Sizing mechanism of alkylketene dimers

Part 1. Possibility for AKD to form β-ketoesters in papersheets

Akira Isogai. Ryu Taniguchi, Fumihiko Onabe and *Makoto Usuda,* Department of Forest Products, Faculty of Agriculture, The University of Tokyo, Japan

Keywords: Sizing, Alkylketene dimers, Cellulase, Extraction, Cellulose, Amorphous. β-Ketoesters, Retention.

SUMMARY: The possibility for alkylketene dimer (AKD) to form β-ketoesters with hydroxyl groups of cellulose and/or hemicellulose in pulp fibers during papermaking and conditioning processes was examined by the following three methods: 1) extractions of AKD and its related compounds from AKD-sized sheets under neutral and alkaline conditions, 2) chemical analyses of enzymatically-hydrolyzed residues of AKD-sized sheets, and 3) chemical analyses of cured mixtures of amorphous cellulose and AKD. Amounts of AKD and ketones extracted under neutral conditions were almost equal to those extracted under alkaline conditions for AKD-sized sheets with over wide range of Stockigt sizing degrees, when the extractions were associated with fiberization of the sheets. AKD contents were increased by removal of cellulose and hemicellulose in AKD-sized sheets with cellulase. IR and other chemical analyses of the enzymatically-hydrolyzed residues revealed that AKD was physically adsorbed to pulp fibers and fillers without formation of P-ketoesters. All model experiments using amorphous cellulose samples showed that no β-ketoesters were formed between AKD and hydroxyl groups of polysaccharides during curing and conditioning treatments. as long as water is present in the system. Furthermore, AKD and ketones, once trapped in amorphous cellulose by curing treatments, could not be extracted completely even by Soxhlet extractions with chloroform. These results show that AKD and ketones (hydrolyzed AKD) are most likely to be present in sheets by physical interactions without formation of β-ketoesters. Furthermore, fiberization of AKD-sized sheets and swelling of pulp fibers are found to be necessary for complete extractions of AKD and ketones trapped in the part of interfiber and/or intrafiber bonding.

ADDRESS OF THE AUTHORS: Faculty of Agriculture, The University of Tokyo, 1-1-1 Yayoi. Bunkyo-ku. Tokyo 113. Japan.

Alkylketene dimers (AKD) and alkenyl succinic anhydrides (ASA) are typical neutral-sizing chemicals, and have been used increasingly with increase in the use of calcium carbonate as a filler. Although AKD is superior to ASA in terms of emulsion stability, it is often difficult to control sizing features of AKD-sized sheets. Namely, the sizing features strongly depend on conditions of papermaking, such as pH of pulp suspensions, dryer temperature, drying sequence, kinds of pulp and fillers, and others. Especially, one of the typical phenomena for AKD sizing is that sizing features often appear gradually during conditioning process. Particularly this leads to serious problems for on-machine coating of AKD-sized paper. Thus, it must be significant for controlling sizing features of AKD-sized paper to make clear the sizing mechanism of AKD.

AKD is reactive to hydroxyl groups, and forms ketones and P-ketoesters by being reacted with water and alcohols, respectively, in the presence of base as a catalyst. Thus, the formation of P-ketoesters between AKD and hydroxyl groups of cellulose and hemicellulose in pulp fibers during papermaking and conditioning treatments has been reported as one mechanism for the appearance of the sizing features of AKD-sized paper (Davis et al. 1956; Dumas 1981; Roberts, Garner 1985; Lindstrom, Soderberg 1986: Lindstrom, O'Brian 1986; Nahm 1986; Odberg et al. 1987; Marton 1990). The primary reasons for supporting this hypothesis are as follows; 1) some of AKD in sheets could not be extracted completely with organic solvents, where radio-active AKD was synthesized and used for determining amounts of "reacted AKD", 2) most of sizing features were remained even after Soxhlet extractions of AKD-sized paper with organic solvents, 3) P-ketoesters were isolated from reaction products of cellobiose and AKD under non-aqueous conditions in the presence of an organic base, and 4) absorption due to carbonyl groups of esters were detected in FT-IR spectra of AKD-sized paper. The above reasons 1) and 2) must be strong proofs for the formation of P-ketoesters, if free AKD and ketones physically mixed in sheets could be extracted completely by the extraction methods, where the sheet form was maintained (Roberts, Garner 1985; Lindstrom, Söderberg 1986; Lindstrom, O'Brian 1986; Ödberg et al. 1987). However, these extraction methods in the sheet form may not completely extract small amounts of free AKD and ketones trapped in the part of interfiber bonding, unless the sheet form is destroyed to swollen single fibers (Robertson 1970).

On the other hand, some reports showed that AKD may not form β-ketoesters with hydroxyl groups of cellulose and hemicellulose in pulp fibers under the conditions of papermaking or conditioning, and that sizing features of AKD must be explained in terms of other reasons than the β-ketoester formation, such as formation of β-ketoacids, migration of AKD, and others (Garner, Roberts 1984; Merz et al. 1985; Rohringer et al. 1985). IR spectroscopy using the frustrated multiple internal reflection method (FMIR) and differential scanning calorimetry (DSC) were used to support these negative ideas of the P-ketoester formation. Thus, at this point, it has not been concluded whether AKD forms P-ketoesters with pulp fibers in AKD-sized paper or not. Naturally, therefore, sizing mechanism of AKD also has not been clarified yet.

In this paper, the possibility for AKD to form β-ketoesters in AKD-sized sheets was examined from some new aspects of analyses. Namely, solvent extractions associated with fiberization were carried out on AKD-sized sheets, and the possibility for AKD to form β-ketoesters was examined by comparing amounts of extracted AKD and ketones between neutral and alkaline conditions. Here, P-ketoesters were stable during the neutral extraction, whereas they were saponified to form ketones during the alkaline extraction. Since AKD content in the usual AKD-sized sheets was too low to detect β-ketoesters, if they were present, by IR and other spectroscopic methods, AKD-rich fractions were collected by cellulase treatments of AKD-sized sheets to remove large amounts of cellulose and hemicellulose.