hard urethane-type segments derived from diisocyanates, and on soft domains which have been built from flexible segments derived from polyol components [13,18,19]. By controlling variables such as functionality, chemical composition and the molecular weight of the different reactants, a wide class of materials with significantly varying properties can be obtained [20].

Waterborne polyurethanes (WPU) are widely used in different fields such as coatings, adhesives and paints, since they are non-hazardous, nonflammable and do not pollute the air due to no or little volatile organic compounds in final formulation [21–24]. WPU have emerged as an important class of polymeric materials in the paint and ink industries because of their environment-friendly nature [25,26]. Technical literature and scientific writings have reported possible applications of WPU for impregnation of materials [27]. Polyacrylate (PAC) emulsions and polyurethane (PU)

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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	Blends ratio (cotton/polyester)	Types of processed fabrics
1	Plain weave poly cotton	(60 × 60/20 × 20)	50/50	White
2	Plain weave poly cotton	(60 × 60/20 × 20)	49/51	Grey
3	Plain weave poly cotton	(76 × 68/30 × 30)	51/49	Dyed (using reactive dyes)
4	Plain weave poly cotton	(76 × 68/30 × 30)	51/49	Printed

aqueous dispersions have been extensively used in coating applications. Both the AC and PU, being hetro-polymer have shown some handicap of properties, i.e., acrylic polymers are lacking in better film forming properties, show less chemical resistance, and rough mechanical properties while PU on the other hand represents the high cost, low pH stability, and limited outdoor durability [28]. To achieve all the required properties in a single polymeric material, the molecular engineering is required. Polyurethanes (PU) can present better mechanical stability, good solvent and chemical resistance, and toughness against loading [29,30], while poly acrylates (PAC) component on the other hand shows high outdoor resistance and lower cost [31]. So, blending of properties of ACs and PUs definitely will help in getting a polymer with improved properties.

Regarding textile applications of the material, a few reports on amino silicone based softeners are also available [32–35]. Great efforts have been dedicated to combine the PUs with acrylic polymers to increase the performance-to-cost ratio of the coatings [36,37]. There are only a limited number of reports about the preparation and application of eco-friendly binders for textile finishing [29,30]. Keeping in view the excellent outdoor resistance of PACs and versatile properties of PUs, the present project is designed to synthesize a series of PUACs copolymers by varying molecular weight of polycaprolactone diols and molar ratio of vinyl terminated polyurethane prepolymer and butyl acrylates (BuAc) components. The effect of molecular weight of soft segment of prepolymer on the performance of the final copolymers has been studied by testing the behavior of the treated and untreated fabrics for various tests.

2. Experimental

2.1. Materials

2.1.1. Chemicals

Isophorone diisocyanate (IPDI), butyl acrylate (BuA), 2-hydroxy ethyl acrylate (HEA) were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). Polycaprolactone diol 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 ($\text{Na}_2\text{S}_2\text{O}_3$), polyoxyethylene glycol, 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 volatile material 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 moisture 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 [38]. All the other materials including IPDI were used as received. All of the reagents used in this study were of analytical grade.

2.1.2. Polycotton fabric—A substrate

For comparative study four different fabric samples were used as substrate for application of synthesized copolymer. These are:

(a) mill de-sized, un-scoured, un-bleached grey poly cotton fabrics; (b) de-sized, scoured, bleached, white poly cotton fabrics; (c) pigment printed poly cotton fabrics and (d) dyed poly cotton fabrics (using reactive dyes). The fabric samples were plain weaved and of similar blend ratio of cotton/polyester (50/50) and were supplied by Arzoo Textile, Khurrianwala, Faisalabad, Pakistan. The characteristics i.e., quality of the fabrics, construction, count, blend ratio, etc., were determined and are presented in Table 1. Before application of PUACs, the fabric samples were 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: $\text{C}_8\text{H}_{17}-(\text{C}_6\text{H}_4)-(\text{O}-\text{C}_2\text{H}_4)_{125}-\text{OH}$: (Triton X-100) a nonionic surfactant (BASF). The fabric was then washed several times with hot water and finally dried at ambient conditions after rinsing with cold water.

2.2. Synthesis of polyurethane acrylate copolymer

Two steps are involved in the synthesis of polyurethane acrylate copolymer samples (Fig. 1).

2.2.1. Synthesis of vinyl terminated polyurethane prepolymer

Three (3) moles of isophoron diisocyanate (IPDI) were reacted with 2 mol of hydroxyl terminated polycaprolactone diols (polyol) to get isocyanate (NCO) terminated polyurethane prepolymers [13]. In this reaction, a four-necked reaction kettle equipped with mechanical stirrer, heating oil bath, reflux condenser, dropping funnel and N_2 inlet and outlet was used. The temperature of the oil bath was increased to 60 °C. Then diisocyanate was added and the temperature was raised and kept at 100 °C under continuous stirring. It took almost 1.0 h to obtain NCO terminated PU prepolymer. A Fourier transform infrared (FTIR) spectrum of the PU prepolymer was obtained to confirm the completion of the reaction (Fig. 2).

After the confirmation regarding the preparation of isocyanate (NCO) terminated PU prepolymer, the temperature of the reaction vessel was decreased to 60 °C. Then 2 mol of 2-hydroxyethylacrylate (HEA) was added into the reaction mixture in portions. The reaction was continued for 30 min and there was a viscous and milky material formed in the reaction vessel [30]. The FT-IR analysis confirmed the formation of the vinyl terminated PU prepolymer (Fig. 1).

2.2.2. Synthesis of urethane-butyl acrylate copolymers

At the second step, copolymerization of vinyl terminated PU resin with butyl acrylate (BA) was carried out through emulsion polymerization process. So, aqueous solution of PVA 3% w/v and emulsifier (Montane 80:Montanox 80; 30:70) 6% v/v were prepared separately, and then the butyl acrylate was added into the reaction flask with 10 mL of 0.2% w/v initiator solution slowly. This addition was completed in almost 3.5 h with continuous stirring at 55 °C to 60 °C. The reaction was continued for another hour till a homogenous emulsion was obtained. A series of copolymers were synthesized by varying the molecular weight of polyol in the polymerization of vinyl terminated PU prepolymer and molar ratio of butyl acrylate in the final

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