

REVIEW

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Separation and analysis techniques for bound and unbound alkyl ketene dimer (AKD) in paper: A review

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Abstract Alkyl ketene dimer (AKD) is the reactive synthetic sizing agent that is used in alkaline or neutral papermaking conditions to provide certain level of hydrophobicity to the paper and board. The sizing mechanism of AKD involves its reaction with the hydroxyl groups on cellulose. However, all of AKD does not chemically react with fibers; some of it may undergo hydrolysis in water to form unstable β-keto acids, which decarboxylate to the corresponding ketone. This portion of AKD remains non-reacted (unbound) and adsorbs onto fibers. The sizing effect depends mainly on the quantity of chemically reacted (bound) AKD in paper, while the role of unbound forms, that is ketone and oligomer, is still not clear. Both bound and unbound portions of AKD have their own effect on paper. It is important to know the proportion of bound and unbound form of AKD in paper. The different techniques have been adopted for the separation and analysis of bound and unbound AKD present in paper. The aim of this paper is to review and summarize the various techniques provided by the researchers to separate the different forms of AKD and highlight the most important aspects for their separation.

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1. Introduction

Paper is composed of cellulosic fibers and highly water-absorbent. However, writing & printing grades of paper or packaging grades of paperboards need to be resistant to some degree on wetting with polar liquids such as water, aqueous solutions and suspensions. Therefore, papermaking components, such as fibers are rendered partially hydrophobic by introducing chemical additives in the pulp stock; this phenomenon is known as internal sizing of paper. The main internal sizing chemicals currently in use around the world are based on emulsions of rosin, alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA). In all three cases the aim is to retain hydrophobic molecules in the sheet of the paper. Internal sizing aims at establishing a hindrance toward penetration and spreading of the liquids through the porous structure of paper. In addition to improving the edge penetration properties of liquid packaging, sizing also improves paper printability by controlling ink absorption and spreading, and reducing the effect of aqueous fountain solution on loss of paper strength (Evans, 1989; Neimo, 1999; Sharma et al., 2010; Chen et al., 2012).

The paper industry has moved from rosin to ASA or AKD sizing i.e. from acid to neutral or alkaline. The new neutral and alkaline sizing techniques have been found to be more efficient owing to their better hydrophobicity and lesser size reversion i.e. higher durability of paper as compared to conventional rosin sizing. AKD is widely used since its inception in late 1950s. It is a reactive size as it forms covalent bonds with cellulose at neutral or alkaline pH during the papermaking system (Lee and Luner, 2005; Song et al., 2012).

Sizing efficiency through AKD depends on several factors including retention, particle distribution on the fiber surfaces and the extent of chemical reaction of the size (Mourao et al., 2011). Different forms of AKD in paper affect the hydrophobicity of paper (Girardi 1989; Lindström and Söderberg, 1986a; Voutilainen 1996). Bottorff (1994) and later on Hardell and Woodbury (2002) confirmed the existence of both forms of AKD along with oligomeric form. Hardell and Woodbury (2002) also separated and quantified the oligomeric form in commercially available AKD waxes and reported that oligomeric form was present up to 10% by weight.

Many papers have been published on the mechanism of sizing development and role of papermaking variables including retention and drying on AKD sizing (Lindström and Söderberg, 1986a; Roberts and Garner, 1985; Shen et al., 2003; Taniguchi et al., 1993; Yu and Garnier, 1997,2002). Many researchers investigated the sizing mechanism of AKD and studied the role of bound and unbound AKD on sizing development. Lindström and Söderberg (1986a) carried out studies on different pulps with AKD and found that bound AKD enhanced hydrophobicity to paper many folds as compared to unbound AKD. On the other hand, Marton (1990) reported that after chloroform extraction of the AKD sized paper that removed more than 50% of the retained AKD material from the paper did not show marked difference in the Hercules size tester (HST) data, which was later on confirmed by studies of Zimmerman et al. (1995); (Lee and Luner 2005); Zeno et al. (2005), Zhang et al. (2007).

It is important to determine the proportion of the AKD retained in the paper, and existence in various forms, in order to properly understand the sizing process, and to make the process cost effective. The aim of this review is to investigate the published literature on the separation and analysis of bound/ unbound and oligomeric form of AKD in paper for the benefit of the papermakers and researchers.

2. Chemistry of AKD and sizing mechanism

AKD is a waxy material, insoluble in water with a melting point around 50 °C depending on the chain length and structure of the fatty acids used in its preparation. Commercial AKD used in different pulp and paper industries is prepared from natural fatty acid containing 14–20 carbon. Due to change in different side chain originated from its source, industrial AKD might have a variety of chain lengths (Roberts 1996; Karademir 2002; Shen et al. 2002).

Being waxy in nature AKD needs an elevated temperature to get molten and emulsified. It is dispersed in high-pressure homogenizer in the presence of some stabilizers viz., cationic starch as a protective colloid in conjunction with lignosulfonates/naphthalene sulfonic acids. Waxy maize starch with no propensity to retrogradation is generally preferred (Isogai 1997). It is important to avoid surface active substances in the dispersion formulation, because they may interfere with sizing. The dispersion is usually made slightly cationic in order to provide it more susceptibility to negatively charged fibers, however anionic dispersions are also available commercially. In order to reduce the hydrolysis of the AKD, the pH of the dispersion is kept below 4. The stability of the AKD emulsion increases with increasing the presence of AKD oligomers (Asakura et al., 2006). The particle size range of AKD emulsion is typically 0.2-2 µm. These dispersions are added to the aqueous fiber suspension. The mechanism of AKD sizing with paper has been the focus of intensive research for a number of years. It is generally accepted that AKD sizing can be divided into the following steps (Lindström and Söderberg, 1986a; Champ and Ettl, 2004; Ravnjak et al., 2007; Seppänen et al., 2000; Shen et al., 2001):

- Retention of AKD particles in the paper web;
- Spreading of the AKD wax over the fiber surface during drying of the web; and
- Reaction of the AKD molecules with the cellulosic molecules in the paper.

The retention mechanism is, in theory, heterocoagulation, where cationic particles are attached to the negatively charged fibers, however, an effective retention aid chemical program is essential for the purpose. Heterocoagulation, can not be used to retain the particles of AKD under high fiber–fiber shear conditions. A high single pass retention of AKD is important as the amount of AKD drained through the forming wire of the paper machine gets hydrolyzed with time in the presence of water and higher pH (neutral or alkaline) (Lindström and Söderberg, 1986b; Champ and Ettl, 2004).

In general it is believed that AKD reacts with cellulose fiber and forms a beta-keto ester bond, hence makes paper hydrophobic (referred as bound/reacted) (Eklund and Linstrom, 1991; Roberts, 1996; Seppänen and Tiberg, 1999; Seppänen and Zhmud, 2003) (Fig. 1). AKD also reacts with water molecules producing an unstable β -keto acid which spontaneously decarboxylates forming the corresponding ketone (referred as unbound/non-reacted/not-retained with paper) while AKD molecule may react together to form oligomer (Bottorff and Sullivan, 1993; Lindström and Söderberg, 1986b) (Figs. 2 and 3). The reaction rate between AKD and water is reported to be faster than that with cellulose fiber (Roberts and Garner, 1985: Seo and Cho. 2005). There have been different explanations for the sizing effects of these two reaction products. Some researchers claim that the reaction between AKD and cellulose is essential for paper water repellency (Ödberg et al., 1987; Eklund and Linstrom, 1991; Roberts, 1996), whereas others believe that such a reaction does not take place at all and is not necessary for sizing (Rohringer et al., 1985).

The required amount of AKD for sizing of a given pulp depends on a number of factors and is linked with the papermak-



 $(\beta$ -keto ester – bound form)

Figure 1 Reaction of AKD with cellulose.

ing parameters and conditions. It is important to retain the AKD as high as possible in the paper matrix, as the recirculated AKD can easily be hydrolyzed. The extent of reaction depends on the drying conditions together with the presence of size accelerators. The extent of reaction of AKD with cellulose lies in the range between 15 to 40%.

3. Separation and analysis of bound and unbound AKD from paper

The high dosage of AKD with papermaking suspension can interact negatively with the paper and may harm the paper machine runnability. It can lead to the formation of stickies which is formed from the hydrolyzed AKD. The dosage of AKD is also linked with the cost of sizing. In order to reduce the dosage of AKD in paper, it is important to first know the amount of AKD retained in paper.

Lindström and O'Brian (1986), Lindström and Söderberg (1986a,b), and Nahm (1986) reported the evidence of different forms of AKD in a sized paper. They also reported that hydrophobicity in paper depends mainly upon the bound AKD while the role of unbound AKD could not be understood. Ödberg et al. (1987) reported the separation of unbound AKD in paper with chloroform and estimated its amount through Gas chromatography (GC) and Fourier transform infrared (FTIR) respectively.

Dart and McCalley (1990) developed the capillary GC procedure for the analysis of the bound and unbound AKD in the paper prepared in laboratory. The method was based on the hydrolytic extraction and quantification of long-chain ketones, the identities of which were confirmed by combined gas chromatography-mass spectrometry (GCMS). The procedure holds good precision and acceptable recoveries of AKD products from both surface and internally sized papers. The technique can also be used to determine the fate of AKD in continuously operated papermaking machine.

Girardi (1989) determined the amount of both forms of AKD through radioactive tracer studies with ¹⁴C nuclear magnetic resonance spectroscopy (NMR) while ¹³C solid state NMR studies were used to quantify the same by Bottorff and Sullivan (1993), and Bottorff (1994).

As reported earlier, in a paper sample both forms of AKD may be present and affect the sizing efficiency. Bottorff



Figure 2 Hydrolytic decomposition of AKD; (i) hydrolysis, (ii) decarboxylation.



Figure 3 Formation of AKD oligomer.

(1994) used the solvent extraction technique to separate the two forms of AKD by tetrahydrofuran (THF). Extraction of AKD sized papers with THF resulted in removal of the ketone group while the β -keto ester group was found present in paper as evident from NMR. The study revealed that unbound AKD can be extracted with THF but the simple extraction was not good enough to extract the bound AKD in paper. The bound AKD was extracted with 50% dioxane-water mixture for 8 h at 80 °C which indicated that the severe conditions are required to separate the bound form of AKD from paper. The results provided good precision and reproducibility but could not correlate the different forms of AKD on the basis of total AKD added to paper during papermaking.

Nyarku and Sithole (1994) determined the unbound form of AKD in paper through potentiometric titrations. The unbound AKD was extracted with chloroform and its content was estimated by titration, and results were compared with analysis of same extract with capillary GC reported by Ödberg et al. (1987). The study also emphasized on the stability of AKD emulsion. AKD was converted into its ketone form before analysis with GC. Bound AKD in paper samples was separated by digestion of the paper with either hydrochloric acid or sodium carbonate. A separation scheme based on solidphase extraction was also developed for the determination of unbound AKD. The Soxtec extraction (rather than Soxhlet extraction) was also employed for the determination of AKD followed by quantification through GC.

Karademir (2002) separated the unbound AKD with dichloromethane (DCM) and the same sample was used to extract the bound AKD. Alcoholic potassium hydroxide solution was used to extract the bound AKD. The paper sample was kept in solvent at 40–50 °C for 3 h followed by acidification with hydrochloric acid. Toluene was used as a solvent to extract the bound AKD from this mixture. Both extractions were evaporated and mixed with internal standard, and their amounts were determined with GC. The proportion of bound AKD in paper was comparatively lower as compared to the unbound one in paper.

Hardell and Woodbury (2002) separated the bound and unbound AKD in paper and also proposed that it was not feasible to extract the oligomeric form from the paper. They separated the oligomeric form of the AKD from wax itself and quantified with the size exclusion chromatography (SEC). Paper sample was treated with acetone for 2 h at 70 °C to extract the bound AKD. The unbound AKD was also extracted from backwater with DCM to balance the total AKD. Pyrolysis GCMS was used to estimate the bound and unbound AKD in paper and backwater while size exclusion technique was used to quantify the oligomeric AKD in AKD wax. The results showed that only 10% of AKD remained bound with cellulose.

Odermatt et al. (2003) also carried out the separation and identification of AKD with pyrolysis GCMS using flame ionization detector (FID). Py-GC/FID proved a good technique for the determination of AKD containing different alkyl groups.

Zule and Dolenc (2003) also used GC to separate the two different forms of AKD in paper. The unbound AKD in paper was extracted with hexane as solvent. For the determination of bound AKD, the hexane extracted paper was dried and used for further extraction. The acidified sample was refluxed with iso-octane for 2 h. After filtrations the remaining fibers were washed with hexane and the organic phase was used to determine the bound AKD with GC. The parameter set for GC was found different for different researchers. Zule and Dolenc (2005) further reconfirmed the existence of two forms after acidic hydrolysis. They also suggested that ester form can only be determined after hydrolyzing the AKD. Bound and unbound AKD in samples were determined.

Laitinen (2007) during his doctoral study separated the unbound AKD using isooctane as a solvent. The bound AKD in pilot papers was extracted using THF followed by liquid chromatography (LC) MS.

Martorana et al. (2009) used a different technique, near infrared (NIR) spectroscopy to quantify the bound AKD in paper sample. This technique was less robust as compared with other but required a new instrument for their estimation. But the mechanism and interaction of AKD can be studied more easily and faster with this technique.

The different techniques used for separation and quantification of bound and unbound form of AKD in paper as reviewed in this paper have been compiled and tabulated for better understanding (Table 1) (Downey, 1949; Isogai, 1999; Jaycock and Roberts, 1994; Mattson et al., 2003; Mattsson, 2002; Pyda et al., 1993; Ravnjak et al., 2006; Roberts and Zhou, 1996; Seo



et al., 2008; Seppanen, 2007; Seppanen, 2009; Sitholé et al., 1995; Vrbanac and Dixon, 1997; Vrbanac et al., 1999; Yano et al., 1992).

4. Conclusions

The retention of AKD in paper is crucial to enhance its efficacy toward increasing hydrophobicity in paper. Through heteroflocculation cationic size particles are attached to the negatively charged fibers; retention of AKD in paper can be increased with the selection of an effective retention aid chemical program. High single pass retention of AKD is important as the amount of AKD drained through the forming wire of the paper machine gets hydrolyzed with time in the presence of water and at higher pH.

AKD reacts with cellulose and present in three forms viz., bound, unbound and oligomer. Bound AKD attribute sizing to paper and is accepted whereas the role of unbound AKD is of mixed nature. The role of oligomer is not yet clear. Several techniques have been used in literature to separate the unbound and bound forms of AKD from paper. The unbound AKD can be separated through extraction with different solvents viz., tetrahydrofuran, hexane, isooctane, methyl t-butyl ether, dichloromethane etc. The analysis of unbound AKD involves the instrumental techniques viz., Gas chromatography (GC), Liquid chromatography - mass spectrometry (LC-MS), Nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FTIR) along with one potentiometric titration technique. The method to separate the bound form of AKD involves the extraction through different solvents. Its analysis is also reported through above mentioned instrumental techniques along with few more techniques viz., UV-vis spectrophotometer, Near-infrared spectroscopy etc. The most commonly used separation and analytical technique in both the cases was GC which gives comparatively higher repeatability and reproducibility while other techniques could not provide so profound results.

Though AKD is being used as a commercial sizing agent for more than six decades, studies on separation, extraction and determination of different forms of AKD present in the paper, and their role is needed to better understand the mechanism of AKD sizing.

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