Colloids and Surfaces A 539 (2018) 132–139

Contents lists available at ScienceDirect

Colloids and Surfaces A

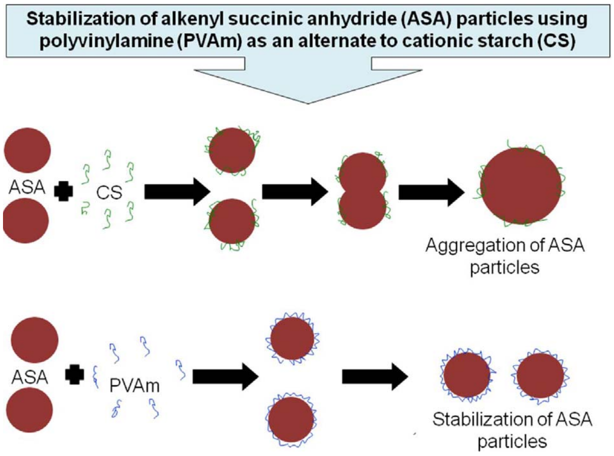
journal homepage: www.elsevier.com/locate/colsurfa

Sizing performance of alkenyl succinic anhydride (ASA) emulsion stabilized by polyvinylamine macromolecules

Ashish Kumar[a,b], Nishi K. Bhardwaj[b,*], Surendra P. Singh[a]

[a] *Department of Paper Technology, Indian Institute of Technology Roorkee, Saharanpur Campus, Saharanpur, 247 001, India*
[b] *Avantha Centre for Industrial Research & Development, Yamuna Nagar, 135 001, India*

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Alkenyl succinic anhydride
PVAm
Cationic starch
Alkaline sizing
$Cobb_{60}$
Contact angle

ABSTRACT

It is well known that alkenyl succinic anhydride (ASA), an alkaline sizing agent, when applied to cellulosic fibers will impart a resistance to the absorption of water. High reactivity of ASA to cellulosic fiber compared to that of alkyl ketene dimer (AKD) is the main advantage of ASA sizing. However, there are some drawbacks associated with the ASA sizing viz. poor stability of ASA emulsion and formation of stickies and deposits as a result of hydrolyzed ASA. Present study deals with the stability of ASA emulsions prepared by using synthetic vinylamine polymers of different colloidal charge as alternate to conventionally used cationic starch and sizing performance using mixed hardwood kraft pulp furnish. The better colloidal stability and sizing performance with polyvinylamines compared to cationic starch was due to the coverage of the ASA droplets with polyvinylamines which extends in to the continuous phase of ASA emulsion. Emulsion stability was achieved even with low dosage of vinylamine polymer.

1. Introduction

Internal sizing is a process to provide the resistance to liquid penetration to paper with the use of sizing agents in paper making. Alkenyl succinic anhydride (ASA) is commonly used in the neutral/alkaline papermaking process. It is an oily monomer and is added to pulp stock in a form of aqueous emulsion at room temperature. It provides on machine sizing because of its high degree of reactivity

---

* Corresponding author.
E-mail addresses: ashish@avanthareasearch.org (A. Kumar), bhardwaj@avanthareasearch.org (N.K. Bhardwaj), chandrafpt@gmail.com (S.P. Singh).

https://doi.org/10.1016/j.colsurfa.2017.12.014
Received 29 September 2017; Received in revised form 4 December 2017; Accepted 4 December 2017

with the hydroxyl groups on polysaccharide components in the paper substrate [1]. Alkyl ketene dimer (AKD) and ASA are the two sizing agents used in alkaline paper making conditions which are costly. These sizing agents have to be added very precisely to avoid problems during paper making such as formation of deposits, and to get the required quality of paper. The anhydride ring of the ASA molecule is mainly responsible for its high reactivity. An ester bond is formed between hydroxyl group of cellulose and ASA molecule. The rate of hydrolysis of ASA is much faster than that of AKD due to the higher reactivity of ASA compared to AKD. Thus, ASA emulsion cannot be stored and shipped as ready to use emulsion to paper industry. Conversion of ASA oil in aqueous form is required just before the addition to paper making stock. This process is called as emulsification. Cationic starch and synthetic polymers are used as stabilizers for ASA emulsification [2]. Maximum reduction in time between its preparation and addition would help in turn to minimize the hydrolysis. Bajpai et al. [3] showed that two parts of cationic starch in one part of ASA oil is sufficient to get the better particle size distribution and sizing performance. High reactivity of ASA with cellulose indicated that it hydrolyses rapidly which means ASA suffers from extensive hydrolysis if conditions are not carefully controlled. The hydrolysis product is a dicarboxylic acid which is quite detrimental to sizing and machine runnability. For many years, hydrolysis resistant ASA emulsion has been in search by the paper makers. Lee et al. [4] prepared a hydrophobically modified corn starch, to obtain a stable ASA emulsion. The stability of ASA emulsion was determined by pH measurement with the passage of time. Martorana et al.; Merisalo [2,5] studied the stability of ASA emulsion prepared by using different polymers up to 1 h and 4 h respectively. It was said that hydroxyl group of glucose component of cellulose forms a covalent bond with ASA molecule as shown in Fig. 1.

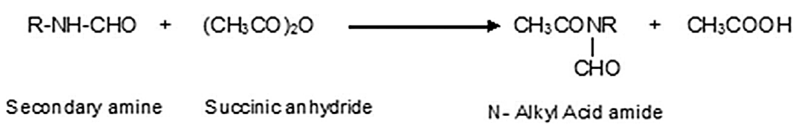
Emulsion droplets can be stabilized against coalescence by polymers, nano and microparticles and surfactants. Demulsification can be prevented by adding the stabilizers (which are non surface active macromolecules) to continuous phase of emulsion which reduces the mobility of the droplets. For an efficient ASA emulsion stability to hydrolysis (hydrolysis stability) along with the stability of particle size (emulsion stability) is the second main quality parameter. Smaller is the particle size higher will be specific surface area resulting in a good sizing level and vice versa. Emulsion stability can be understood by the stability of particle size and the hydrolysis stability in regards to hydrolysis. [2] Hydrolysis stability is generally lost if the protecting action of the stabilizer surrounding the ASA molecule surface is lost. As water diffuses through the stabilizer barrier, hydrolysis occurs, the emulsion becomes destabilized leading to increase in the rate of hydrolysis [5]. According to the DLVO theory, the dispersed particles are subject to two independent forces: electrostatic force of repulsion and the Van der Waals force of attraction arising from the presence of electrical double-layers at the particle surfaces. By adding these two terms, the net interaction between the particles is obtained. If the repulsion potential exceeds the attraction potential, an energy barrier opposing collision results. If the kinetic energy of the particles is less than the magnitude of this energy barrier, the suspension is stable. The Van der Waals negative potential becomes significant only when the distance between the particles is quite small. According to Martorana et al. [2] faster hydrolysis also causes the aggregation of ASA particles, so hydrolysis stability goes parallel to emulsion stability mostly. Both the stability parameters should be considered simultaneously because hydrolysis should not cause higher aggregation according to rule (Fig. 2).

The laponite and short amines such as ethylamine, *n*-propylamine and *n*-butylamine were used to stabilize the partly hydrolyzed (PH) ASA emulsions. However, the partly hydrolysed ASA emulsions lose most of their sizing effect by hydrolysis within 60 min [1].

The sizing performance of ASA emulsion stabilized with montmorillonite (MMT) was improved by using the chitosan with low molecular weight and low dosage without reducing the emulsion stability [8]. Encapsulation of ASA particles with cationic/anionic polymeric substances provides a protective layer to the exposed area of the ASA particles without interfering in the sizing mechanism. If a polymer, which is extended in to the continuous phase of emulsion is used to cover the surface of a particle or droplet, the polymer segment reduces the aggregation of the ASA molecules. The film of the polymer acts as a stearic barrier against adhesion of particle to particle thereby preventing to destabilize the ASA emulsion [5]. As polymer coated particles approach, the polymers are forced into close proximity and repulsive forces arise, keeping particles apart from each other [9]. Generally, the destabilization phenomenon other than coalescence of particles in emulsion includes creaming, phase inversion, flocculation, Oswald ripening, and sedimentation [5]. Zhang et al. reported that the formation of particle barrier around ASA droplets is also expected to reduce the interaction of water and ASA by reducing the rate of hydrolysis of ASA [10]. Furthermore, particle size plays an important role during the evaluation of hydrolytic stability and deposition [11].

Li et al. [12] mentioned that a strong film acting as a physical barrier to particle coalescence will be developed by the adsorption of solid particles to oil-water interface which will develop strong lateral interactions and will prevent the direct contact of water and ASA reducing the hydrolysis reaction of ASA.

Present communication is based on the particle size distribution of ASA particles, sizing performance with respect to Cobb$_{60}$ and contact angle with time, to measure colloidal stability of ASA emulsion prepared by using cationic/anionic synthetic stabilizers such as polyvinylamine macromolecules which include the amine as reactive group which reacts with the anhydride group present in ASA molecules. It is also well documented that amines react with acid anhydride and form the N alkyl acid amide as per the following reaction [13].



$$\text{R-NH-CHO} + (\text{CH}_3\text{CO})_2\text{O} \longrightarrow \underset{\text{CHO}}{\underset{|}{\text{CH}_3\text{CONR}}} + \text{CH}_3\text{COOH}$$

The later will interact with hydroxyl groups of cellulose molecule simply through hydrogen bonding providing the sizing.