WATER-BORNE, LOW-TEMPERATURE CURABLE POLYACRYLATE COATINGS

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A water-borne, low-temperature curable polyacrylate (PA) coating was developed by introducing crosslinkages in polymer chains with a polyfunctional comonomer. The effect was investigated of amount of comonomer on the properties of coating latex, such as mechanical properties, solvent resistance, Tg, and surface morphology of polymer. The particle size, size distribution, and the dispersion stability were also measured. Comparisons of the product were carried out with some coatings available from the market.

INTRODUCTION

Polycrylate (PA) coating agents are the most common products as regards the ease of production, the low cost, and the final properties of the finished material. However, solvent-borne PA coatings have a number of deficiencies causing a variety of problems for processors. The aromatic and chlorinated hydrocarbon solvents in coating systems not only damage the health of workers but also adversely influence the environment. Therefore, over the last decade regulations to protect the environment, personal safety, and health have caused coating to move away from solvent-based to water-borne systems [1].

But the normal water-borne PA coating agents have poorer solvent resistance and lower resistance against water pressure than solvent-borne coatings. As is well known, introducing crosslinks into a latex

film can increase its physical and chemical properties [2–5]. The crosslinkage could only be formed under intensive curing conditions such as high temperature and catalyst. Traditional N-methylolacrylamide-containing coatings are used in this way. These processes not only might emit formaldehyde but also run the risk of weakening the substrate during the finishing process. Alternatively, introducing suitable crosslinks in polymer chains in the polymerization stage may improve effectively the film properties.

The aim of this study was to develop, through the pre-crosslinking technique and optimizing the processing conditions, a kind of low-temperature curable and water-based PA coating, which can impart on the coated fabric a high water pressure resistance, and good moisture permeability properties.

EXPERIMENTAL

Materials

In this study the following materials were used; methyl methacrylate (MMA), n-butyl acrylate (n-BA), Styrene (St), 2-ethyl hexylacrylate (2-EHA), methyl acrylic acid (MAA) as monomers; Glycol dimethylacrylate, used as the comonomer, was purchased from the market; $(NH_4)_2S_2O_8$ as the initiator; Sodium dodecylsulfate, Emulator TX-30, and Emulator OS as emulsifiers.

Latex Synthesis

First the emulsifiers were dissolved in deionized water at room temperature in a three-necked reactor equipped with a reflux condenser, a stirrer, and a thermometer. The system was maintained at a temperature of 70°C with continuous stirring. The initiator aqueous solution was charged to the reactor; several minutes later the mixture of monomers and comonomer was added dropwise in a period of 2 to 3 h. Little monomer accumulation was observed at any time, therefore it was assumed that reaction was starve-fed. When monomer addition was finished, the reaction was continued for half an hour. An amount of additional initiator solution was added, and the system was heated to about 85°C and kept for about 1 h to complete the reaction. The latex was then gradually cooled down to ambient temperature under stirring. Finally the latex was filtered through a 100-mesh screen to remove the minimal amount of grit formed during the polymerization.

Fabric Coating

The coating was neutralized to pH 7−8 with aqueous ammonia and thickened by small amount of PTF thickener, and then the paste was spread on the fabric (nylon: 210T) surface with a knife. The fabric was then dried at 80°C.

MEASUREMENTS

Particle Size Determination

Latex particle sizes and size distribution were determined using TSM Grain Size Analyzer. All the latexes were monodispersed.

Differential Scanning Calorimeter (DSC)

DSC was used to determine the Tg of the emulsion polymers. Latexes were dried under ambient conditions until they lost opacity. The temperature scan ranged from an initial temperature of −100°C to a final temperature of 100°C, at a heating rate of 10°C/min. The inflection point of the curve was assigned as Tg.

Tensile Testing

Ultimate tensile strength and elongation were measured on tensile tester. Testing was done on films that were 6 mm wide, 10 mm long, and approximately 0.5 mm thick. And the extension rate was 200 mm/min. Five replicate measurements were made. The values reported were the mean ultimate tensile strength and the mean percent elongation at break.

Water Absorbency of the Film

Films of known weight (W_i) were immersed in distilled water at room temperature for different time intervals. The surfacial water was removed, and the film was re-weighed (W_2). The absorbency in percentage was obtained according to the equation:

$$\text{Water absorbency}\,(\%) = (W_2 - W_1)/W_1 \times 100$$

Weight Loss of the Binder Membrane in Cold Water

Sample films were cured at 80, 100, and 160°C in a chamber for 3 min, respectively; then they were immersed in distilled water at room temperature and occasionally shaken for 24 h and dried until constant

weight; finally the percentages of the weight loss were calculated according to the following equation:

$$\text{Weight loss}\,(\%) = (W_3 - W_4)/W_3 \times 100$$

Where W_3 is the original weight of the sample film and W_4 is the weight of the sample film after immersion and drying.

Surface Characteristics of Sample Film

Atomic force microscopy (AFM) was used to investigate the morphologies of the sample film on a commercially available force microscope (Digital Instrument Nanoscope) [6].

Measurement of Physical Properties of Coated Fabric

]Water Pressure Resistance

The water resistance hydrostatic pressure head test was carried out on a hydraulic tester made by KYOTO according to ISO811-1981.

Tearing Severity

The tearing test was done on the Elmendorf Tearing tester according to ISO/DIS13937-1: 1995.

Water Vapor Permeability

The moisture value ($g/m^2/24$ h) was measured at 40°C, 65% R.H. according to GB/T12704-91.

Weight of Coated Fabric (g/m^2)

The weight of the coated fabric was determined in units of grams per square meter.

RESULTS AND DISCUSSION

Characterization of Emulsion Latex

The water-borne PA coatings were prepared through a compounded emulsion systems composed of anionic and nonionic surfactants. In this study the dodecylsulfate was used to achieve a fine particle size, and emulator TX-3, which has larger number of polyoxyethylene, was selected to reduce the probability of collision of particles and ensure the emulsion stability. The particle size and size distribution not only affect the stability of latex emulsion, but also have effects on the film properties such as minimum film-forming temperature (MFT) and Tg [7−8]. Figure 1 showed that the particle size distribution was narrow,
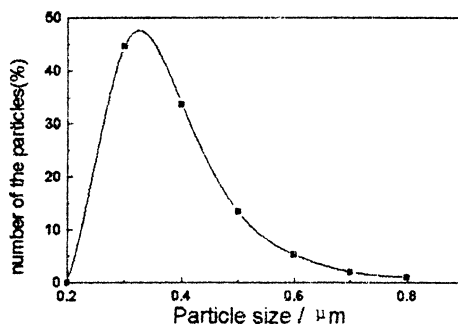
FIGURE 1 Emulsion particle size distribution.

and the particle size was concentrated in the range of 0.3 to 0.5 μm. And the number percentage of size 0.3 μm accounts for 44.6% approximately, the size of 0.4 μm is probably 33.67%. The pot life was over one year. When diluted by water or electrolyte (10% aqueous calcium chloride solution, the system could stand over one week without any change in appearance.

Effect of Amount of the Comonomer on the Properties of the Coating

The commercial PA coatings were normally composed of linear long chain polymers. On applying to the fabric, crosslinks could only be introduced by the inherent curable groups in the polymer system or by the addition of external-crosslinking agents, both needing intensive curing conditions such as high temperature. These processes not only exhausted much energy but also the water pressure resistance of the coated fabric was relatively poor.

In this study the suitable crosslinkages were already introduced into the copolymers during the polymerization stage. When the coatings were applied to the web and dried, the particles became deformed into space-filling polyhedra, which packed together to form a strong film. It must be emphasized that the suitable extent of crosslinking was the key to obtain satisfactory properties because the crosslinkage played a dual role during the film formation. On one hand, the crosslinkage in the interior of particles confined the shift and deformation of molecular chains, thus enhanced the strength of the film formed from the latex; and on the other hand, the development of cohesive strength in the films was achieved through the interdiffusion of polymer chains across particle–particle interfaces, which was

referred to as "further coalescence." This coalescence of polymer molecules across the interfacial membrane that made the particle fuse together had been recognized as an essential step in the applications of latex-based coatings [9]. If the extent of crosslinkage exceeded some proper value, the mobility of the polymer molecules, and thus the ability of the latex to form films, would be reduced. There would be minimal interdiffusion of latex particles, and the film would be held together by only a few interparticle entanglements along with interparticle crosslinks, and the toughness of the film would decline. The limitations to diffusion imposed by the presence of crosslinks depended on the extent of pre-crosslinkage.

In this article the effect of the amount of comonomer on pre-crosslinkage was investigated and the solvent-resistance, Tg, the mechanical properties as well as the surface morphologies are discussed.

The Water-Resistance of the Film

The extent of crosslinking in the polymer chain could be determined indirectly from the degree of swelling of the film in water. The water absorbency at different intervals and the weight loss of thin film in water in different temperature are listed in Tables 1 and 2.

As is shown in Tables 1 and 2, the water absorbency and the weight loss in water fell gradually, accompanying the increasing concentration of comonomer. These results provided clear evidence that the extent of crosslinkage increased with the content of comonomer. But it was worthy to note that when the amount of the comonomer reached to 7.6%, a slight increase in water absorbency and weight loss occurred. This small increase in the water absorbency and weight loss indicated that the excessive crosslinkage limited the extent of interdiffusion, leading to a reduction in the quality of the film.

TABLE 1 Water Absorbency of Film with Different Content of the Comonomer (Dried at Room Temperature)

Sample no.	Amount of the comonomer (%)	Water absorbency (%)		
		1 h	2 h	24 h
1	0.50	8.60	11.3	21.04
2	2.02	6.21	9.12	16.52
3	3.93	4.32	6.30	13.12
4	5.81	3.20	4.85	9.89
5	7.60	3.63	5.02	9.99

TABLE 2 Weight Loss of Thin Film in Water Cured at Different Temperatures

Sample no.	Amount of the comonomer (%)	The weight loss of thin film (%)		
		80°C	100°C	160°C
1	0.50	9.21	6.72	2.91
2	2.02	5.80	3.54	1.60
3	3.93	3.52	2.21	0.86
4	5.81	2.10	1.10	0.40
5	7.60	2.40	1.12	0.45

The Glass Transition Temperature of the Film

The "hand" of coated fabric depended on the Tg of the applied coating polymer. The higher the Tg, the tougher the film, and the "hand" of the fabric was stiffer. But when the Tg was too low, the fabric tended to be tacky.

The glass transition temperature (Tg) characterized, to some extent, the structure and uniformity in composition of latex particles. The Tg depended on the polymer composition and molecular weight, but also on the extent of crosslinkage, and the latex particle size [10]. In this study the influence of crosslinkage on Tg was investigated and the result are shown in Figure 2.

From Figure 2, it could be seen that Tg went up with the amount of comonomer. Especially when the content of comonomer changed from 5.81% to 7.6%, the Tg shifted to a higher temperature by 11.8°C. This was due to the fact that as the amount of comonomer increased, the crosslinkage density in the polymer also increased, the length of the dangling chain became shorter and the mobility of polymer was reduced.
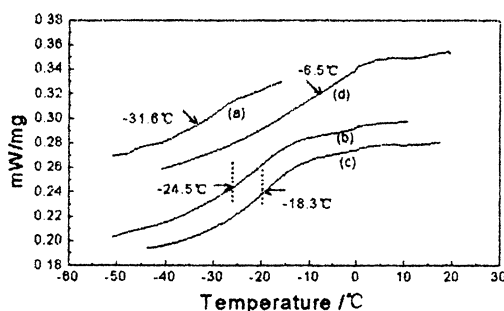
FIGURE 2 The DSC curve of the film with different amount of the comomer
Note: (a) comonomer%:0.50%; (b) comonomer%:3.95% (c) comonomer%:5.81%; (d) comonomer%:7.60%.
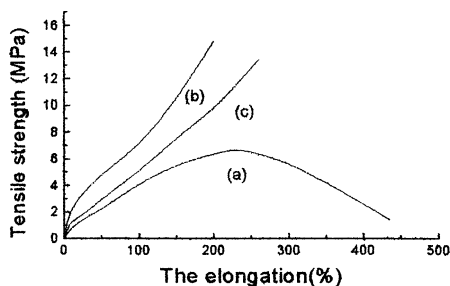
FIGURE 3 The stress-strain curve of film Note: (a): the amount of comonomer: 0% (b): the amount of comonomer: 5.9% (c): the amount of comonomer: 7.6%.

Effect on Tensile Properties

Tensile measurements required great care because defects in the sample could lead to premature rupture. For each set of five samples examined, one or two might have a significantly lower strain-at-break than the others. In this case, the data from these samples were discarded and the results from the remaining were averaged. In Figure 3 stress−strain curves for different amount of comonomer for films are presented. The curve labeled (a) was for uncrosslinked film. For this film, the curve showed a peak in stress-at-break (6 Mpa) and had a large elongation. It did not break at the highest tensile strength until the elongation reached to 475%. The curves labeled (b) and (c) were the pre-crosslinked films. There were significant changes compared to curve (a), exhibiting a large increase in tensile strength and decrease in strain-at-break. Compared to curve (b), the stress-at-break of curve (c) appeared to decrease slightly and the strain-at-break increased, which might be interpreted that when the excess crosslinkage was introduced in the polymer chains the interdiffusion between particles was hampered, and these impaired the film properties.

Surface Morphology of the Film

In this article, AFM was used to observe the surface morphology of the films directly and to show the influence of crosslinkage on film formation. Film made from latex without comonomer was considered as the reference sample (Figure 4). The topologies of films made from latex with pre-crosslinkage were given in Figures 5 and 6. Contrary to the film in Figure 4, the surface morphologies of Figures 5 and 6

RMS.4.531nm
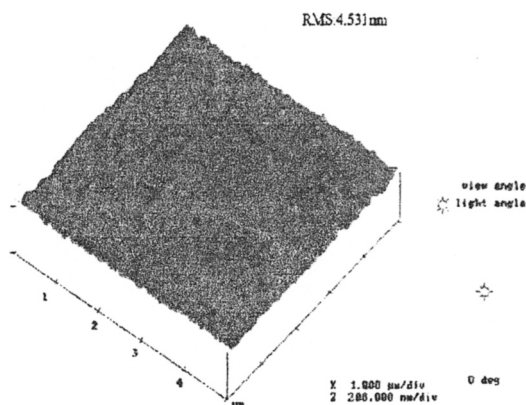
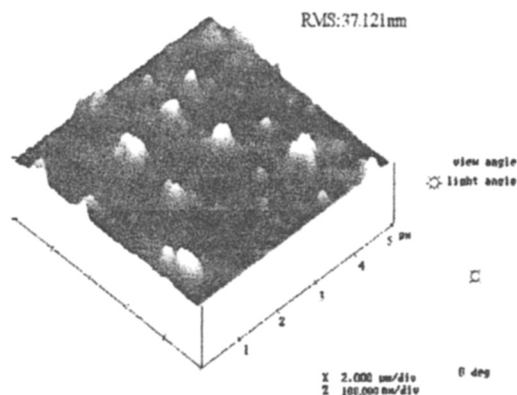FIGURE 4 The image of film with 0% comonomer.

were covered with "hills" and "valleys." This was consistent with the surface roughness of the film. These appearances suggested the incomplete particle coalescence in the film formation due to the crosslinkage.

Comparison with Other Coatings

The product and some coatings available in the market were applied to nylon fabric (210 T) by knife coating. The procedure was as follows: the substrate → coating (a thin layer covered on the surface of the

RMS:26.293nm
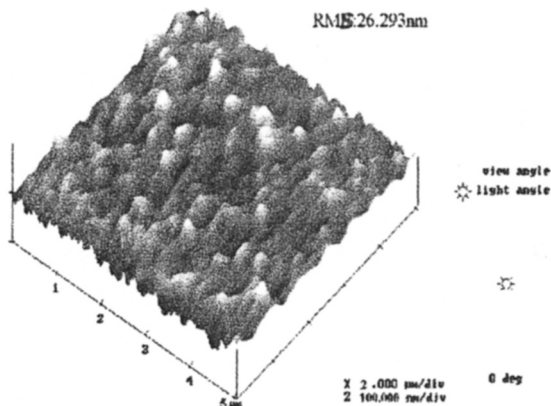
FIGURE 5 The image of film with 5.81% comonomer.

FIGURE 6 The image of film with 7.6% comonomer.

web) → dried (80°C). The coated samples with commercial coatings were cured at 160°C for 3 min. The results are listed in Table 3, which illustrated that the coated fabric covered with the product had satisfactory properties after being dried. The water-pressure resistance reached to 1103 mm H_2O, which was much higher than that of the common coatings, whereas the moisture permeability was as high as 2650 g/m^2 24 h, and the loss in tearing strength of fabric was below 30%. The water resistance hydrostatic pressure reached to 2000 mm H_2O when the add-on was 10 g/m^2.

Conclusions

From the earlier experimental results the following could be drawn: A low temperature curable water-borne PA coating was developed by

TABLE 3 Comparison of the Product with Other Coating

Types	Add-on (g/m^2)	Water pressure resistance (mm H_2O)	Moisture permeability (g/m^{2}24 h)	Tearing strength (gf) Warp	Weft	The appearance of coated fabric
The product	6−7	1103	2651.9	1772.8	1324.8	Smooth, soft
The coating A	8−9	562	2313.5	1561.6	1231.9	Smooth, soft
The coating B	6−7	410	2521.9	1660.5	1378.5	Smooth, soft
Substrate	/	/	4627.7	2990.9	1747.2	/

Note: Coatings A and B are commercial products available in the market.

pre-crosslinking technology. The water proofing and moisture permeability of the coated fabric dried at 80°C were satisfactory. The water-pressure resistance was much higher than that of common PA coatings, which not only lowered the energy consumption but also enlarged the application field of water-borne coatings. The particle size of latex was mainly concentrated in the range of 0.3 to 0.5 μm, therefore the emulsion had a good dispersion stability and long pot life. The extent of pre-crosslinkage increased with the amount of comonomer, which improved the coating properties. However, excessive crosslinkage in polymer chains could hinder the film formation, thus impairing the film properties. The optimal amount of comonomer was about 5 to 6% in weight percentage of the total monomers in each reaction batch.

REFERENCES

[1] Traubel, Harro (Leverkusen, D. E.), Reiner et al., U.S. Patent 5,518,764 (1996).
[2] A. Iosel and G. Ley, *Macromolecules* 26, 2222 (1993).
[3] W. T. Brown, *J. of Coatings Technology* 72(904), 63 (2000).
[4] P. Pinenq and M. A. Winnik, *J. of Coatings Technology* 72(903), 45 (2000).
[5] T. Tamai, P. Pinenq, and M. A. Winnis, *Macromolecules* 32, 6102 (1999).
[6] R. M. Rynders, C. R. Hegedus, and A. G. Gilicinski, *J. of Coatings Technology* 67, (1995).
[7] S. K. Charles, *J. of Coatings Technology* 71(896), 89 (1999).
[8] D. P. Jensen and L. W. Morgan, *J. Appl. Poly. Sci.* 42, 2845 (1991).
[9] A. Iosel and G. Ley, *G. Polymer Bulletin* 27, 459 (1992).
[10] A. Rudin and D. Burgin, *Polymer* 16, 291 (1975).