UDK 676.026:54.021
Strokovni članek

ISSN 1580-2949
MTAEC9, 39(1–2)55(2005)

THE INFLUENCE OF THE CHEMICAL COMPOSITION OF SYNTHETIC REACTIVE SIZES ON THE SIZING EFFICIENCY OF PAPER

VPLIV KEMIJSKE SESTAVE SINTETIČNIH REAKTIVNIH KLEJIV NA UČINKOVITOST KLEJENJA PAPIRJA

Janja Zule, Jožica Dolenc
Pulp and Paper Institute, Bogišičeva 8, 1000 Ljubljana, Slovenia
janja.zule@icp-lj.si

Prejem rokopisa – received: 2004-09-20; sprejem za objavo – accepted for publication: 2005-01-31

Sizing is a process of producing paper of hydrophobic character which becomes suitable for printing purposes due to its enhanced liquid penetration resistance.. Alkylketene dimers (AKD) are the most common sizing agents in neutral or slightly alkaline papermaking systems. They may be applied together with $CaCO_3$ as filler. Consequently, the paper produced is typically more chemically stable and durable.

Some practical results of AKD analyses of different label paper grades are also presented and discussed.

It is well known that sizing efficiency depends on the properties of fibre, filler and sizing agent as well as on pH, system temperature, contact time and method of drying .

The results of our extensive research show that the chemical properties of sizing agents, such as the percentage of active substance, the proportion of C_{16}/C_{18} chains on the AKD structure or the content of impurities and addition of promoters, all significantly influence the sizing quality which is represented by the total amount of retained AKD in paper as well as by the proportion between adsorbed and chemically bound portions of the sizing agent.

Key words: reactive sizing agents, alkyl ketene dimers, sizing efficiency, long chain ketones, gas chromatography

Klejenje je postopek, pri katerem hidrofilna celulozna vlakna v papirju hidrofobiramo, pri čemer postane papir odpornejši proti penetraciji tekočin in s tem primeren za tiskanje. Najpogosteje uporabljena klejiva v nevtralnem ali rahlo alkalnem papirniškem sistemu so alkilketenski dimeri (AKD). Možno jih je uporabljati skupaj s polnilom $CaCO_3$, narejeni papir pa ima dobro kemijsko stabilnost ter obstojnost.

Znano je, da je učinkovitost klejenja odvisna od lastnosti celuloznih vlaken, klejiva in polnil, od pH in temperature sistema, kontaktnega časa in metode sušenja.

Naša raziskava je pokazala, da kemijske lastnosti klejiva, na primer delež aktivne snovi, razmerje C_{16}/C_{18} organskih verig v osnovni strukturi, vsebnost nečistoč in dodatek promotorja bistveno vplivajo na kakovost klejenja oziroma na celotno vsebnost klejiva v papirju ter na razmerje med adsorbiranim in kemijsko vezanim deležem klejivnega sredstva.

V članku so prikazani tudi rezultati določanja različnih oblik klejiva v nekaterih vrstah etiketnega papirja.

Ključne besede: reaktivna klejiva, alkilketenski dimeri, učinkovitost klejenja, ketoni z dolgimi verigami, plinska kromatografija

1 INTRODUCTION

Sizing is one of the most important stages in paper production. Its purpose is to impart hydrophobicity to the manufactured paper by addition of different water repellent chemicals known as sizing agents. Due to its enhanced liquid penetration resistance, only sized paper is suitable for printing purposes. The most important sizing chemicals currently in use around the world are based on emulsions of rosin, alkenyl succinic anhydride (ASA) or alkyl ketene dimers (AKD). The advantage of the latter is their applicability in combination with $CaCO_3$ as filler in neutral to slightly alkaline pH of the papermaking system. Paper produced in this way is typically more chemically stable and durable [1].

AKD belong to a group of reactive sizes which are supposed to form covalent bonds with cellulose fibers during paper web drying. The reaction of AKD lactonic rings with free OH groups on the cellulose molecule when forming β-keto esters is presented by **Figure 1**. R_1 and R_2 are long alkyl chains composed of 16 and 18 C atoms respectively [2, 3].

Unfortunately, this is not the only process that occurs during the sizing stage of paper production. As water is always present in the papermaking system, it may promote hydrolysis of the sizing agent. This unavoidable side reaction leads to the formation of corresponding ketones which do not contribute to sizing efficiency.

Numerous experiments have shown that AKD is either chemically bound to the fibers forming a paper web,

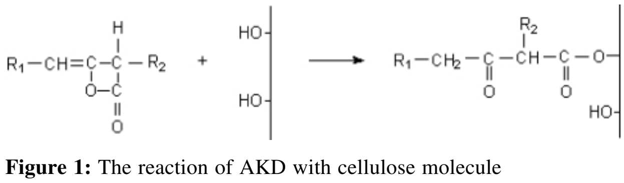

Figure 1: The reaction of AKD with cellulose molecule
Slika 1: Reakcija AKD s celulozno molekulo

or else it may be physically adsorbed on their surface in its original form (lactonic rings) or as a hydrolysed product (ketones). Whereas the first two forms are responsible for adequate sizing performance, ketones actually represent the loss of sizing agent.

Sizing chemicals are relatively expensive raw materials. Therefore, it is necessary to optimise their usage, meaning that they should be properly applied and maximally retained in paper structure or otherwise they may enter and pollute process water [4].

Many AKD agents differing in their physical and chemical properties as well as in their efficiency are commercially available to papermakers. Their most significant characteristics are activity, namely the quantity of active dimer in emulsion, the proportion between C_{16} and C_{18} chains on the lactonic ring, chemical purity, and the content of additives such as cationic starch or synthetic polymers which stabilize AKD emulsions and promote chemical bonding to fibers. The necessary addition of commercial agent is 1 %, calculated from the weight of o.d. fibers [5].

In order to thoroughly understand and thus optimize the process of sizing, it is necessary to evaluate the retention of AKD in paper structure and characterize its chemically bound and adsorbed or unbound portions related to the chosen technological parameters. This can be performed by means of successive extraction and hydrolysis steps to isolate the individual forms of AKD from paper, after which quantitative determination of separated portions is conducted by means of gas chromatography [6,7].

The purpose of our research was to characterise several commercial AKD emulsions and specify the connection between their chemical composition and performance in a papermaking system. The most appropriate agent for industrial paper production at different technological conditions was chosen with regards to its chemical characteristics. Paper samples from various production programmes were analysed in order to determine the content of bound and unbound AKD. The results were compared to each other. In addition, we evaluated the sizing efficiency.

2 EXPERIMENTAL

2.1 Samples

Three widely used commercial sizing agents (AKD 1, AKD 2 and AKD 3) made by different producers were tested for their activity, C_{16}/C_{18} proportion and chemical purity.

Paper samples were obtained from four slightly different label paper production programmes, using the same quantities of selected AKD. They were evaluated for the content of total, bound and unbound AKD. The ratio between both portions was also determined.

2.2 Chemical analyses

Sizing agents were dried in vacuum at 30 °C. Afterwards, their dry matter content was determined.

100 mg portion of dried sample was dissolved in 10 mL of hexane, after which the content of ketones representing the originally present inactive hydrolysed form of the agent was analysed by GC.

Total AKD was determined after acidic hydrolysis of 100 mg portion, for which 5 mL of 6M HCl was added. The mixture was heated for 1 h at 120 °C, and cooled and extracted several times by hexane so that the final volume of the extract amounted to 10 mL. The concentration of ketones corresponding to the total AKD was determined by GC. The difference between the total and the hydrolysed form represented the active form or activity if expressed as the percentage of active sizing agent in emulsion.

As the active lactonic form of AKD can not be detected directly by GC, it is necessary to hydrolyse the sizing agent to obtain the corresponding ketones which are easily chromatographed. Three ketones differing in the length of alkyl chains attached on both sides of carbonyl group are usually produced.

The C_{16}/C_{18} proportion was calculated from the chromatograms by integrating peak areas of the corresponding three ketones and chemical purity by integrating peak areas not belonging to AKD.

Bound and unbound AKD in paper samples was determined according to the procedure descrbied in reference nr. 7.

2.2.1 Gas chromatography (GC)

GC analyses were performed on HP 5890 at the following experimental conditions: capillary column SPB-1 (15 m) from Supelco, injector temp. 350 °C, split ratio 1:15, init. oven temp. 230 °C (0 min), heating rate 5 °C/min, final oven temp. 300 °C (10 min), det. FID temp. 350 °C, N_2 flow 1.5 mL/min. Major ketone peaks were integrated and their concentrations calculated from the calibration curve of the corresponding standard ketone mixture. Calibration was conducted by means of using the following concentrations of standard ketone mixture in hexane: (0.1; 0.5; 1; 2.5; 5; 7.5 and 10) mg/mL.

All experiments were performed in 5 parallels. Therefore, the results are the average values of individual determinations.

3 RESULTS AND DISCUSSION

All three tested sizing agents showed different chemical characteristics such as the content of active AKD and impurities, and the C_{16}/C_{18} proportion. Consequently, their technological behaviour in the chosen papermaking system varied. GC chromatograms are presented in **Fig-**

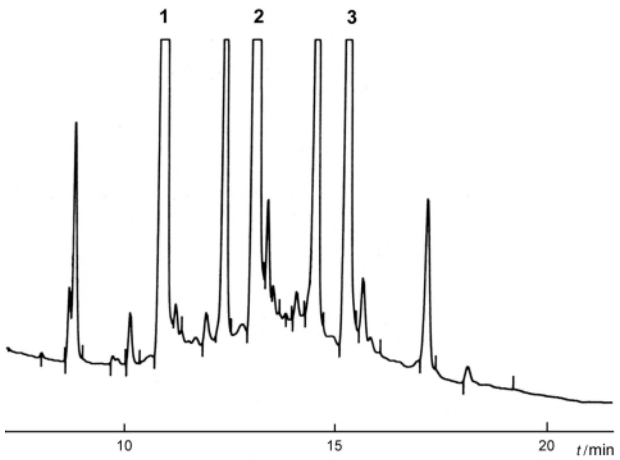

Figure 2: GC chromatogram of total AKD 1 (1-$C_{16}COC_{16}$, 2-$C_{16}COC_{18}$, 3-$C_{18}COC_{18}$)
Slika 2: Plinski kromatogram celotnega klejiva AKD 1 (1-$C_{16}COC_{16}$, 2-$C_{16}COC_{18}$, 3-$C_{18}COC_{18}$)

ures 2, **3** and **4,** and chemical properties are shown in **Table 1**.

AKD 1 had the most inhomogeneous structure and the highest content of impurities as it was obviously synthesized from impure raw materials (**Table 1**). Thus, its technological behaviour was highly inpredictable and its retention in paper web relatively poor. A substantial portion of it (up to 20 %) was therefore lost in process water.

AKD 2 had a much more uniform structure and performed better on paper machine. The sizing degree of the produced printing paper was high enough for it to be used

for most printing purposes. The GC chromatogram is presented in **Figure 3**.

AKD 3 proved to be the most efficient sizing chemical due to its homogeneous structure and higher activity

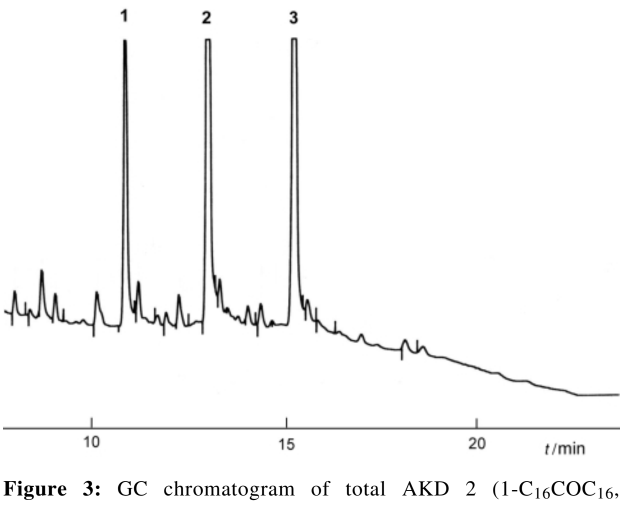

Figure 3: GC chromatogram of total AKD 2 (1-$C_{16}COC_{16}$, 2-$C_{16}COC_{18}$, 3-$C_{18}COC_{18}$)
Slika 3: Plinski kromatogram celotnega klejiva AKD 2 (1-$C_{16}COC_{16}$, 2-$C_{16}COC_{18}$, 3-$C_{18}COC_{18}$)

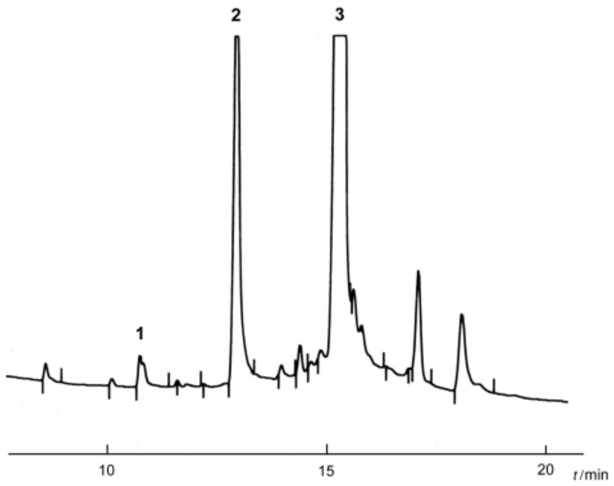

Figure 4: GC chromatogram of total AKD 3 (1-$C_{16}COC_{16}$, 2-$C_{16}COC_{18}$, 3-$C_{18}COC_{18}$)
Slika 4: Plinski kromatogram celotnega klejiva AKD 3 (1-$C_{16}COC_{16}$, 2-$C_{16}COC_{18}$, 3-$C_{18}COC_{18}$)

(**Table 1**, **Figure 4**). Its retention was the highest (95 %) and the sized papers manifested excellent printing properties. The longer C_{18} chain predominated in structure (peak 3) and had more favourable physical characteristics, for example a higher melting point which is an important factor on modern paper machines where we have to deal with increased temperatures caused by a high level of process water recycling.

Table 1: Chemical properties of tested AKD sizing agents
Tabela 1: Kemijske lastnosti preizkušanih AKD-klejiv

Sample	Activity (%)	Proportion C_{16}/C_{18}	Impurities (%)
AKD 1	4,8	50 : 50	33
AKD 2	5,2	38 : 62	8
AKD 3	6,4	6 : 94	6

As AKD 3 showed the most suitable chemical properties expected of a sizing agent, it was applied in four different production programmes of industrial label paper manufacture. The results of paper analyses for the content of total, bound and unbound portions as well as the proportion between the two forms are collected in **Table 2** and are expressed as mg AKD on kg of o.d. paper.

Table 2: AKD determination for different label paper grades
Tabela 2: Določitev vsebnosti AKD v različnih vrstah etiketnega papirja

Paper sample	Total mg/kg	Unbound mg/kg	Bound mg/kg	Proportion unbound/ bound
1	340	320	20	94 : 6
2	380	350	30	92 : 8
3	370	330	40	89 : 11
4	390	300	90	77 : 23

Though the amount of added AKD was the same in all four cases, the sizing agent behaved differently in the same papermaking system due to the changes of technological conditions, such as fiber composition, filler concentration, pH and basis weight of paper. The samples differ in the total amount of retained AKD as well as in adsorbed and chemically bound portions. Sample 4 exhibited the greatest sizing efficiency due to the good retention and the highest amount of esterified AKD, while the differences between other samples were not so distinctive. At the same time, this sample showed, due to its more homogeneous surface structure, better printing characteristics, such as lower liquid absorptivity and penetration of printing ink into fiber structure, as well as weaker bleeding effect [8, 9]. These parameters are of crucial importance for paper to be extensively used as printing material.

4 CONCLUSION

The chemical composition of individual AKD sizing chemical is strongly related to its performance in paper production. The higher is its activity, purity and content of longer C_{18} alkyl chains in the active lactonic molecule the better is its behaviour in the system. The retention of such an agent is usually very high and its distribution in the paper web convenient, meaning that a relatively large amount is chemically bound to fibers. The results of paper analyses for the content of different forms of chosen AKD indicated that the amount of chemically bound AKD is at the same time also strongly dependent on numerous technological parameters in paper production, such as fiber composition, filler concentration, pH of the system, process water temperature as well as drying temperature and time.

By means of chemical analyses, we are able to learn interesting facts about sizing mechanisms. The newly obtained knowledge may help optimise this important stage of the papermaking process.

5 REFERENCES

[1] E. Bobu: Old and new aspects on the AKD sizing system, Wochenblatt für Papierfabrikation (**2000**) 14/15, 976–981

[2] T. Lindström, G. Södberg: On the mechanism of sizing with alkyl ketene dimers. Part 1. Studies on the amount of alkyl ketene dimer required for sizing different pulps, Nordic Pulp and Paper Research Journal (**1986**) 1, 26–33

[3] A. Isogai, R. Taniguchi, F. Onabe, M. Usada: Sizing mechanism of alkylketene dimers. Part 1. Possibility for AKD to form β-ketoesters in papersheets, Nordic Pulp and Paper Research Journal (**1992**) 4, 193–199

[4] L. Odberg, T. Lindström, B. Liedberg, J. Gustavsson: Evidence for β-ketoester formation during the sizing of paper with alkylketene dimers, Tappi Journal 70 (**1987**) 3, 135–139

[5] J. Zule, J. Dolenc: Klejenje papirja z alkilketenskimi dimeri, Papir 30 (**2002**) 3/4, 94–97

[6] J. Zule, J. Dolenc: Kvantitativno vrednostenje AKD klejiva, Papir 31 (**2003**) 3, 27–28

[7] J. Zule, J. Dolenc: Determination of AKD sizing agents in papermaking systems by gas chromatography, Acta Chimica Slovenica 50 (**2003**) 1, 115–122

[8] R. N. Jopson: Improved surface performance, Paper 216 (**1991**) 6, 29–31

[9] T 558 om-95: Surface wettability and absorbency of sheeted materials using an automated contact angle tester, TAPPI Test Methods, TAPPI Press, Atlanta 2002