AKD Sizing Mechanism (III)
- The Nature of AKD and Ketone -

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1. Introduction

It was well known that a dialkyl ketone was produced by the hydrolysis of AKD in AKD sized paper. Zhou (*1*) reported that considerable amounts of AKD were hydrolyzed during storage from the observation of the IR spectra of the extracts of AKD sized paper. Akapio and Roberts (*2*) suggested that one gram of tetradecyl ketene dimer required theoretically only 0.04 g of water to completely convert it to palmitone, therefore, about 8-10% moisture content of paper would be enough to hydrolyze the dimer to palmitone. However, a lot of researchers (*1-4*) reported that hydrolyzed AKD did not provide sizing effect because the hydrolyzed AKD could not react with cellulose to form a covalent linkage. Isogai *et al.* (*5*) reported that the partial hydrolysis of AKD on the surface of emulsion particles probably brings about the remarkable decrease in dispersibility of the emulsion through the increase in hydrophobicity of emulsion, and that the decrease of dispersibility leads to the decrease in sizing effect. In our previous paper (*6*), it revealed that AKD reacted rarely with cellulose in the presence of water and most of AKD was converted to a dialkyl ketone through the reaction with water. Therefore, the actual sizing agents should not be beta-ketoesters of cellulose, but unreacted AKD and hydrolyzed AKD (ketone). Comparison of hydrophobicity of the sizing agents, as reported by Shin et al. (*7*), it was shown that ketone could give higher hydrophobicity to cellulosic fibers than unreacted AKD.

In this paper, to investigate the effects of the melting and spreading features of AKD and ketone on the sizing development of AKD sized paper, the spreading behavior of particles of the sizing agents in paper web were observed by scanning electron microscopy. Stöckigt size degree was also measured before and after heat treatments.

2. Experimental

2-1. Materials

A commercial alkylketene dimer (AKD, Nippon Oils Co., Ltd., Japan) was used as a wax form. Hydrolyzed AKD (ketone) was prepared by the hydrolysis of AKD as previously described (6). AKD and ketone was recrystallized from hexane solution for three times, and characterized by FTIR, ^{1}H-NMR, and ^{13}C-NMR. Whatman No. 1 filter paper was used as a base paper for sizing. HPLC-grade dimethylformamide (DMF) was purchased from Aldrich Chem Co. Inc., and used without further purification.

2-2. Methods

DMF was used as a solvent for AKD and ketone. AKD and ketone solution (1.0 wt.%) in DMF was prepared by stirring at 50°C over 3 hours, respectively. Whatman No. 1 filter paper was immersed in 50 mL of the solutions at 50°C and then 50 mL of 30°C distilled water was added to produce particles of both AKD and ketone in the filter paper. By the addition of water, which acted as a non-solvent for both AKD and ketone solved in DMF solution, AKD and ketone were much less soluble in the solutions. Consequently, AKD and ketone homogeneously solved in DMF solution became to be small particles in the filter paper and on the fiber surface. Finally, DMF was removed from the papers by careful washing with distilled water. Thereafter, these samples were dried at room temperature. SEM micrographs was obtained to see the formation of AKD or ketone particles in the filter paper and on the fiber surface. Pick-up of AKD and ketone in the filter paper was 9.30 wt.% and 8.85 wt.% respectively. The papers including AKD or ketone particles were heated on a rotary drum dryer for 30 seconds at various heating temperatures. Before and after heating treatments, the papers were used for the observation of SEM and the measurement of Stöckigt size degree.

2-3. Measurements

SEM micrographs were taken from JEOL JSM-840A (Japan). Sizing degree was measured by Stöckigt method according to KS M7025 just after the heat treatments. Differential scanning calorimeter (DSC) was used for measurement of melting points of AKD and ketone used. DSC spectra were obtained from TA Instrument Model No. 1200-42910DSC at the heating rate of 5°C/min in nitrogen atmosphere.

3. Results and Discussion

The papers including the particles of AKD or ketone were heated on the rotary drum dryer at various temperatures for 30 seconds. Before and after the heat treatment, the morphology of the particles in the filter paper was observed by scanning electron microscopy. The SEM images are shown in Fig. 1.

Fig. 1(A) shows the surfaces of the filter papers before heating, which contain AKD and ketone particles. Particle shapes and sizes of AKD and ketone are different. The spreading behaviors of both AKD and ketone particles can easily be observed from changes of particle shapes and sizes in the SEM-micrographs. In Fig. 1(B), no changes of both AKD and ketone particles in the papers heated at 35°C are observed. In the case of heat treatment at 50°C, most of AKD particles disappears, while the ketone particles remains without any changes in its morphology as shown in Fig. 1(C). Fig. 1(D) shows that AKD particles lose their shapes and the ketone particles start to melt when the paper is treated at 75°C. Finally, Fig. 1(E) shows that both AKD and ketone lose completely their particle shapes by heating at 100°C. Disappearance of the wax particles in the SEM images implies that the wax particles of both AKD and ketone melt and then spread on the fiber surface.

Fig. 2 shows DSC spectra of AKD and ketone. From the spectra, it can be known that the melting points of AKD and ketone were around 50 and 75°C, respectively. These temperatures correspond with the temperatures that AKD and ketone particles disappeared in the paper. Therefore, it can be considered that the spreading behaviors of AKD and ketone were related directly to their melting points.

After heating of the papers containing AKD or ketone particles, their size degrees were measured by Stöckigt test method and the results are illustrated in Fig. 3. AKD treated papers show about 40 seconds and 60 seconds of Stöckigt size degrees when they heat treated at 50 and 75°C, respectively, while the papers treated with ketone does not show sizing effect. However, in the case of the heat treatment over 100°C, the ketone shows superior sizing effect than AKD. This result indicates that ketone can also contribute to sizing development of sized paper, when it spreads well on the fiber surfaces. Especially, ketone treated papers show higher size degree than that treated with AKD when they are heated over 100°C. In other words, ketone can give higher sizing effect than unreacted AKD when it spreads well on the fiber surface.

However, it has been thought that ketone could not contribute for sizing development. Ketone could be introduced to AKD sized papers by using old AKD emulsion partially hydrolyzed to ketone. Marton (*8*) reported that a commercial AKD

emulsion lost about 15 % of its reactive groups through the hydrolysis during five weeks storage at room temperature. It was reported that an old AKD emulsion brought about a remarkable decrease in sizing development. The reason was thought as decreasing of the reactivity of AKD by its hydrolysis and poor spreading of hydrolyzed AKD (ketone). Ketone could also be introduced in AKD sized paper during drying process and storage of the AKD sized papers by the hydrolysis of AKD retained in the paper. Zhou (*1*) reported that there was no ketone just after drying, but considerable amounts of ketone was detected after 23 days storage of AKD sized paper. In this case, ketone should not exist in the form of solid particle, but in the form of well spread thin-layer on AKD sized paper. The reason was that ketone was produced by the hydrolysis of AKD, which is already melted and spread on the fiber surface. Therefore, it was proposed that ketone could contribute for AKD sizing development when it produced by the hydrolysis of AKD in AKD sized paper.

Literature cited

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