Carbohydrate Polymers 86 (2011) 928–935

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Improvement of performance behavior of cellulosic fiber with polyurethane acrylate copolymers

Misbah Sultan[a], Haq Nawaz Bhatti[a], Mohammad Zuber[b,*], Ijaz Ahmad Bhatti[a], Munir Ahmad Sheikh[a]

[a] *Department of Chemistry and Biochemistry, University of Agriculture, Faisalabad 38040, Pakistan*
[b] *Department of Applied Chemistry, Government College University, Faisalabad 38030, Pakistan*

ARTICLE INFO

Article history:
Received 26 April 2011
Received in revised form 14 May 2011
Accepted 24 May 2011
Available online 1 June 2011

Keywords:
Cellulose fibers
Polyurethane acrylates
Emulsion stability
Pilling evaluation

ABSTRACT

Polyurethane acrylate (PUA) copolymers were synthesized following three step synthesis using toluene-2,4-diisocyanate, poly (2-methyl-1,3-propylene glutarate) diol terminated, 2-hydroxyethylacrylate (HEA) and butyl acrylate (BuA) via emulsion polymerization technique. The conventional spectroscopic characterization of the samples with FT-IR was in accordance with proposed PUA copolymer structure. The synthesized PUA copolymer samples were applied using dip-padding techniques on mill desized, scoured, bleached, printed, 100% cotton combed satin, striped weave fabrics. The emulsion stability evaluation and pilling rating showed reciprocal dependence on the percentage of butyl acrylate (BuA) and dual dependence on the concentration of vinyl terminated polyurethane prepolymer. The results revealed that by decreasing the mole ratio of polyol the emulsion stability and pilling rating drastically increased.

1. Introduction

Cellulosic fabrics are prone to develop balls of fiber on the surface, which are known as pills. The pills are formed during wearing and washing, when fibers have lose ends on the fabric surface “tease out” and become entangled. Under the influence of the rubbing action these loose fibers develop into small spherical bundles anchored to the fabric by a few unbroken fibers (Booth, 1968).

Ever since the discovery of polyurethanes by Otto Bayer and co-workers in 1937, these have been developed as a unique class of synthetic polymers with wide variety of applications (Woods, 1990; Zia, Bhatti, & Bhatti, 2007). The urethane linkage is formed by the reaction of an isocyanate group of one reactant with the alcohol group of another component. The microstructure of a polyurethane 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 connected with soft domains which have been built from flexible segments derived from polyol components (Barikani, Zia, Bhatti, Zuber, & Bhatti, 2008). By controlling variables such as the functionality, chemical composition and the molecular weight of the different reactants, a wide class of materials with significantly varying properties can be obtained. This flexibility has led polyurethanes to find use as synthetic polymers in foams, elastomers, coatings, sealants, and adhesive based products. Some of the applications of polyurethanes lie in the textile finishing, automotive, furniture, construction, and thermal insulation and footwear industries (Zia et al., 2007).

Regarding up-to-date study on polyurethane, extensive work on detailed molecular characterization (Zia, Barikani, Zuber, Bhatti, & Bhatti, 2008), XRD studies (Zia, Barikani, Bhatti, Zuber, & Bhatti, 2008), and thermal properties (Zia, Barikani, Zuber, Bhatti, & Sheikh, 2008) of chitin-based polyurethane elastomers (PUEs) have also been previously discussed and reported. In vitro biocompatibility and non-toxicity of chitin/1,4-butanediol blends based polyurethane elastomers has also been reported elsewhere (Zia, Zuber, Bhatti, Barikani, & Sheikh, 2009a, 2009b). Some reports are also available on molecular characterization and shape memory properties of chitin-based shape memory polyurethane elastomers (Barikani et al., 2008; Zia, Zuber, Barikani, Bhatti, & Khan, 2009). For the application of PU, their stability against terrestrial weathering is very important. One of the greatest factors in the terrestrial weathering of PUEs is ultraviolet (UV) radiation in the wavelength range 330–410 nm. Attempts have been made to study the effect of UV-irradiation on surface properties of some common polymers (Kaczmarek & Chaberska, 2006; Kaczmarek & Podgorski, 2007; Zia et al., 2007). Photooxidative behavior and effect of chain extender length in polyurethane on photooxidative stability have also been reported (Zia, Barikani, Bhatti, Zuber, & Bhatti, 2008; Zia, Barikani, Zuber, Bhatti, & Islam-ud-Din, 2008). Surface morphology of starch (Matsushita et al., 2008), cellulose (Yokota, Kitaoka, & Wariishi, 2008), and chitin–humic acid (Santosa, Siswanta, Sudiono, & Utarianingrum, 2008) have also been investigated and well documented. XRD studies and surface characteristics of UV-irradiated and non-irradiated chitin-based polyurethane elastomers have also

---

* Corresponding author. Tel.: +92 321 6682375; fax: +92 041 9200671.
E-mail address: mohammadzuber@gmail.com (M. Zuber).

0144-8617/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2011.05.045

been presented elsewhere (Zia, Bhatti, Barikani, Zuber, & Bhatti, 2009; Zia, Barikani, Khalid, Honarkar, & Ehsan-ulHaq, 2009; Zia, Barikani, Zuber, Bhatti, & Barmar, 2009e, 2009f).

The scientific writings and other professional literature have for some time been reporting possible applications of water-borne polyurethane binders not only for the production of environmentally friendly lacquers and/or adhesives, and for impregnation of materials with considerably high surface areas like fibrous mineral fillers, and adhesive for powdered ceramic materials as well (Król, Król, Pikus, & Skrzypiec, 2005). Water-borne polymer emulsions are an important class of materials, especially in the paint and coating industry. Increasing concern for health, safety, and the environment restrictions has driven many researchers to prepare water-borne polymers with sophisticated composition and architecture, which are expected to exhibit almost the same performance as conventional solvent-borne systems. Acrylic (AC) emulsions and polyurethane (PU) aqueous dispersions have been used extensively in coating applications. Both systems have some disadvantages such as reduced film formation, lower chemical resistance, and coarse mechanical properties of acrylic, a high cost, low pH stability, and limited outdoor durability of PU (Hegedus & Kloiber, 1996). To improve the properties of an individual polymer system it is common to mix them. Better mechanical stability, solvent and chemical resistance, and toughness are obtained from the PU portion. Outdoor resistance, pigment ability, and lower cost are due to the acrylic (AC) component (Kukanja, Golob, Ic-Valant, & Krajnc, 2000). Polyurethane acrylates are also applied as UV-curable, pressure-sensitive adhesive (PSA) due to decrease in emission of volatile organic compounds (Czech, 2004; Horigome, Ebe, & Kuroda, 2004; Yaobin, Huiming, Longsi, Jianming, & Yongqiang, 2006). Regarding textile applications of the material few reports on amino silicone based softener are also available (Zia et al., 2011; Zuber et al., 2011). There are only a limited number of reports about the preparation and application of eco-friendly binder for textile finishing purposes. Great efforts have been dedicated to the combination of polyurethanes with acrylic polymers to increase the performance-to-cost of the coatings (Wang, Hu, & Tu, 2008). In this way, extensive possibilities are offered to obtain the polymer structure which will be compatible for particular intention (Król et al., 2005). Polyurethane acrylate oligomers have gained more and more attention and speedy development. Considering excellent outdoor resistance of acrylic and versatile properties of polyurethanes the present project is designed to synthesize polyurethane acrylate copolymers with potential to reduce pilling capacity of the textile finished goods.

2. Experimental

2.1. Materials

2.1.1. Chemicals

The chemicals used in this study for the synthesis of polymer are: toluene-2,4-diisocyanate (TDI) (Fluka Chemicals), poly (2-methyl-1,3-propylene glutarate) diol terminated (molecular weight 1020, Aldrich Chemicals), 2-hydroxyethylacrylate (HEA) (Aldrich Chemicals), butyl acrylate (BuA), ammonium persulphate (APS), sodium thiosulphate ($Na_2S_2O_3$), Tween 60 (polyoxyethylene sorbitan monolaurate – an emulsifier), polyvinyl alcohol (PVA), Na_2CO_3 and polyoxyethylene glycol octylphenol ethers. 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 (ASTM, 2004). TDI and all of the other materials were used as received. All of the reagents used in this study were analytical grade.

2.1.2. Cotton/satin fabric – a substrate

Mill desized, scoured, bleached, printed, 100% cotton comed satin fabrics; satin striped weave was supplied by Arzoo 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 copolymers, 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 condition.

2.2. Synthesis of polyurethane acrylate copolymers

Polyurethane acrylate copolymers have been synthesized by following three step syntheses.

2.2.1. Synthesis of isocyanate (NCO) terminated polyurethane (PU) prepolymer

The synthesis of PU prepolymers was carried out according to the recommended procedure (Barikani & Hepburn, 1986). First of all (18.54 g, 2 moles) of poly (2-methyl-1,3-propylene glutarate) diol terminated (polyol) was charged into a four-necked round bottom flask equipped with a mechanical stirrer, a thermometer, a reflux condenser, heating oil bath and a nitrogen gas inlet system. The temperature of the oil bath was increased to 60 °C. Poly (2-methyl-1,3-propylene glutarate) diol terminated was stirred continuously under the blanket of nitrogen gas for 30 min. Then 3.89 mL (3 moles) of toluene-2,4-diisocyanate (TDI) was added to the reaction vessel and temperature was raised to 80 °C. It took almost 1.0 h to obtain NCO terminated polyurethane (PU) prepolymer (Scheme 1a). The NCO contents of the prepolymer were determined and the experimental values found close to the theoretical value (experimental value 9.31%; theoretical value 9.29%). A Fourier Transform Infrared (FTIR) spectrum of the PU prepolymer was obtained to confirm the PU prepolymer reaction (Fig. 1).

2.2.2. Synthesis of vinyl terminated polyurethane prepolymer

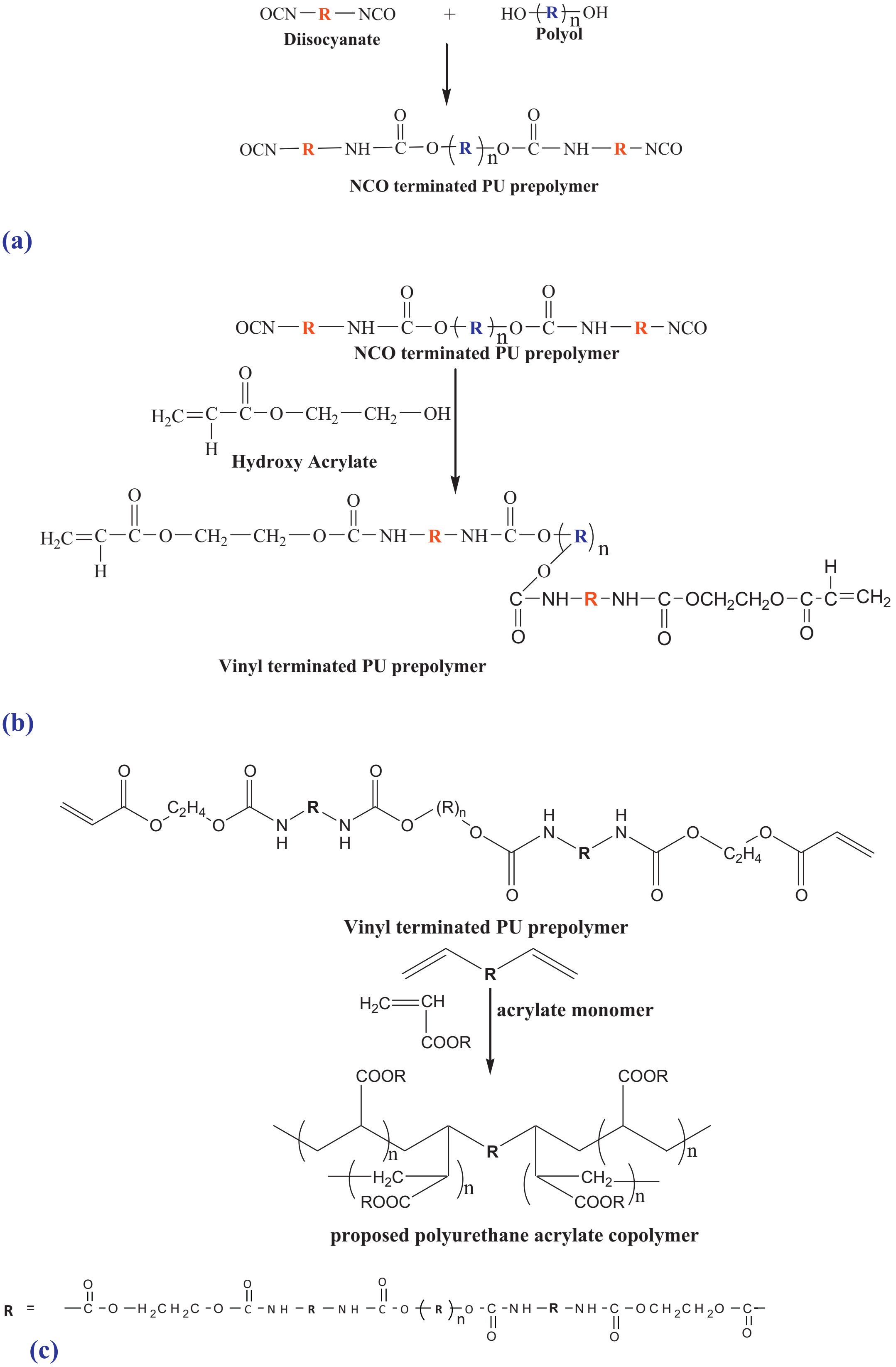
Over the formation of the isocyanate (NCO) terminated PU prepolymer synthesis confirmed, the temperature of the reaction vessel was lowered down to 60 °C. Then 4.22 mL of 2-hydroxyethylacrylate (HEA) was added into the reaction mixture. The reaction was continued for 30 min and there was a thick, viscous and transparent material in the reaction vessel (Wang et al., 2008) which indicates the formation of vinyl terminated PU prepolymer (Scheme 1b). The formation of the vinyl terminated prepolymer was confirmed by FT-IR (Fig. 1).

2.2.3. Copolymerization of vinyl terminated PU prepolymer with butyl acrylate (BuA)

Copolymerization of vinyl terminated PU prepolymer with butyl acrylate (BuA) was carried out through emulsion polymerization, in the presence of polyvinyl alcohol (PVA), Tween 60 (polyoxyethylene sorbitan monolaurate) and ammonium persulphate (APS) with $Na_2S_2O_3$ (as redox initiator). The formulation about the preparation of polyurethane acrylate (PUA) emulsion is presented in Table 2. Aqueous solutions of PVA 3% (w/v) and Tween 60 (an emulsifier) 6% (v/v) were prepared separately following the formulation given in Table 2, and then they were introduced into the reaction flask with 10 mL of 0.2% (w/v) initiator solution slowly.

Table 1
Fabrics specification with quality and processed applications.

S. no.	Quality	Construction/count	Blend ratio cotton/polyester	Application
01	Printed stripe satin/cotton (satin stripe = 1 cm)	(140 × 100/40 s × 40 s)	100% combed cotton	Combination of pigments



Scheme 1. Synthesis of polyurethane acrylate co-polymers: (a) preparation of NCO terminated polyurethane (PU) prepolymer, (b) vinyl terminated PU prepolymer, and (c) proposed polyurethane acrylate co-polymers.

Table 2
Preparation of polyurethane acrylate (PUA) emulsions.

S. no.	Ingredients	Quantity
1	PVA[a]	6 g (3% of emulsion)
2	Tween 60[b]	24 mL (12% of emulsion)
3	$Na_2S_2O_3$	One crystal
4	Distilled water	150 mL
5	PU prepolymer[c]	Varied from 5% to 30% of BuA
6	BuA[d]	Varied from 95% to 70%

[a] Polyvinyl alcohol.
[b] An emulsifier.
[c] Polyurethane prepolymer.
[d] Butyl acrylates.

This addition was completed in almost 3.5 h with continuous stirring at 55 °C (Scheme 1c). Total of the 30 samples, (5 series, 6 samples in each series) of the emulsion of BuA and vinyl terminated PU prepolymers, ratio of both were assorted progressively, were prepared. White milky emulsions were obtained which were saved for further investigations. A schematic illustration of the chemical route for synthesis of PU acrylate copolymer is given in Scheme 1a–c.

2.3. Treatment of fabrics with polyurethane acrylate copolymers

Various dilutions of polyurethane acrylate copolymer samples were applied onto the satin/cotton fabric. The fabric samples were treated with an aqueous solution of polyurethane acrylate copolymer samples (following the formulation given in Table 3) with various dilutions (i.e., 25 g/L, 30 g/L and 35 g/L) dried at 100 °C for 4 min. The curing of the printed treated fabrics was done at 140 °C for 5 min.

2.4. Measurements

Molecular structure of the synthesized PU acrylate copolymer was confirmed using Fourier Transform Infrared (FT-IR) spectroscopy. FT-IR spectra of the PU acrylate copolymer samples were obtained in the transmission mode using a Shimadzu Fourier Transform Infra-red (FT-IR) spectrometer. FTIR scans were collected on completely dried thin films cast on KBr discs from N,N′-dimethylformamide (DMF) solution. The spectra covered the infrared region 4000–500 cm^{-1}, the number of scans per

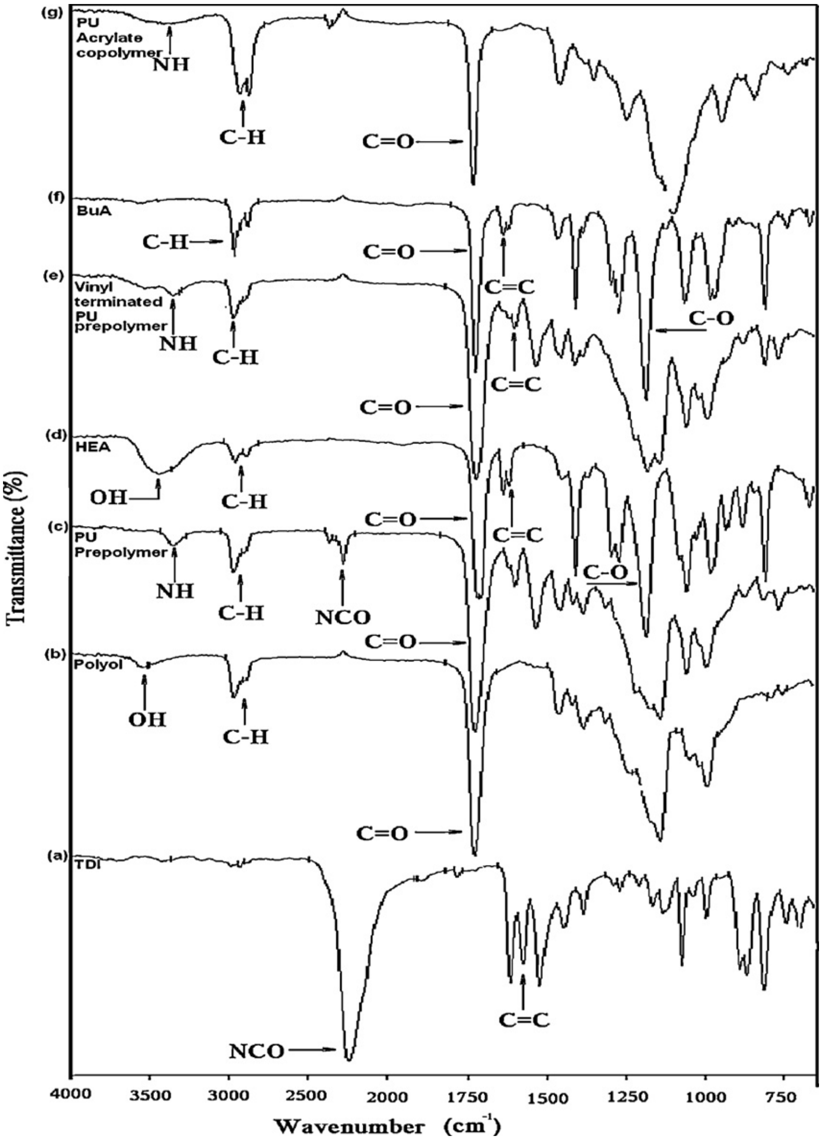


Fig. 1. FT-IR spectra (a) toluene-2,4-diisocyanate (TDI); (b) 2-methyl-1,3-propylene glutarate-diol terminated polyol; (c) isocyanate (NCO) terminated PU prepolymer; (d) 2-hydroxyethylacrylate (HEA); (e) vinyl terminated PU prepolymer; (f) butyl acrylate (BuA); (g) polyurethane acrylate copolymers.

Table 3
Formulations of polyurethane acrylate emulsions, emulsion stability and pilling evaluation ratings of printed fabrics.

S. no.	Composition of polyurethane acrylate emulsion					Pilling rating of printed fabrics[f]	Emulsion stability of the samples	S. no.	Composition of polyurethane acrylate emulsion					Pilling rating of tested fabrics[f]	Emulsion stability of the samples
	Polyol[a] (mole)	TDI[b] (mole)	HEA[c] (mole)	VT-PU[d] (%)	BuA[e] (%)				Polyol[a] (mole)	TDI[b] (mole)	HEA[c] (mole)	VT-PU[d] (%)	BuA[e] (%)		
1	2	3	2	5	95	3	A_1	16	1.8	3	2	20	80	3/4	D_3
2	2	3	2	10	90	3	B_1	17	1.8	3	2	25	75	3/4	E_3
3	2	3	2	15	85	3	C_1	18	1.8	3	2	30	70	4	F_3
4	2	3	2	20	80	3/4	D_1	19	1.7	3	2	5	95	3	A_4
5	2	3	2	25	75	3/4	E_1	20	1.7	3	2	10	90	3	B_4
6	2	3	2	30	70	3/4	F_1	21	1.7	3	2	15	85	3/4	C_4
7	1.9	3	2	5	95	3	A_2	22	1.7	3	2	20	80	3/4	D_4
8	1.9	3	2	10	90	3	B_2	23	1.7	3	2	25	75	4	E_4
9	1.9	3	2	15	85	3	C_2	24	1.7	3	2	30	70	4	F_4
10	1.9	3	2	20	80	3/4	D_2	25	1.6	3	2	5	95	3	A_5
11	1.9	3	2	25	75	3/4	E_2	26	1.6	3	2	10	90	3/4	B_5
12	1.9	3	2	30	70	3/4	F_2	27	1.6	3	2	15	85	3/4	C_5
13	1.8	3	2	5	95	3	A_3	28	1.6	3	2	20	80	4	D_5
14	1.8	3	2	10	90	3	B_3	29	1.6	3	2	25	75	4	E_5
15	1.8	3	2	15	85	3/4	C_3	30	1.6	3	2	30	70	4	F_5
31[g]	EFD (commercial standard sample no. 1)					3	S_1	32[h]	SE (commercial standard sample no. 2)					3	S_2

[a] Poly (2-methyl-1,3-propylene glutarate) diol terminated.
[b] Toluene-2,4-diisocyanate.
[c] 2-Hydroxyethylacrylate.
[d] Vinyl terminated polyurethane prepolymer.
[e] Butyl acrylate.
[f] Pilling of untreated fabrics = 2.
[g] Commercial standard sample no. 1 (EFD).
[h] Commercial standard sample no. 2 (SE).

experiment was 16 and resolution was 4 cm^{-1}. The stripe satin fabrics (Table 1) after application of PU acrylate copolymer were evaluated applying pilling standard test method ASTM D-3514-02 (ASTM, 2004).

3. Results and discussion

3.1. FT-IR spectral studies

All the emulsion samples were cured in the dry oven at 45 °C, for 48 h. These films were used for further analysis. FTIR spectra of monomers toluene-2,4-diisocyanate (TDI) (Fig. 1a), 2-methyl-1,3-propylene glutarate-diol terminated polyol (Fig. 1b), isocyanate (NCO) terminated PU prepolymer obtained by the reaction of TDI and poly (2-methyl-1,3-propylene glutarate) diol terminated polyol (Fig. 1c), 2-hydroxyethylacrylate (HEA) (Fig. 1d), vinyl terminated PU prepolymer (Fig. 1e), butyl acrylate (BuA) (Fig. 1f) and polyurethane acrylate copolymers (Fig. 1g) are jointly presented in Fig. 1 and discussed.

FTIR spectra of toluene-2,4-diisocyanate (TDI) (Fig. 1a) show an intense peak at 2233.66 cm^{-1} due to characteristic isocyanate (–NCO) groups attached to the toluene-2,4-diisocyanate. The FT-IR spectrum shows sharp peaks at 1527 cm^{-1}, which is due to the C=C stretching of benzene ring. The observed peaks in the functional group region of FT-IR spectrum of poly (2-methyl-1,3-propylene glutarate) diol terminated polyol (Fig. 1b) were assigned as: 3506 cm^{-1} (OH stretching vibration); 2963 cm^{-1} (asymmetric CH_2 stretching); 2865 cm^{-1} (symmetric CH_2 stretching); 1726 cm^{-1} (C=O stretching). FT-IR spectrum of NCO terminated PU prepolymer has also been presented in Fig. 1c. It is clearly observed that the signal for the OH groups disappeared and that of the intensity of isocyanate (–NCO) groups has reduced to some extent resulting that isocyanate group has entirely reacted and a signal for NH units appeared at 3239 cm^{-1} suggesting that PU prepolymer had been formed (Fig. 1c). The other observed peaks in the FT-IR spectrum of PU prepolymer were assigned as: 2931 cm^{-1} (CH symmetric stretching of CH_2); 2889 cm^{-1} (CH asymmetric stretching of CH_2 groups); 2272 cm^{-1} (isocyanate (–NCO) group); 1727 cm^{-1} (C=O stretching of soft segment of poly (2-methyl-1,3-propylene glutarate) diol terminated polyol). Disappearance of intense peak 2233 cm^{-1} (–NCO) and appearance of less intense peak at about 2272 cm^{-1} (–NCO), indicates that the NCO group has been reacted with OH groups of poly (2-methyl-1,3-propylene glutarate) diol terminated polyol and confirms that isocyanate terminated PU prepolymer has been formed. In Fig. 1c PU prepolymer exhibited the characteristic absorption peaks at about 810 cm^{-1} (C=C band), 1600 cm^{-1} (C=C bond), 1532 cm^{-1} (N–H bending and C–N stretch), 1720 cm^{-1} (C=O stretch) and 3339 cm^{-1} (N–H stretching) (Yaobin et al., 2006). The free ends of isocyanates group were further reacted with hydroxyl ethyl acrylate (HEA) (Wang et al., 2008). The observed peaks in the FT-IR spectrum of HEA (Fig. 1d) were assigned as: 3486 cm^{-1} (OH stretching vibration); 2946 cm^{-1} (asymmetric CH_2 stretching); 2833 cm^{-1} (symmetric CH_2 stretching); 1723 cm^{-1} (C=O stretching); 1533 cm^{-1} (C=C stretching); 1135 cm^{-1} (C–O, C–C stretching). After the reaction of NCO terminated PU prepolymer (Fig. 1c) with that HEA (Fig. 1d), the vinyl terminated PU polymer was formed. FTIR spectra of vinyl terminated PU polymer (Fig. 1e) show small stretching at 3330 cm^{-1} (N–H stretching) due to formation of urethane linkage in the vinyl terminated PU prepolymer. The CH stretching of CH_2 group was observed at 2931 cm^{-1}. The FT-IR spectrum shows sharp peaks at 1727 cm^{-1} and 1530 cm^{-1} which is due to the C=O and C=C stretching of the synthesized material, respectively. It can be observed in the vinyl terminated PU prepolymer spectrum that NCO peak has been disappeared indicating the complete utilization of the NCO group with that of HEA forming vinyl terminated PU prepolymer. Also, appearance of peaks at 809 cm^{-1} and at 1600 cm^{-1} delegates the incorporation of HEA in the PU backbone. The vinyl terminated PU prepolymer chain was further extended with the addition of butyl acrylate. The FT-IR of butyl acrylate (BuA) is given in Fig. 1f. The observed peaks in the FT-IR spectrum of BuA (Fig. 1f) were assigned as: 2949 cm^{-1} (asymmetric CH_2 stretching); 2830 cm^{-1} (symmetric CH_2 stretching); 1726 cm^{-1} (C=O stretching); 1530 cm^{-1} (C=C stretching); 1131 cm^{-1} (C–O, C–C stretching). Fig. 1g represents the complete synthesis of PU acrylate copolymers. It shows presence of N–H groups at about 3450 cm^{-1}, carbonyl group at 1731 cm^{-1} and peaks at 2929 cm^{-1}, 2870 cm^{-1} for CH anti-symmetric and symmetric stretching, respectively. To provide clear information about the vibrational mode changes due to involvement of butyl acrylate to the polyurethane backbone during the polymerization reaction, FT-IR spectrum obtained from the sample is shown in Fig. 1g. In the FT-IR analysis obtained for the final PU acrylate sample, the disappearance of the NCO peak at 2272 cm^{-1} and the appearance of N–H peak at 3393 cm^{-1} confirmed the completion of polymerization reaction. FT-IR spectrum of the final polyurethane obtained support the proposed structure of the final polymer. The observed peaks in the spectrum imply that the reaction was completed and the predesigned PU acrylate was formed.

3.2. Emulsion stability of the synthesized samples

The results regarding emulsion stability of the prepared polyurethane acrylate samples and the pilling evaluation of the printed satin treated fabrics are presented in Table 3. In five (5) sets of 30 experiments (e.g. A_1–F_1, A_2–F_2, A_3–F_3, A_4–F_4, and A_5–F_5) the stability of the emulsions decreased by increasing the concentration of vinyl terminated polyurethane prepolymer or by decreasing the amount of butyl acrylate (BuA). Furthermore, in five sets of 30 experiments when mole ratio of polyol is decreased, the stability of emulsions (for the period over one year) continually increases as mole ratio decrease from 2.0 moles to 1.9 and 1.8 moles, but when it further decreases to 1.7 and 1.6 moles, the emulsions were less stable comparatively. The resulting order of emulsion stability of the prepared samples have great influenced on the treated fabrics samples imparting high tensile strength and stretchability, excellent film forming characteristics, good body and handle for finished fabrics, excellent wash-fastness, resistant to dry cleaning, high crease-resistance and excellent pill resistance.

3.3. Pill characterization and evaluation

Pills are localized minor disturbances randomly distributed on the surface, while protruding yarn, which are part of the fabric structure; appear to be periodical and associated only with the pattern of interlacing (weave) or interloping (knit). These give a very unsightly look to the garments. In the visual evaluation, observers intend to rate the pilling appearance of a fabric by comparing pill properties such as density, size and height, to those of the visual standards. (a) Pill density is the first impression that an observer probably will get when examining a pilled sample. The pill density is often estimated by the number of pills in a unit area. This definition is accurate only if pills are randomly or uniformly distributed over the area selected for counting pills. When clumping occurs the result will substantially vary with the area. A more rational estimator of pill density can be constructed based on the distances of pills to their nearest neighbors. The nearest distance of two pills is the length between the two centers. (b) The average size of pills is another important factor influencing pilling appearance. Someone can locate and count the pill, and then calculate the following statistical data: mean, standard deviation, maximum, minimum and area percentage, which is equal to the ratio of the total area of pills to the image area. The size distribution curve can be calculated as well. (c) The contrast between a pill and its surrounding region reflects the height of the pill. In a gray-scale image, the contrast between two regions is measured by the difference in intensity.

In order to make the rating results generated by the pilling evaluation system consistent with the visual standards, the ASTM photographic pilling standards is first analyzed using the system and the rating equations is built based on the measurements of pill properties of these photographs. Although the average size of pills has a decreasing trend when the pilling grade increases, there is no significant difference between grades 1 and 2. This is because pills are worn off as their sizes increase to a certain level. Hence, the average pill size alone is not sufficient for rating pilled samples. The density and % area of pills show relatively coherent decreases with the pilling grade, though the relationships are non-linear.

The results presented in Table 3 show clear separation lines among the five pilling propensity groups and a progressive trend between the no pilling (rating 5) and the most severe pilling (rating 1) samples. The results in Table 3 show that the 32 pilling samples (30 experimental samples and 2 standard samples) in each standard test set are successfully classified into five pilling grades. Pilling evaluation results of 32 samples (A_1–F_1, A_2–F_2, A_3–F_3, A_4–F_4, A_5–F_5, S_1 and S_2) showed that pilling rating improved by decreasing the amount of butyl acrylate (BuA) and/or by increasing the percentage of vinyl terminated PU prepolymer and vice versa. Furthermore, in all sets of 30 experiments and two standard samples when mole ratio of poly (2-methyl-1,3-propylene glutarate) diol terminated polyol is decreased, the pilling rating continually improved as mole ratio decrease from 2.0 moles to 1.6 moles. It can be observed that all sets of experiment have shown comparatively good results as compared to standard sample available in the market. In comparison to all the 5 sets, the samples (A_5–F_5) have shown excellent results. This behavior may be attributed to the good emulsion stability and compatibility of the co-polymerized samples.

4. Conclusion

Pilling is a fabric surface fault characterized by little pills of entangled fibers clinging to the surface. These are formed during wearing or washing by the entanglement of the loose fibers which protrude from the fabric surface and development of these into spherical bundles anchored to the fabric by a few unbroken fibers. Polyurethane acrylate copolymers have been synthesized by following three step synthesis processes. Structural characteristics of the synthesized polyurethane (PU) acrylate copolymer were studied using Fourier Transform Infrared (FT-IR) spectrophotometer. The stripe satin cotton printed fabrics after application of PU acrylate copolymer was evaluated applying pilling standard test method. The results revealed that emulsion stability and pilling rating improved by decreasing the percentage of butyl acrylate (BuA) and or by increasing the concentration of vinyl terminated PU prepolymer. The emulsion stability and pilling rating continually improved as mole ratio of the polyol decrease from 2.0 moles to 1.6 moles. Density, size and contrast are the important properties of pills that describe the degree of pilling, and are used as independent variables in the grading equations of pilling.

Acknowledgements

This work is a part of PhD thesis of Ms Misbah Sultan. Financial support of Higher Education Commission (HEC), Government of Pakistan regarding indigenous 5000 scholarship and international research support initiative program (IRSIP) is highly appreciated and acknowledged for the conduct of this work.

References

ASTM Standards. (2004). *Standard test method for pilling resistance and other related surface changes of textile fabrics: Elastomeric Pad1 (D 3514-02)*. USA: American Society of Testing Material, ASTM International.

Barikani, M., & Hepburn, C. (1986). Isocyanurate crosslinking as a means of producing thermally stable polyurethane elastomers. *Cellular Polymer*, *5*, 169–185.

Barikani, M., Zia, K. M., Bhatti, I. A., Zuber, M., & Bhatti, H. N. (2008). Molecular engineering and properties of chitin based shape memory polyurethane elastomers. *Carbohydrate Polymers*, *74*, 621–626.

Booth, J. E. (1968). *Principles of textile testing* (3rd ed.). London: Butterworths.

Czech, Z. (2004). Development in the area of UV-crosslinkable solvent-based pressure-sensitive adhesive with excellent shrinkage resistance. *European Polymer Journal*, *40*, 2221–2227.

Hegedus, C. R., & Kloiber, K. (1996). Aqueous acrylic-polyurethane hybrid dispersions and their use in industrial coatings. *Journal of Coatings Technology*, *68*(860), 39–48.

Horigome, K., Ebe, K., & Kuroda, S. (2004). UV curable pressure-sensitive adhesives for fabricating semicondutors. II. The effect of functionality of acrylate monomers on the adhesive properties. *Journal of Applied Polymer Science*, *93*, 2889–2895.

Kaczmarek, H., & Chaberska, H. (2006). The influence of UV-irradiation and support type on surface properties of poly(methyl methacrylate) thin films. *Applied Surface Science*, *252*, 8185–8192.

Kaczmarek, H., & Podgorski, A. (2007). The effect of UV-irradiation on poly(vinyl alcohol) composites with montmorillonite. *Journal of Photochemistry and Photobiology A: Chemistry*, *191*, 209–215.

Król, P., Król, B., Pikus, S., & Skrzypiec, K. (2005). Study on the synthesis and on supermolecular structures of a water-dilutable urethane-acrylic copolymer applicable as a binder for powdered Al_2O_3. *Colloids and Surfaces A: Physicochemical & Engineering Aspects*, *259*, 35–44.

Kukanja, D., Golob, J., Ic-Valant, Z., & Krajnc, A. M. (2000). The structure and properties of acrylic–polyurethane hybrid emulsions and comparison with physical blends. *Journal of Applied Polymer Science*, *78*, 67–80.

Matsushita, Y., Suzuki, A., Sekiguchi, T., Saito, K., Imai, T., & Fukushima, K. (2008). Mapping of the cationic starch adsorbed on pulp fibers by ToF-SIMS. *Applied Surface Science*, *255*, 1022–1024.

Santosa, S. J., Siswanta, D., Sudiono, S., & Utarianingrum, R. (2008). Chitin–humic acid hybrid as adsorbent for Cr(III) in different of tannery wastewater treatment. *Applied Surface Science*, *254*, 7846–7850.

Wang, F., Hu, J. Q., & Tu, W. P. (2008). Study on microstructure of UV-curable polyurethane acrylate films. *Progress in Organic Coatings*, *62*, 245–250.

Woods, G. (1990). *The ICI polyurethanes book* (2nd ed.). John Wiley and Sons.

Yaobin, R., Huiming, P., Longsi, L., Jianming, X., & Yongqiang, Y. (2006). Synthesis of polyurethane acrylate and application to ultraviolet-curable pressure-sensitive adhesive. *Polymer-Plastics Technology and Engineering*, *45*, 495–502.

Yokota, S., Kitaoka, T., & Wariishi, H. (2008). Surface morphology of cellulose films prepared by spin coating on silicon oxide substrates pretreated with cationic polyelectrolyte. *Applied Surface Science*, *253*, 4208–4214.

Zia, K. M., Barikani, M., Bhatti, I. A., Zuber, M., & Bhatti, H. N. (2008b). Synthesis and thermo-mechanical characterization of polyurethane elastomers extended with α,ω-alkane diols. *Journal of Applied Polymer Science*, *109*, 1840–1849.

Zia, K. M., Barikani, M., Bhatti, I. A., Zuber, M., & Bhatti, H. N. (2008e). Synthesis and characterization of novel biodegradable thermally stable chitin based polyurethane elastomers. *Journal of Applied Polymer Science*, *110*, 769–776.

Zia, K. M., Barikani, M., Khalid, A. M., Honarkar, H., & Ehsan-ulHaq. (2009). Surface characteristics of UV-irradiated chitin based polyurethane elastomers. *Carbohydrate Polymers*, *77*, 621–627.

Zia, K. M., Barikani, M., Zuber, M., Bhatti, I. A., & Barmar, M. (2009e). Surface characteristics of polyurethane elastomers based on chitin/1,4-butane diol blends. *International Journal of Biological Macromolecules*, *44*, 182–185.

Zia, K. M., Barikani, M., Zuber, M., Bhatti, I. A., & Barmar, M. (2009f). XRD studies of UV-irradiated chitin-based polyurethane elastomers. *Carbohydrate Polymers*, *77*, 54–58.

Zia, K. M., Barikani, M., Zuber, M., Bhatti, I. A., & Bhatti, H. N. (2008). Morphological studies of polyurethane elastomers extended with α,ω-alkane diols. *Iranian Polymer Journal*, *17*, 61–72.

Zia, K. M., Barikani, M., Zuber, M., Bhatti, I. A., & Islam-ud-Din. (2008). Surface characteristics of UV-irradiated polyurethane elastomers extended with α,ω-alkane diols. *Applied Surface Science*, *254*, 6754–6761.

Zia, K. M., Barikani, M., Zuber, M., Bhatti, I. A., & Sheikh, M. A. (2008). Molecular engineering of chitin based polyurethane elastomers. *Carbohydrate Polymers*, *74*, 149–158.

Zia, K. M., Bhatti, H. N., & Bhatti, I. A. (2007). Methods for polyurethane and polyurethane composites, recycling and recovery: A review. *Reactive and Functional Polymer*, *67*, 675–692.

Zia, K. M., Bhatti, I. A., Barikani, M., Zuber, M., & Bhatti, H. N. (2009). XRD studies of polyurethane elastomers based on chitin/1,4-butane diol blends. *Carbohydrate Polymers*, *76*, 183–187.

Zia, K. M., Tabassum, S., Barkaat-ul-Hasin, S., Zuber, M., Jamil, T., & Jamal, M. A. (2011). Preparation of rich handles soft cellulosic fabric using amino silicone based softener. Part-I: Surface smoothness and softness properties. *International Journal of Biological Macromolecules*, *48*, 482–487.

Zia, K. M., Zuber, M., Barikani, M., Bhatti, I. A., & Khan, M. B. (2009). Surface characteristics of chitin based shape memory polyurethane elastomers. *Colloids and Surfaces B: Biointerfaces*, *72*, 248–252.

Zia, K. M., Zuber, M., Bhatti, I. A., Barikani, M., & Sheikh, M. A. (2009a). Evaluation of biocompatibility and mechanical behavior of polyurethane elastomers based on chitin/1,4-butane diol blends. *International Journal of Biological Macromolecules*, *44*, 18–22.

Zia, K. M., Zuber, M., Bhatti, I. A., Barikani, M., & Sheikh, M. A. (2009b). Evaluation of biocompatibility and mechanical behavior of chitin polyurethane elastomers. Part-II: Effect of diisocyanate structure. *International Journal of Biological Macromolecules*, *44*, 23–28.

Zuber, M., Zia, K. M., Tabassum, S., Jamil, T., Barkaat-ul-Hasin, S., & Khosa, M. K. (2011). Preparation of rich handles soft cellulosic fabric using amino silicone based softener. Part II: Colorfastness properties. *International Journal of Biological Macromolecules*, *49*, 1–6.