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Surface modified cellulose obtained by acetylation without solvents of bleached and unbleached kraft pulps

Summary — Heterogeneous acetylation to a low extent of bleached and unbleached commercial kraft pulps was performed with acetic anhydride without solvents and in the presence of sulfuric acid catalyst. The process was conducted in an effort to change the polarity of studied kraft pulps and to improve their compatibility with synthetic polymers without changing their fibrous structure. It was observed that the fiber morphology does not change up to a reaction time of 3 h for both investigated materials. The hydrophilic character of the bleached pulp was decreased by acetylation to a low extent, while the unbleached material showed an initial increase of water retention capacity. At higher degrees of modification, both pulps exhibited similar hydrophilic properties. For both materials, an initial slightly increased susceptibility to enzymatic attack with cellulase from *Trichoderma reesei* was observed, however the acetylated bleached cellulose fibers were more susceptible to enzymatic attack than those of the unbleached material.

Keywords: cellulose, acetylation, crystallinity, FT-IR, X-ray diffraction analysis.

CELULOZA MODYFIKOWANA POWIERZCHNIOWO OTRZYMANA METODĄ ACETYLOWANIA BEZ ROZPUSZCZALNIKÓW BIELONEJ I NIEBIELONEJ CELULOZOWEJ MASY SIARCZANOWEJ

Streszczenie — Używając bezwodnika octowego przeprowadzono bez rozpuszczalników, w obecności kwasu siarkowego jako katalizatora, heterogeniczne acetylowanie bielonej (AC) i niebielonej (ACM) celulozowej masy siarczanowej (rys. 1 i 3). Miało to na celu zmianę jej polarności i poprawę kompatybilności z tworzywami polimerowymi bez zmiany struktury włókien celulozy. Badano wpływ czasu trwania tego procesu na właściwości otrzymywanych próbek. Zaobserwowano, że w przypadku obu rodzajów masy celulozowej (AC i ACM) morfologia włókien nie ulega zmianie jeżeli proces prowadzi się nie dłużej niż 3 h (rys. 6). Hydrofilowy charakter bielonej masy celulozowej uległ zmniejszeniu dzięki przeprowadzonemu w niewielkim stopniu acetylowaniu. Próbki niebielonej masy charakteryzował początkowo wzrost zdolności pochłaniania wody, ale przy wyższych stopniach acetylacji oba rodzaje mas wykazywały taki sam charakter hydrofilowy. W przypadku obu mas podatność na enzymatyczny atak z użyciem celulozy pochodzącej z *Trichoderma reesei* początkowo słabo wzrastała ze wzrostem stopnia acetylacji, aby następnie zmniejszyć się do poziomów niższych niż początkowe. Włókna bielonej i acetylowanej celulozy były bardziej wrażliwe na ten atak niż te zawarte w niebielonej próbce (rys. 9).

Słowa kluczowe: celuloza, acetylowanie, krystaliczność, FT-IR, dyfrakcyjna analiza rentgenowska.

Cellulose and its derivatives have drawn much attention in recent decades for their applications in various areas of modern life, as a consequence of the high versatility, renewability, non-toxicity and abundance of this natural polymer. One of the most studied cellulose polymer, cellulose acetate, is well known for its applications in plastics, textile fibers, separation membranes, medical and technological products, etc. Also, cellulose fibers exhibit specific properties that focused the interest toward their use as reinforcing fillers in polymeric composites [1—6].

Many physical and chemical methods are available to improve the compatibility and surface adhesion between natural fibers and synthetic polymers [7—9]. Thus, heterogeneous acetylation is one suitable way to reduce the high polarity of cellulose fibers and to increase their hydrophobic character. In numerous papers, a variety of condition to perform heterogeneous acetylation of cellulose as well as different goals for the final products utilization is reported. This acetylation reaction may be rea-

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lized with [10, 11] or without [12, 13] organic solvents as reaction media. Thus, Frisoni *et al.* [12] modified the surface properties of fibers from flax by heterogeneous acetylation with acetic anhydride and sulfuric acid as catalyst in order to obtain biodegradable fibers for application as polymer composite reinforcements. Cellulose from commercial cotton was acetylated without solvents by Adebajo *et al.* [14] in an attempt to develop hydrophobic materials for application in oil spill cleanup.

Recently, other procedures have been developed for solvent-free acetylation with acetic anhydride using iodine as a catalyst [15—17]. Iodine is also reported as an excellent catalyst for heterogeneous acetylation of sisal cellulose [18]. Fibrous acetates with lower degrees of substitution obtained by heterogeneous acetylation are also suitable for other applications like hydrophobic biodegradable sorbent materials [12—14].

The aim of the present work was to modify the ratio of the hydrophilic/hydrophobic properties of cellulose fibers from bleached and unbleached kraft pulps in order to improve their compatibility with synthetic polymers without changing their fibrous structure. For this purpose, surface acetylation to a low extent was achieved by a heterogeneous procedure without solvents using acetic anhydride and in the presence of sulfuric acid as a catalyst. According to our knowledge, such a procedure was not previously applied to kraft pulps in order to change their polarity. Structural modification of cellulose fibers were investigated by means of FT-IR spectroscopy, X-ray diffractometry and scanning electron microscopy (SEM) methods. The variation of water and gas oil retention capacity of both acetylated celluloses was followed as a function of acetylation degree. The biodegradability of acetylated pulps was also comparatively investigated by means of enzymatic hydrolysis with cellulase from *Trichoderma reesei*.

EXPERIMENTAL

Materials

The bleached and unbleached kraft pulps were commercial batch cooked pulps supplied by Södra Cell Varö Sweden. The spruce (*Picea abies*) to pine (*Pinus sylvestris*) ratio was 79:21. The relative hardness described by kappa number equals 26.8 and 3.2 for unbleached and bleached pulps, respectively. Intrinsic viscosity was equal to 1109 and 728 cm^3/g for unbleached and bleached pulps, respectively.

Both pulps were wet-defibrated and air-dried at room temperature for several days then oven-dried at 80 °C for 24 h.

The enzyme used for biodegradability studies was a cellulase complex from *Trichoderma reesei* supplied by Fluka.

Other chemicals (acetic anhydride, sulfuric acid, sodium acetate) were of reagent grade and were used without further purification. Acetic anhydride was supplied by Merck and sulfuric acid and sodium acetate were purchased from Sigma-Aldrich.

Acetylation process

1.5 g of each sample were suspended in a mixture of 7.5 cm^3 of acetic anhydride and 0.015 cm^3 of sulphuric acid 98 wt. % (used as a catalyst) and vigorously stirred.

Acetylation was performed at 30 °C for different reaction times: 1, 3, 5 or 24 h. When the desired reaction time expired, each sample was separated from suspension by filtration, then washed several times with distilled water and air-dried at room temperature.

Methods of testing

X-ray diagrams for cellulose acetates were recorded on a diffractometer Bruker AXS D8 Advance with CuKα radiation.

FT-IR spectra (attenuated total reflectance, ATR) were recorded with a spectrometer Bruker VERTEX 70, in the frequency range 600—4000 cm^{-1}.

Scanning electron microscopy and energy dispersive X-ray (SEM-EDX) analyses were performed by means of a system SEM/ESEM-EDAX Quanta 200.

DSC analysis was carried out on a differential calorimeter Mettler DSC 12E at a heating rate of 10 deg/min. Before measurements, samples have been conditioned for 48 h at 25 °C and 65 % humidity.

For determination of gas oil retention capacity (amount of g of gas oil retained by 100 g of dried material), the dried samples have been immersed in gas oil for 24 h, then centrifuged at 3000 rpm for 2 min and weighted.

Enzymatic degradation experiments were performed in aqueous suspensions as follows: 0.2 g of an oven-dried (2 h at 105 ± 2 °C) sample was suspended in 40 cm^3 acetate buffer (0.05 M sodium acetate) containing 0.2 cm^3 of a *Trichoderma reesei* cellulase solution (0.6 g/10 cm^3 in acetate buffer). Samples were allowed to hydrolyze for 260 h at 25—28 °C, then filtered out and washed with distilled water. The final step was drying at room temperature then in oven for 2 h at 105 ± 2 °C. The susceptibility to enzymatic attack was evaluated by % weight loss of the initial sample.

RESULTS AND DISCUSSION

FT-IR spectra, presented in Figure 1, provide evidence of structural modification of bleached (AC) and unbleached (ACM) cellulose fibers during acetylation in the studied conditions.

Thus, spectra of acetylated samples show three new bands characteristic to acetyl group vibration at about 1740—1750 cm^{-1} (carbonyl C=O stretching), 1368 cm^{-1} [C-H bond bending in $-O(C=O)-CH_3$] and 1230—1240 cm^{-1} (C-O stretching of acetyl group) [12—14]. The

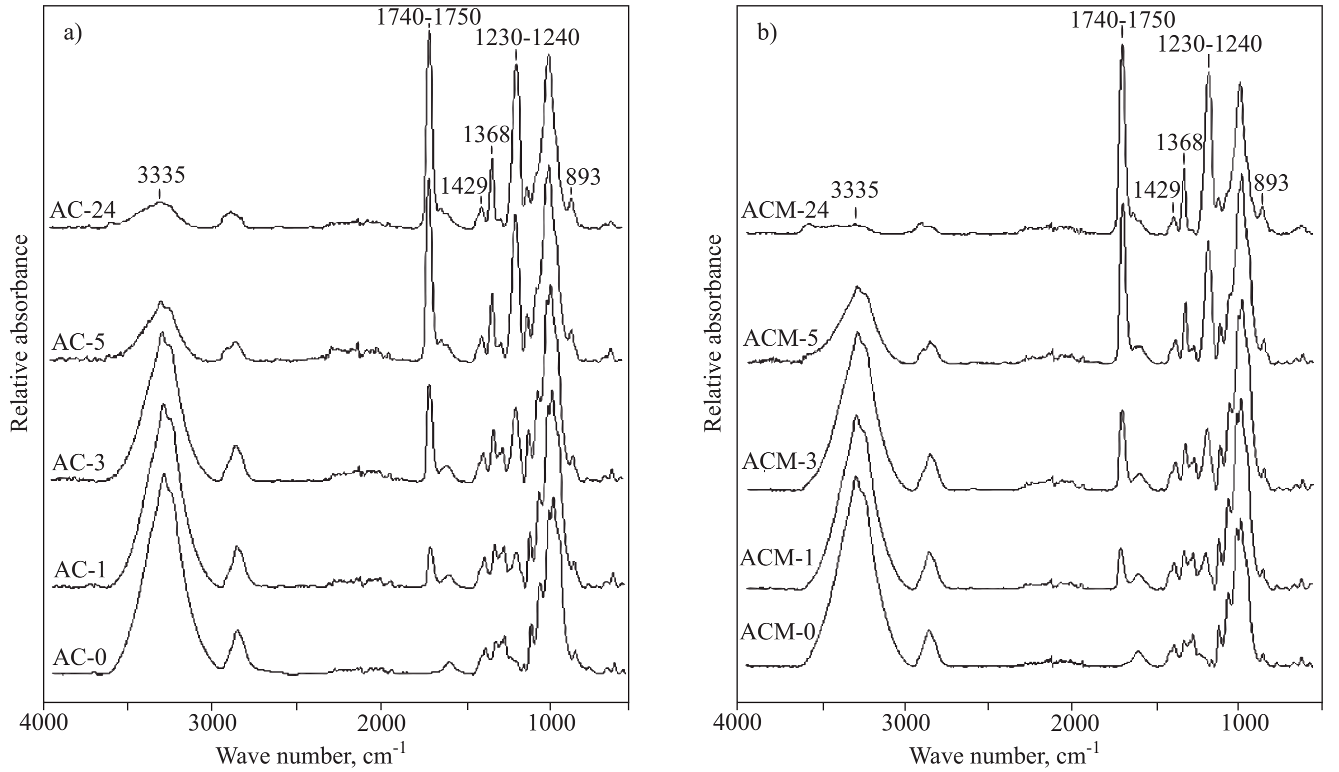

Fig. 1. FT-IR spectra of bleached (a) and unbleached (b) cellulose pulps before (AC-0, ACM-0) and after heterogeneous acetylation for 1 h (AC-1, ACM-1), 3 h (AC-3, ACM-3), 5 h (AC-5, ACM-5), and 24 h (AC-24, ACM-24)

intensity of these bands increases with increasing the acetylation time. Simultaneously, it was observed that with the increase of reaction time the intensity of the band at 3335 cm^{-1} attributed to cellulose OH groups stretching vibrations progressively diminishes in the acetylated samples.

FT-IR spectra can also be used as a measure of crystallinity in cellulose. In literature several absorbance ratios between infrared absorptions such as $A(1372\ cm^{-1})/A(2900\ cm^{-1})$ and $A(1429\ cm^{-1})/A(893\ cm^{-1})$ for measuring crystallinity in unmodified cellulosic materials [19] are proposed. In the case of acetylated cellulose, the band at 1372 cm^{-1} attributed to C-H bending mode is overlapped with the band at 1375 cm^{-1} characteristic to acetyl group (C-CH_3 stretching and C-H bending vibration), therefore the ratio $A(1372\ cm^{-1})/A(2900\ cm^{-1})$ cannot be used as a measure of crystallinity. Instead of this, the band at 1429 cm^{-1} corresponding to CH_2 scissoring mode vibration and the band at 893 cm^{-1} corresponding to the vibration of anomeric C_1 [19, 20] are not overlapped with other bands of acetylated celluloses. Crystallinity (CR_{FT-IR}) for our cellulosic materials could be estimated in that case using ratio:

$$CR_{FT-IR} = \frac{A(1429\,\mathrm{cm}^{-1})}{A(893\,\mathrm{cm}^{-1})} \tag{1}$$

Figure 2 shows the evolution of CR_{FT-IR} during acetylation. It can be seen that in the first 3 hours of reaction, CR_{FT-IR} does not change significantly since the acetylation process takes place mainly in amorphous regions.

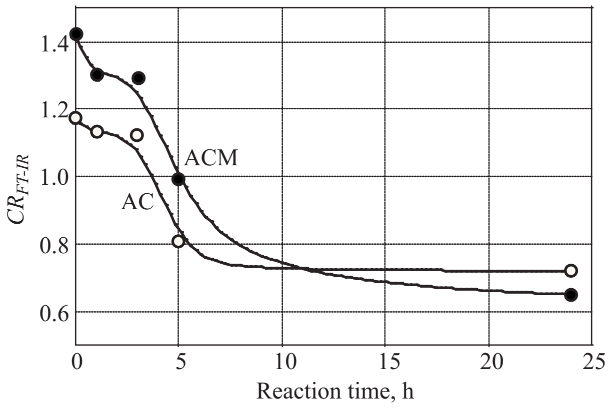

Fig. 2. FT-IR crystallinity ratio (CR_{FT-IR}) as a function of reaction time for bleached (AC) and unbleached (ACM) samples

X-ray diagrams presented in Figure 3, of bleached and unbleached samples also revealed no significant change of crystallinity for both celluloses during acetylation in the first 3 hours of reaction (AC-3 and ACM-3 samples). At higher levels of modification, the intensity of the peak at $2\Theta = 22°$ decreases and the peaks at $14 < 2\,\Theta < 16°$ are broadened. Also, new and broad reflection peak in the 2Θ range from 5° to 10° characteristic to cellulose acetate appears. These modifications in the crystalline structure of cellulosic substrates are consistent with variation of CR_{FT-IR}, as evidenced in Figure 2. A good correlation of CR_{FT-IR} with empirical crystallinity index (*CRI*) by Segal *et al.* [21] is found. *CRI* is defined by equation:

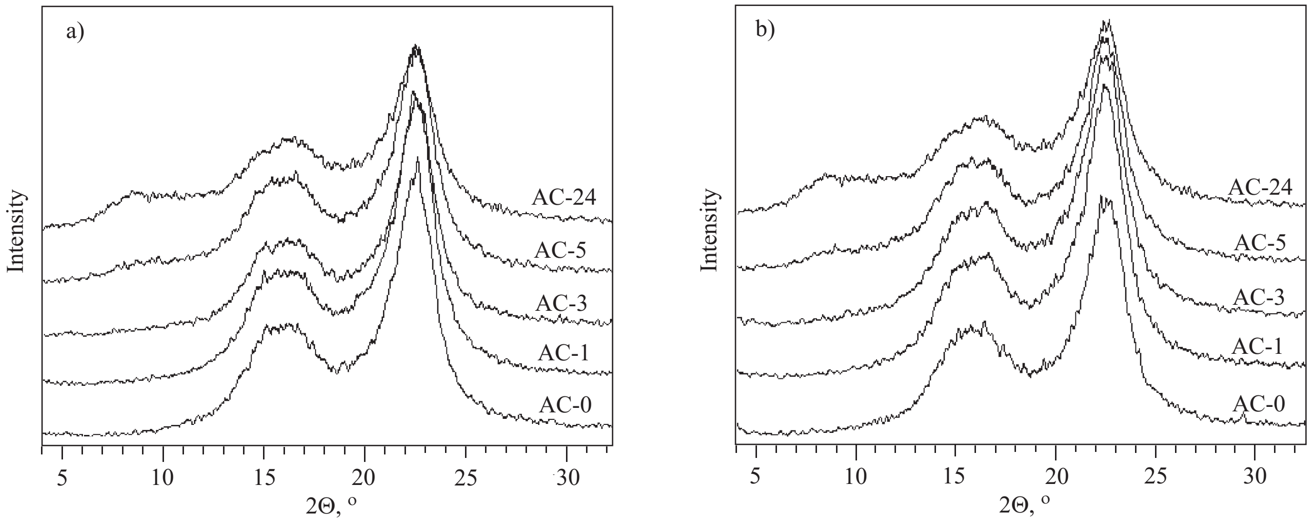

Fig. 3. X-ray diagrams of bleached (a) and unbleached (b) pulps before (AC-0, ACM-0) and after heterogeneous acetylation for 1 h (AC-1, ACM-1), 3 h (AC-3, ACM-3), 5 h (AC-5, ACM-5) and 24 h (AC-24, ACM-24)

$$CRI = \frac{I_{002} - I_{AM}}{I_{002}} \cdot 100 \qquad (2)$$

where: I_{002} — *the intensity of the 002 reflectance,* I_{AM} — *the minimum intensity at* $2\Theta = 18°$.

The graphical representation of those correlations for bleached and unbleached cellulose is presented in Figure 4. The correlation coefficient *R* is equal to 0.934, and 0.988 for AC and ACM samples, respectively.

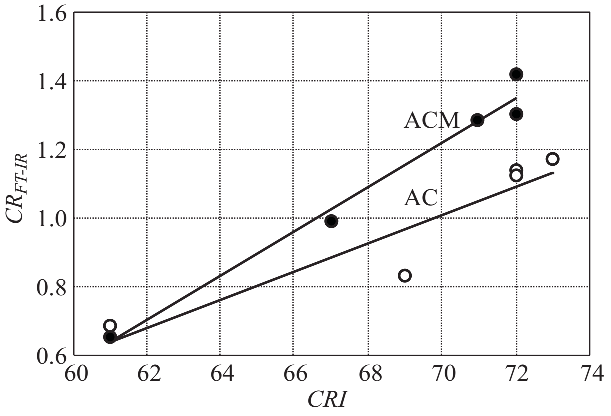

Fig. 4. Correlation of $CR_{FT\text{-}IR}$ *with CRI*

The extent of acetylation was estimated using FT-IR spectra by calculating the ratio (*r*) between the absorbance of the C=O stretching band at 1740—1750 cm^{-1} and the intensity of the C-O stretching band of the cellulose backbone at about 1020—1050 cm^{-1}:

$$r = \frac{A_{C=O}}{A_{C-O}} \qquad (3)$$

As it was shown in Figure 5 there is no important difference in reactivity between the two materials. This is probably because, in the reaction medium a fraction of the lignin in ACM sample is removed and similar accessibilities of OH groups in both materials can be achieved. Similar results were described in [6].

SEM micrographs depicted in Figure 6 show no significant change of morphology for both bleached and unbleached pulps after 1 h as well as 3 h of acetylation. Prolonged reaction time produces morphology changes that can be associated with reduced surface areas of the fibers.

The results of EDX analysis is presented in Figure 7. Potential sulfate esters deriving from the use of sulfuric acid as reaction catalyst have not been detected in the reaction product. The peaks corresponding to the energy level of sulfur atoms (designed by symbol S) have the same intensities as in the starting materials.

As a consequence of surface acetylation performed in heterogeneous conditions, variations of accessibility and hydrophilic properties during the process are expected. Curves shown in Figure 8 (a and b) depict the evolution of water retention capacity and gas oil retained, respectively, for AC and ACM samples as a function of different degrees of modification. Water retention capacity of the

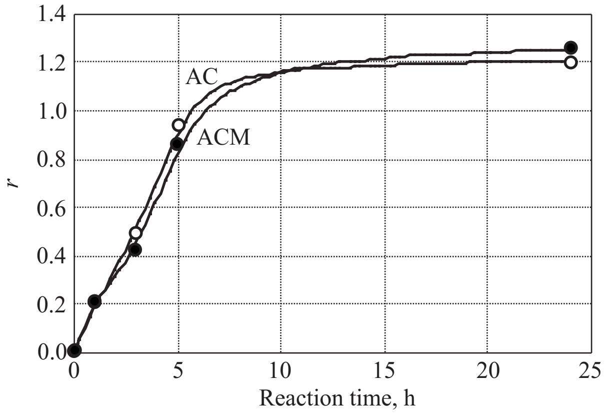

Fig. 5. Degree of modification (r) of acetylated bleached (AC) and unbleached (ACM) samples

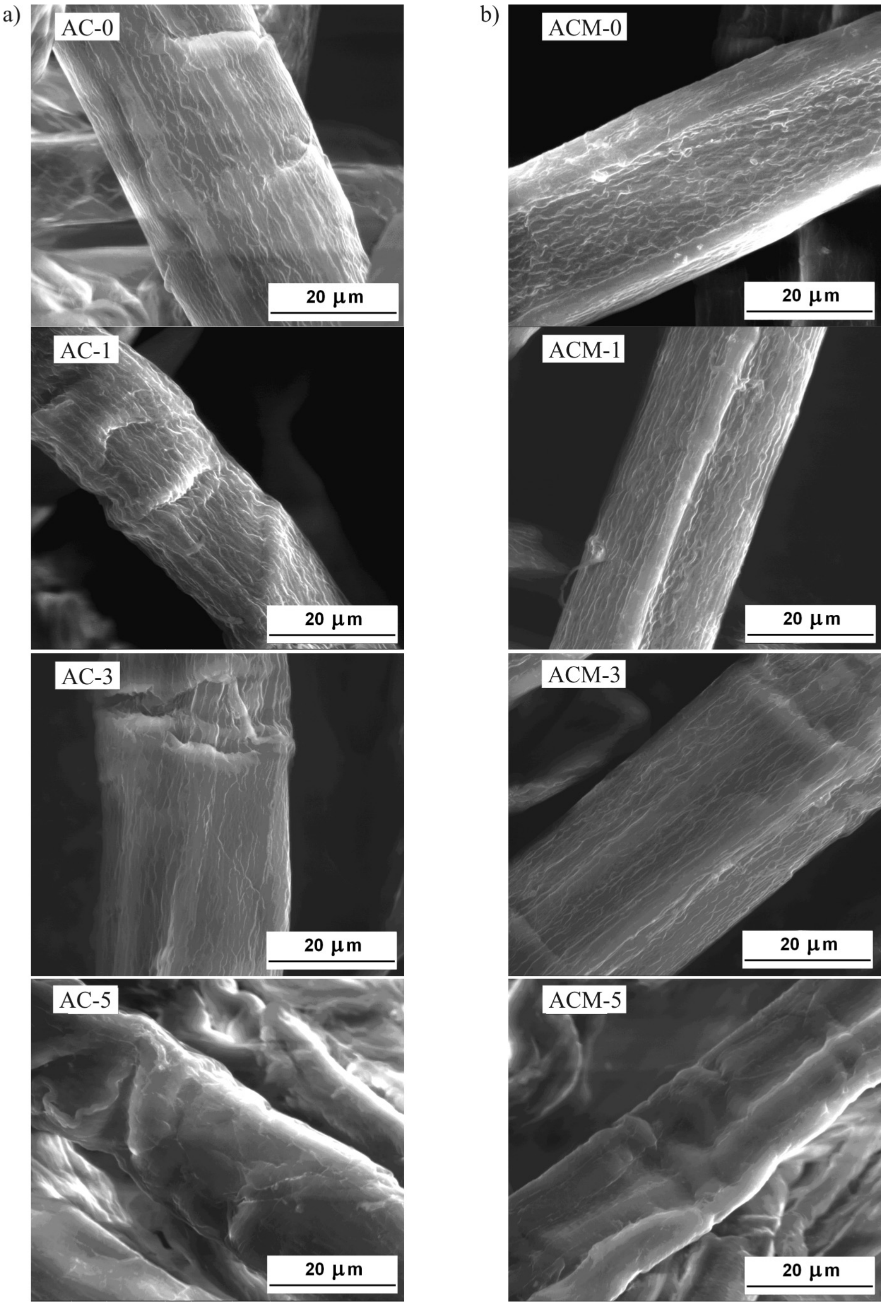

Fig. 6. SEM micrographs of bleached (a) and unbleached (b) pulps before (AC-0, ACM- 0) and after acetylation for 1 h (AC-1, ACM-1), 3 h (AC-3, ACM-3), and 5 h (AC-5, ACM-5)

acetylated pulps, which depends on the number of hydroxyl groups available to absorb water molecules, was estimated as areas of endothermic peaks in DSC thermograms corresponding to water loss (the dehydration enthalpy is proportional to peak area [22]). All the areas were measured for 1 mg of the sample (Fig. 8a).

In the case of unmodified pulp, this capacity is slightly lower for unbleached cellulose (ACM) due to the presence of lignin which is less hydrophilic than cellulose. It is observed that the bleached cellulose undergoes a pronounced decrease of hydrophilic character by introducing acetyl groups even for a low degree of modification, *r* about 0.2. At this point, curve AC demonstrates the lowest peak area (Fig. 8a), and correspondingly, the highest percent of gas oil retained (Fig. 8b). This fact suggests that the most accessible OH groups in the amorphous domain of bleached cellulose were acetylated within the first hour of reaction. When AC pulp is allowed to react for 3—5 hours, peak area increases, though the degree of acetylation is increased. This is probably caused by rearrangement of macromolecules in the amorphous region, so that more hydroxyl groups become available to water molecules. Therefore, acetylation only to a low extent (*r* about 0.2) is adequate to reduce the hydrophilic character of bleached kraft pulp. On the contrary, the unbleached pulp (curves ACM in Fig. 8) exhibits an increase of hydrophilic character for low degree of acetylation, probably due to partial removal of lignin

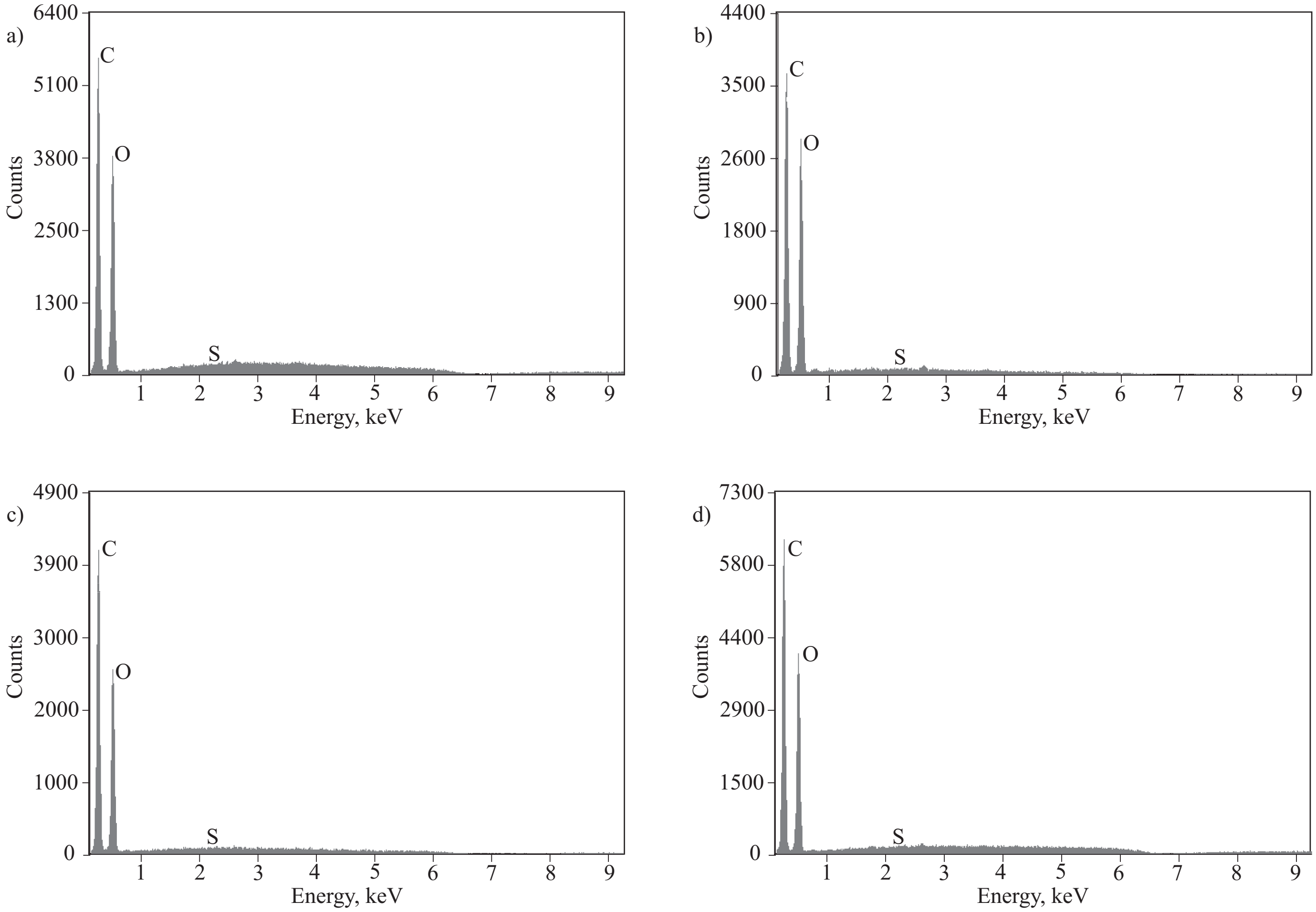

Fig. 7. EDX spectra of samples: a) unmodified bleached (AC-0), b) unbleached (ACM-0) pulps, c) 5 h acetylated bleached (AC-5), d) 5 h acetylated unbleached (ACM-5)

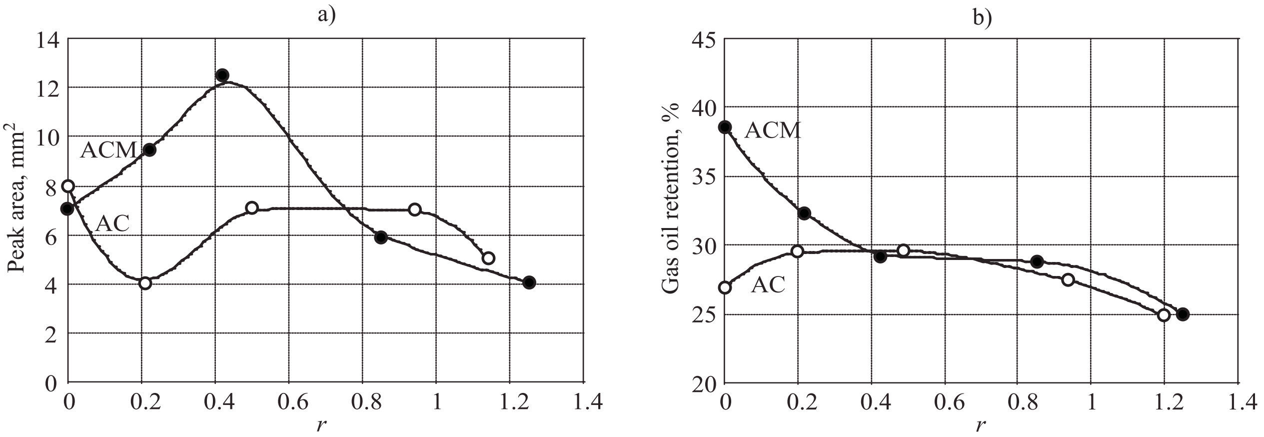

Fig. 8. Peak areas from DSC curves (a) and gas oil retained (b) for bleached (AC) and unbleached (ACM) pulps as a function of degree of modification (r)

during acetylation which may increase the accessibility of OH groups to water molecules. For higher degree of modification, the affinity to water decreases for both AC and ACM pulps, as a result of higher amount of hydrophobic acetyl groups introduced in cellulose matrix. Curves in Fig. 8b show a constant level of the amount of gas oil retained by bleached and unbleached samples acetylated for 3 to 5 hours.

Biodegradability of the two materials investigated in this paper is determined by their susceptibility to cellulase attack. As shown in Figure 9 both acetylated celluloses exhibit a slightly increased weight loss at low degree of modification ($r \approx 0.2$) probably because in the early stage of acetylation cellulose substrates are activated and subsequently become more accessible to enzymatic complex. The decrease of biodegradability occurs with increasing the degree of acetylation of the fibers because the formation of the complex enzyme-substrate is hindered by higher amount of acetyl groups. It is also observed that due to the presence of lignin, all unbleached samples are less susceptible to enzymatic attack than the bleached substrates.

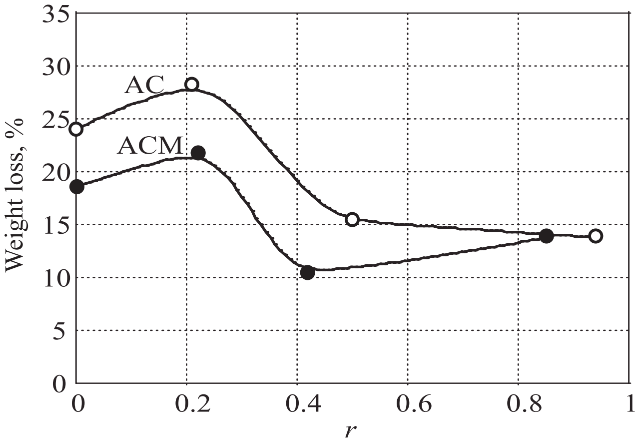

Fig. 9. Weight loss after enzymatic degradation of initial and acetylated bleached (AC) and unbleached (ACM) kraft pulps as a function of degree of modification (r)

CONCLUSIONS

Heterogeneous acetylation of bleached and unbleached pulps was successfully performed without solvents and in the presence of sulfuric acid as a catalyst. Both investigated materials exhibit almost the same reactivity and similar crystallinity modifications during acetylation. The hydrophilic character of the bleached pulp was decreased by acetylation to a low extent (r about 0.2), while the unbleached material showed an initial increase of water retention capacity (r about 0.4) followed by a pronounced decrease for higher values of r. At higher levels of modification ($r > 0.7$), both pulps exhibit almost the same water retention values and percent of gas oil retained. The acetylated bleached cellulose fibers are more susceptible to enzymatic attack than those of unbleached material.

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