Research of Fluorinated Acrylate Copolymer on Flax Fabric

DOI: 10.5604/01.3001.0010.5376

Zhihui Sui, Kangle Yang, Jie Chen, Xin Zhao, Shuzhen Gao

Qiqihar University, School of Light Industry and Textile, Qiqihar 161006, P.R. China
E-mail: szh2736@163.com

Abstract

A fluorine-containing acrylate copolymer emulsion was prepared in this study, which was applied to finishing linen fabric. Dodecafluorohexyloxy methacrylate (G04) was used as a modified monomer, butylacrylate (BA) and methylacrylate (MMA) as soft and hard monomers, respectively, and acrylic acid as a functional monomer. Structure and properties of the products were characterised and analyzed by FTIR, TEM, PSD and CA measurements, respectively. The water and air permeability as well as the breaking force of the fabric treated were also investigated. The results showed that the fluorine-containing acrylate copolymer emulsion obtained had a core-shell structure, and the microsphere was of nanoscale size. Because of the latex film on the fabric surface, it became smooth and flat. And the increase in G04 was beneficial to the mechanical properties, waterproofness and antifouling ability of the linen fabric. When the content of G04 were increased from 0% to 20%, the water tension of the linen sample and hexadecane contact angles to the copolymer film increased from 113.0° to 136.0° and from 65.1° to 87.6°, respectively. Furthermore the breaking force of the linen samples was enhanced from 648 N to 721 N. However, the increasing content of G04 had negative effects on the flexural rigidity as well as water and air permeability of the fabric, which were essential requirements for the fabric’s application. However, the wash resistance was excellent and the wear-resistance of the finished linen fabric was better than the unfinished linen fabric.

Key words: fluorine-containing acrylate, core-shell polymerization, linen fabric, finishing agent, hydrophobicity, lipophobility.

Introduction

The electronegativity of F atoms is extremely strong [1, 2]. The C – F chain is a flexible chain. The intermolecular forces of containing a lot of C – F keys are small [3]. A fluoride group could significantly reduce the copolymer molecular surface free energy and critical surface tension if fluorine-containing organic compounds were introduced, [4, 5]. The fluoroalkyl groups tend to enrich at the film-air interface and extend the air interface directionally, which makes it possess some special surface properties, such as hydrophobicity and lipophobicity, the self-cleaning property and good chemical resistance (to acids, bases and solvents) [6-8]. Fluorinated polycrlylate latexes have become an excellent finishing agent of construction, coating, fabric, leather, and other substrates [9-11], while the fluorine monomer is very expensive [12]. Therefore the polymerisation process should be improved actively by improving the polymer performance as well as reducing the fluorine monomer content to reduce the production cost. Yan Zhang [13] prepared fluorinated acrylate polymer on antifouling coating by free radical polymerisation, which used fluorinated acrylate quardopolymer (QPFA), acrylate bipolar (BPFA) and acrylate homopolymer (HPFA). Edja F. Assanvo [14] synthesised novel ricinodendron heudelotii oil-based alkyl-acrylate hybrid latexes as a waterborne environmentally friendly binder for coating systems. Flax is a kind of natural plant fibre which has many excellent unique advantages, such as fast moisture absorption and wet dissipation, good rubbing resistance, high temperature resistance, small conductivity, low dust absorption and the antibacterial property. Flax is the only bundle fibre which is formed from flax single cells by means of colloidal adhesions. It has excellent thermal conductivity (air permeability) because of a lack of air-free conditions, and has fast moisture absorption and wet dissipation because of the imitation hammer-shaped structure and unique pectin oblique hole structure. In addition, flax is a kind of hidden spice plant, the faint smell of which could kill many bacteria and inhibit the growth of a variety of parasites. Linen has been favoured by more and more consumers of all ages in the international and domestic markets. It can be used for clothing, decoration, national defense as well as for industrial and agricultural special cloth. However, the wrinkle and wear resistance of linen fibre is poor.

With living standards increasing, people have higher requirements of textile quality. For example, water and oil repellent finish on fabric is becoming more widespread, with the fluorine-containing acrylate emulsion finishing agent being one of the main varieties of fabric finishing agents today. H. H. Ye [15] successfully synthesised fluorinated polymer by continuous process emulsion copolymerisation using acryloyl tri (1,1,2,2-tetrahydroperfluoro-octyl) citrate (FOC), β-acryloyloxy 1,1,2,2-tetrahydroperfluoro-octyl propionate (FOP) and butyl acrylate. Moreover the water and oil repellency of the polymers used as a textile finishing agent on cotton fabrics was investigated. Hybrid fluorocarbon coating was applied to a wool substrate together with UV/O3 treatment by Jalal Rahmatinejad [16].

Although researchers are working on finishing agents, reports of applying them to finish linen textile are few. Our research used dodecafluorohexyloxy methacrylate modify acrylate polymers and successfully obtained fluorinated acrylate copolymer emulsion with a core-shell structure, whose application is becoming more and more widespread because of the integrat-
ed advantages of both. The fluorinated acrylate copolymer emulsion prepared was used to finish linen fabric, resulting in waterproof and oil properties especially. The present study was focused on its effects on the finished linen fabric which included the linen fabric tensile strength, bending resistance, moisture and air permeability, waterproofness, oil resistance, etc.

## Experimental

### Materials

Linen samples: 45 tex × 45 tex × 228 roots/10 cm × 161 roots/10 cm × 137 cm.

Dodecafluoroheptyl methacrylate (G04) was purchased from the Harbin Xeogia Group Co., Ltd. (Harbin, China); n-butyryl acrylate (BA), methacrylate (MMA) & sodium dodecyl sulfate (SDS) were obtained from the Tianjin Secco romoe Chemical Reagent Co., Ltd. (Tianjin, China); acrylic acid (AA) & potassium persulfate (KPS) were attained from the Tianjin Kaitong Chemical Reagent Co., Ltd. (Tianjin, China); and Alkyd phenol polyoxyethylene ether – 10 (OP – 10) was purchased from the Tianjin Nankai Chemical factory (Tianjin, China). All chemicals were analytical grade and used as received without further purification, except OP-10 and sodium bicarbonate. Distilled water was used for all experiments.

### Preparation of fluorine modified copolymerisation emulsion

Core-shell G04/MMA/BA/AA latexes were synthesised by the semi-continuous seeded emulsion polymerization technique in two stages, i.e., the seed and pre-emulsion preparation stages. Their recipes were established based on the aim of our present work and also with reference to the work of Sui et al. [17]. The detailed steps were as follows: We took a certain quantity of OP-10 and the mixed emulsifier solution in a mass ratio of 5:3 with SDS set aside. KPS was used to prepare an initiator solution of 2%.

10 ml of the emulsifier solution above, 3.6 g of MMA, 3.6 g of BA and some G04 were separately added into a 250 ml four-neck flask, then intensively homogenised for 20 minutes using an ultrasonic cleaner, and uniformed mixing was performed for 20 min slowly, after which the pre-emulsion can be obtained, named solution a.

In addition, a mixed kettle liquid (20 ml of the emulsifier solution above, 1.8 g of MMA, 5.4 g of BA, 0.9 g of AA, a little sodium bicarbonate) and 20 ml of distilled water were introduced into a four-neck flask equipped with a reflux condenser, mechanical stirrer and thermometer. The mixture solution was dispersed by the ultrasonic dispersion technique, then heated to 50 °C in a water bath and reacted for 20 min. Then KPS (6 ml) was added dropwise to the flask when the temperature was heated to 80 °C. The pre-emulsion of solution a and KPS was added simultaneously after the emulsion polymerisation occurred. Then the polymerisation was kept at 80 °C for 2 h to ensure complete monomer conversion. Finally the hybrid emulsion of FPAE (fluoride polyacrylate emulsion) with a core-shell structure was obtained.

### Finishing technology of flax textile

The hybrid emulsion of FPAE was diluted into finishing liquor of 60 g/l. Linen fabric was finished through „dip – rolling – baked” sample processing (the mangle rate was about 75%). Finally the samples were dried at 80 °C for 3 min and cured at 160 °C for 3 min.

### Characterisation and test analysis

#### FTIR spectra of copolymer films

FTIR spectra were detected by a Spectrum One Fourier Transform Infrared Spectrometer in the wave number range from 4000 to 500 cm⁻¹ at 25 °C.

#### Characterisation of FPAE hybrid emulsion

Transmission electron microscopy (TEM) micrographs of the FPAE particles were taken with an H-7650 transmission electron microscope (Hitachi Company, Japan) at an acceleration voltage of 200kV. The samples were stained with 2% phosphotungstic acid (PTA) solution [18].

---

**Figure 1.** FTIR spectra of copolymer films: a) pure polyacrylate film b) FPAE film.

**Figure 2.** TEM photos of FPAE emulsion particle; a)×200000 and b)×100000: a) unfinished flax sample, b) finished flax sample by FPAE.
XPS of fabric surface

XPS is a surface chemical analysis technique for analysing the surface chemistry of a material in the as-received state or after some treatment [19].

XRD analysis of fabric surface

XRD patterns were recorded on a Rigaku D/MAX2200 X-ray diffractometer using Cu Ka radiation, operating at 40 kV and 40 mA. The measurements were performed within a scanning range of 20°-40° [13].

SEM analysis of fabric surface

Scanning electron microscopy (SEM) can be directly used to observe the sample surface with respect to the material properties of the surface material.

Flax fabric application performance test

In order to study the effect of FPAE hybrid emulsion on flax fabric, we conducted tests of the following: breaking strength, air and moisture permeability, contact angle etc.

Results and discussion

Chemical composition and structure of copolymers

FTIR spectra of copolymers pure polyacrylate (a) and FPAE (b) are shown in Figure 1. All the monomers exhibit the characteristic peak of -CH₂ stretching vibrations at 2968 cm⁻¹ and 2871 cm⁻¹, and the characteristic absorption peak of C=O stretching vibrations was at 1730 cm⁻¹. The absence of C=O characteristic stretching vibrations (1600-1700 cm⁻¹) and the C-H stretching vibration peak (3000-3300 cm⁻¹) confirmed that all the monomers had been polymerized in FPAE.

Compared with the curve a, the frequency doubling of the stretching vibration peak of C=O was at 3455 cm⁻¹ on curve b. Generally the strong peaks at 1256 cm⁻¹ and 1177 cm⁻¹ were assigned to the stretching absorption of C-F bonds, which overlapped with the characteristic absorption peaks of C-O in -COO⁻ at 1240 cm⁻¹ and 1160 cm⁻¹. Moreover on curve b, the absorption peak of CF₂ was 743 cm⁻¹, and the C-F stretching vibration peaks were at 616 cm⁻¹ and 688 cm⁻¹, which indicated that the incorporation of dodecafluoroheptroethy methacrylate into the FPAE copolymers was effective.

Transmission electron microscopy (TEM) analysis

Transmission electron microscopy (TEM) was used to observe the microstructure of transparent emulsion. Figure 2 shows TEM images of FPAE whose fluorine content was 16% (a) and 20% (b), respectively. Spherical structures are seen in both of the pictures. The latex particle surface was very smooth, and we can clearly see the core-shell structure with a black shell and white core, because it was dyed with phosphotungstic acid solution. Particles were dispersed evenly in the emulsion. Furthermore the distribution and size of latex particles were more well-distributed with an increase in fluorine. Ultimately the size of the emulsion particle generated was of a nanoscale, which indicated that the FPAE emulsion had excellent dilution stability.

XPS analysis of fabric

A surface analysis of the flax fabric unfinished (a) and finished (b) by XPS with FPAE is shown in Figure 3. The absorption peaks of O1s (533.1 eV), C1s (287.5 eV) appeared in (a) and (b). In addition, the peak at 688.5 eV assigned to F1s was observed slightly in (b), indicating that fluoride copolymers were linked together with the fabric in some way. Copolymer formed a thin layer of film on the surface of the fabric, which can reduce the surface tension, and effectively prevent fabric from being soaked by water, so as to make excellent waterproof fabric. Combined with the FTIR spectra of the copolymer, it can also illustrate that the preparation of the copolymer was the target product.

XRD analysis of fabric

XRD was introduced to further investigate crystallisation formation. The diffraction spectra performed on flax fabric at room temperature are shown in Figure 4. The diffraction peak of (a) and (b) appeared at around 22.7° and 34.6°. After calculation [20], the crystallinity of a was 85.20% and b - 83.32%; the crystallization index was 88.87% (a) and 87.45% (b), respectively. The conclusion showed that the structure of flax fabric was not obvious after finishing agent treatment.

Figure 3. XPS of flax sample: a) unfinished flax sample, b) finished flax sample by FPAE.

Figure 4. XRD patterns of flax sample: a) unfinished flax sample, b) finished flax sample by FPAE.
were assigned to the stretching absorption of C-F bonds, which overlapped with the C=O stretching vibrations at 3455 cm\(^{-1}\). The absence of C=C characteristic stretching vibrations (1600-1700 cm\(^{-1}\)) confirmed that all the monomers had been polymerized in FPAE. Moreover the distribution and size of latex particles dispersed evenly in the emulsion. Furthermore the distribution and size of latex particles decreased. With an increase in fluoride, the finished fabric became more smooth, and the adhesion among the fibres got more intensive, which can effectively reduce the surface energy and decrease the critical surface tension of the fabric. Moreover the fabric was not wet from water, and thus waterproof fabric was achieved eventually.

**Contact angle to water on the flax fabric**

The contact angle can reflect the waterproof performance of treated fabric. Hence film morphologies of linen fabrics untreated (a) or treated (b-f) with FPAE were studied in this work and a series of photographs of the contact angle are presented in Figure 6.

The contact angle on the untreated linen sample (Figure 6.a) was only 97.45°. However, when water was dropped on the treated linen sample, water droplets were approximately spherical. When the content of G04 was increased from 0% to 20%, the water contact angles (Figures 6.b to 6.f) increased from 113.02° to 136.08°. The reason was that copolymer emulsion formed a protective film on the surface of the linen fabric and the fibres were wrapped. Fluoride-groups on the sample surface increased with an increase in fluoride. Fluoride-groups in copolymer can greatly reduce the critical surface tension. Besides this, in the process of forming, fluorine atoms migrated into the air-polymer interface and fluoride segments stretched into the air interface, which can defend the backbone structure and internal molecules.

A comparison of results of the water contact angle before and after washing is shown in Table 1.

**Table 1.** Comparison of the water contact angle before and after washing. Note: 1 represents the water contact angle of the fabric which was not washed and soaped, and 2 – the water contact angle of the fabric which was washed and soaped for 10 minutes, respectively.

| Water contact angle | Contents of fluoride, % |
|---------------------|------------------------|
|                     | Unfinished | 0  | 5 | 10 | 15 | 20 |
| 1                   | 97.45°     | 113.02° | 121.76° | 128.43° | 131.86° | 136.08° |
| 2                   | –          | 106.33° | 116.77° | 121.54° | 123.16° | 126.55° |

**Table 2.** Application performance of linen fabric.

| Contents of fluoride | Breaking force, N | Gas permeability, mm/s | Moisture permeability, g/(m\(^2\)·h) | Bending rigidity | Hexadecane contact angles on film, ° | Abrasion resistance, rings |
|----------------------|-------------------|------------------------|--------------------------------------|-----------------|-----------------------------------|---------------------------|
| Unfinished           | 498               | 6.44                   | 223.0                                | 5.63            | –                                 | 302                       |
| 0%                   | 648               | 4.78                   | 215.9                                | 6.47            | 65.1                              | 320                       |
| 5%                   | 684               | 4.41                   | 218.0                                | 6.72            | 70.2                              | 336                       |
| 10%                  | 693               | 4.30                   | 204.0                                | 7.05            | 77.2                              | 335                       |
| 15%                  | 699               | 4.17                   | 175.0                                | 7.21            | 81.7                              | 339                       |
| 20%                  | 721               | 4.09                   | 149.9                                | 7.58            | 87.6                              | 336                       |
| Standard deviation   | 26.7              | 0.27                   | 29.4                                 | 0.43            | 8.95                              | 7.53                      |

**Scanning electron microscope (SEM) analysis**

SEM photos of unfinished and finished flax fibre are shown in Figure 5 (×1000). A, B, C and D represent unfinished samples, a finished fibre sample of 16% fluoride (total mass of monomer), a finished fibre sample of 20% fluoride, and a finished fibre sample of 25% fluoride, respectively.

Figure 5 shows that the surfaces of the flax fibres had an obvious difference. The unfinished flax fibre surface was rough and had many impurities. The gaps among the fibres were also larger than in the finished ones, and as a result it was easy to absorb moisture. The finished flax fibre surface was smooth and the adhesion among fibres was clearly observed. The gaps were partially filled by the finishing liquid; the finished fabric fibre gaps decreased, and the relative area with water decreased. With an increase in fluorine, the finished fabric became more transparent emulsion. Figure 2 shows TEM images of FPAE whose fluorine content was 16%.

**Figure 5.** SEM photos of flax unfinished a) and finished b-d) by FPAE. a) unfinished, b) 16%, c) 20%, d) 25%.

**The contact angle can reflect the waterproof performance of treated fabric.**

Hence film morphologies of linen fabrics untreated (a) or treated (b-f) with FPAE were studied in this work and a series of photographs of the contact angle are presented in Figure 6.

The contact angle on the untreated linen sample (Figure 6.a) was only 97.45°. However, when water was dropped on the treated linen sample, water droplets were approximately spherical. When the content of G04 was increased from 0% to 20%, the water contact angles (Figures 6.b to 6.f) increased from 113.02° to 136.08°. The reason was that copolymer emulsion formed a protective film on the surface of the linen fabric and the fibres were wrapped. Fluoride-groups on the sample surface increased with an increase in fluoride. Fluoride-groups in copolymer can greatly reduce the critical surface tension. Besides this, in the process of forming, fluorine atoms migrated into the air-polymer interface and fluoride segments stretched into the air interface, which can defend the backbone structure and internal molecules.

A comparison of results of the water contact angle before and after washing is shown in Table 1.

Contrasting 1 and 2, the results show that the water contact angle on the fabric (washed with water and soap) decreased slightly (about 10°); but the fabric still had relatively high hydrophobicity; the finished effect was excellent, and the wash resistance was satisfactory.

**Fabric application performance test**

FPAE copolymer-emulsion synthesised in the same conditions was prepared as finishing liquor with a certain concentration and used to treat linen fabric. Some application properties of linen fabric were studied, such as the breaking force, moisture and gas permeability, bending rigidity and oil repellency. The results are shown in Table 2.
were more well-distributed with an increase in fluorine. Ultimately the size of the emulsion and surface tension, and effectively prevent fabric from being soaked by water, so as to make Copolymer formed a thin layer of film on the surface of the fabric, which can reduce the spectra performed on flax fabric at room temperature are shown in Figure 4. The diffraction unfinished flax fibre surface was rough and had many impurities. The gaps among the fibres fluoride, respectively.

C and D represent unfinished samples, a finished fibre sample of 16% fluoride (total mass of gas permeability, bending rigidity and oil repellency. The results are shown in Table 2 hydrophobicity; Fluoride-groups in copolymer can greatly reduce the critical surface tension. Besides this, in XPS analysis of fabric XRD analysis of fabric indicating that fluoride copolymers were linked together with the fabric in some way.

Table 2 shows that the breaking force of the unfinished linen sample was 498 N, and that of the finished samples increased significantly compared with unfinished samples. When the content of G04 was increased from 0% to 20%, the breaking force increased from 498 N to 721 N (standard deviation was 26.7), which may be flexible C-F chains making the finished fabric have a certain coherence. Furthermore the fluorine atom was small, which tightly surrounded the main chain of the C-C, enhancing the physical and mechanical properties of the fluorinated polyacrylate material. Finally the breaking force of the finished sample was also improved.

The air and moisture permeability of the untreated flax sample were 6.44 mm/s and 223.0 g/(m²·h), respectively. These properties of the finished sample decreased compared with unfinished samples, while not affecting the wearability of the fabric. When the content of G04 was increased from 0% to 20%, the moisture and gas permeability gradually decreased, with the lowest air permeability being 4.09 mm/s, and the minimum moisture permeability – 149.9 g/(m²·h). This was because FPAE emulsion formed a film on the fabric surface, and the gaps could be immersed. At the same time, dried emulsion induced adhesion among fibres, which reduced the gaps of fibre fabric, thus reducing air or water through the cloth sample reduced in time.

The increase in G04 was beneficial to the waterproof and antifouling ability of the flax fabric, with the standard deviation of hexadecane contact angles on the film being about 8.95. However, it had a negative effect on bending rigidity. Because polymers formed a latex film on the fabric surface, C-F segments of FPAE extended in the direction of the air, and hence the fabric had excellent water-proofness and oil resistance. In addition, along with an increase in the C-F flexible chain segment, rigid chain segments also increased, which enhanced the rigidity of copolymerisation and then the fabric.

From the last column of Table 2, the abrasion resistance of the modified linen fabric was superior to that of the unmodified linen fabric because of the elongation and elasticity of the fibre. The tensile deformation energy and elasticity of the fibre increased with an increase in elongation. The finished linen fibre was wrapped by the emulsion film (or combined with FPAE). The FPAE was a kind of flexible polymer with a straight chain structure, and thus the elongation of the fibre became larger. During wearing, the fibre was subjected to repeated stress which was much smaller than the breaking force. The fibre (large deformability and excellent elasticity) had relatively small morphological changes in the process of repeated tensile stress. That is to say, this finished fibre was given small variable deformability and excellent abrasion resistance.

In summary, the water repellency of the finished linen fabric was obviously improved (the fabric’s bending rigidity, air permeability and moisture permeability were slightly changed, and due to not affecting the performance of the linen fabric itself, it could still maintain serviceability). The research mainly aimed at developing clothing, waterproof raincoats, household tracery, bedding, car cushions and backrests as well as daily textiles.

**Conclusions**

FPAE emulsion with a core-shell structure was synthesised by semi-continuous seed emulsion polymerisation. Then linen fabrics were treated with the FPAE. It was confirmed that the as-prepared latex particles had a uniform spherical core-shell structure. FPAE could form a smooth resin film on the treated fabric/fibre surface, as seen by SEM observation. XPS analysis showed that the linen fabric was integrated successfully with FPAE. XRD...
analysis indicated that FPAE can slightly reduce fabric crystallinity and the crystallization index from 85.20% to 83.32% and from 88.87% to 87.45%, respectively. It was concluded that FPAE emulsion had less of an effect on the internal structure of flax. In addition, some application properties of linen fabric were tested and the results indicated that the increase in G04 was beneficial to the breaking force as well as the waterproof and antifouling ability of the linen fabric. Moreover the wash resistance was excellent and the wear-resistance of the finished linen fabric was better than for the unfinished linen fabric; however, it had a negative effect on bending rigidity as well as the air and moisture permeability.

Acknowledgements

This research is supported financially by the Heilongjiang Provincial Natural Science Foundation of China (E201468), Foundation of Heilongjiang Provincial Educational Committee (12531768) and Graduate Foundation of Heilongjiang Provincial Educational Committee of China (E201468), Foundation of the Heilongjiang Provincial Natural Science Foundation of Leather Science and Engineering in coating. Journal of Surface coating Technology 2015; 211, 165-173.

10. Xianfei Chen, Peng Qi, Yanjun Liu. Preparation and application of the water-solubility fluoroacrylic copolymer for stone protective agent. New Chemical Materials 2012; 40(9): 135-137.

11. Jianhua Zhou, Xin Chen, Hao Duan, et al. Synthesis and characterization of nano-SiO2 modified fluorne-containing polycrylate emulsion-free emulsion. Applied Surface Science 2015; 504-511.

12. Monica Periolatto, Franco Ferrero. Cotton and polyester surface modification by methacryl silane and fluorinated alkoxysilane via sol-gel and UV-curing coupled process. Surface & Coating Technology 2015; 271, 165-173.

13. Yan Zhang, Yuhong Qi, Zhanping Zhang, et al. Synthesis of fluorinated acrylate polymer and preparation and properties of antifouling coating. J. Coat. Technol. Res. 2015; 12 (1) 215–223.

14. Edja F. Assanvo, Shashi D. Baruah. Synthesis and properties of Ricinodendron heudeloti oil based hybrid alkyd-acrylate latexes via miniemulsion polymerization. Progress in Organic Coatings 2015; 86: 25-32.

15. Ye H H, Li Z X, Chen G Q. Preparation and properties of acryloyloxy carboxylperfluorooctyl ester copolymer for liquid repellent finishing of cotton. Fibers and Polymers 2014; 15(5): 908-913.

16. Jalal Rahmatinejad, Akbar Khoddami, and Ozan Avinc1. Innovative Hybrid Fluorocarbon Coating on UV/Ozone Surface Modified Wool Substrate. Fibers and Polymers; 2015, 2416-2425.

17. Zhihui Sui, Weiwei, Pang Jia Song, Lei Zhang and Xin Zhao. The Preparation of silicone-modified acrylic ester emulsion adhesive with core - shell structure [J]. Asian Journal of Chemistry 2014; 26 (14): 4435-4438.

18. Zhifang Zhao, Xiao Li, Peizhi Li, et al. Study on properties of waterborne fluorne-containing polyurethane/acrylated hybrid emulsion and films. J Polym Res. 2014; 21:460.

19. Shin MS, Lee YH, Rahman MM, Kim HD. Synthesis and properties of water fluorinated polyurethane-acrylate using a solvent-emulsifier-free method. Polymer 2013; 54: 4873-4882.

20. Long Li, Guanzhong Sheng. Analysis on crystalline structure of cellulose fiber from cotton-straw bast by X-ray diffraction method. Journal of cellulose science and technology 2009; 17 (4) 37-40.