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Properties of the modified cellulosic fabrics using polyurethane acrylate copolymers

Shazia Tabasum, Mohammad Zuber, Abdul Jabbar, Khalid Mahmood Zia*

Institute of Chemistry, Government College University, Faisalabad 38030, Pakistan

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ABSTRACT

Polyurethane acrylate copolymers (PAC) were synthesized via emulsion polymerization following three step synthesis process using toluene-2,4-diisocyanate, hydroxy terminated poly(caprolactone) diol, 2-hydroxyethylacrylate (HEA) and butyl acrylate (BuA). Structural characteristics of the synthesized polyurethane acrylate copolymer (PAC) were studied using Fourier Transform Infrared (FT-IR) spectrophotometer and are with accordance with the proposed PAC structure. The physicochemical properties such as solid contents (%), tackiness, film appearance and emulsion stability were studied, discussed and co-related with other findings. The plain weave poly-cotton printed fabrics after application of PAC was evaluated applying colorfastness standard test method. The results revealed that emulsion stability is the main controlling factor of the synthesized material in order to get better applications and properties. The emulsion stability of the synthesized material increased with increase in molecular weight of the polycaprolactone diol.

1. Introduction

The hard and soft segments of polyurethane result to form a microphase separated structure, which brings them to be used in various ways such as adhesives, coatings, biomedical materials and elastomers (Barikani & Hepburn, 1986, 1987). Polyurethane elastomers (PUEs) are possibly the most versatile classes of polymers as they can be molded, injected, extruded and recycled (Zia, Bhatti, & Bhatti, 2007). Molecular characterization and morphological studies of PUEs have been reported by many researchers (Rogulska, Podkoscielny, Kultys, Pikus, & Pozdzik, 2006; Zia, Barikani, Zuber, Bhatti, & Bhatti, 2008). The effect of the diisocyanate structure (Rogulska et al., 2006) and chain extender (CE) length using α,ω-alkane diols on the crystallinity, surface morphology (Zia, Barikani, Zuber, Bhatti, & Bhatti, 2008) and thermo-mechanical properties (Zia, Barikani, Bhatti, Zuber, & Bhatti, 2008a) of PUEs have also been investigated and well documented. Regarding established literature on chitin based polyurethane synthesis, characterization and application, extensive work on structural characterization, crystalline patterns, and thermal properties of chitin-based polyurethane elastomers (PUEs) have been comprehensively reported elsewhere (Zia, Barikani, Bhatti, Zuber, & Bhatti, 2008b; Zia, Barikani, Zuber, Bhatti, & Sheikh, 2008; Zia, Bhatti, Barikani, Zuber, & Sheikh, 2008). In vitro biocompatibility and cytotoxicity of chitin/1,4-butanediol blend based polyurethane elastomers have been reported in the literature (Zia, Zuber, Bhatti, Barikani, & Sheikh, 2009c, 2009d). Few reports have been found on the structural characterization of chitin-based polyurethane elastomers and their shape memory characteristics (Barikani, Zia, Bhatti, Zuber, & Bhatti, 2008; Zia, Zuber, Barikani, Bhatti, & Khan, 2009). 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 and alkane diols based polyurethane elastomers have also been presented elsewhere (Zia, Barikani, Khalid, Honarkar, & Ehsan-ulHaq, 2009; Zia, Barikani, Zuber, Bhatti, & Barmar, 2009a, 2009b). 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, and on soft domains which have been built from flexible segments derived from polyol components (Barikani et al., 2008; Zia, Zuber, Barikani, Jabbar, & Khosa, 2010; Zia, Zuber, Mahboob, Sultana, & Sultana, 2010). 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 (Zuber, Zia, Mahboob, Hassan, & Bhatti, 2010).

Waterborne polyurethanes (WPUs) are widely used in different fields such as coatings, adhesives and paints, since they are

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* Corresponding author. Tel.: +92 300 6603967; fax: +92 041 9200671.
E-mail address: ziakmpkpolym@yahoo.com (K.M. Zia).

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non-hazardous, nonflammable and do not pollute the air due to no or little volatile organic compounds in final formulation (Dieterich, 1981; Rahman, Kim, Yun Kwon, Yoo, & Kim, 2008; Zuber, Zia, Bhatti, Ali, et al., 2012; Zuber, Zia, Bhatti, Jamil, et al., 2012). WPUs have emerged as an important class of polymeric materials in the paint and ink industries because of their environment-friendly nature (Guo, Li, Wang, Ma, & Hang, 2012; Zia et al., 2012). The professional literature and scientific writings have reported possible applications of water-borne polyurethanes for impregnation of materials (Król, Król, Pikus, & Skrzypiec, 2005). Polyacrylate (AC) emulsions and polyurethane (PU) aqueous dispersions have been extensively used in coating applications. Both the AC and PU have shown some drawback such as acrylic represents the lack of better film forming properties, show less chemical resistance, and rough mechanical properties and PU on the other hand represents the high cost, low pH stability, and limited outdoor durability (Hegedus & Kloiber, 1996). 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 (Sultan et al., 2012). Acrylic (AC) component on the other hand shows high outdoor resistance and lower cost (Kukanja, Golob, Ic-Valant, & Krajnc, 2000). So, blending of properties of AC & PU definitely will help to get such a polymer with required properties. Polyurethane acrylates are also applied as UV-curable, pressure-sensitive adhesive (PSA) due to decrease in emission of volatile organic compounds (Horigome, Ebe, & Kuroda, 2004; Yaobin, Huiming, Longsi, Jianming, & Yongqiang, 2006).

Regarding textile applications of the materials, few reports on amino silicone based softener are also available (Bhatti, Zia, Ali, Zuber, & Fazal-Ur-Rehman, 2012; Zia, Tabassum, et al., 2011; Zia, Zuber, et al., 2011; Zuber et al., 2011). Great efforts have been dedicated to combine the polyurethanes with acrylic polymers to increase the performance-to-cost ratio of the coatings (Wang, Hu, & Tu, 2008). There are only a limited number of reports about the preparation and application of eco-friendly binders for textile finishing purposes (Tabasum, Zuber, Jamil, Shahid, & Hussain, 2013; Sultan et al., 2012). Polyurethane acrylate oligomers have gained more and more attention and speedy development. Considering excellent outdoor resistance of polyacrylates and versatile properties of polyurethanes, the present project is designed to synthesize polyurethane acrylate copolymers varying by molecular weight of polycaprolactone diols in order to study the effect of molecular weight on the properties of the treated and untreated fabrics.

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. (Saint 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, Ohio. Potassium persulfate (KPS), sodium thiosulfate ($Na_2S_2O_3$), 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 (ASTM, 2004). 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, scoured, bleached, printed, poly cotton (cotton/polyester ratio 44:56), plain weaved fabrics 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 copolymers, the fabric was completely 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. Step 1: synthesis of isocyanate (NCO) terminated polyurethane (PU) prepolymer (PAC-1)

The synthesis of PU prepolymers was carried out according to the recommended procedure (Barikani & Hepburn, 1986). First of all (2 mol) of hydroxyl terminated polycaprolactone diols (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. Polycaprolactone diols was stirred continuously under the blanket of nitrogen gas for 30 min at 60 °C. Then 3 mol of toluene-2,4-diisocyanate (TDI) were added to the reaction vessel and temperature was raised to 80 °C. During optimization of the experimental conditions it was confirmed that the formation of isocyanate (NCO) terminated polyurethane (PU) prepolymer completes in 1 h (Fig. 1a – Step 1). A Fourier Transform Infrared (FTIR) spectrum of the PU prepolymer was also obtained to confirm the progress of polturethane (PU) prepolymer reaction (Fig. 2). The NCO contents of the PU prepolymer were determined and the experimental values were found close to the theoretical value (experimental value 9.27%; theoretical value 9.29%).

2.2.2. Step 2: synthesis of vinyl terminated polyurethane prepolymer

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. The reaction was continued for 30 min and there was a thick, viscous and milky material in the reaction vessel (Wang et al., 2008) which indicates the formation of vinyl terminated PU prepolymer (Fig. 1b-Step 2). The formation of the vinyl terminated PU prepolymer was also confirmed by FT-IR (Fig. 1).

2.2.3. Step 3: copolymerization of vinyl terminated PU prepolymer with butyl acrylate (BuA)

As the formation of vinyl terminated PU prepolymer was confirmed, the copolymerization of vinyl terminated PU prepolymer was carried out with butyl acrylate (BuA) through emulsion polymerization. The following components were put to smooth and precede the polymerization reaction: polyvinyl alcohol-PVA (as protective colloid), a mixture of Montane 80 (HLB = 4.3) and Montanox 80 (HLB = 15) in the ratio of 30:70 in order to get the

Table 1
Fabrics specification with quality and processed applications.

S. no.	Quality	Construction/count	Blend ratio cotton/polyester	Processed application
01	Plain weave poly cotton	(76 × 68/30 × 30)	44/56	Pigments printed

Emulsifier systems of HLB value = 11.79, which is required for the such polymerization reaction, potassium persulfate (KPS) with $Na_2S_2O_3$ (as redox initiator). Sample code designation and different formulation of polyurethane acrylate copolymers (PAC) varying molecular weights of polycaprolactone diols is presented in Table 2. Aqueous solutions, i.e., 10% Montane 80:Montanox 80 (30:70), 3% (w/v) of PVA and 0.2% of potassium persulfate (KPS) were prepared separately following the formulation given in Table 3.

For this purpose 50% portions of the prepared above three solutions (emulsifier, PVA, KPS) were charged into the reaction vessel with one third (6 g) of butyl acrylate with continuing stirring for 1 h and labeled as 'A'. The remaining butyl acrylate (two-third, i.e., 12 g)

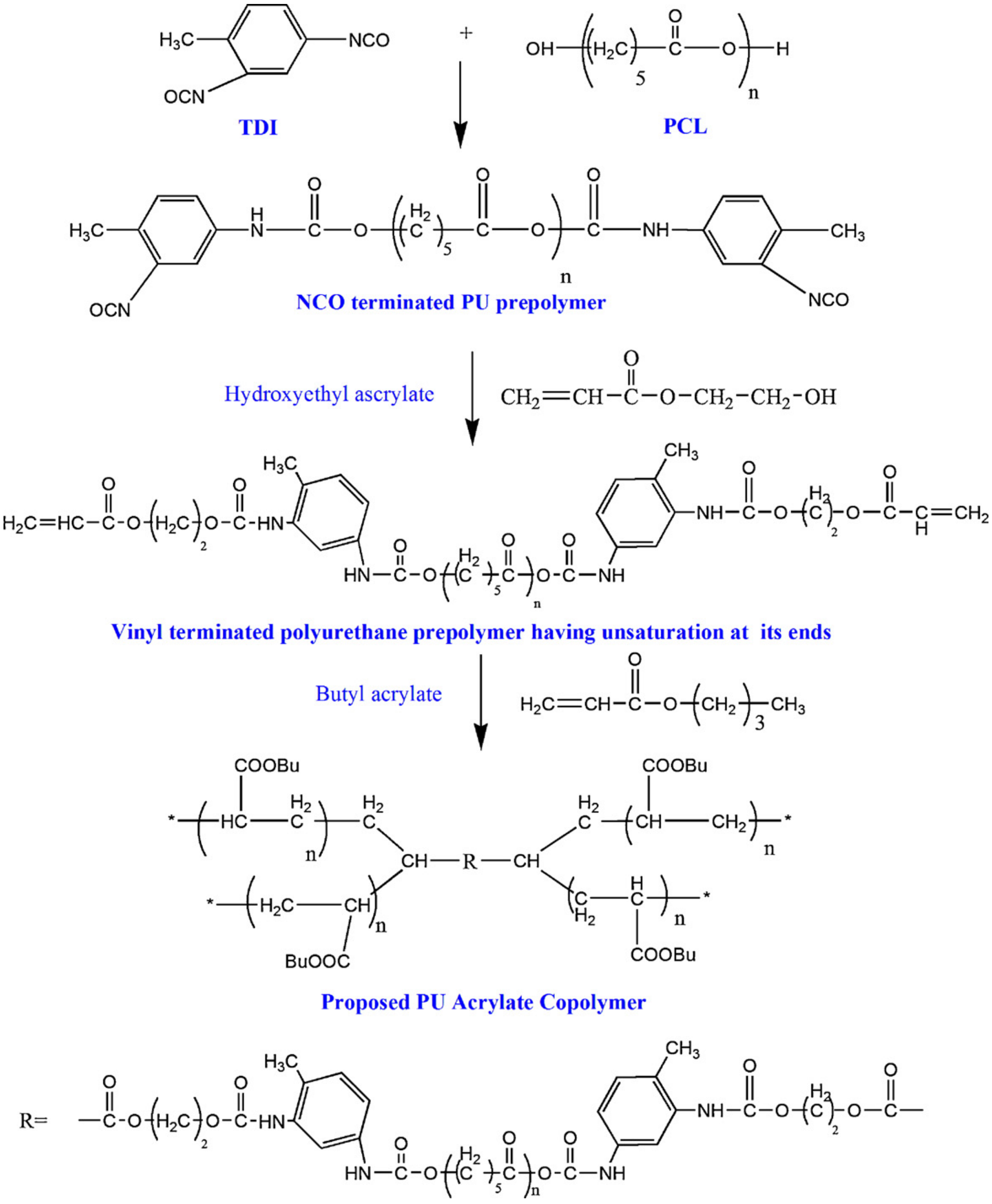


Fig. 1. Synthesis of polyurethane acrylate co-polymers containing polycaprolactone as a soft segment: (a) Step 1: preparation of NCO terminated polyurethane (PU) prepolymer, (b) Step 2: vinyl terminated PU prepolymer, and (c) Step 3: proposed polyurethane acrylate co-polymers.

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 (%).

was mixed up with 2 g of vinyl terminated polyurethane prepolymer using magnetic stirrer and labeled as the reagent 'B'. After 1 h stirring of the above reagent mixer 'A'; remaining halves of the solutions (emulsifier, PVA, KPS), and half of the reagent 'B' were charged into the 'A' with continuous stirring at 60 °C and the reaction was continued for another 1 h. The viscosity of the reaction mixture was observed to increase gradually with time. After 2 h of the reaction progress, the remaining half of the 'B' was charged into the reaction vessel and the reaction was continued for other 1 h with continuous stirring. As a result the emulsion polymerization of the above reactants was completed in almost 3 h with continuous stirring at 60 °C (Fig. 1c – Step 3).

Following the detailed procedure mentioned above, a total of the 7 samples of the emulsion of butyl acrylate and vinyl terminated polyurethane prepolymers were prepared varying the molecular weight of polycaprolactone diol in the PU prepolymer step. The detailed formulation of all these samples is given in Table 2. White and translucent white 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 Fig. 1a–c (Steps 1–3).

2.3. Dry weight contents (solid contents)

Dry weight contents (solid contents) of PAC copolymers were determined by drying a weighed volume of emulsion in aluminum cups using dry heating oven at 60 °C for 3 h till constant weight. The calculation was done as following:

$$\text{Solid contents}\quad (\%) = \frac{C - A}{B} \times 100$$

Weight of empty aluminum cup = A; weight of aluminum cup and PAC = B; weight of the aluminum cup and PAC after heating = C.

Table 3
Preparation of polyurethane acrylate copolymer (PAC) emulsions.

S. no.	Ingredients	Quantity
1	Vinyl terminated polyurethane prepolymer	2 g (2% of emulsion)
2	Butyl acrylates	18 g (18% of emulsion)
3	Polyvinyl alcohol	3 g (3% of emulsion)
4	Montane 80:Montanox 80 (30:70)	10 g (10% of emulsion)
5	Potassium persulphate (KPS)	0.2 g (0.2% of emulsion)
6	$Na_2S_2O_3$	One crystal added in KPS
7	Distilled water	Water to make the volume up to 100 mL

2.4. Molecular characterization

Molecular characterization of synthesized polyurethane acrylate copolymer sample containing different molecular weights was confirmed using Fourier Transform Infrared (FT-IR) spectroscopy. FT-IR scans of the prepared copolymer samples were obtained in the transmission mode using a Shimadzu Fourier Transform Infrared (FT-IR) spectrometer.

2.5. Treatment of fabrics with polyurethane acrylate copolymers emulsion

After the preparation of polyurethane acrylate copolymers emulsions containing different molecular weight of polycaprolactone diol, various dilutions (i.e., 15 g/L, 30 g/L and 50 g/L) of the prepared PAC samples were made and applied onto the printed poly-cotton fabric. After application, the treated printed fabric samples were dried at 100 °C for 4 min and then cured at 140 °C for 5 min.

2.6. Physical characterization and colorfastness properties

The solid contents (%), emulsion stability and emulsion appearance were also observed continuously and reported. The colorfastness to rubbing and change in shade of the printed treated fabrics after application of PU acrylate copolymer were evaluated applying standard test method (AATCC, 1968; ASTM, 2004).

3. Results and discussion

3.1. Molecular characterization

FTIR spectra of all the monomers and individual polymerization steps were recorded and presented in Fig. 2. FTIR spectra of toluene-2,4-diisocyanate (TDI), hydroxy terminated polycaprolactone diol, isocyanate (NCO) terminated PU prepolymer obtained by the reaction of TDI and hydroxy terminated poly(caprolactone diol), 2-hydroxyethylacrylate (HEA), vinyl terminated polyurethane (PU) prepolymer, butyl acrylate (BuA) and polyurethane acrylate copolymers are jointly presented in Fig. 2. The peaks assignment of the important functional group are presented and interpreted. FTIR spectrum of toluene-2,4-diisocyanate (TDI) (Fig. 2a) show a very sharp and an intense peak at 2241.28 cm^{-1} which corresponds to the isocyanate (—NCO) groups attached to the TDI structure. The FT-IR spectrum shows sharp peaks at 1516.05 cm^{-1} attributed to the C=C stretching of benzene ring. The peaks assignment appeared in FTIR spectrum of poly(caprolactone) diol (PCL) is presented in Fig. 2b. The observed peaks in the functional group region of PCL were assigned as: 3534 cm^{-1} (OH stretching vibration); 2937.59 cm^{-1} (asymmetric CH_2 stretching); 2876 cm^{-1}

Table 4
Physical characteristics of polyurethane acrylate copolymers (PACs) coatings varying molecular weight of polycaprolactone diols.

Sample code	Emulsion stability	Emulsion appearance	Tackiness	Film appearance	Solid content (%)
PAC-1	>1 year and ~9 months	White	Tack free	White	33.91
PAC-2	>1 year and ~10 months	White	Tack free	White	34.12
PAC-3	<1 year	White	Tack free	Translucent white	34.43
PAC-4	<1 year	White	Tack free	Translucent white	34.69
PAC-5	<1 year	Translucent white	Tack free	Opaque white	34.96
PAC-6	<1 year	Translucent white	Tack free	Off white	35.11
PAC-7	<1 year	Translucent white	Tack free	Off white	35.45

(symmetric CH_2 stretching); 1724.36 cm^{-1} (C═O stretching); 1168.86 cm^{-1} (C—O stretching). These two monomers (TDI & PCL) were reacted in the reaction flask and the reaction was lasted for 1 h at 100 °C. After optimization of the experimental conditions, it was observed that formation of polyurethane prepolymer is completed in 1 h and isocyanate terminated PU prepolymer has been produced. FT-IR spectrum of NCO terminated PU prepolymer has been given in Fig. 2c. It can be clearly observed from the spectrum that isocyanate (—NCO) group has been reacted with the OH group of the PCL and therefore the signal for the OH groups disappeared and that of the intensity of isocyanate (—NCO) groups has reduced to some extent resulting that isocyanate terminated PU prepolymer has been formed with a signal for NH units appeared at 3239 cm^{-1} (Fig. 2c). The other peaks observed in the FT-IR spectrum of PU prepolymer were assigned as: 2930 cm^{-1} (CH symmetric stretching of CH_2); 2893 cm^{-1} (CH asymmetric stretching of CH_2 groups); 2267 cm^{-1} (isocyanate (—NCO) group); 1726 cm^{-1} (C═O stretching of soft segment of poly(caprolactone) diol); 1190 cm^{-1} (C—O stretching of soft segment). Disappearance of intense peak 2241.28 cm^{-1} (—NCO) and appearance of less intense peak at about 2267 cm^{-1} (—NCO), confirms the completion of reaction and formation of the NCO terminated PU prepolymer. The PU prepolymer has also shown some characteristic absorption peaks (Fig. 2c) which were assigned as: 1534 cm^{-1}, 1530 cm^{-1} (N—H and C—N, bending and stretching respectively), 1605 cm^{-1} (C═C), 1720 cm^{-1} (C═O stretching) and 3339 cm^{-1} (N—H stretching). The isocyanate terminated PU prepolymer was further reacted with 2-hydroxyl ethyl acrylate (HEA) following the established reported method (Sultan et al., 2012). The FTIR spectrum of 2-HEA (Fig. 2d) has shown many characteristics peaks, i.e., a broad peak at 3433.29 cm^{-1} corresponds to OH stretching vibration; 2923.78 cm^{-1}, attributed to asymmetric CH_2 stretching; 2883.58 cm^{-1}, assigned to symmetric CH_2 stretching; 1714.15 cm^{-1}, ascribed to C═O stretching; 1545 cm^{-1} relates to C═C stretching; 1193.94 cm^{-1}, consigned to C—O, C—C stretching. The vinyl terminated PU prepolymer was formed by the reaction of isocyanate terminated PU prepolymer with that of 2-hydroxy ethyl acrylates. FTIR spectra of vinyl terminated PU polymer show a well-defined peak of N—H stretching at 3333 cm^{-1} attributed to the formation of urethane linkage in the vinyl terminated PU prepolymer (Fig. 2e). The CH stretching of CH_2 group was observed at 2929.87 cm^{-1}. The FT-IR spectrum shows very sharp peaks at 1716.65 cm^{-1} and 1531.48 cm^{-1} which are attributed to the C═O and C═C stretching of the synthesized material, respectively. It is clearly observed in the FTIR spectrum of vinyl terminated PU prepolymer that isocyanate (NCO) peak has been disappeared indicating the complete utilization of the NCO contents with that of 2-hydroxy ethyl acrylate forming vinyl terminated PU prepolymer. The chain extension of vinyl terminated PU prepolymer was carried out with the addition of butyl acrylate. The FT-IR spectrum of butyl acrylate (BuA) is presented in Fig. 2f. The FTIR spectrum of BuA showed distinct characteristic peaks which are assigned as: 2949.16 cm^{-1} (asymmetric CH_2 stretching); 2832 cm^{-1} (symmetric CH_2 stretching); 1724.36 cm^{-1} (C═O stretching); 1534 cm^{-1} (C═C stretching); 1188.15 cm^{-1} (C—O, C—C stretching). The reaction of butyl acrylate with that of vinyl terminated polyurethane prepolymer leads to the formation of PU acrylate copolymers. The FTIR spectrum of finally synthesized PU acrylate copolymers is presented in Fig. 2g. The FTIR spectrum shows characteristic peaks, i.e., 3371.57 cm^{-1}, attributed to N—H stretching; 1693.49 cm^{-1}, corresponds to carbonyl stretching; and 2929.87 cm^{-1}, 2847.70 cm^{-1} ascribed to CH anti-symmetric and symmetric stretching, respectively. The clear information about the vibrational mode changes due to involvement of butyl acrylate to the polyurethane backbone during the polymerization reaction can be obtained and hence the completion of the reaction can also be best studied through FTIR analysis technique. It is worth mentioning that the completeness of polymerization reaction can be confirmed by the appearance or disappearance of some characteristic peaks. As in the case, the FTIR spectra the isocyanate (NCO) peak at 2267 cm^{-1} disappeared and the N—H peak at 3371.57 cm^{-1} appeared, confirm the completion of polymerization reaction and hence formation of proposed polyurethane acrylate copolymer.

3.2. Physical characterization

The results regarding physical characteristics of polyurethane acrylate copolymers (PAC) varying molecular weight of polycaprolactone diols are presented in Table 4. Physical characteristics of PAC samples such as solid contents (%), emulsion appearance, tackiness, film appearance and emulsion stability are reported in Table 4. These parameters are essential for further use of emulsions in various applications. Solid content of the synthesized material is in the ranges of 33–36% which are in good agreement with that of Sultan et al. (2012). The reported results in Table 4 emphasis that dry weight content of PU acrylate copolymer sample PAC-1 is lesser as compared to the PAC-7, although, equal amount of the vinyl terminated polyurethane prepolymer was taken during emulsion polymerization with BuA. This slight continual increase in the solid contents can be explained on the basis of the gradual increase in the macrodiols. So, by increasing the molecular weight of the polycaprolactone diol the resultant emulsion showed gradual increase in solid contents (%). It is worth mentioning that high solid contents sample have a short drying time and form an adjustable film thickness in fewer passes.

Emulsion appearance in all the studied samples is almost same, i.e., white or translucent white, however sample containing molecular weight up to 1250 g/mol show white and remaining show translucent white appearance. A gradual increase in translucency of the emulsion with increase in molecular weight of polycaprolactone diols has been observed. It looks that the relatively more polarity of the ester linkage in the polycaprolactone diols (CAPA) moiety is responsible for this effect. The results presented in Table 4 revealed that the emulsion stability of all the prepared polyurethane acrylate copolymer samples continually increases by increasing the molecular weight of the soft segment (PCL). By using low molecular weight PCL, i.e., 400 and 750, the stability of the emulsion is ~9 and ~10 months, respectively. However by using higher molecular weight of PCL (>1000) the stability of the emulsion is observed greater than 1 year. The preparation of polyurethane dispersion has been reported by many researchers (Dieterich &

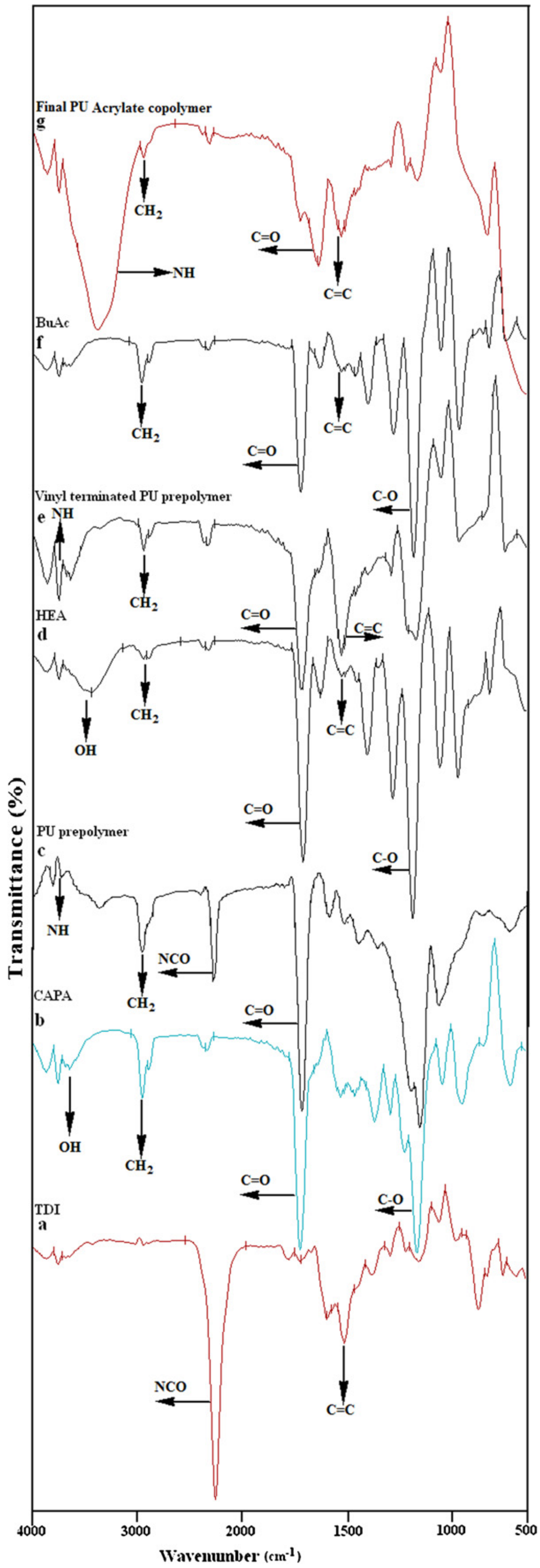
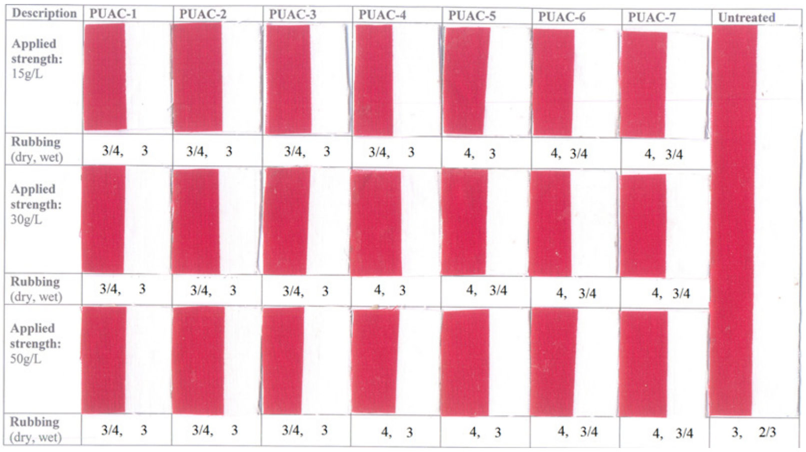


Fig. 2. FT-IR spectra: (a) toluene-2,4-diisocyanate (TDI); (b) polycaprolactone diol (CAPA); (c) NCO terminated polyurethane prepolymer; (d) 2-hydroxyethylacrylate (HEA); (e) vinyl terminated polyurethane prepolymer; (f) butyl acrylate (BuA); (g) Final polyurethane acrylate copolymers (PUAC).

Dieterich, 1973) and polyelectrolyte properties of polyurethane have also been filed time to time. Polyelectrolyte phenomenon of PU well defines the stability of emulsions. Polyurethane may only show polyelectrolyte properties if there are some specific functional groups (capable of carrying positive or negative charge) attached to the polyurethane backbone. However in this case, no such group is attached and the emulsion stability may be attributed to the biphase nature of the PAC emulsion. It has been observed and reported in the above lines that the color of the emulsion changes from white to translucent white by increasing the molecular weight of the polycaprolactone diol. The acrylate based PU samples having high molecular weight of CAPA gave translucent emulsion. This might be due to better interaction because of more hydrophilic regions in the polymer chain. Therefore, with increasing the molecular weight of the polyurethane acrylates copolymers, the stability increases. However, if the molecular weight is too high, it will not dissolve in the solution and instead of increasing stability it will form gel lumps, and ultimately results to decrease the emulsion stability (Wang, Kimura, & Dubin, 2000). Therefore it can be concluded that up to the use of molecular weight of CAPA 4000 g/mol (CAPA 2403A), the emulsions remain stable. The resulting order of emulsion stability of the prepared samples will surely be great influenced on the treated fabrics samples imparting high tensile strength and stretch-ability, 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. *Colorfastness properties*

The properties of the fabrics to resist the change in color towards the various testing parameters are called the colorfastness properties. The results of colorfastness to rubbing (dry and wet) are presented in Fig. 3. The results revealed that the treatment of polyurethane acrylates copolymers has pronounced effect on the crock fastness properties of all the treated fabric swatches. The untreated fabric swatch has shown dry and wet rubbing rating 3 and 2/3, respectively, whereas all the treated fabrics swatches have shown dry rubbing rating in the range of 3/4 to 4, and wet rubbing rating in the range of 3 to 3/4. It is clear from the results (Table 4) all the treated fabrics swatches have shown some better resistance to crocking. However, the samples treated with polyurethane acrylate copolymer containing low molecular weight of PCL have shown some slightly poor crock fastness as compared to those containing high molecular weight. The display of such results might be because of formation of stable tough coating layer on the treated fabrics. The performance of PAC emulsion based on high molecular weight PCL is slightly better than those of containing lower molecular weight PCL. This is very interesting display of structure property correlation. It looks that in case of high molecular weight PCL the resulting PAC has higher number of polar ester groups incorporated in the polymer chain. These provide more opportunity and have maximum inter-chain interaction and polymer substrate interaction which results in better performance. This improvement in the crock fastness of all the treated fabric swatches may also come jointly with a remarkable chemical versatility due to the presence of the acrylic and urethane (—NHCOO—) groups. It has been reported in the established literature that PU show better solvent and chemical resistance, and toughness (Sultan et al., 2012) and polyacrylates (AC) component on the other hand shows high outdoor resistance and pigment ability (Kukanja et al., 2000). The combination of both these components will ultimately show the better resistance against crocking. It is also well know that acrylate polymer belongs to a group of polymers which could be referred to generally as plastics and are noted for their transparency and resistance to breakage and elasticity. These lines also support



Description	PUAC-1	PUAC-2	PUAC-3	PUAC-4	PUAC-5	PUAC-6	PUAC-7	Untreated
Applied strength: 15g/L								
Rubbing (dry, wet)	3/4, 3	3/4, 3	3/4, 3	3/4, 3	4, 3	4, 3/4	4, 3/4	
Applied strength: 30g/L								
Rubbing (dry, wet)	3/4, 3	3/4, 3	3/4, 3	4, 3	4, 3/4	4, 3/4	4, 3/4	
Applied strength: 50g/L								
Rubbing (dry, wet)	3/4, 3	3/4, 3	3/4, 3	4, 3	4, 3	4, 3/4	4, 3/4	3, 2/3

Fig. 3. Colorfastness to rubbing data of treated and untreated printed poly-cotton fabric (ISO X12).

the stability and resultant properties of the synthesized PAC emulsion.

4. Conclusion

Polyurethane acrylate copolymers (PAC) samples were prepared varying molecular weight of polycaprolactone diol reacting with toluene-2,4-diisocyanate (TDI), and chain was extended with 2-hydroxy ethyl acrylate to form vinyl terminated PU preploymer, and finally the co-polymerization was completed by free radical polymerization using butyl acrylate in emulsification process. The FTIR spectra of the monomers, prepolymers and copolymers confirmed the proposed PACs structure. The physical characterization such as solid contents (%), emulsion appearance and emulsion stability were studied and discussed. The different dilutions of synthesized polyurethane acrylate copolymer were applied on to the mill desized, bleached, printed poly-cotton plain weave fabrics using dip-padding techniques. The outcome of the results fully correlates the structure property relationship of the synthesized materials.

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