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Synthesis and Properties of Pigment Printing Adhesive with Core-Shell Structure for Textiles

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Nano-TiO_2/polyacrylate emulsion adhesive with core-shell structure was synthesized by seed-emulsion polymerization with methyl acrylate, ethyl methacrylate, butyl acrylate, 2-acrylamide-2-methyl propane sulfonic acid and nano-TiO_2 as the main raw materials. Its structure was characterized and performances used as a pigment printing adhesive were discussed. FT-IR spectrum and ^1H NMR spectrum analysis showed that copolymerization reaction happened among all kinds of monomers. The core-shell structure of the emulsion adhesive was obviously showed by both DSC test and TEM photograph. The experimental results showed that, compared with the commercial adhesives, the fastnesses of nano-TiO_2/core-shell emulsion adhesive were obviously improved. The dry and wet friction fastness could reach level 5, brushing fastness and soaping fastness could be to level 4.

Key Words: Acrylate, Core-shell polymerization, Pigment printing, Adhesive, Nano-TiO_2.

INTRODUCTION

Pigment printing process equipment is simple, just fixation without washing after printing, therefore, it is suitable for all kinds of fiber and blended fabrics printing[1]. At present, the waterborne polyacrylic ester adhesive is widely used in domestic printing industry, but the adhesive has problems of the limitation called"sticky when heated and fragile when cooled", bad wet rubbing fastness and handle[2], it is difficult to be used for high-grade printing products. In order to overcome the above shortcomings, the polyacrylate emulsion has been modified by many research methods[3-6]. The modifying methods are basically the following two categories: One is that the polyacrylate latex is modified by organic silicon, organic fluorine, polyurethane, nano-materials, casein, cellulose derivatives and other polymer materials; the other is that the performance of polyacrylate emulsion is improved using the new polymerization methods such as core-shell emulsion polymerization, interpenetrating polymer network technology, micro emulsion copolymerization technology, soap-free emulsion polymerization technology and so forth.

The quality and grade of pigment printing products depend largely on pigment printing adhesive performance, therefore, an important trend to improve the printing technology and quality is to prepare a new high performance adhesive.

In this paper, a kind of core-shell nano-TiO_2/acrylate emulsion polymers was prepared by the method of seed emulsion polymerization. The chemical structure characteristics were analyzed in detail and its performance used for pigment printing adhesive was also discussed.

EXPERIMENTAL

100 % cotton fabric; methyl acrylate (MA), analytical reagent (AR); ethyl methacrylate (EMA), AR; butyl acrylate (BA), AR; 2-acrylamide-2-methyl propane sulfonic acid (AMPS), industrial grade; sodium dodecyl sulfate (SDS), AR; OP-10, AR; nano-TiO_2, industrial grade; potassium persulfate (KPS), AR; polyacrylate adhesives, commercially available; pigment printing ink scarlet, industrial grade; Thickener PTF, industrial grade.

Precise power mixer JJ-2, purchased from Jintan medical instrument factory; drying oven 202-1, supplied by Shanghai experimental instrument factory; precision thermostat water bath cauldron HH.S, supplied by Jintan medical instrument factory; Numerical control ultrasonic cleaner KQ-100DE, supplied by Kunshan Ultrasonic instruments limited company; Infrared spectrometer Spetrum-one, produced by US; Nuclear magnetic resonance (NMR) spectrometer Avance 400, produced by US; transmission electron microscopy (TEM) JEM-100 CXII, produced by Japanese; Diamond differential scanning calorimeter (DSC), PerkinElmer company products; Y571B friction fastness tester, produced by Wenzhou textile factory; YB571C brushing fastness tester, produced by Wenzhou Darong textile instruments factory.

Preparation method of core-shell emulsion adhesive: The allyl monomers were washed with 2 % NaOH solution to

remove the inhibitor, then washed to neutral with deionized water and remained on stand-by:

Preparation of reaction solution: The ingredients of the reaction solution were shown in Table-1.

Operation steps: According to the ingredients in Table-1, first, all emulsifier solution and 20 mL initiator solution were put into a 500 mL four-mouth flask, stirring up to 50 ºC, adding 3.5 g of nuclear monomers and temperature up to 80 ºC. After blue phase appeared, the remaining nuclear monomers were dropped off in 1 h, during this time, initiator solution was added for 2 times and each for 4 mL, keeping warm for 1 h. At this temperature, 4 mL initiator solution was added and the shell monomer and dispersive nano-TiO_2 solution began to drop off in 1 h. In the meantime, the initiator solution was added for 2 times and each for 4 mL and keeping the temperature, reacted for 1 h. Then cooled down to 50 ºC, the ammonia was added to attain a pH 6-7 and nano-TiO_2/polyacrylate core-shell emulsion adhesive was obtained after filtering with gauze.

FT-IR spectrum measurement of the core-shell emulsion adhesive: The sample was prepared by solution film-making method. A certain concentration of core-shell emulsion was painted on a clean slide. After film was formed, the film samples on the glass slide together with the slide were immersed in distilled water. The thin film samples were obtained after being fully wetted, peeled and thoroughly dried. Its spectrogram was measured by spetrum-one Fourier transform infrared (FTIR) spectrometer.

Nuclear magnetic resonance (^{1}H NMR) spectroscopy determination: Core-shell emulsion was treated by flocculation, washing, drying, acetone dissolve, Soxhlet extraction and then dried again. The latex was determined by Avance 400 nuclear magnetic resonance spectrometer (USA). While determined, added dimethyl sulfoxide as solvent for 16 times.

TEM observation: 2 to 3 drops of core-shell emulsion was mixed well with 10 mL distilled water and a drop of the mixture was taken to the copper net with Formvar supporting film. After dry, the copper net was put in a culture dish, adding 1-2 drops of 1 % phosphotungstic acid. The product was dyed by 1 % (mass fraction) of phosphotungstic acid, putting aside for 12 h, after drying, determined by TEM JEM-100 CXaII (Japan).

DSC method: After core-shell emulsion adhesive film formed by decompression and drying at room temperature, its glass transition temperature (T_g) was determined by Diamond DSC (PerkinElmer company) under the atmosphere of helium. The heating rate was 10 ºC/min and temperature ranged from -50 to 300 ºC.

Application test of core-shell emulsion adhesive: Dry and wet rubbing fastness: tested according to GB/T3920-1997; washing fastness: tested according to GB/T420-90 and rated by colour card; soaping fastness: tested according to GB/T3921.1-1997.

RESULTS AND DISCUSSION

FT-IR spectrum analysis: The FT-IR spectrum of prepared core-shell emulsion adhesive is shown in Fig. 1. The stretching vibration absorption peak of N-H in amide group near 3445 cm^{-1}, -CH_3 and -CH_2 in the range of 2959-2865 cm^{-1}, the ester carbonyl C=O at 1732 cm^{-1}, C-O in the ester at 1163 cm^{-1}, Ti-O-C at 1229 cm^{-1} and Ti-O at 680-630 cm^{-1}, the bending vibration absorption peak of -CH_3 and -CH_2 at 1455 cm^{-1} and the antisymmetric stretching vibration absorption peak of SO_2 in R-SO_2-OR (sulphonate) at 1386-1372 cm^{-1} can be seen from Fig. 1. This shows that the characteristic absorption peak of reaction monomer units is present in the product structure and that polymerization reaction occurred among the monomers.

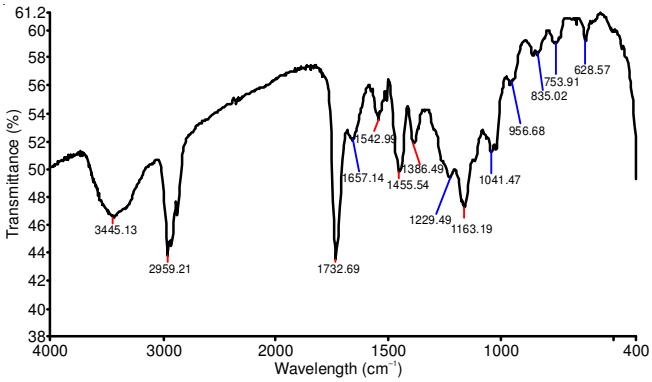

Fig. 1. FT-IR spectrum of the core-shell emulsion adhesive

^{1}H NMR spectrum analysis: The ^{1}H NMR spectrum of core-shell emulsion adhesive is shown in Fig. 2. Fig. 2 showed the absorption peak of methyl on butyl acrylate as well as ethyl ester methyl-terminated and substituted-methyl on ethyl methacrylate is near 0.8-0.9 ppm. The absorption peak near 1.3 ppm should be methylene adjacent to methyl on butyl acrylate; the absorption peak near 1.7 ppm should be methylene away from methyl a methylene on butyl acrylate. The absorption

TABLE-1
INGREDIENT PROPORTIONS OF REACTION SOLUTION

Name of the reagent	Nuclear monomer	Shell monomer	Emulsifier	Initiator	Nanomaterials
MA (g)	8.38	1.6	–	–	–
EMA (g)	8.38	1.6	–	–	–
BA (g)	5.0	16	–	–	–
AMPS (g)	3.24	0.8	–	–	–
SDS (g)	–	–	0.7	–	–
OP-10 (g)	–	–	1.4	–	–
Deionized water (mL)	–	–	40	40	10
Nano-TiO_2 (g)	–	–	–		0.01
KPS (g)	–	–	–	0.3	

Note: Before reaction, nanometer TiO_2 solution must be dispersed by ultrasonic oscillation apparatus. Dispersion time was 20 min and temperature was 75 ºC.

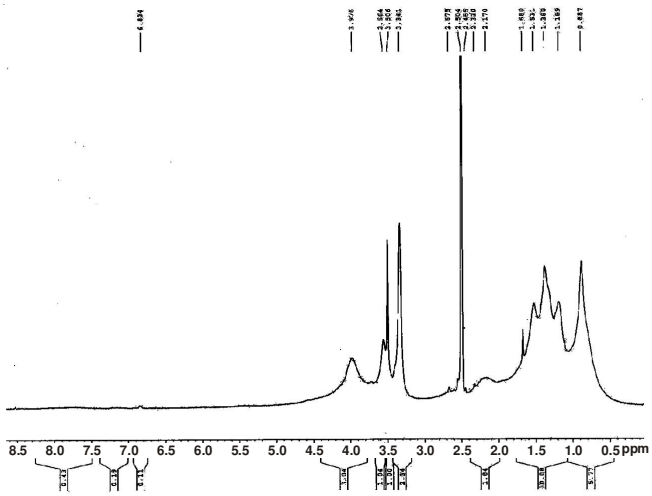

Fig. 2. ^{1}H NMR spectrum of the core-shell emulsion adhesive

peak of two methyls of 2-methyl-2-acrylamide propanesulfonic acid range from 1.1-1.7 ppm. The absorption peak of methyl on dimethyl sulfoxide is near 2.5 ppm; the absorption peak area from 3.3-3.6 ppm is due to methyl on methacrylate, methylene connected to the oxygen on ethyl methacrylate and methylene connected to sulphur on 2-methyl-2-acrylamide propanesulfonic acid. The absorption peak near 4.0 ppm is methylene connected to the oxygen on butyl acrylate.

DSC analysis: Fig. 3 is DSC analysis diagram of core-shell emulsion adhesive. It can be clear seen from Fig. 3 that, two glass transition temperature (T_g) of emulsion polymer appear and the span is relatively large rather than fixed in a certain range, so the core-shell structure can be deduced. Experiments find that the emulsion stability is good under the condition of both lower and higher temperature and the problem of polyacrylate emulsion called "sticky when heated and fragile when cooled" is well solved by core-shell structure after modified reaction.

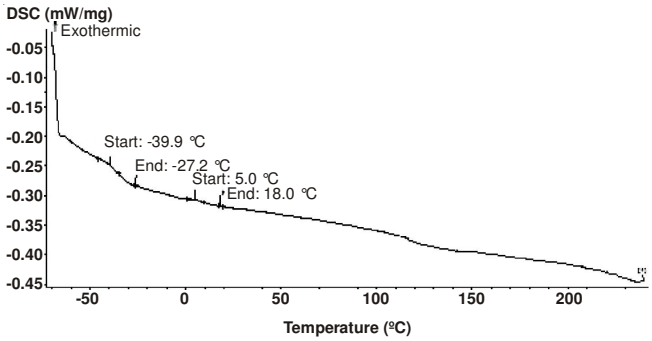

Fig. 3. DSC curve of the core-shell emulsion adhesive

TEM analysis: TEM photograph of core-shell emulsion adhesive is shown in Fig. 4. The methods of phosphotungstic acid dyeing and transmission electron microscopy observing can be used for determining whether the prepared emulsion particles is with core-shell structure. This is because the core-shell emulsion is heterogeneous polymer emulsion and the medial and lateral of colloidal particles is enriched with different components. The solubility of phosphotungstic acid is different with different composition, the dye is different too, so the obvious core-shell structure will appear after phosphotungstic acid dyeing. After the emulsion adhesive is dyed by phosphotungstic acid, latex particle morphology is observed by transmission electron microscope. As is shown in Fig. 4, the emulsion particles has a dyed crust, center area is brighter than the edge and the obvious core-shell structure of emulsion particles is clearly shown by photographs. This is the same as the aforementioned DSC analysis results.

Fig. 4. TEM photo of the core-shell emulsion adhesive

Application properties of the core-shell emulsion adhesive

Fabric fastness: The prepared core-shell emulsion adhesive was used for pigment printing test of cotton fabrics and its fastnesses were tested and compared with commercially available acrylate pigment printing adhesive. The pigment printing test process was as follows[7,8]: Pure cotton fabric was treated by screen mesh coating paste made in advance, dried at 100 ºC for 3 min and baked at 150 ºC for 3 min.

The fabric fastnesses after pigment printing were shown in Table-2. Table-2 shows that, compared with the commercially available acrylate emulsion adhesive, the various fastnesses of nanometer TiO_2 modified core-shell emulsion adhesive are obviously improved. This is because that the prepared adhesive in this study belongs to organic-inorganic composite materials. On the basis of keeping the polyacrylate emulsion good flexibility, grafting makes the prepared polymer very close to the nanoscale structure. The emulsion particles are very small, small size effect and high specific surface area lead to strong permeability and the solid focus between the adhesive and fiber is enhanced by the significantly increased specific surface area, therefore, the various fastnesses of adhesive are obviously improved.

Fabric handle: By sensory evaluation, a soft, smooth and clean handfeel and good elasticity was obtained after pigment printing with the prepared adhesive, however, printing with commercially available adhesive, only got a rough, viscous, heavy and hard handfeel.

Conclusion

Core-shell type TiO_2/acrylate emulsion polymer adhesive was prepared by the method of seed emulsion polymerization. The structure analysis by FT-IR and ^{1}H NMR spectrum showed that the preparation of the adhesive was a success. DSC analysis showed that T_g of the preparation emulsion polymer was not constant in a certain range, but two T_g with a large span. Thus the problem of traditional polyacrylate emulsion called "sticky when heated and fragile when cooled" could be obviously

TABLE-2
PRINTING FASTNESS OF THE CORE-SHELL EMULSION AND COMMERCIAL ADHESIVE

Adhesive	Dry friction fastness/grade	Wet rubbing fastness/grade	Wash fastness/grade	Soaping fastness/grade
Commercial adhesive	3-4	3-4	3	3-4
Core-shell adhesive	4-5	4-5	4	4

improved and the obvious core-shell structure of emulsion polymer was shown by TEM analysis. When the prepared core-shell latex polymer was used as a pigment printing binder, a good effect was achieved by preliminary test. Compared with the commercially available acrylate emulsion adhesive, the various fastnesses of prepared adhesive were obviously improved, dry and wet rubbing fastness reached level 5, brushing and soap washing fastness reached level 4. Soft, smooth and clean handfeel and good elasticity was obtained when it was used as pigment printing adhesive.

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