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Waterborne Polyurethane/Acrylics Interpenetrating Networks Polymer:Preparation,Characterization and Application for antipilling coating materials

Ren yan[1,2,a], Zhangjian Fei[1,b] , Dingchang Bo[2,c] and Chen Jun[2,d]

[1] College of Textile, Tianjin Polytechnic University, 300387 Tianjin , China
[2] College of Textile and Material , Xi′ an Polytechnic University, 710048 Xi′ an , Shannxi, China
[a] ry901@163.com, [b] zhangjianfei1960@126.com, [c] wl830507@163.com, [d] 527811502 @qq.com

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Abstract. Aqueous polyurethane dispersions with C=C double bonds were synthesized by using Isophorone diisocyanate, Polyether diol 218, polyether-tribasic alcohol 310 and dimethylolbutanoic acid without any organic solvents. Then waterborne polyurethane-acrylic hybrid emulsion interpenetrating network were prepared with the method of pre-emulsification semi-continuous. Based upon the FT-IR, DSC, TG and particle size analysis, the experimental results showed that polyurethane with C=C double bond and acrylate has good compatibility and exhibits phase separation morphology with interpenetrating networks. Thermal stability and emulsion stability is good. Anti-pilling grade of different fabrics rise two or three levels after finishing by using waterborne polyurethane and acrylic ester interpenetrating networks polymer.

1. Introduction

An interpenetrating polymer networks, IPN, can be defined as a combination of two polymers in network form, at least one of which is synthesized and / or crosslinked in the immediate presence of the other.[1] An IPN can be distinguished from monomer copolymerization and polymer blending system, because it emphasizes the throughout or intersection between polymer network in molecular scale.[2-4] It doesn't mean chemical reaction between different polymer, neither does the piling up of consented state in remote structure. So in recent years, An IPN has rapidly become one of the effective methods to solve the composite of polyurethane (PU) and acrylic polymer (PA), and also become one of the major areas in polymer composite field.[5-7]

The preparation of an IPN hybrid emulsion exists two major problems at present. One is that pre-emulsion swelling method is both time-consuming and incomplete reaction.8,9 Actually, only a small part of the PA monomers can be swelled into the colloidal particles of PU during the process of synthesis, the great mass of which adsorbed on the surface of micelle or is outside in free form.10

This will result in high gel content and instability of emulsion. In order to get the stable emulsion, adding emulsifiers separately was carried out during the composition of PU and PA by C.S. Chen et.al.11 However, due to the existence of emulsifier micelle, PA monomers were carried on the free radical copolymerization reaction without swelling to the PU colloidal particles. Despite the gel rate was reduced and emulsion was stable in appearance, PU and PA weren't compound in real and still in the two-phase incompatible state. The other one is the addition of hydrophilic groups.12-14 In order to achieve excellent hydrophilicity in pre-polymer, 2,2- dihydroxy methyl propionic acid (DMPA) was added to the PU molecular chain frequently. But meanwhile, the demand of organic solvents was growing gradually, which used to dissolve DMPA and reduce the PU pre-polymer viscosity. Use of organic solvent is bound to cause serious damages to the environment and human health.[15-17]

The purpose of this work was to solve above problem. The first good action to deal with was adding hydrophilic groups into the molecular structure of isocyanate pre-polymer. Secondly, hydroxyethyl acrylate (HEA) was adopted as end-capped reagent to prepare waterborne blocked polyurethane by self-emulsifying. Last but not least, the synthesis of waterborne polyurethane (WPU) containing unsaturated C=C double bond which has set the stage for forming interpenetrating network. Then, the waterborne polyurethane/acrylate interpenetrating network (WPUA IPN) was prepared without emulsifier by using emulsification semi-continuous method. The morphology structure and microscopic properties of WPUA IPN were studied and then applied to pilling resistance finishing of various fabrics.

2. Experimental

2.1. Materials

The following reagents were used as received: Polyether diol 218(number-average molecular, Mn=1744g/mol, Jinhai chemical Co., Ltd, China), Polyether triols 310(number-average molecular, Mn=1000g/mol, Jiuling chemical Co., Ltd, China), dimethylolbutanoic acid (DMBA, Dongying Saimeike chemical Co., Ltd, China), Isophorone diisocyanate (IPDI, 98wt% purity, Guangdong Fuchen chemical Co., Ltd, China), tri-ethylamine (TEA, Xilong chemical Co., Ltd, China), hydroxyethyl acrylate (HEA, Shanghai Huayi acrylate Co., Ltd, China), 1,4-butanediol (BDO, BASF), ethylenediamine(EDA, BASF), Butyl acrylate (BA, Damao chemical Co.), methyl methacylate (MMA, Damao chemical Co., Ltd, China), JFC, deionized water. The other reagents were used as received without further purification.

2.2. Preparation of PU/PA IPN Emulsions

2.2.1. Preparation of waterborne polyurethane

WPU emulsions were prepared by a self-emulsification method. A poly-addition reaction was conducted in a 500-ml four-necked flask equipped with a reflux condenser, a mechanical stirrer, a thermometer and a nitrogen gas inlet. Polyether diol 218, Polyether triols 310 and DMBA were dried and dehydrated at 115 ℃ under vacuum for 3.0h, and then the temperature was cooled to the environmental temperature. IPDI was added to the mixture and reacted with polyols mentioned above at 85℃ for 4h. Afterwards, the reaction temperature was lowered to 70℃ and HEA was added as the blocking agent. The mixture stirred continuously for 1h. The pre-polymer was then neutralized and chain extended by adding EDA and TEA respectively. The WPU emulsion with a solid content of 25 wt% was obtained by adding a calculated amount of deionized water to the mixture solution. The synthetic route is shown in figure 1.

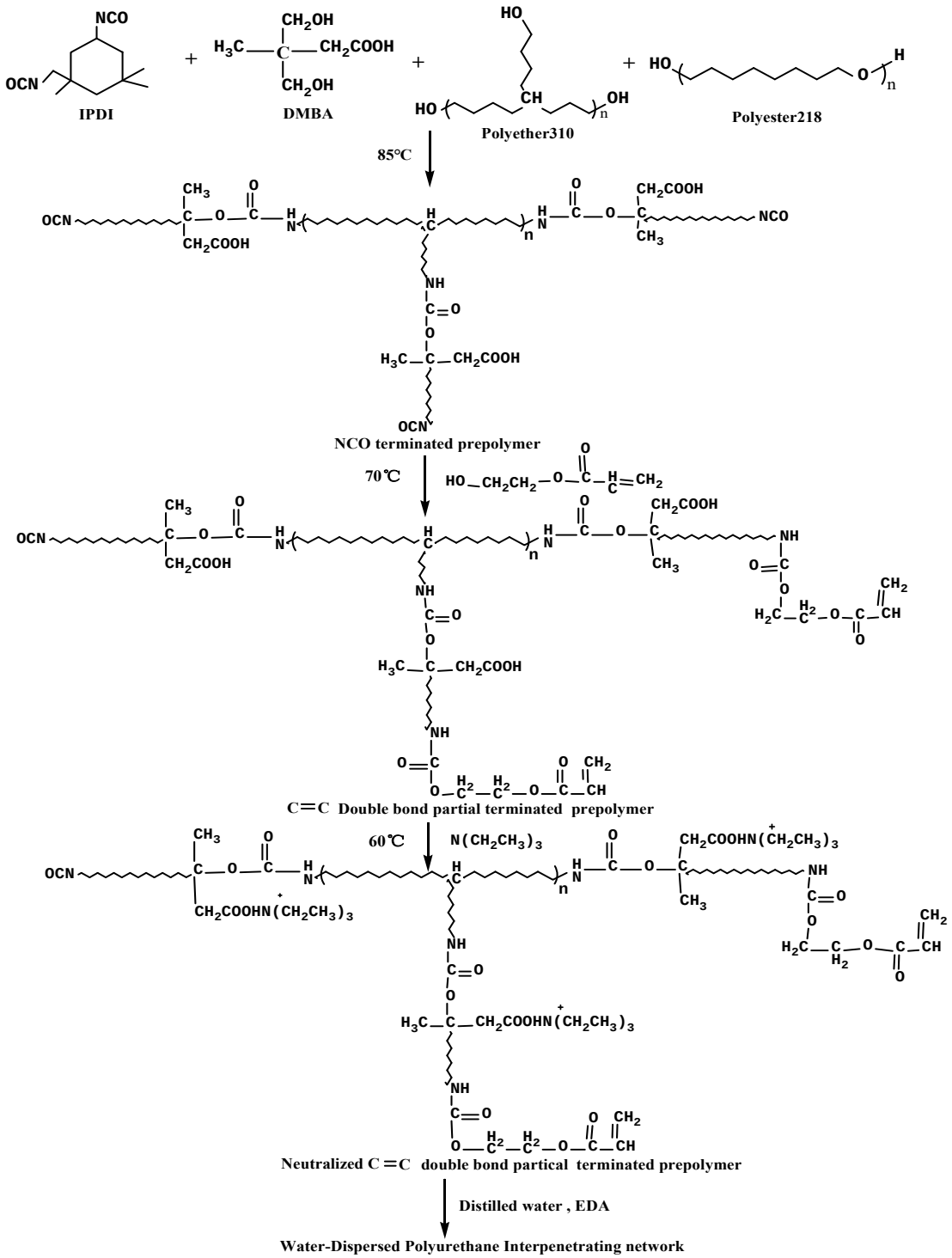
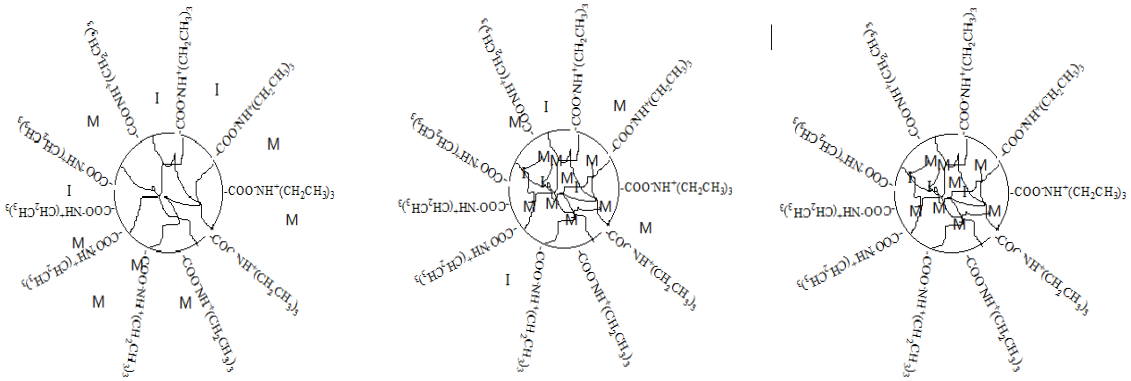


Figure 1 Synthetic route of the waterborne polyurethane

2.2.2. Preparation of PU/PA IPNs

The preparation of PU/PA LIPNs was carried out by using soap free polymerization, which used PU dispersions as the seed emulsions. The synthetic route is shown in scheme 1.



Step one, monomer and initiator began swelling to the WPU emulsion micelle.

Step two, part of the monomer and initiator swelled to the WPU emulsion micelle.

Step three, monomer and initiator swelled to the WPU emulsion micelle completely.

Figure 2 Synthetic reaction of WPUA IPN emulsion

2.2.3. Film formation

Films for the tests were prepared by casting emulsions onto a Teflon plate, followed by drying for 1 week at ambient temperature (20～23℃). The thickness of the dried films was about 0.5 mm.

2.3. Characterization

FITR spectra of the films were recorded between 4000 and 500 cm^{-1} with an FITR spectrometer (Nexus 670, Nicolet, USA). The dynamic mechanical properties of WPU and WPUA IPN hybrid film samples were obtained using a DSC (DSC-1, STAR^e system, Mettler Toledo, USA) with 10℃/min heating rate range from –80～100℃. The average particle size was measured using laser-scattering equipment (Zetasizer Nano, Malvern, UK). Apparent properties of WPUA IPN were measured in according to the GB/T 11175-2002 standard.

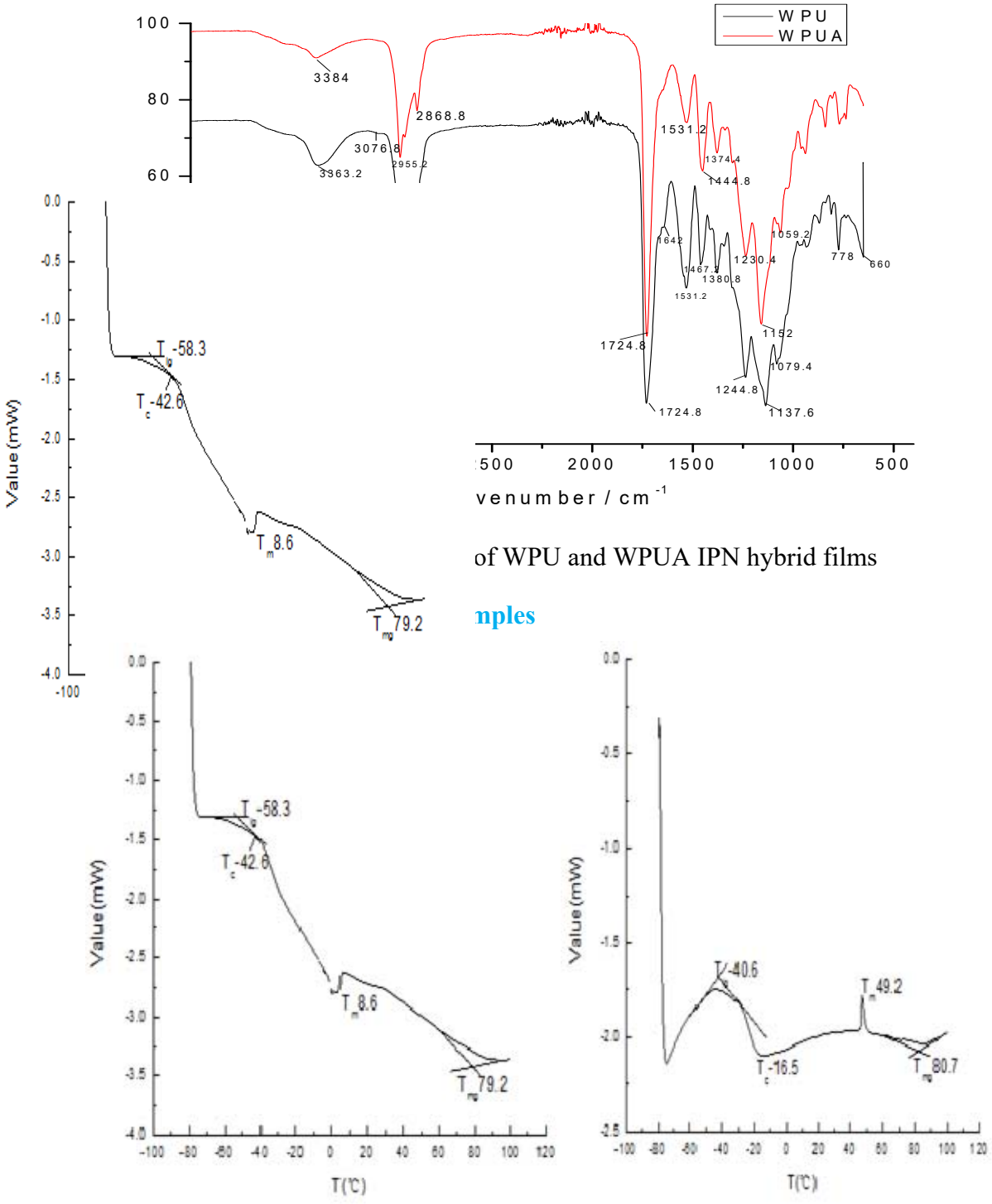
3. Results and discussion

3.1. FTIR Characterization

Figure 3 shows the FTIR spectrum of WPU and WPUA IPN hybrid films prepared in this study. No strong absorption bonds between 2000 and 2500 cm^{-1} in WPU spectrum was observed, indicating the complete reaction of all - NCO groups. In the NH stretching region, the major absorption around 3300 cm^{-1} was attributed to the completely hydrogen-bonded NH groups. The asymmetric stretching vibration peak of C-O at 1137.6 cm^{-1} and 1152 cm^{-1}, C=C at 1642.2 cm^{-1} and characteristic absorption peak of C-H at 3076.8 cm^{-1} were all detected in the WPU film. These are strong evidence of existence of C=C in WPU, proving that HEA has reacted to the –NCO with partial blocking. And the corresponding spectrum of WPUA, no characteristic peaks of C=C and C-H indicated that acrylate monomer has polymerized completely and WPU/PA hybrid emulsion was synthesised. On the other hand, it shows that the completely reaction of C=C end group in pre-polymer contributed the copolymerization of PU and PA to the closer interpenetrating network.

Compared the two spectrums, the N-H peak at 3384 cm^{-1} of WPUA while at 3343.2 cm^{-1} of WPU showed that the degree of hydrogen bonding in the N-H has decreased. Absorption frequency tended to move to – NH which is in free state. Research has pointed out that the formation of the

interpenetrating network structure attributed to the disorder increasing of hard segment and space structure hindrance structure of block is not conducive to the formation of hydrogen bonds. It seems that the WPU emulsion beforehand in acrylate monomer graft has formed network structure, achieve the goal of interpenetrating network.



of WPU and WPUA IPN hybrid films

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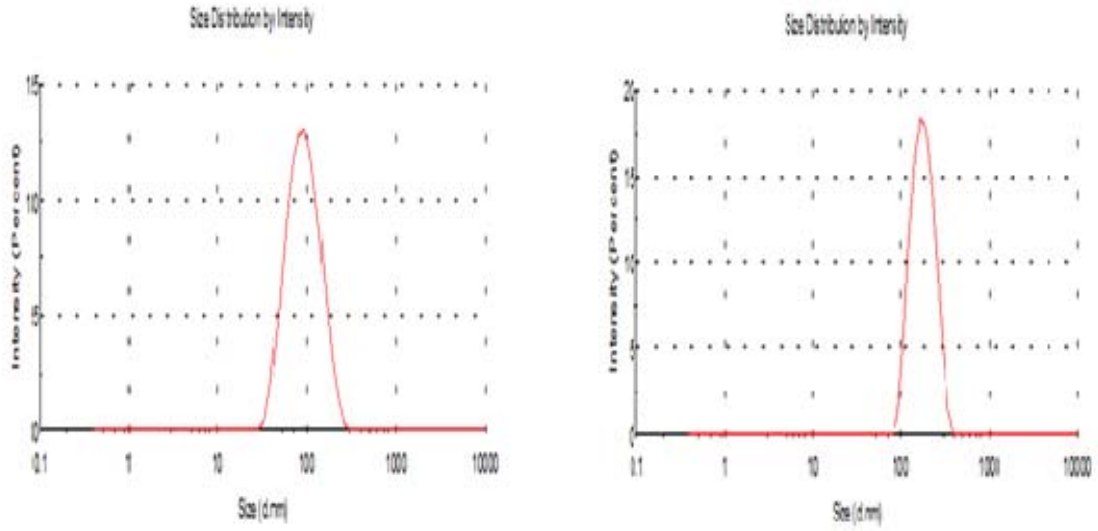
Figure 4 DSC curves of WPU and WPUA IPN hybrid films

Figure 4 shows the differential thermal scanning calorimetry analysis of WPUA. Polyurethane has two phases (soft segment and hard segment phases), so two glass transition temperature in each

curves was detected. The broad span between two Tg refers to the obvious micro phase separation. As seen in Fig.4, the Tig of WPU's soft segment was 58.3 ℃, the Tmg of hard segment was 79.2 ℃, and the Tig of WPUA's soft segment was 40.6 ℃, the Tmg of hard segment was 80.7 ℃. Obviously, the glass transition temperature of WPUA IPN hybrid film increased, especially the soft segment. Crystallization temperature of WPU is 42.6 ℃, the melting temperature Tm is 8.6 ℃, while the crystallization temperature of WPUA IPN is 16.5 ℃, the melting temperature Tm is 49.2 ℃. Crystallinity and mechanics performance were both enhanced after forming interpenetrating network between polyurethane and acrylic ester.

3.3. Particle size of composite emulsion



a. WPU：Average particle size 82.52nm, Dispersion coefficient 0.137　　b. WPUA IPN：Average particle size 82.52nm, Dispersion coefficient 0.096

Figure 5　The Particle size distribution curve of WPU and WPUA

Figure 5 lists the particle size of WPU and WPUA IPN emulsions. The average particle size of two former was respectively 82.52nm and 155.6nm. It is well known that the grain size was increased after compositing. Dispersion coefficient of WPU was larger than the WPUA IPN, because PU containing the double bond and acrylic ester which has excellent compatibility and bigger applied force resulting in the shrinkage between two phases. Therefore, the particle size distribution became narrow and emulsion stability got enhanced.

3.4. Fundamental characteristics of PU/PA LIPN

Table 1 lists the basic properties of WPUA IPN emulsion. The results show that each indicator can meet the commercial requirements. Meanwhile, the emulsion appearance presented semi-transparent and faint blue light. High solid content and good film properties are also advantages.

3.5. Application in anti-pilling finishing for textile

The experiments found that WPUA IPN can be used as anti-pilling finish agent for all kinds of fabric. The pilling resistance effect would comparable with commercial one.

Table 1 Apparent properties of WPUA IPN

Technical index	Sampling results
Apparent	faint blue light, semi-transparent
Solid content	50%±2
Viscosity / mPa.s	52.4
Water absorption /%	4.8
Tensile strength /MPa	8.6
Elongation at break /%	352.6
Electrolyte (Ca^{2+})stability	No delamination and demulsification phenomenon after seven days.
Centrifugal stability	No delamination and demulsification phenomenon at 4000r/min after 15min.
Storage stability	No delamination and demulsification phenomenon at room temperature for three months. There is also no change of the emulsion appearance.
Film property	Good gloss, transparent, smooth, elastic and good flexibility.

a. Cotton knitted fabric
(Anti-Pilling property is level 2)

b. Cotton knitted fabric after anti-pilling finish
(Anti-Pilling property can be up to level 4)

c. Polyester/Cotton blended knitted fabric
pilling finish
Anti-Pilling property is level 1-2.

d. Polyester/Cotton blended knitted fabric after anti-
Anti-Pilling property can be up to level 3-4.

Figure 6 The anti-pilling property of two types of fabrics

The figure 6 (a,c) shows that the pilling in surface of cotton and polyester/cotton blended fabrics were serious. After finishing with WPUA IPN, two kinds of fabrics (b,d) were obtained smooth and clean surface. It is obvious that the resistance to pilling grade of each fabric has improved 2-3 level.

4. Conclusions

Without emulsifier, the interpenetrating network polymer was synthesised with waterborne polyurethane containing unsaturated C=C double bond and acrylic ester by the pre-emulsification semi-continuous method. Infrared spectroscopy showed that unsaturated C=C double bond was existed in WPU which end-capped by HEA. While, no C=C absorption peak in the spectrum of WPUA IPN meant that PA monomers had polymerized completely with WPU and interpenetrating network was formed. Differential calorimeter scanning analysis indicated that WPUA IPN existed two glass transition temperature and micro phase separation was obvious. Particle size and its distribution illustrated that polyurethane and acrylic ester had an excellent compatibility. The emulsion stability was good. Pilling resistance grade of cotton and cotton/polyester blended knitted fabric were up to 2-3 level after finishing.

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