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THERMAL ANALYSIS IN THE CELLULOSE, PAPER AND TEXTILE INDUSTRY

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ABSTRACT

The present paper reports the main results presented at the 8th ICTA Conference on the thermal analysis of the cellulose, paper and textile industry. An attempt was made to classify the presentations.

Thermodestruction studies on cellulose allow the thermooxydative effect of various ions to be classified.

Experimental results give evidence that boron-containing cellulose fibres present a different combustibility mechanism than phosphorus-containing antipyrenes. The relaxation and phase transition of cellulose are evidenced by DTA and calorimetry and a classification of plasticisers is made.

An original clamping technique for TMA is presented to study very thin paper samples.

Interactions between dyes and fibers are analysed and a kinetic model, expressing sorbed dye rate, is proposed.

The use of microwaves in the textile industry is described for polymerization, thermal treatment and dyeing. It appears that the use of microwaves gives a very uniform dye migration with a 50 times higher kinetic rate for acrylic compounds and 200 times higher for viscose.

INTRODUCTION

In thermophysical research, paper, cellulose and cellulose derivatives are widely investigated. Posters were presented on various aspects, which can be classified as follows: thermal treatment and thermodestruction of cellulose and its derivatives; thermal analysis of cellulose, its derivatives and paper; and thermal analysis and thermal methods in the textile industry. These posters are summarized in this paper.

Thermal Analysis Highlights, 8th ICTA, Bratislava, Czechoslovakia.

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I. THERMAL TREATMENT AND THERMODESTRUCTION OF CELLULOSE AND ITS DERIVATIVES

Simkovic et al. presented a poster entitled "Thermooxidation of trimethylammoniumhydroxypropyl (TMAHP) cellulose depending on its anionic form" [1]. This work was carried out under oxidative and inert atmospheres using semi-quantitative DTA. The experimental results enabled a classification of thermooxidative effects of various ions to be established; this is a valuable result which may have applications in research and in industry.

Kogerman described the thermal destruction of some cellulose derivatives by stepwise pyrolysis [2]. The results indicated that boron-containing cellulose fibres undergo a different combustion mechanism than phosphorus-containing antipyrenes. This study allows one to determine the thermal stability of cellulose derivatives, which is important for industrial applications.

Skoropanov presented a poster entitled "Influence of ammonium chloride on the regenerated cellulose thermodestruction process" [3]. Viscose fibres were impregnated with aqueous ammonium chloride solutions of various concentrations between 1 and 7%, DTG and DTA techniques were applied under argon and air. The results showed that there are an "active" and an "inactive" form of the salt in regenerated cellulose. This result is an important contribution to cellulose science.

II. THERMAL ANALYSIS OF CELLULOSE, ITS DERIVATIVES AND PAPER

Uryash et al. presented a poster entitled "Thermal and calorimetric analysis of cellulose, its derivatives and their mixtures with plasticizers" [4]. DTA and vacuum adiabatic calorimetry were applied in the temperature range 4–600 K. Various cellulose derivatives were studied, as acetates, nitrates, acetobutyrate, ethylcellulose and their mixtures with various plasticizers (phthalate esters, triacetin, etc.). Diagrams of the physical states in the polymer–plasticizer binary system were displayed. From the temperature concentration dependence, relaxation and phase transition temperatures were observed and β-transitions as two glass transitions were studied. The results showed that the relaxation and phase transition temperatures increase with increasing replacement of hydroxide groups of cellulose by acetate groups. For cellulose nitrate with various nitrogen contents, the β-transition temperature increases with increasing replacement of hydroxyl groups with ONO_2 groups; this corresponds to an increase in polymer ordering with such a substitution. A classification of the efficiency of plasticizers was formulated, which is valuable especially for industrial applications.

Skripchenko et al. presented a poster entitled "Polyconjugated systems formed during thermal treatment of cellulose" [5]. A cellulose sulphate into which 5% of phosphoric acid was introduced at room temperature was studied from 20 to 500°C. Physico-chemical transformations of cellulose were investigated by DTA, TG and ESR and IR spectroscopy. The results showed that the number of polyconjugated blocks and their dimensions increase with increasing temperature. It was shown that phosphoric acid accelerates the dehydration of cellulose and increases the thermal stability of intermediate structures.

Toth et al. presented a poster entitled "Dynamic mechanical analysis of paper samples" [6]. A clamping technique for thin cellulose samples and small paper sheets was devised for investigations on paper ageing. This clamping technique, providing an arched sample cross-section, enables one to work on thin samples (below 0.1 mm), which are not easy to study with conventional apparatus.

Various paper samples were studied at 50% relative humidity in air. Experimental curves of resonance frequency and damping are similar to those of synthetic polymers. Aged samples show a broad damping maximum whereas the original samples have a constant damping level. This interesting subject was also studied by Wiedemann [7], who applied DTA, TG, TMA and thermomicroscopic techniques to papyrus and ancient paper materials. Differences in thermal behaviour and the shape and position of peaks may be ascribed to changes in composition due to "paper technology" or the influence of fungi. These thermoanalytical methods are also valuable for studies of ancient chinese silk materials and their production methods.

III. THERMAL ANALYSIS AND THERMAL METHODS IN THE TEXTILE INDUSTRY

Popescu et al. presented a poster entitled "Thermal analysis in the textile industry" [8] and described studies of cotton and wool fibres dyed with direct or acid dyes. Interactions between dyes and fibres were analysed. Results obtained with a MOM derivatograph allowed the identification of the nature of the fibre and the class of dye used for dyeing.

Another poster by the same group was entitled "Non-isothermal kinetic method for the analysis of dyeing processes" [9]. Three steps were considered: transfer of dye from the solution to the fibre surface, absorption of the dye on the fibre surface and diffusion from the fibre surface to the bulk. A dyeing diagram was presented, together with equations for expressing the sorbed dye fraction versus time and the heating profile versus sorbed dye fraction and activation energy. These interesting considerations may be developed into an industrial process.

The poster by Karmazsin and Satre, entitled "Use of continuous and pulsed microwaves for quick polymerization of epoxy resins: study of some thermomechanical properties" [10], was realized in collaboration with the

French Textile Institute, Lyon. The mechanical and thermomechanical properties of an epoxy resin, polymerized under continuous or pulsed microwave energy in a few minutes, were compared with those of the same resin polymerized for 1 h at 100°C in a conventional furnace. The results indicate that the use of microwave energy not only allows an important gain of time, but also gives better mechanical and thermomechanical properties. This assertion was confirmed by further work. The use of microwave energy is very valuable in the cellulose, paper and textile industry.

In the conventional paper industry, energy represents 20% of the total costs and half of this energy is used for drying. The industry uses water to transport cellulose fibres, so the drying phase is very important; 1.5 kg of water must be evaporated per kg of paper and most of the properties (mechanical resistance, permeability to air, etc.) are developed during this operation. Conventional drying of paper is achieved through several mechanical and thermal steps in which the last 5 or 10% of water must be removed by very energetic methods, which may lead to overdrying, which is expensive and harmful to the final quality of the paper [11]. With microwave techniques there is an isotropic repartition of water, with the same rate of drying in each direction and no overdrying, so not only is energy saved but the paper quality is increased [12].

The textile industry uses 12% of the overall industrial power consumption. For drying, conventional hot air needs 7 therms per litre of water evaporated for polyester cotton whereas microwave techniques need only 1.2–2 therms for the same result [13]. The thermal treatment is very short (30–60 s) and the polyester does not degrade or turn yellow.

Microwaves are also very valuable in the dyeing industry. For instance, with conventional heating, dye migration is often observed, giving a non-uniform result. This problem does not occur with microwave techniques.

It is possible to achieve dye fixation by microwave techniques on cotton textiles without any water vapour. Good results have been obtained with wool and polyamide with the same efficiency for acid dyes as with conventional techniques [14,15], but the dye fixation kinetic rates are 25–50 times higher with microwave techniques; for instance, on viscose the dye fixation rate is 200 times higher. For acrylic products the efficiency with respect to the basic components is the same as in the vapour phase (with conventional heating) but the dye fixation rate is 50 times higher.

The use of microwaves is finding increasing applications in the cellulose, paper and textile industries as research in this field is expanding.

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