Industrial Crops & Products 124 (2018) 244–253

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop

Preparation and characterization of natural rosin stabilized nanoparticles via miniemulsion polymerization and their pressure-sensitive adhesive applications

Jifu Wang[a,b,*], Chuanwei Lu[a], Yupeng Liu[a,b], Chunpeng Wang[a,b], Fuxiang Chu[a,b]

[a] Institute of Chemical Industry of Forest Products, CAF; National Engineering Lab. for Biomass Chemical Utilization; Key and Lab. on Forest Chemical Engineering, SFA; Key Lab. of Biomass Energy and Material, Jiangsu Province, Nanjing 210042, China
[b] Institute of Forest New Technology, CAF, Beijing 100091, China

ARTICLE INFO

Keywords:
Rosin
Rosin derived acrylic monomer
Miniemulsion polymerization
Pressure-sensitive adhesive

ABSTRACT

A series of rosin stabilized nanoparticles were prepared by miniemulsion polymerization. The hydrophobicity of dehydroabietic acid (DA) from rosin or from DA derived acrylic monomer (AEDA) was employed to stabilize the monomer miniemulsions. Then miniemulsion polymerizations of these monomer miniemulsions were performed separately and achieved the rosin stabilized nanoparticles with a near-monodisperse spherical morphology, respectively. This approach can effectively incorporate DA or AEDA into polyacrylate miniemulsion. Herein, AEDA played a role as both costabilizer and reactant in miniemulsion polymerization, and high molecular weight AEDA-MMA copolymers were achieved. The introduction of rosin's moiety also could afford its copolymers with an improved thermal stability and mechanical property. Unlike conventional usage of rosin derivatives as a tackifying resin in pressure-sensitive adhesives (PSA), AEDA served as a hard component and improved the holding power of PSA, which opens a new platform for the using of rosin.

1. Introduction

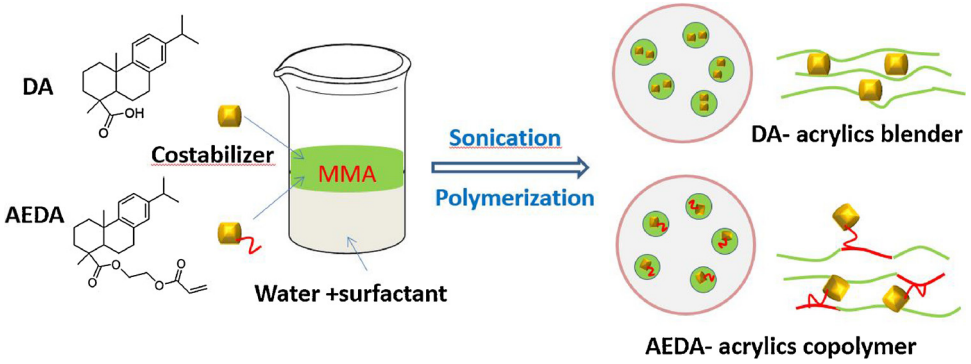
Seeking a renewable feedstock to fabricate the polymeric materials attracts much attention, as these materials have a great potential to replace or partially replace the petroleum based materials (Gandini, 2011; Gandini and Lacerda, 2015; Miller, 2014; Sheldon, 2014). Rosin, one of important naturally renewable resources, has approximately 1.2 million tons annual production. Resin acids are the major component (~80%) of rosin and bear a bulky hydrophobic hydrophenanthrene structure. The characteristic bulky hydrophenanthrene structure, as well as its intrinsic acidity and rigidity has enabled rosin to be used in the field of adhesives, paper sizing agents, printing inks, solders and fluxes, surface coating, insulating materials, etc (Maiti et al., 1989; Silvestre and Gandini, 2008). In recent years, a largely number of resin acids derived monomers have been developed and used to fabricate rosin based polymers (Huang et al., 2013; Liu et al., 2009; Wilbon et al., 2013; Yan et al., 2017; Yao and Tang, 2013; Zhang, 2012).

However, manufacturing and utilizing of these rosin based polymers are still challenging. For example, most of rosin based monomers and the polymers, were fabricated by using organic solvents as reaction media due to the inherit hydrophobicity and steric effect of the moiety of rosin. It really does harms to the environment. As a results, many efforts have dedicated to convert rosin and its derivatives into emulsion by emulsification with surfactants (Li et al., 2015). In some cases, this method in some cases would lead to the poor stability of the emulsion, when emulsified rosin was added. The core-shell emulsion strategy was adapted in order to improve the stability of rosin based emulsion. People incorporated the rosin and its derivatives into latexes during emulsion polymerization (Dong et al., 2007; Li et al., 2015). However, rosin could still leakage from the latexes during the emulsion polymerization.

Miniemulsion polymerization is a robust and environmental friendly mean that can prepare the high molecular weight polymer by using water as dispersed phase. Generally, the typical formulation for miniemulsion polymerization includes water, monomer mixture, costablizier, surfactant and initiator system. Miniemulsion polymerization takes place in monomer droplets within a size range of 50–500 nm. Comparing with the conventional emulsion polymerization that monomers diffuse from droplets to particles for polymerization, miniemulsion polymerization is carried out in monomer droplets stabilized

* Corresponding author at: Institute of Chemical Industry of Forest Products, CAF; National Engineering Lab. for Biomass Chemical Utilization; Key and Lab. on Forest Chemical Engineering, SFA; Key Lab. of Biomass Energy and Material, Jiangsu Province, Nanjing 210042, China.
E-mail addresses: wjf118@126.com, wangjifu@icifp.cn (J. Wang).

https://doi.org/10.1016/j.indcrop.2018.07.079
Received 23 February 2018; Received in revised form 23 June 2018; Accepted 27 July 2018



Scheme 1. Synthesis strategy of natural rosin stabilized nanoparticles (DA- acrylics blenders and AEDA- acrylics copolymers).

by hydrophobic materials. Miniemulsion polymerization thus enables hydrophobic materials that can't diffuse from droplets in aqueous phase, to be incorporated into final latexes particles (Asua, 2002; Cao et al., 2015; Lopez et al., 2011; Yao et al., 2017). So far, various hydrophobic materials including alkyd resins, polyesters, polyurethanes, et al, have been introduced into polymer latexes via miniemulsion polymerization (Degrandi-Contraires et al., 2011). As a naturally hydrophobic material, rosin and its derivatives were first reported to be employed in miniemulsion polymerization in our previous work. But in this case, rosin was just physically incorporated in the poly(methyl methacrylate) (PMMA) miniemulsions, leaving much room for further investigation (Lin et al., 2006).

Herein, we report a "miniemulsion polymerization" strategy to prepare rosin stabilized nanoparticles containing rosin based co-polymers. Scheme 1 demonstrates a preparation of rosin stabilized nanoparticles via miniemulsion polymerization. The surfactant dissolved in water and the costabilizer dissolved in monomer are mixed under stirring at the first step. The mixture is then homogenizated through sonication to achieve monomer miniemulsion before polymerization. 2-acryloyloxyethyl dehydroabieticcarboxylate (AEDA) is a novel acrylic monomer derived from dehydroabietic acid (DA, one of resin acids in rosin).

In this work, AEDA was copolymerized with methyl methacrylate (MMA) in the monomer droplets. For comparative purpose, DA- acrylics blenders were also developed with the aim to investigate the effect of the moiety of resin acid on stability of miniemulsions, conversion of acrylic monomer, particle size of miniemulsions, molecular weight, thermal properties and mechanical properties. Additionally, the rosin stabilized nanoparticles were also designed as a pressure-sensitive adhesives (PSA) by tailoring the composition of acrylic monomer. The performance of PSA containing AEDA was evaluated. It should be pointed out that AEDA plays a new role in formation of PSA, which is different from the counterparts (rosin derivatives) that are usually used as a tackifying resin in PSA (Dong et al., 2007; Li et al., 2015; Zhang et al., 2016). To the best of our knowledge, it is the first report on the miniemulsion stabilized by the rosin derived acrylic monomer AEDA, as well as on its application in PSA. We believe that the results obtained from this research could be employed as a proof-of-concept to study the copolymerization of AEDA with other monomers, and the feasibility of replacing some existing petrochemical acrylic monomers.

2. Materials and methods

2.1. Materials

Dehydroabietic acid (DA, ~98%) was obtained from Wuzhou Chemicals. Methyl methacrylate (MMA, stabilized, 99%), butyl acrylate (BA, stabilized, 99%), n-hexadecane (HD, 99%), sodium dodecyl benzene sulfonate (SDBS) were purchased from Acros. Toluene, tetrahydrofuran (THF) and methanol were purchased from Sinopharm Chemical Reagent Co Ltd, China. Ascorbic acid, H_2O_2 (37%, analytical grade), azobisisobutyronitrile (AIBN, analytical grade) were obtained from Shanghai No.4 Reagent & H.V. Chemical Co Ltd, China. All the chemicals were analytical grade and used as received. 2-acryloyloxyethyl dehydroabieticcarboxylate (AEDA) was synthesized according to early reports (Wang et al., 2011; Yu et al., 2014).

2.2. Preparation of monomer miniemulsion

All experiments performed in this work were according to the recipe shown in Table 1 unless otherwise specified. $AEDA_1M_{100}$ was used as an example. As shown in Scheme 1, 0.1 g AEDA was dissolved in 10 g MMA to prepare oil phase. Surfactant (SDBS, 0.1 g) and ascorbic acid (0.1 g) were dissolved in deionized water (48.8 g) to prepare the water phase. Then the oil phase and the water phase were mixed in a beaker by stirring for 30 min to generate the pre-emulsion. Followed by miniemulsifying sonication in an ice bath (Scientz JY98-3D ultrasonic cell disruptor; ultrasonic frequency was set at 1000 KHz; duty cycle at 70% for 3 min), the uniform AEDA /MMA monomer miniemulsion was obtained.

2.3. Miniemulsion polymerization

The AEDA/MMA monomer miniemulsion prepared in Section 2.2, was transferred into a four-neck round bottom flask equipped with a reflux condenser, N_2 inlet, thermometer and mechanical stirrer. When the temperature was heated to 85 °C, initiator (0.38 g H_2O_2) was added to the flask and activated the polymerization. Samples were taken at timed interval to measure the conversion of MMA and the particle size of miniemulsion. Mass ratio of DA or AEDA in final miniemulsion polymers can be calculated by Eq. (1) and summarized in Table 1.

$$Mass(DA - or - AEDA)/Mass(MMA) = \frac{3 \times M}{3 \times 100} \times \frac{A_d}{A_m} \quad (1)$$

Where M is the molecular weight of DA or AEDA, A_d is the ^{1}H NMR integration area of aromatic protons in DA or AEDA at 6.7–7.2 ppm, 100 is the molecular weight of MMA, A_m is the ^{1}H NMR integration area of the methyl protons of ester group in MMA at 3.6 ppm.

2.4. Film formation for DMA test

The films containing DA were first cast in polytetrafluoroethylene mold and drying at 50 °C for 24 h. The polymers (films) was then quickly washed with deionized water to get rid of the emulsifier, and was dried again at 60 °C under vacuum until constant weight. The films containing AEDA were cast by a different procedure. The resulting miniemulsions containing AEDA were first dried at 60 °C for 24 h to remove the water. Then the solids were re-dissolved in THF and predicated in methanol to get rid of un-polymerized AEDA and emulsifier. The collected copolymers were then dried at 40 °C under vacuum until