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Synthesis of Guar Gum Derivatives in [BMIM]Cl Ionic liquids and their Application on Pulping and Papermaking

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Abstract:

In this paper, Dodecenyl succinic anhydride(DDSA), Octadecenylsuccinic Anhydride(ODSA), and Octenylsuccinic Anhydride(OSA) with catalyst TMAOH was used to modify guar gum in 1-Butyl-3-methyl imidazolium chloride ionic liquid. The modified guar gum exhibit good retention and drainage properties in reconstituted tobacco pulp. The results of this study demonstrated that the modified guar gum could be used as a useful retention and drainage aid in reconstituted tobacco pulp.

Keywords: *dodecenyl succinic anhydride; ctadecenyl succinic anhydride;octenyl succinic anhydride;guar gum;[Bmin]Cl ionic liquids;retention and drainage*

1. Introduction

During tobacco harvesting and processing, lots of tobacco wastes were produced that cannot be incorporated directly into cigarettes, such as tobacco dust, leaf scraps, mid-ribs, and tobacco stems[1].In order to fully utilize these tobacco wastes,"reconstituted tobacco sheet (RTS)" was introduced into the tobacco waste utilization. In order to retain fiber fines of pulp, a variety of retention and drainage aids have been developed[2-4].Nevertheless, when buring, most commonly used wet-end additives will produce unpleasant flavors. Guar gum (GG), a natural polysaccharide, is obtained from Indian cluster beans. It is biocompatible, biodegradable, non-toxicity and low cost. More importantly, when burning there aren't yielding an adverse smoke flavor. All these special nature allows its usage in reconstituted tobacco pulp as a retention and drainage aid. Ionic liquids are solvents that solely consist of ions. Ionic liquids (ILs) have attracted a great interest to chemists because of their unique properties. Kinetics of reaction in ILs is different from conventional molecular solvents. It has low vapor pressure, on-flammability, excellent dissolving ability, high thermal stability, a wide liquid range, high ionic conductivity, and a wide voltage window [5]. In this paper, guar gum (GG) was modified by Dodecenylsuccinic anhydride(DDSA), octenyl succinic anhydride(ASA) and Octadecenylsuccinic anhydride (ODSA) in [Bmin]Cl ionic liquids in order to improve its retention and drainage properties. The retention and drainage properties of the modified guar gum were also evaluated. In general, this study could provide a valuable way to utilize agricultural fiber wastes.

2. Experimental

2.1. materials

The Guar gum from FoShan He Feng Biological Technology was used without further purification. Dodecenylsuccinic anhydride(DDSA), octenyl succinic anhydride(ASA) and Octadecenylsuccinic anhydride (ODSA) were provided by Wuxi Huilong Electronic Materials Co., Ltd. Tetramethylammonium hydroxide Beilstein (TMAOH) were procured from Sinopharm chemical Reagent Co., Ltd. Ionic liquid [BMIM]Cl, lab homemade. The tobacco pulp was provided by Guangdong Jinye tobacco company. All other chemicals used are analytical reagents.

2.2 Synthesis of [Bmin]Cl

[Bmin]Cl was prepared by the reaction of 1:2 molar amounts of 1-methylimidazole and 1-chlorobutane at 80°C in a three-necked round-bottom flask fitted with a reflux condenser for 48h to give a yellow solid. Then, the product was washed several times with diethyl ether and heating under vacuum to give the product in 90% yeild.

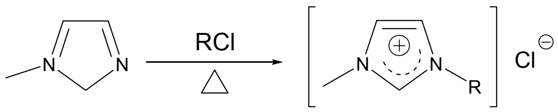

***Fig.1** The reaction equation of ionic liquid synthesis*

2.3 Synthesis of Guar Gum Succinate derivatives

Guar Gum Succinate (GGS) with various degrees of substitution (DS) were prepared by reacting GG aqueous solution with various amounts of DDSA in presence of TMAOH in [Bmin]Cl liquids. Different reaction parameters were tested at a range of values to get the optimal conditions for synthesis of guar gum succinate. The reaction was carried out under mechanical stirring. Thereafter, the formed product was neutralized with NaOH and precipitated with ethanol. Thereafter, the product was dried under vacuum and stored in desiccators until further use. At the optimal conditions, Guar Gum Succinate (GGS) with various degrees of substitution (DS) were prepared by reacting GG aqueous solution with various amounts of DDSA in presence of TMAOH. Different reaction parameters were tested at a range of values to get the optimal conditions for synthesis of guar gum succinate. The reaction was carried out under mechanical stirring. Thereafter, the formed product was neutralized with NaOH and precipitated with ethanol. Thereafter, the product was dried under vacuum and stored in desiccators until further use.OSA modified guar gum and ODSA modified guar gum were synthesized at the same conditions with the optimal DDSA modified guar gum.

3. Characterization

3.1 Rheological measurements

The aqueous concentration of GG and GGS samples were 0.1% (w/v). Rheological measurements were performed using a Viscometer (Brookfield).

3.2 Contact Angle Measurements

The surface wettability of the GG and the GGS was evaluated by contact angle measurement, using a Contact Angle System OCA40 Micro (Data Physics Instruments), combined with a high-speed camera. During the test, a droplet(3μL) of deionized water was deposited on the surface of the samples. The contact angle values are calculated using the contact angle meter software on basis of the droplet shape in the image. For each sample, measurements are repeated at several different positions, and its contact angle is finally determined by averaging these contact angle values from various measurements.

3.3 Retention and Drainage

The dynamic drainage jar (DDJ) is a common and reliable tool to evaluate retention of single or multi component flocculation systems under conditions that are quite similar to large-scale paper-making processes. In the present work, a DDJ with a 200-mesh bottom screen was used. The FPR of pulp suspension can be calculated based on Eq (1):

$$FRP = (1 - C / C0) \times 100\% \qquad (1)$$

Where, C and C0 are the stock before drainage and of the filtrate.

4.Results and discussions

GGS was synthesized by reacting GG with DDSA in the presence of DMAP as a catalyst. In this paper, succinylation of the crude GG was carried out in[Bmin]Cl Ionic liquids system to esterify GG's O-H groups. DDSA reacts with GG to form the monoester are shown in Fig.2.

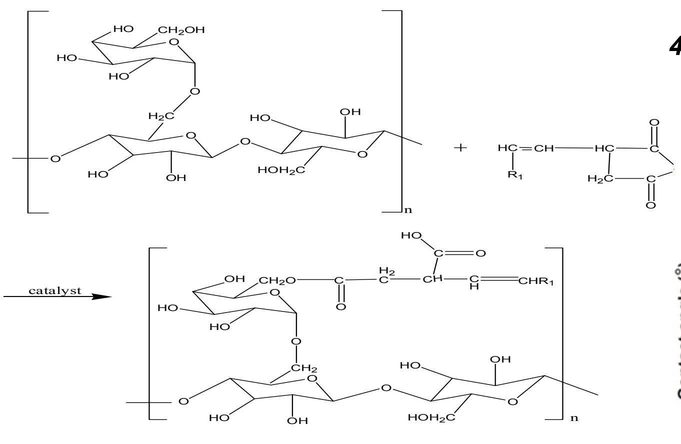

Fig.2 Reaction of Guar gum with Dodecenyl succinic anhydride

4.1 Rheological properties

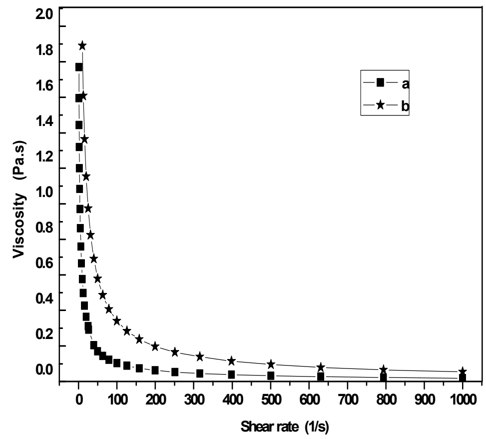

Fig.3 Rheological behavior of Guar solution at 1% w/v. (a)Pristine guar gum and (b) DDSA modified guar gum

Figure 3 shows the Rheological behavior of guar gum and DDSA modified guar gum solution studied at 1% concentration. Under the same shearing speed, the viscosity of DDSA modified guar gum were observed to be higher than that of pure guar gum(Fig.6). This is probably due to the existence of grafted DDSA side chains on guar gum. Furthermore, entanglements of the long chain could produce "steric hindrance" and then making the aggregation of particles difficult. Overall, it can be ascribed to physical chain entanglements in the amorphous phase that affect the behavior of DDSA modified guar gum. As the shearing speed increase, the viscidity behavior index decreased. The results showed that the guar gum and DDSA modified guar gum solution belongs to the typical shear-thinning fluid. This phenomenon can be attributed to the long chain entanglements structure of guar gum and DDSA modified guar gum were broken down by the shear stress to alter their structures or form new structures, which could lead to the decrease of the viscosity. When submitted to a higher shear rate, guar gum and DDSA modified guar gum molecules are fully oriented of the direction of flow. Therefore, the fluid of the guar gum and DDSA modified guar gum incline toward Newtonian fluid.

4.2 Contact Angle

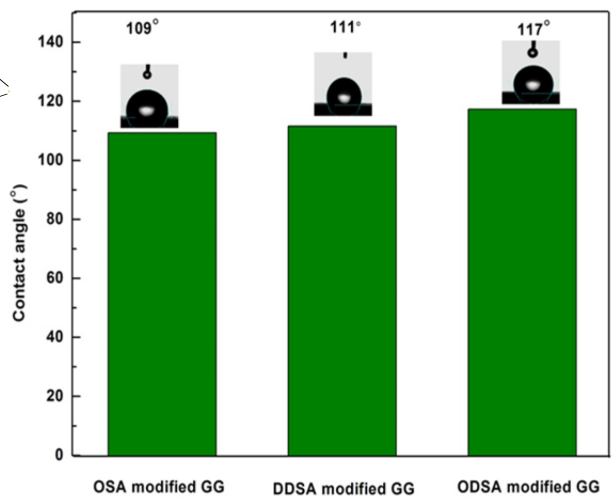

Fig.4 *the contact angles of OSA modified guar gum, DDSA modified guar gum and ODSA modified guar gum*

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Figure 4 shows the contact angle (CA) change of a water droplet on guar gum and modified guar gum. As shown in Fig.5, The water CAs of the OSA modified guar gum, DDSA modified guar gum and ODSA modified guar gum were ~109°, ~111° and~117° respectively. This indicated that the graft of long alkyl carbon chain side chains significantly improved the water resistance of the surface. In summary, the guar gum derivatives which have long alkyl chains shows superior hydrophobic property than shorter alkyl chains.

4.3 Retention and Drainage

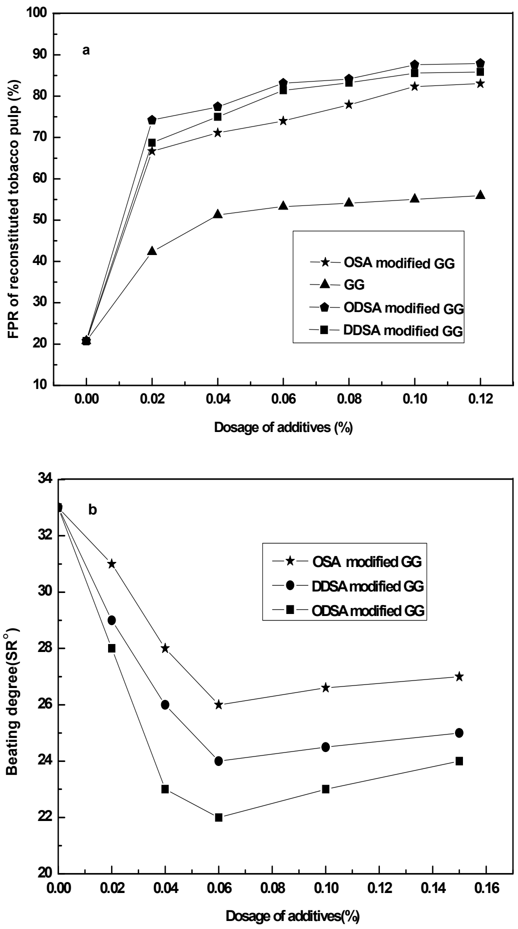

Fig.5 Effect of different substituents of modified guar gum on FPR(a) and on SR°(b)

From Fig.5a we can conclude that the FPR of tobacco reconstituted pulp increased with increasing alkyl chains of substituted groups. At the same dosage of 0.02%, OSA modified guar gum, DDSA modified guar gum and ODSA modified guar gum could reach the maximum FPR of 75%,69% and 65% respectively. This is because guar gum and guar gum derivatives have similar structures with that of tobacco cellulose. Therefore, they could link with cellulose molecules through hydrogen bond, from which excellent retention effect of copolymer initiated. The birding mechanism may be main mechanism for guar gum and guar gum derivatives, for the long chain of guar gum derivatives can easily bind the tobacco pulp through bridging and form the flocs.

The beating degree can reflect the drainability of reconstituted tobacco pulp. The higher the beating degree the lower the drainability of reconstituted tobacco pulp. The beating degree of tobacco pulp with different substituents of modified guar gum were displayed in Fig.5b. As shown in Fig.5b, the beating degreed of tobacco reconstituted pulp was affected by the side chains of guar gum. In general, Under the same dosage of additives, the beating degree of ODSA modified guar gum were observed to be higher than DDSA modified guar gum and OSA modified guar gum.

5. Conclusions

The Guar gum was successfully modified by OSA, DDSA, ODSA in [Bmin]Cl Ionic liquids. The results demonstrated that the modified Guar gum could be an efficient retention and drainage aids used in the reconstituted tobacco sheet industry.

6. References

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