Research Progress of Polymer Latex Modified With Rosin

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SUMMARY

Polymer latexes have been widely used in paints, adhesives, binders, paper coatings, textile finishes, pharmaceuticals, floor polishes, printing inks, etc. because of the reduced volatile organic compound emissions afforded by these water-based systems. Rosin has excellent properties of corrosion, moisture, insulation, emulsifying and thickening. The rosin is introduced into polymer latexes to produce polymer latex modified with rosin via blending or copolymerization methods, which not only broadens the use of deep-processing of rosin, but also widens the scope of application of polymer latexes. The research progress of polymer latexes including water dispersible polymers modified with rosin was reviewed. The tendency of polymer latexes modified with rosin is brought forward.

INTRODUCTION

Rosin is an abundantly available and renewable resource. It is mainly obtained from the exudation of pines and conifers. The presence of a carboxyl group and double bond in the structure imparts to it a high chemical reactivity. In addition, rosin and its derivatives are analogous to many aromatic compounds in rigidity owing to their characteristic fused ring structure. Recently, the major uses of rosin are in the production of derivatives for papermaking, adhesives, coatings, printing inks, solders, plasters, etc. [1-3].

Polymer latexes have been widely used in paints, adhesives, binders, paper coatings, textile finishes, pharmaceuticals (including sustained and controlled
release formulations), floor polishes, printing inks, etc. because of the reduced volatile organic compound (VOC) emissions afforded by these water-based systems. It may be anticipated that the range of applications of polymer latexes will continue to increase in the future. Presently, there is a tendency that the rosin and its derivatives used as tackifying resin were usually introduced into polymer latexes to improve their properties. Although polymer latexes are the primary focus of this review it should be recognised that water-soluble and water dispersible polymers may also be used in water-based coating systems. Polyurethanes and epoxies with low-to-moderate molecular weights prepared by step growth polymerisation and then dispersed in water can have advantages of toughness in relation to film formation temperature as compared with polymer latexes. Pseudo-latex dispersions of polyurethanes, for example, can be prepared without surfactant addition, whose sizes are as low as 20-100 nm and offer low film formation temperatures as a consequence of their water-swollen and plasticised nature [4]. In this paper, the recent advances in the polymer latexes modified with rosin in the last decade are reviewed and summarized. In addition, the tendency of polymer latexes modified with rosin is brought forward.

**ARYLATE LATEX MODIFIED WITH ROSIN**

Acrylate latex modified with rosin is mainly prepared by two methods. One is blending and the other is copolymerization.

**Blending**

Blending is that two and more kinds of homopolymers or copolymers are blended to form a uniform mixture from macro perspective. The consistency among components is vital to the stability of latexes. The consistency is the mutual dissolution in thermodynamics, i.e. the mixing free enthalpy $\Delta r G$ is not more than 0, which reflects the ability that the blend does not produce a repulsive separation. The method of blending is simple and convenient. And the scale can be controlled easily and it also has important industrial value. Furthermore, the cost of blending method is lower than that of copolymerization method. The blending method of preparing the acrylate latexes modified with rosin often includes physical blending and chemical blending, which the schematic plan is presented in Scheme 1 and Scheme 2, respectively. In Scheme 1 and Scheme 2, $M_1$ stands for the polymer latex and $M_2$ stands for rosin.
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The physical blending is dependent on the physical action. The rosin latex and acrylate are mixed to form a homogeneous and stable mixture according to a certain proportion. This method is widely used in the industrial production. Xie et al. prepared the acrylate latex modified with rosin through physical blending. Effects of composite of rosin latex and acrylate latex on storage stability, workability and scrub resistance of resultant emulsion paint were studied in detail. It was found that this composite emulsion paint had good property and low cost [5]. Wu et al. also prepared the cationic acrylate latex modified with the cationic rosin. The promoting effects of the cationic acrylate latex on the sizing efficacy of the cationic rosin latex were investigated on a pulp. The results show that the mixture of the acrylate latex and the rosin latex exhibits much larger sizing efficacy than the rosin latex does at the same dosage, while the acrylate latex show s no sizing efficacy. And it was also found that the acrylate latex could enhance the surface charge density and hydrophobicity of the rosin latex [6]. Hu et al. prepared a series of acrylate latex modified with rosin via physical blending. A series of polycrylate emulsions were blended with tackifier resin emulsions such as modified rosin emulsion, C5 resin and C9 resin emulsion. The results show that the peel strength is improved as the amount of the tackifier resin increases and comes to a maximum at a specific content. The ball tack property decreases slightly and the hold strength changes complicationly as the tackifier resin increases [7].

Chemical blending method is that the rosin is blended in the course of the emulsion copolymerization of acrylate monomers. The rosin and the acrylate latex can be mixed fully. Thus, the properties are usually superior to those of physical blending method. Lin et al prepare rosin-acrylics hybrid latexes, which is synthesized by semi-continuous emulsion as seed. The hybrid fine-particle rosin emulsion is prepared by inverse emulsification. Results shows that introduction of rosin derivatives improves remarkably the bonding properties of acrylic polymers [8]. In addition, Lin et al. also synthesized the composite
latex particles of disproportionated-rosin (DPR) and polyacrylates, which is prepared with mini-emulsion polymerization. It was found that polymerization rate was increased with the increased dosage of initiator or surfactant. Particle size of mini-emulsion was kept relatively stable during polymerization when an initiator of lower solubility was used. An increase in dosage of DPR reduced polymerization rate, but had no significant influence on the final monomer conversion. It was also demonstrated that rosin in hybrid polymer functioned as a plasticizer to reduce glass transition temperature, which resulted in the reduction of strength and increase of elongation of polymer films [9]. Ren et al. prepared a HR/acrylate hybrid miniemulsion by miniemulsion polymerization with hydrogenated rosin (HR) as a tackifying resin. The results showed that the miniemulsion had smaller particle size, more narrow particle size distribution, higher monomer conversion, lower coacervation ratio, higher Zeta potential and more stable system. HR could effectively improve bonding properties of pressure sensitive adhesive [10].

Copolymerization

The blending method of preparing the acrylate latex modified with rosin will lead to non-uniform latex. Furthermore, the stability of the acrylate latex can be destroyed. Therefore, the better method of preparing the acrylate latex modified with rosin is copolymerization of the rosin and acrylate monomers, which the schematic plan is presented in Scheme 3. The stability of the acrylate latex modified with rosin can be improved remarkably in this method. Chen et al. synthesized polyacrylate/polymerized rosin composite emulsions, which were prepared by seeded semi-continuous emulsion polymerization of acrylate monomers in which polymerized rosin was dissolved. The results showed that with an increase of polymerized rosin content gel fraction and sol molecular weight decreased obviously but monomer conversion was basically unchanged. In contrast, with a further increase of polymerized rosin content, the decreasing rates of gel fraction, and sol molecular weight were slowed down. Meanwhile, monomer conversion decreased remarkably. Moreover, interface failure changed into cohesive failure after the addition of polymerized rosin, and the peel adhesion and shear resistance of composite latex films declined with the increase of polymerized rosin content. Thermal analysis showed that polymerized rosin and polyacrylate were compatible and the composite latex films had good thermal stability [11]. Xu et al. also prepared the acrylate emulsion surface sizing agent modified with rosin. In their study, a series of core-shell type cationic soap-free latex were prepared by using styrene, butyl acrylate, and methyl methacrylate as main materials and introducing rosin as the functional monomer. Cationic starch (CS-8),
which has low relative viscosity, was used as the emulsifier and dispersant. The results showed that the excellent performance and good sizing effects of latex were achieved. The water-resistant performance of paper was improved significantly when latex was modified with rosin [12]. Chen et al. also prepared the polyacrylate emulsions tackified by polymerized rosin via seeded semi-continuous emulsion polymerization. The instantaneous conversion, gel fraction, crosslinking density and sol molecular weight decreased significantly due to the chain transfer and inhibition of the abietic acid. The relationship between the main adhesive properties of tackified latex films and polymer microstructure was obtained [13]. Lin et al. prepared the pressure sensitive adhesive (PSA) based on disproportionated rosin, which was synthesized by miniemulsion polymerization. The molecular weight of the copolymers was decreased with the increasing dosage of rosin when using ammonium persulfate (APS) as initiator, so the primary adhesion and peel strength were increased and the retained adhesion was decreased rapidly; but the primary adhesion, peel strength and retained adhesion of the copolymers had good balance when using benzoyl peroxide (BPO) as initiator. Pressure sensitive adhesive with good performance was obtained by this method [14]. Gao et al. synthesized the rosin modified acrylate latex with the particle of core-shell structure, which was prepared by seeded semicontinuous emulsion polymerization. The effect of the amount of rosin and its addition style, and the proportion of core and shell monomers on the properties of the latex was studied. The optimal condition of preparing the rosin modified acrylate latex was obtained [15]. Liu et al. prepared a rosin derivatives acrylate copolymer emulsion with radical-polymerizable rosin derivatives as tackifying resin. The resultant latex, which was prepared by
pre-emulsifying and semi-continuous emulsion polymerization, was used as matrix resin of pressure-sensitive adhesive. The results showed that the rosin derivative participates in copolymerization of system and the compatibility between rosin derivative and systems was good [16].

**POLYURETHANE LATEX MODIFIED WITH ROSIN**

Waterborne polyurethanes (PU) are known to be environment-friendly materials with good adhesion, elasticity, and chemical resistance. Based on water, they are of low VOC emission or VOC-free. Water-based PU materials have been widely applied in adhesives, coatings, surface finishing, paper and textile industries [17, 18]. However, pure PU is highly costing, and its latex films are of low water resistance and low gloss. Wang et al prepared the new cationic rosinyl polyurethane sizing agent by copolymerization of rosin, toluene, 2, 4-diisocyanate, N-methyldiethanolamine and 1, 4-butanediol. And the synthetic method and the affecting factors are discussed in their study. The applied paper size has good quality characteristics [19]. Liu et al. also synthesized the rosin-based polyurethane latex by using 2, 4-diisocyanate, rosin and sodium bisulfite as raw materials. When the rosin-based polyurethane was used as a paper sizing agent, it not only shows high sizing performance, but also significantly enhances paper strength. In addition, Guo et al. prepared the waterborne polyurethane adhesive modified by rosin. Effects of the amounts of DMPA, rosin, and NCO/OH value on the properties of the latex were studied in their work. The adhesive property of modified and unmodified polyurethane for laminated package films was compared in their study. And the experimental results showed that the modified waterborne polyurethane adhesive meets the need of laminated package films [20]. Furthermore, Wang also prepared the polyurethane latex modified with rosin, which was made from acrylpimaric acid polyester polyols and maleopimaric acid modified polyester polyols. The relationship between structure and properties of rosin modified waterborne polyurethanes was studied. It was found that the addition of rosin ring structure could increase gloss, hardness, heat resistance and water resistance of waterborne polyurethane [21].

**HYBRID LATEX MODIFIED WITH ROSIN**

Hybrid latex is composed of at least two kinds of organic latexes, normally incompatible, and again covalently bonded to each other. The hybrid latex intimately combines the properties of the different kinds of latexes. The main applications of hybrid latex lie in the waterborne coatings, such as paints,
paper coating products, adhesives, textile sizing, and printing inks. For example, polyurethane (PU) improves properties of waterborne acrylic latexes such as resistance to solvent, film formation or toughness [22-24]. Given the attractive properties of PU-modified films, such systems have been widely used in the as binders for paints, inks and adhesives. However, the high cost of hybrid latex has a negative influence on the commercial application. It is possible to save the production costs and offer other new properties when the natural biomass resources were applied to modify the hybrid latex. Thus, the market competitiveness of the hybrid latex was improved further. Cui et al. prepared the polyurethanes-acrylate hybrid latex modified with rosin. In their work, fumaropimaric acid-type waterborne polyurethanes-acrylate hybrid emulsion (FWPUA) were prepared from fumaropimaric acid-type waterborne polyurethanes, methylacrylate and butyl acrylate. FWPUA with excellent comprehensive properties was obtained when azo-bis-isobutyronitrile and ammonium persulfate was used as composite initiator [25]. In addition, Guo et al. synthesized the polyurethane-epoxy hybrid latex modified with rosin. In their study, waterborne polyurethane hybrid emulsions were prepared from polycaprolactone glycol (PCL), toluene diisocyanate (TDI) and dimethy lolpropionic acid (DMPA), with trimethylol-propane (TMP) as the crosslinking agent and with epoxy resin and rosin as the modification agents. The results indicate that the preparation of WPU is due to the formation of urethane groups via the react ion between the hydroxyls in epoxy resin and the diisocyanate groups in TDI, to the grafting of epoxy resin on to the polyurethane (PU) molecules via a ring-opening reaction, and to the participation of carboxyls in rosin in the reaction. Moreover, it is found that the average particle size of WPU hybrid emulsions increases with the contents of epoxy resin and rosin. And the epoxy resin, PU and rosin all have good compatibility after the modification. In addition, the decomposition temperature of the cast films revealed strong adhesion strength of the adhesive formulated by the modified WPU emulsion for various laminated package films [26].

**CONCLUSIONS**

Rosin has excellent properties of corrosion, moisture, insulation, emulsifying and thickening. The rosin is introduced into polymer latexes to produce polymer latex modified with rosin via blending or copolymerization methods, which not only broadens the use of deep-processing of rosin, but also widens the scope of application of polymer latexes. Rosin is a natural and renewable resource, which can be used as raw materials in line with the direction of development of green chemistry. In comparison with blending, copolymerization can offer polymer latexes more and better properties. The tendency of polymer latexes
modified with rosin is as follows: (1) Rosin will be modified to contain more active group, which can be copolymerized with other monomers easily and high efficiently; (2) Elemental fluorine and silicon elements will be introduced into the molecular structure of the polymer latexes, which will bring the unique properties of modified polymer latexes; (3) Novel emulsion polymerization technique such as micro-emulsion polymerization, soap-free emulsion polymerization and inverse emulsion polymerization will be used to produce the polymer latexes modified with rosin.

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REFERENCES

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