Adsorption of Sizing Emulsion on Various Cellulosic Fibres

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Abstract: Adsorption of any chemicals over pulp stock during wet-end operations in paper manufacturing is extremely important for effectiveness, waste treatment, close system operation and so on. This paper investigates the adsorption characteristics of AKD emulsions over various pulp blends containing bleached, unbleached fibres and secondary fibres obtained from some waste paper grades. Fibre suspensions with different properties were mixed with various amounts of sizing emulsions under different conditions and the amount of adsorbed sizing agents were monitored by gas chromatography studies. The optimum amount of sizing adsorption needs to be achieved giving higher retention, clear drainage and good water repellent properties. Work is believed to offer some useful information to especially papermills utilising waste papers at neutral or alkaline conditions.

Keywords: Paper making, adsorption, sizing, retention, waste water, GC.

Introduction

Many paper and paper products are required to show some degree of resistance to liquids, such as water, drinks and so on. Various water-repellent materials, called sizing agent, have been tried to bring such properties to papers and some of them are currently used in the industry. Sizing agents can be added into the pulp suspension before formation or can be applied over dry paper. The first one is known as "internal sizing" while the latter is called as "surface sizing". Until recently rosin was the most commonly used sizing agent which had been introduced to paper industry around 1850 by Morritz Illig. Rosin emulsion is prepared by the saponification of resin which is extracted from stands of softwoods and/or obtained from some chemical pulping processes as byproducts. Rosin emulsion must be used with alumunium sulphate to maintain attachments of rosin over cellulosic fibres in a pulp suspension. System works best at pH between 4,5-5,5, hence it is called as acid system and the product produced is named as acid paper (Roberts, 1992; Karademir and Imamoglu, 2005).

Around 1990'ies, a new waxy sizing agent took a significant attention from papermakers which is manufactured from a stearic and palmitic acid, alkyl keten dimer (AKD). AKD is melted and mixed with cooked cationic starch to produce a milky emulsion. AKD is accepted a widespread wellcome from papermakers since it works at neutral-alkali conditions and attach to fibres via cationic starches on its particle shell. During drying, tiny wax in its particle melt and spread over fibres then eventually develop ester bonds with cellulose. AKD is, therefore, called as reactive sizing agent. Detailed information on subject is available in the literature (Roberts, 1991; Karademir et al, 2004; Hubbe, 2006). Paraffin is also a water repellent chemical which consists of a long aliphatic hydrocarbon chain. Some fibreboard and particle board manufacturer normally use paraffin emulsion as surface application. It is also used paper manufacturing too.

Retention of sizing chemicals used in a pulp suspension is a crucial mechanism which must be maintained at high degree. Sizing chemicals must be firstly adsorbed onto the stock, preferably fibres, and should be evenly distributed in the paper matrix. The chemical retention mechanism plays real important role in the retention of such paper additives when using pulps with long fibres. If pulps having lots of fines, fillers and small particles are used, then the mechanical retention too would be very important in addition to chemical one. In such situation, sizing particles normally tend to attach on small components of pulp due to their greater surface area. Therefore, it is critically important to maintained higher fine retention (first pass retention) to be able to hold sizing chemicals in the forming sheets (Roberts, 1991; Voutilainen, 1996; Jian and Deng, 2000; Karademir et al, 2005; Hubbe, 2006; Ravnjack et al, 2007). Mechanical retention is quite difficult in recycling papermills since pulps naturally contain lots of small ingredients, fines and chemicals. The problem should be solved to run a close up system efficiently where used water is circulated in a loop and offers many environmental benefits (Imamoglu et al, 2005a; Imamoglu et al, 2005b).

Experimental Materials and Methods

Fibres and Chemicals

Bleached both long and short fibres and also unbleached long fibres were used as virgin wood pulps. Pulps from old office paper, newspaper and corrugated box were also prepared as secondary fibres. Just long fibres (bleached and unbleached) were beaten in a PFI mill in accordance with Tappi T 248 sp-08 method until 37 SR° values are reached.

Three commercial sizing emulsions were used. AKD and rosin emulsions were obtained from Kahramanmaraş Papermill (Kahramanmaras, Turkey) and paraffin emulsion was obtained from Caran Chemical (Izmir, Turkey). The solid content of AKD was %25 while rosin and paraffin emulsions were at %40.

Handsheets Making and Testing

Pulp from old newspaper was used to compare the effects of three sizing emulsions on the both Cobb and breaking force values (TAPPI T 494 om-88) of resultant papers. Long unbleached fibres were also used to see the effects of beating and increasing sizing addition on the Cobb and tensile index of sheets (TAPPI T 494 om-88). Tappi 205 sp-95 method was followed for papermaking.

Gas Chromatography Study

Calculated AKD emulsions were added to various pulp slurries prepared at 0,5 consistency in a Dynamic Drainage System (DDS). Mixture was initially stirred at 500rpm for 3 minutes, then at 200 rpm for 1 minute. And then, the suspension was filtered on 200 mesh wire just after 10 seconds waiting without mixing. Filtered fibre mats were allowed to air dry, then retained AKD was extracted from samples according to method followed by Karademir (Karademir, 2002). Extracts were analysed in a capillary gas chromatography (Perkin Elmer, Clarus 500).

Results

Sizing Emulsions and Contributions

Pulp from old newspapers was prepared at a laboratory disintegrator and a number of sheets were made in a British sheet former at 100 g/m^2 grammage with different addition levels of three sizing emulsions. It is clearly seen in figure 1 that AKD and paraffin emulsions were quite effective in making handsheets hydrophobic compared to rosin emulsion. Retention levels of sizing chemicals on dry basis and also reaction mechanisms with cellulosic fibres need to be discussed here to be able to evaluate the sizing emulsions. What is known is that rosin and AKD can develop chemical bonds in sheets during drying stage if retained, whereas paraffin just physically covers the surfaces making a barrier to penetrating liquids. Unfortunately, we can only plot the Cobb values versus theoretical sizing addition levels rather then exact retained amount.

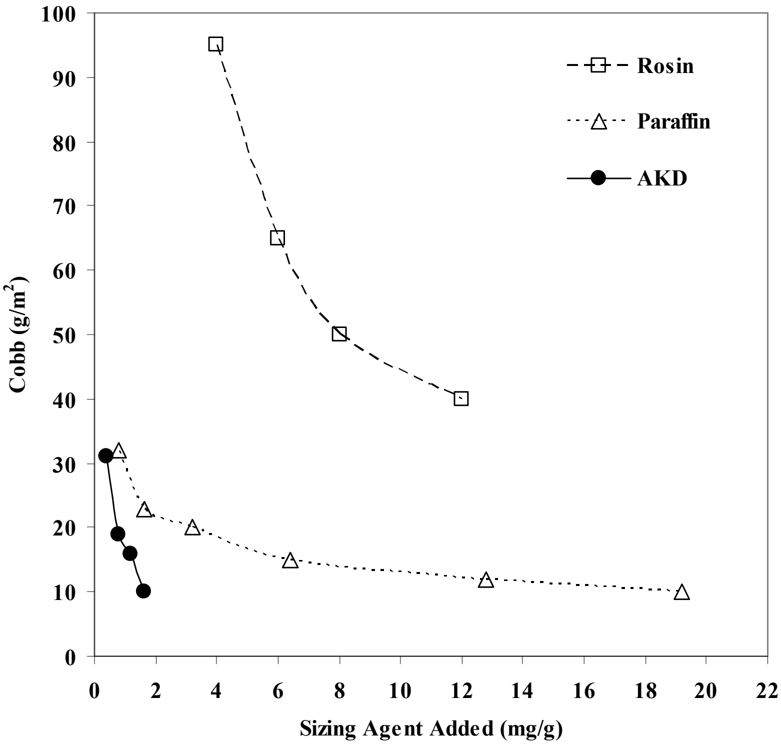

Figure 1: AKD emulsion gave the best Cobb value with little dry content.

Figure 2 shows the contribution of sizing agents on paper strength, represented as the breaking force. It seems that despite presenting in very small amount in papers, AKD molecules are thought to have developed extra bonds between fibres and pulp ingredients hence increasing sheets strength. Paraffin, however, remarkably reduced strength value. Paraffin probably wrapped up fibres in different intensities and just hindered the potential bond formation between fibres. Rosin emulsion was found to be almost stable showing no negative effects on sheet strength (Figure 2).

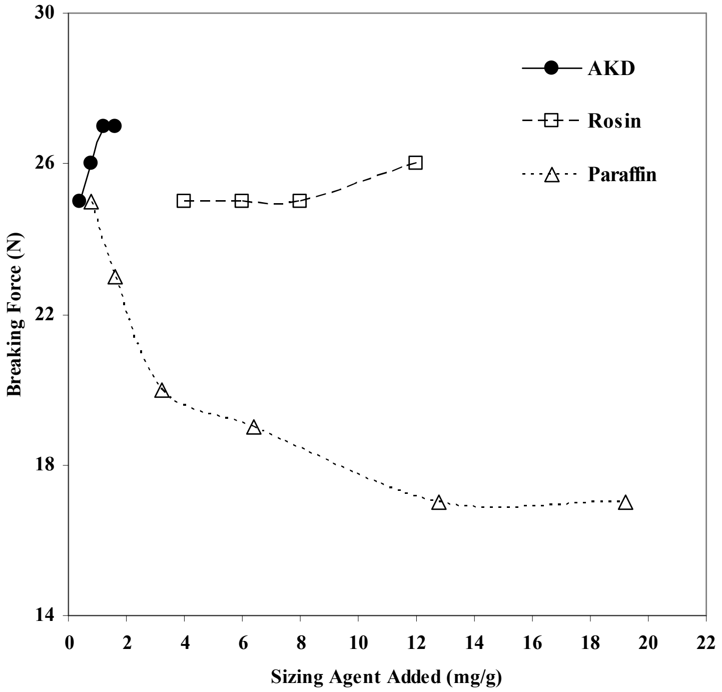

Figure 2: Sizing agents effecting sheet strength.

Beating and Addition Levels on Cobb and Strength

Increasing beatings were performed on the pulp of long unbleached fibres at PFI mill to see the changes on the sheet strength and Cobb value at %0,5 AKD emulsion level. As seen in figure 3, the beating represented, as Shopper Riegler value, improved tensile index of sheets to some degree, then level out. Cobb values show a rapid drop at the first beating, and then headed to gradual increase parallel to beating (Figure 3).

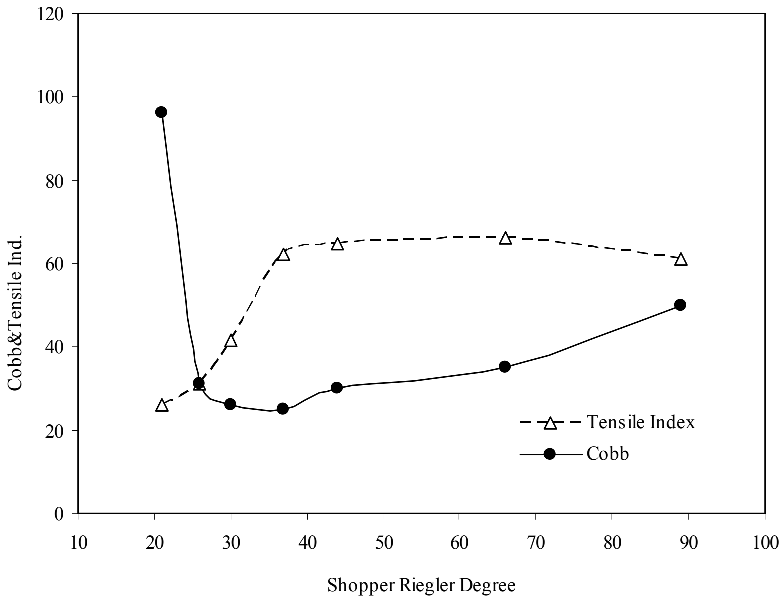

Figure 3: Effects of beating on Cobb and tensile index of sheets.

Moderate beating makes fibres flexible and produces new surfaces as a result of both internal and external fibrillation. These all favour in making stronger, denser and smoother sheets. Excessive beating, on the other hand, causes damages on fibres and produces lots of fibre breaks, fines which may lead to retention problem and weak sheet formation. These depend on the intensity of beating and the real damages generated on the fibres. Fines having greater surface area adsorb huge amounts of sizing chemicals compared to fibres and may not be retained in the sheets. Therefore, sizing degree would be expected to drop in any case if fines in pulps are increased.

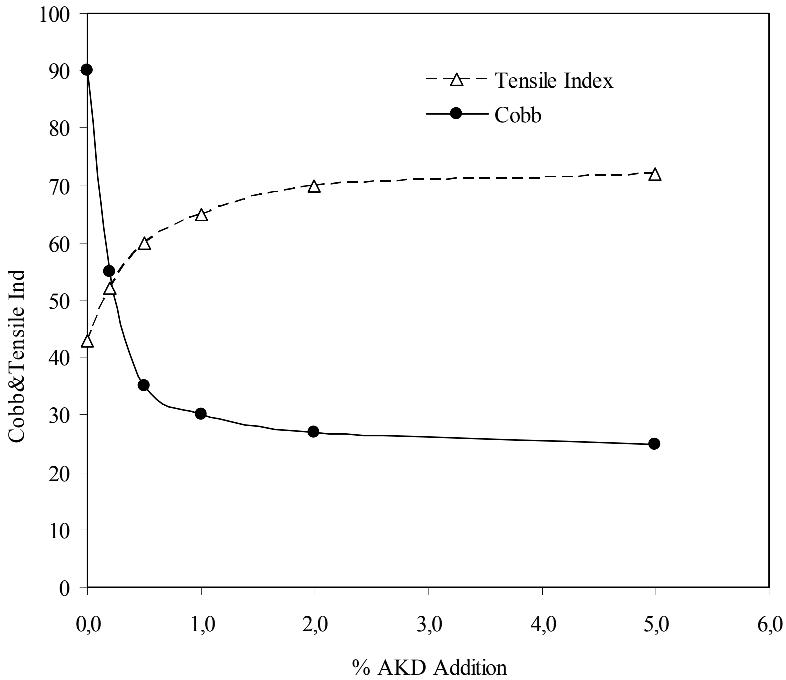

Figure 4: Effects of beating on Cobb and tensile index of sheets.

AKD addition made positive changes on both paper strength and cobb value as seen in figure 4. Findings are in agreements with those presented in both figure 1 and 2 that AKD addition creates new chemical bonds between fibres. It is noted that excessive addition level of AKD above % 1 did not make a significant change.

AKD Adsorption on Pulps

Various pulps were mixed with %0,5 AKD emulsions, filtered, air dried and extracted with dichloromethane for 12 hours. It is known that air drying did not develop any chemical bonds between AKD molecules and cellulose (Ref) since AKD melting point is over 60°C. Therefore it was expected all AKD retained in filtered fibre mat to be extracted. Results plotted in figure 5 as extracted percentage of total added emulsion. Results suggest that most of the emulsion mixed with bleached short fibres were lost to back water. The retention in old office paper was also seen very poor. Newspaper on the other hand, despite being quite dirty pulp, was noted to keep most of the AKD emulsion in it. The adsorption of AKD emulsion in studied pulps were governed by the opposite charge attractions, between cationic starch molecules around AKD droplets and pulp ingredients. Retention of adsorbed AKD particles however depends on how good or bad papermaking ingredients stayed over wire. Flocculation and coagulation in fibre slurry, in this respect, directly increased the AKD retention. It is suggested that fibre suspensions poor in AKD retention should be adjusted in terms of charges and supported by retention aids.

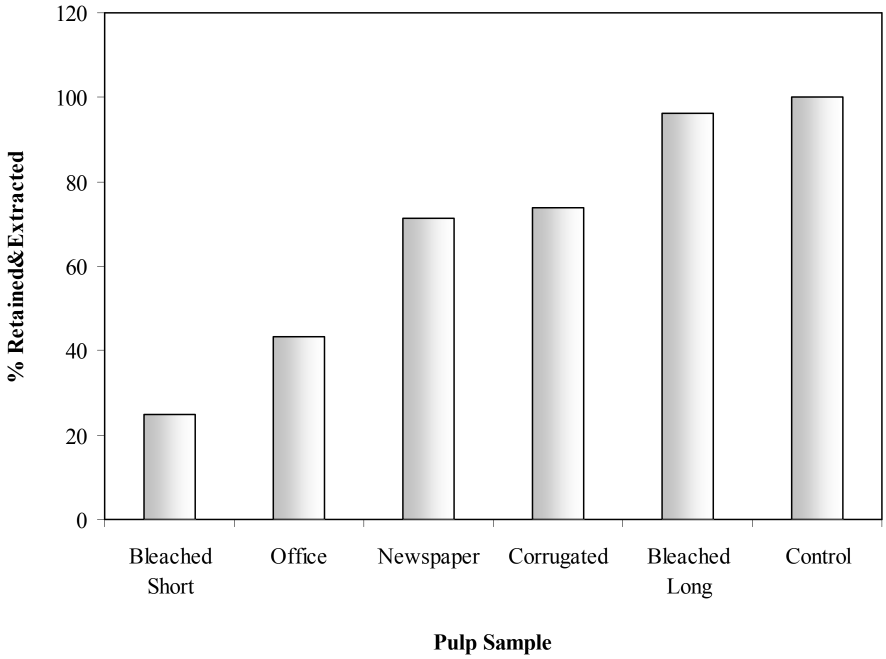

Figure 5: Amounts of retained AKD as extractable portion from filtrated pulps.

Conclusion

Some degree of sizing is required for many papers. Sizing agents should not reduce paper properties other then Cobb value. AKD works well at small addition levels compared to other sizing agents studied here. Beating improved paper strength to some extend and improved Cobb value too. Severe beating, however, may not develop paper strength; but actually may reduce it due to destructive effects over fibres. AKD adsorptions over fibres are improved by opposite charge attractions. Adsorbed AKD on stock may be lost to back water if especially fine retention is not well enough.

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