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Research Article

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Study on the polyurethane acrylate composite emulsion on the paper plastic laminating precoat film

Gao Yanfei[1,2] and Chen Qifeng[*2]

[1]Zhong Shan Torch Polytechnic, Zhong Shan, PR China
[2]State Key Lab of Pulp & Paper Engineering, South China University of Technology, Guangzhou, PR China

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ABSTRACT

In this paper, the Water-borne polyurethane-acrylate hybrid aqueous emulsions which dominate the properties of the adhesive were prepared by the experiments. According to analysis of polyurethane-acrylate hybrid aqueous emulsions and the polyurethane raw materials by the FT-IR, allyl group was observed to take the crosslinking reaction. Through the Malvern particle size analysis, the size and the distribution of emulsion particles were found to become significantly smaller after reaction. Base on the storage stability, dilution stability, water-resistant performance, dry performance of the observation, the acrylic-polyurethane hybrid aqueous emulsions was expect to take stable performance. The experimental results based on the physical properties and image analysis of the precoat adhesive film of paper-plastic lamination showed that: the adhesive film coated by this hot melt adhesive had a high gloss and adhesive force, it improved the application performance of the precoat adhesive film of paper-plastic lamination in the printing and packaging industry.

Key words: Polyurethane, Acrylate, Precoat, Emulsion

INTRODUCTION

The production of precoat adhesive film of paper plastic laminating is usually realized by coating the EVA hot melt adhesive to the BOPP based on the gravure printing, but the coating of this kind of precoat adhesive film is made of screen dot and it will affect the brightness and transparency in application [1]. In order to solve this problem, we have used the method of coating continuous and uniform hot melt adhesive to the EVA hot melt layer which was made of screen dot.

Benlian Zou used the butyl acrylate as soft monomer and the vinyl acetate as the hard monomer , she prepared some adhesive in the non-ionic and anionic emulsion polymerization system, the adhesive showed high brightness[2]; Xianke Ye prepared an acrylic hybrid aqueous emulsion, where acrylonitrile and acrylic acid were used as functional monomer[3]. These research showed that the best quality ratios of acrylonitrile and acrylic acid were 4% and 5% ~ 8%; Zushun Xu prepared an adhesive based on the semi-continuous seeded emulsion polymerization, where acrylate, methacrylate, styrene and acrylonitrile were used as the main monomer[4,5]. In regard to water-borne polyurethane, the research was used as hot melt adhesive[6,7]. Acrylate copolymer emulsion is important component of precoated adhesive film emulsion at present, it shows high hardness, good transparency and good ink affinity[8], while for water-based polyurethane emulsion, it shows outstanding bonding performance, toughness after film forming, good wear resistance,gloss and pigment affinity [9,10]. Therefore, if we combine them together, we will obtain composite emulsion with good transparency and high bonding performance.

This paper studied on the application mechanics and characteristics of the polyurethane acrylate composite emulsion applying to the precoated adhesive film of paper plastic laminating, and presented the synthesis process and batch formula of polyurethane modifying acrylic copolymer emulsion, and the physical properties of the copolymer emulsion was tested by infrared spectroscopy (IR),particle size analysis, gel permeation chromatography (GPC). According to mix the waterborne polyurethane acrylate emulsion to the waterborne rosin emulsion, we obtained the hot melt precoat adhesive. The experimental results based on the physical properties and image analysis of the precoat adhesive film of paper plastic laminating showed that: the adhesive film coated by this hot melt adhesive had a high gloss and adhesive force, it improved the application performance of the precoated adhesive film of paper and plastic laminating in the printing and packaging industry.

EXPERIMENTAL SECTION

Materials and Apparatus:table 1 showed the main materials and reagents,main apparatus include: Nicolet-510 Fourier Transform Infrared Spectrometer (Thermo Co., US); Differential scanning calorimeter Q200 (TA Co., US); LR5KPlus Universal tensile test machine (Lloyd instruments, UK); X-Rite spectroeye 519 (X-Rite,USA).

Table 1 Main materials and reagents

Chemicals	Specification
Water-based polyurethane (PU)	Industrial grade
Butyl acrylate (BA)	Analytical grade
Methyl methacrylate (MMA)	Chemical grade
Acrylic acid (AA)	Chemical grade
Sodium dodecyl sulfate(SDS)	Chemical grade
Potassium peroxydisulfate (KPS)	Analytical grade
Sodium bicarbonate（$NaHCO_3$）	Analytical grade
Rosin	Industrial grade
Antifoaming agent	Industrial grade
Ammonia	Analytical grade

PREPARATION OF WATER-BASED PU/ PA COMPOSITE EMULSION

(1)Preparation of PU pre-emulsion

We added all water-based PU, 1/4 acrylate monomer, half emulsion, and partial deionized water to flask with mixer and stirred for 30 minutes, with temperature kept at 70 ℃, to obtain non-laminated pre-emulsion.

(2)Preparation of PA emulsion [11,12]

We added the remained acrylate monomer, the remained composite emulsion, 3/5 initiator, and some deionized water. Mixed it and increased the temperature. When temperature reached 80℃, slowly dripping added KPS water solution with one-hour metering amount. After dripping was finished, we kept constant reaction temperature for 30 minutes. When there was blue light appearing in the emulsion, it indicated that PA emulsion has been produced. When there was no back flowing for the reaction, kept constant temperature for half an hour to obtain PA emulsion.

(3)Preparation of PU/PA composite emulsion [13,14]

At the temperature of 80±2℃, we added PU pre-emulsion, AA, the remained initiator to PA emulsion, the dripping speed was controlled to make that there was no obvious back flowing in the reaction flask. With the addition of PU pre-emulsion, blue color of PA emulsion was changed to milk white gradually, the result was as shown in Figure 1 and Figure 2. After the dripping, we held the temperature for 2 hours and naturally cooled the temperature below 40℃, then discharged and filtered.

Figure 1 PA emulsion preparation

Figure 2 PU/PA emulsion preparation

PREPARATION OF MODIFIED ACRYLIC RESIN EMULSION

The basic formula was listed as follow: BA 24.7g, VAC12.3g, KPS1.2g, Emulsifier 0.4g, SDS0.6g, Sodium bicarbonate1.2g, Deionized water 60g.Op-10, SDS(as emulsifier) and deionized water 30g were heated to 60 ℃ in a four -necked flask under reflux and stirring, then 20% (by weight) of monomer mixture (mixed with butyl acrylate, vinyl acetate and acrylic acid), sodium bicarbonate (as PH buffer) and about 35% (by weight) of potassium persulfate (as initiator) were put into the reaction flask. When the blue-ray appeared, the reaction temperature was increased to 85 ℃. After 30 minute's reaction, appropriate amount of allyl maleated rosin ester was dissolved in remaining monomer mixture, and then the remaining monomer mixture and initiator were slowly but continuously dropped into the reaction system for 4 hours. At last the product was obtained after 30-minute's reaction at 90℃ [15].

Acid value was calculated as formula. 1:

$$\text{Acid value (mg NaOH/g)} = (V\times m\times 40)/W. \qquad (1)$$

V is the volume (ml) of sodium hydroxide standard solution; m is the molar concentration of potassium hydroxide; W is weight of sample (g).

The weighted sample 1.5g was stoving for 2 hours，and solid content was calculated by the final ratio of remaining sample.

APPLICATION OF COMPOSITE EMULSION ON PAPER-PLASTIC PRECOAT ADHESIVE FILM

We selected self-prepared water-based PU/PA emulsion with solid content of 12% and added water-based rosin emulsion NH-139 according to the calculated ratio, then mixed well to obtain the needed composite adhesive. Finally, we coated the adhesive to the precoat film by using "工" type manual coating device. After the uniform coating, the film was dried for 6 minutes at 70℃ and laminated on electronic laminator at 110℃.

The T-style peel strength of emulsion was determined according to national standard GB / T2791-1995.

Color density of printed matter was tested by color density meter，removal rate of ink was calculated as formula 2:

$$S = (A_0-A_1)\times 100\% / A_0. \qquad (2)$$

S is the removal rate of ink (%), A_0 is the color density (D) of printed matter before peeling test, and A_1 is the color density (D) of printed matter after peeling test.

RESULTS AND DISCUSSION

Figure 3 was the infrared spectrogram of water-based PU/PA composite emulsion. At the 1740cm^{-1}, the strong peak appeared, it proved that there was the ester bond. At the 3300-3400cm^{-1}, the wide peaks appeared, it proved that there was the R-OH group. And there was no characteristic peak in 1600-1680cm^{-1}, indicated the additive reaction of acrylate monomer had been finished.

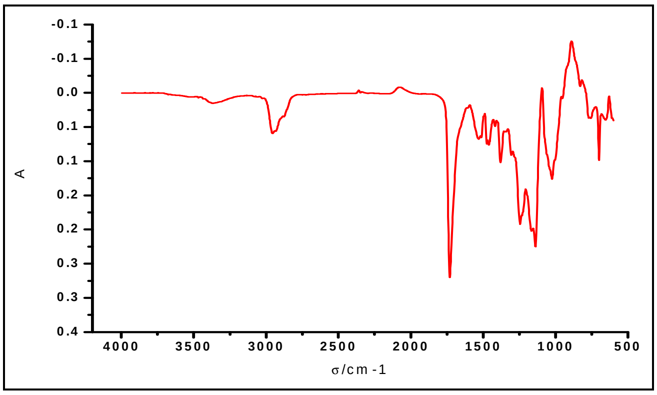

Figure 3 Infrared spectra of composite emulsion

Compared the spectra of allyl maleated rosin ester Figure 4 (a) with maleic rosin Figure 4 (b), the differences were in the spectra of allyl maleated rosin ester, there was absorption at 1735 cm^{-1} from vibration of C=O bond in ester group, but in spectra of maleic rosin there were absorption at 1781 and 1845 cm^{-1}[6] from vibration of C=O bond in anhydride group. So it showed the esterification had happened between maleic rosin and allyl alcohol. The weight ratio to maleic rosin of allyl alcohol, Catalyst and inhibitor were 4, 6.5% and 0.5%. Temperature was 110℃.Reaction time was 5 hours. Acid value of maleic rosin and allyl maleated rosin ester were measured, and the results were 165.5, 71.75. The acid value of product was lower than reactant that indicated the esterification happened.

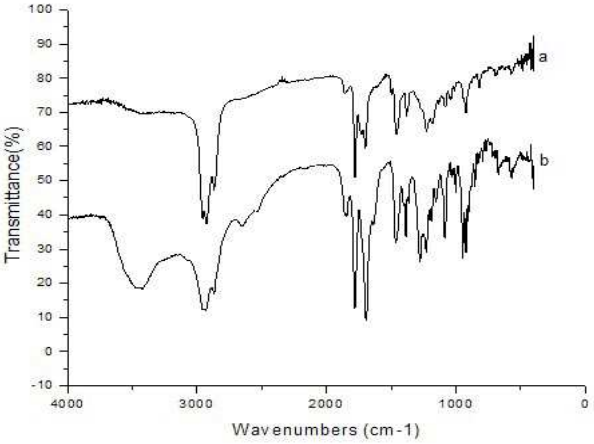

Figure 4 IR spectra of maleic rosin (b) and allyl maleated rosin ester(a)

After the additive reaction of PA monomer was finished, we carried out Malvern particle size analysis on water-based PU/PA composite emulsion in order to further know emulsion particle state, the results were shown in Figure 5.

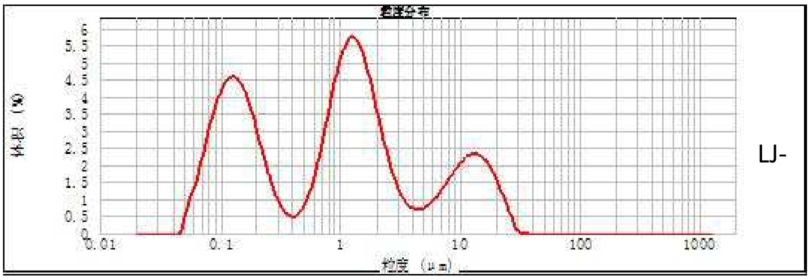

Figure 5 Particle size distribution of PU/PA

The membrane of allyl maleated rosin ester modified acrylic resin and the mixed membrane of allyl maleated rosin ester and acrylic resin were prepared and then compared through DSC analysis.

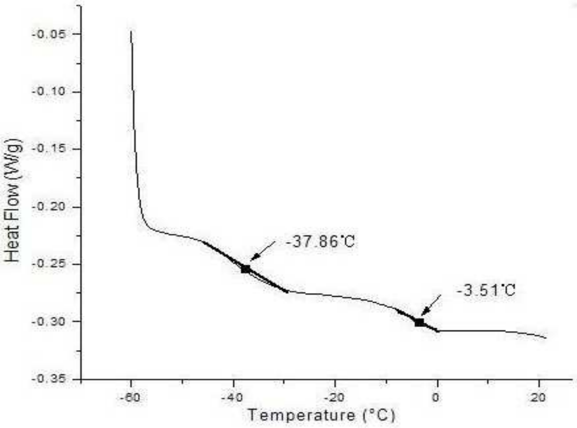

Figure 6 DSC of mixed membrane

Figure 6 showed that the mixed membrane of allyl maleated rosin ester and acrylic resin had two glass transition temperatures (-37.85 and -3.51℃). So the blending emulsion was not stable and easy to separate into two phases. So the modified acrylic resin was a stable homogeneous phase system.

As showed in Figure 7, the absorption at 2959 and 2925 cm^{-1} were from vibration of methyl and methylene C-H. The strong absorption at $1731cm^{-1}$ from vibration of carbonyl group and the absorption at 1239 and 1169 cm^{-1}[7] from vibration of C-O showed the existence of carboxyl group and ester group. The absorption at 1450 cm^{-1}[8] from in-plane bending vibration of six-carbon ring C-H demonstrated the copolymerization between allyl maleated rosin ester and acrylics.

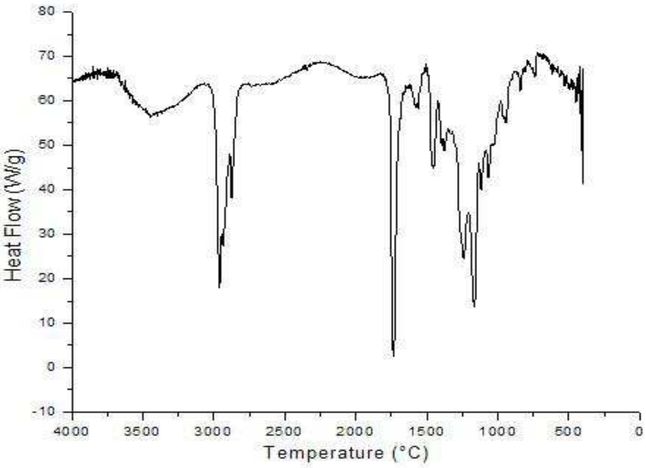

Figure 7 IR spectra of modified acrylic resin

The ink cell image had been clearly and directly obtained through QEA PLASTM-Ⅱimage analyzer, the results were as shown in Figure 8.

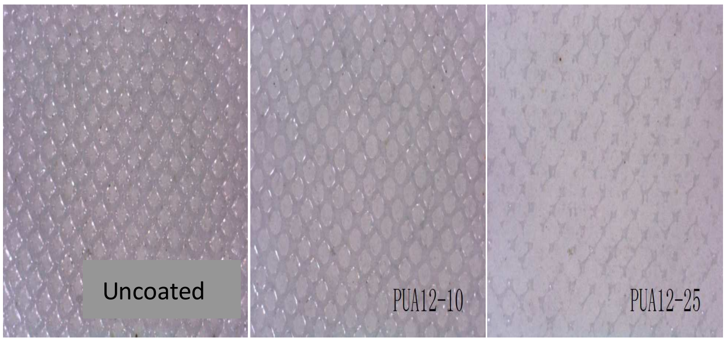

Figure 8 the image of the ink cell on precoat film

We could know that there were some circular dots in the surface of the coating film, the ink cell had a big concave depth. Along with the increase of the rosin, the emulsion viscosity increased, the colliquefaction ability became stronger, and the repelling force of the interface between coating gelatine and primary gelatine decreased. The ink cell was filled gradually, when the ratio of rosin rose to 25%,the emulsion viscosity, the ability of colliquefaction, the affinity force of interface between coating gelatine and primary gelatine were the best. Most of the ink cells were covered by the latex particles; there was a biggest melt viscosity of the gelatine now. When the ratio of rosin further increased to 30%, the aqueous PUA could not bear the internal force of the gelatine, the gelatine could not cover the surface of the cell stably.

The uncoated film had a weaker ability of removing ink than the aqueous PUA. With the adding the rosin, the ink removing rate presented a trend of up and down, when the contents of the rosin were from 20% to 25%,there was a maximum of the ink removing rate, the results were as same as the image examined by QEA PLASTM-Ⅱ.

The peak in the figure was the force record of peeling when the film and paper were separated. We could know that the gelatine had a weaker adsorption capacity to the printing ink than to paper, the results confirmed the bonding mechanism of the precoated film. The Figure 9 showed the ink removing on uncoated film and coated film,

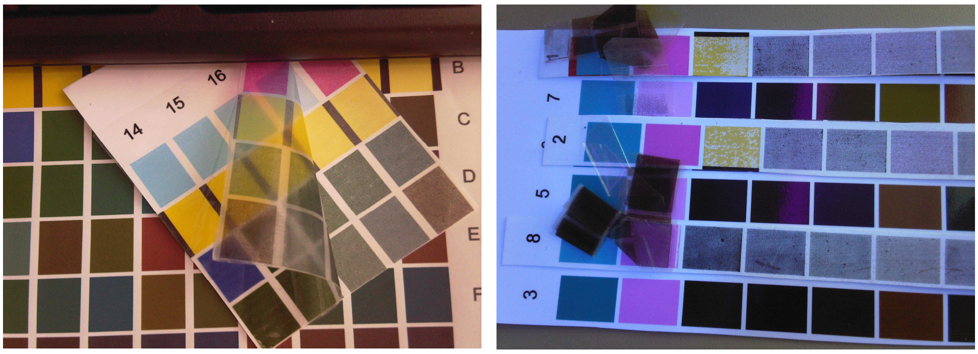

Figure 8 The ink removing on uncoated film and coated film

CONCLUSION

In this paper, we adopted self-prepared water-based polyurethane/acrylate composite emulsion to mix with water-based rosin emulsion to coat on the precoated adhesive film secondly. Physical performance and image analysis of the emulsion had been coated on precoated adhesive film indicated that: the adhesive film coated by this hot melt adhesive had a high gloss and adhesive force, the development of this type of emulsion will greatly improve the application performance of paper-plastics composite precoated adhesive film in printing and packaging industries.

Determination for adsorption effect of adhesives to ink showed that modified acrylic resin had better adsorption effect of adhesives to ink. Compared with unmodified acrylic resin emulsion, the rosin modified acrylic resin emulsion had better adhesive property, more stable performance and excellent compatibility with the ink.

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