Journal of Thermal Analysis and Calorimetry, Vol. 82 (2005) 129–135

# EFFECT OF THE FIBRE-FORMING MATERIAL STRUCTURE AND SILICA NANOPARTICLES

## Thermal properties of alginate fibres

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The paper discusses the thermal properties of alginate fibres made from alginic acid or sodium alginate and from alginates substituted with divalent metal ions during the fibre-forming stage. Alginate fibres with an addition of silica nanoparticles have also been examined. The selection of fibre-forming parameters was intended to obtain the best either sorption or strength properties depending on the specific fibre application. Thermal curves of the fibres under investigations obtained by means of a derivatograph under air atmosphere and differential scanning calorimetry (DSC) under neutral gas atmosphere have been interpreted from the view of physical and chemical changes in the fibre-forming material. Based on thermogravimetric curves, the fibre thermal stability indices have been determined. It has been found that the addition of silica nanoparticles exerts a positive influence on the thermal properties of the examined fibres.

**Keywords:** *alginate fibres, nanoparticles, thermal properties*

## Introduction

Alginate fibres find wider and wider use in the manufacture of modern dressing materials adapted to the type and stage of wound heeling. Their basic advantages are associated with high absorption properties and capabilities to gelatinise under the influence of wound pus, which makes it possible to painlessly remove the dressing, especially important in the case of bedsores difficult to heel and post-burn wounds [1–5]. Sodium alginate fibres can gelatinise completely [6], while this capability of calcium alginate fibres depends on the predominance of guluronic acid blocks ($G$) or mannuric acid blocks ($M$) [7] in the fibre-forming material. The $M/G$ ratio affects also the character of the gel being formed (rigid or elastic gels), its thermo-mechanical properties and dynamic modulus. These parameters depend also on the degree of transition of sodium alginate into calcium alginate. From the studies on calcium alginate hydrogels it follows that the degree of transition is also connected with the immersion time [8]. In the case of alginate fibres, the immersion time is very short and the transition degrees are at similar levels. Good sorption properties of alginate fibres are connected with the hydrophilic character of the fibre-forming material as well as with its porous structure formed during fibre formation [9].

Thermal properties of alginate fibres may be associated with the chemical composition of the fibrous materials such as alginic acid, sodium alginate or alginates substituted with various divalent metal ions during the fibre spinning process. The thermal properties may be also dependent on the character of porous structure and the quantity of incorporated silica nanoparticles into the fibres. The knowledge of thermal changes taking place in various alginate fibres is important because of the utilisation of waste dressing materials or hospital's linen.

The fibres made from calcium alginate containing an addition of silica nanoparticles may constitute a precursor to carbon fibres that owing to the presence of calcium and silicon should assist in the process of bone restoration. Thus, it is important to assess the effect of silica nanoparticles on the thermal changes in calcium alginate fibres in connection with the selection of parameters for the carbonisation of the modified precursor.

The objective of the present study was to assess the yet unreported effect of silica nanoparticles on the chemical changes in calcium alginate fibres and the relationship between the fibre-forming material structure and the thermal stability of various alginate fibres.

### *Object of study*

The object of our study included the following fibres developed by us:

- Fibres made from sodium alginate, alginic acid or zinc alginate designed for the manufacture of modern active dressing materials.

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1388–6150/$20.00

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- Fibres made from copper alginate designed mainly for the manufacture of hospital linen and pressure dressings.
- Precursor calcium alginate fibres containing silica nanoparticles in amounts of 3 and 5% in relation to the polymer mass. The particle size of silica (product AGH University of Science and Technology in Cracow) used by us ranged from 50 to 100 nm as determined by electron microscopy.

During developing the manufacturing conditions for these fibres, the selection of fibre forming parameters was intended to obtain the best sorption or strength properties depending on their specific application. In the case of precursor alginate fibres, the aim was to obtain strength properties that would be appropriate for the carbonisation process with a higher porosity of fibres at the same time. This feature is desirable due to the use of carbon fibres as osteoconductive and osteoproductive materials.

Fibres were spun from 7–7.5% aqueous solutions of sodium alginate, Protanal LF 20/60 (product FMC Biopolymer AS), with a predominance of blocks derived from guluronic acid. The apparent dynamic viscosity ranged from 42 to 43 Pas. The fibres were spun with the use of a laboratory spinning machine, whose construction made it possible to stabilise the technological parameters at a required level under continuous control, using spinnerets with 500 orifices, 0.08 mm in diameter each.

The solidification of sodium alginate fibres was carried out in a bath containing ethyl alcohol under conditions given in [6]. Fibres from alginates substituted with divalent metal ions were solidified in a bath containing chlorides of these metals in a quantity of 3%, while those from alginic acid in a bath of 2% HCl.

The fibres substituted with divalent metal ions were drawn in two stages: in a plasticising bath with the same concentration as the solidification bath at 50–75°C and then under superheated steam at a temperature of 140°C. Sodium alginate fibres were drawn in a 75% solution of ethyl alcohol at a low temperature of 10–15°C, while the fibres of alginic acid were drawn in an aqueous plasticising bath at 50–70°C. After rinsing, the fibres were dried at 20–60°C under isothermal conditions (sodium alginate fibres were not rinsed).

The characteristics of the fibres are given in Tables 1 and 2.

Generally, the fibres of alginate substituted with divalent metal ions are characterised by high values of moisture absorption at 65% RH at a level of

**Table 1** Sorption and strength properties of alginate fibres made under the optimal conditions for the given type of fibres

| Sample symbol | As-spun draw ratio/% | Total draw ratio/% | Moisture absorption at 65% RH | Moisture absorption at 100% RH | Water retention/% | Tenacity/ cN tex$^{-1}$ |
|---|---|---|---|---|---|---|
| Alg.Ca | 70.37 | 54.65 | 23.21 | 45.68 | 69.68 | 23.53 |
| Alg.Ca$_{3\%\mathrm{SiO}_2}$ | 60.00 | 63.66 | 23.48 | 46.42 | 69.44 | 19.93 |
| Alg.Ca$_{5\%\mathrm{SiO}_2}$ | 90.23 | 59.03 | 22.36 | 45.58 | 66.35 | 19.29 |
| Alg.acid | 120.00 | 17.72 | 15.53 | 20.15 | 165.00 | 16.05 |
| Alg.Na | 32.00 | 25.00 | 22.65 | 52.08 | 177.04* | 13.23 |
| Alg.Zn | 30.50 | 64.63 | 25.00 | 43.06 | 101.53 | 21.24 |
| Alg.Cu | 119.90 | 73.25 | 21.35 | 37.58 | 61.54 | 21.41 |

*Percentage of water absorbed by sodium alginate fibres from a moist substrate for 1 h; Alg.Ca – calcium alginate fibres; Alg.Ca$_{5\%\mathrm{SiO}_2}$ – calcium alginate fibres containing 5% of silica nano-particles per polymer; Alg.Ca$_{3\%\mathrm{SiO}_2}$ – calcium alginate fibres containing 3% of silica nano-particles per polymer; Alg.acid – alginic acid fibres; Alg.Na – sodium alginate fibres; Alg.Zn – zinc alginate fibres; Alg.Cu – copper alginate fibres

**Table 2** Total pore volume, internal surface and percentages of capillary sets of alginate fibres

| Sample symbol | Total pore volume/ mm$^3$ g$^{-1}$ | Internal surface of pores/ m$^2$ g$^{-1}$ | Percentage pore content/% | | | |
|---|---|---|---|---|---|---|
| | | | small 4–12.3 μm | medium 12.3–75 μm | large 75–750 μm | very large 750–7500 μm |
| Alg.Ca | 54.32 | 1.80 | 6.82 | 0.0 | 11.36 | 81.72 |
| Alg.Ca$_{3\%\mathrm{SiO}_2}$ | 91.25 | 4.53 | 18.07 | 8.22 | 10.96 | 65.75 |
| Alg.Ca$_{5\%\mathrm{SiO}_2}$ | 90.70 | 5.53 | 16.67 | 11.54 | 10.26 | 61.53 |
| Alg.acid | 58.73 | 3.88 | 18.93 | 21.62 | 13.52 | 45.95 |
| Alg.Na | – | – | – | – | – | – |
| Alg.Zn | 47.67 | 1.60 | 9.76 | 0.0 | 7.2 | 82.90 |
| Alg.Cu | 146.15 | 4.98 | 7.89 | 14.48 | 15.79 | 61.84 |

22–25%, while the alginic acid fibres show an absorption of 15%, which is connected with the hydrophilic character of the fibre-forming material. The value of moisture absorption at 100% RH is also affected by the total pore volume and the character of the formed porous structure, which depend also on the fibre spinning parameters (Table 2).

With a low total pore volume and a low content of pores capable of moisture absorption through capillary condensation, it is clear that the values of absorption at 100% RH are at a similar level 43–46% except for alginic acid fibres for which this value is 20.15% despite a higher cumulative content of small and medium pores from the initial range of this interval. Thus, it is mainly the hydrophilic character of material that exerts a decisive influence on this index. High values of water retention, especially for fibres of zinc alginate, are connected with the quantitative predominance of large and very large pores in the formed structure and with the swelling of fibres due to water penetration into their supermolecular structure. This is particularly clearly seen in the case of alginic acid fibres, for which the value of this index is very high owing to a considerable solvation of COOH groups by water penetrating the material structure.

## Experimental

### *Methods*

The methods used to examine the structure and properties of alginate fibres were the same as those used for fibres made from a modified polyimidoamide [10].

Fibre porosity was measured by means of a mercury porosimeter of Carlo–Erba linked with a computer system to register the numerical values of the measured parameters. The determinations included: the total pore volume, total internal surface, volume of capillary group with a defined radius and pore percentage content. This method allows one to determine the pore percentage content with given ranges in the capillary set with sizes of 5–7500 nm.

Moisture absorption at 65 and 100% RH was determined by the desiccator method according to the Polish Standard PN-71/P-04635.

Water retention was measured by the centrifuge method. Fibre samples were immersed in distilled water containing a surface-active agent (Rokafenol Nx-3 in an amount of 0.1%) for 24 h and then the absorbed water was centrifuged off for 10 min at an acceleration of 10000 m s$^{-2}$.

Fibre tenacity and elongation at break were measured according to the Polish Standard PN-85/P-04761/04, referring the breaking force to the fibre linear density in tex.

The thermal analysis of fibres was carried out by means of a derivatograph, (Paulik–Paulik–Erdey system) and differential scanning calorimetry (DSC-204 microcalorimeter of Netzsch). The TG, DTG and DTA measurements were carried out in air using weighed portions of 60 mg at a heating rate of 7.9°C min$^{-1}$ within the temperature range from 20 to 800°C. In the case of microcalorimetry the measurements were performed in inert gas, using weighed portions of 2.5 mg at a heating rate of 10°C min$^{-1}$ within the temperature range from 30 to 600°C.

IR spectra were recorded by means of a Perkin-Elmer System 2000 with a resolution of 4 cm$^{-1}$, using KBr tablets containing finely cut and ground fibres.

## Results and discussion

From the complex analysis of the fibres it follows that during heating from room temperature to 800°C they are affected by complex physical and chemical processes (Figs 1 and 2, Table 3). Within the temperature range from 40 to 150°C in the DTA curves of all the alginate fibres is shown a broad endothermic peak with its maximum at *T*=90°C corresponding to water desorption. This change is clearly observed in the DSC curves of the examined fibres and its maximum under neutral gas is slightly shifted towards higher tempera-

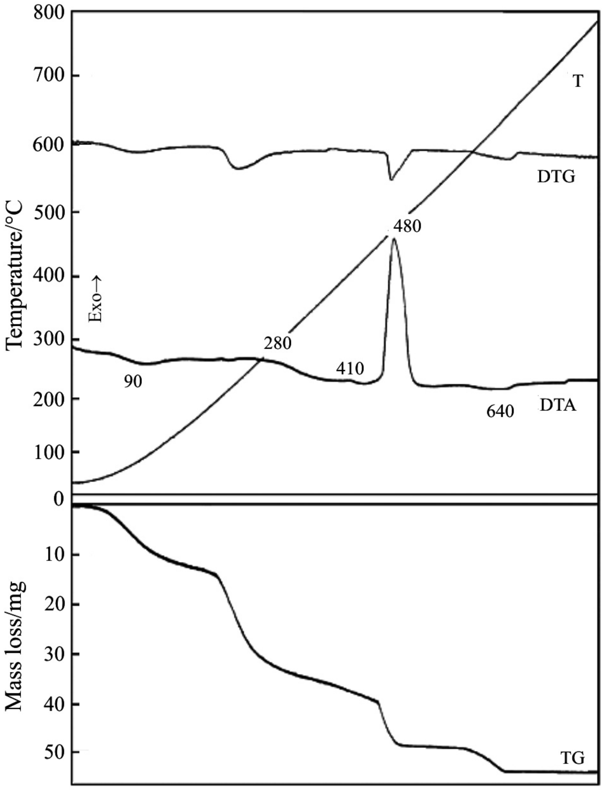

**Fig. 1** TG, DTG, DTA and T curves of calcium alginate fibres

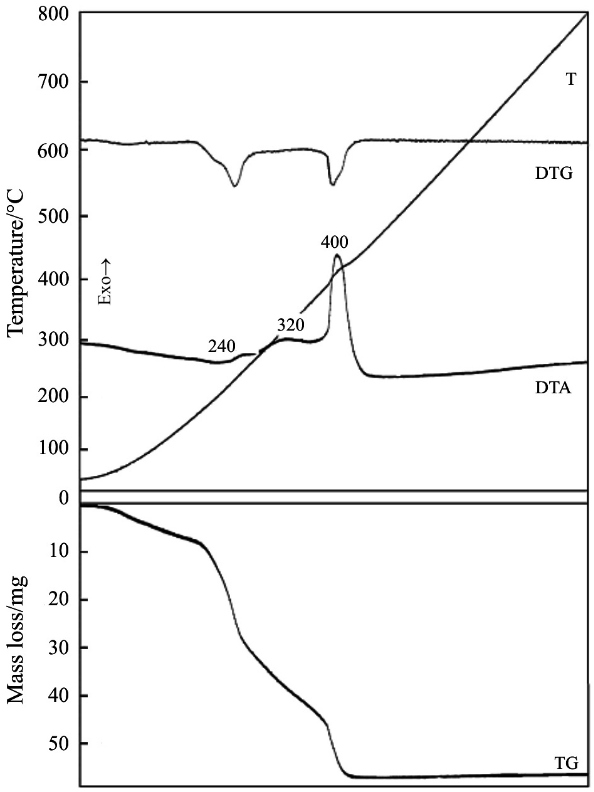

**Fig. 2** TG, DTG, DTA and T curves of alginic acid fibres

tures (Fig. 3). As follows from the TG curves, the absorbed water content in fibres ranges from 12.5 to 23.3%, which is consistent with the moisture content of these fibres at 65% RH (Table 1). The lowest water content, 12.5%, is released in the mentioned temperature range from the fibres made from alginic acid, which results from the lower moisture contents at both 65% and 100% RH. Measurements carried out by IR spectroscopy have shown that the fibres from alginic acid and calcium alginate maintain their characteristic groups when heated in the derivatograph's oven up to 170 and 200°C, respectively (Figs 4 and 5). The IR spectra of both types of fibres show (similarly as those of thermally untreated fibres) bands corresponding to stretching and bending vibration of the glycoside bond at the wavelengths 1128.20, 1086 and 1086.26 $cm^{-1}$ and a strong band of stretching vibration at 1745.16 $cm^{-1}$ confirming the presence of acidic groups in the fibres made from alginic acid (Fig. 4). At wavelengths 1620 and 1419.76 $cm^{-1}$ appear strong, sharp bands related to the presence of stretching vibration on ion carboxylic in calcium alginate fibres (Fig. 5).

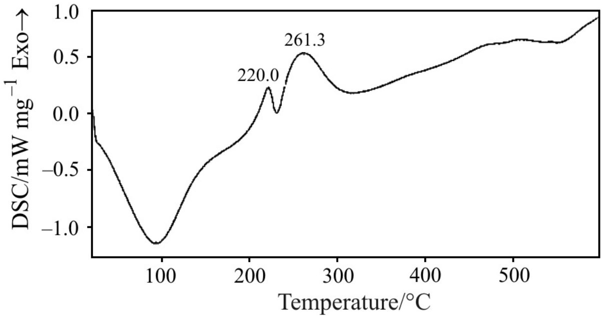

**Fig. 3** DSC curve of calcium alginate fibres

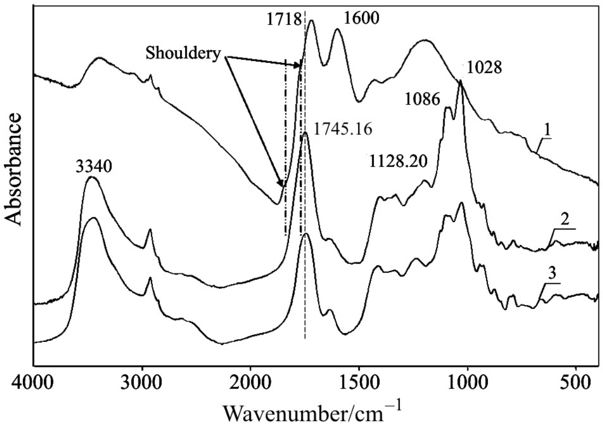

**Fig. 4** IR spectra of alginic acid fibres heated to 170°C and 300°C; 1 – fibres unheated, 2 – fibres heated to 170°C, 3 – fibres heated to 300°C

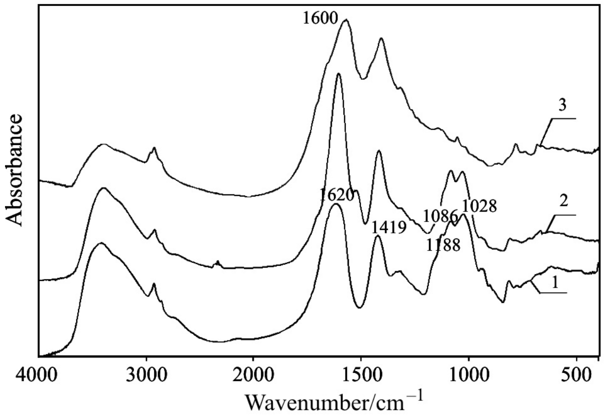

**Fig. 5** IR spectra of calcium alginate fibres heated to 170°C and 300°C;. 1 – fibres unheated, 2 – fibres heated to 170°C, 3 – fibres heated to 300°C

Within the temperature range from 150 to 300°C, the DTA curves of the fibres under investigation show a broad peak with its maximum at *T*=280°C, reflecting the dehydration of the fibre-forming material accompanied by the chemical redevelopment of its macromolecules (Fig. 1) resulting from destruction processes. This is confirmed by considerable differences in the spectra of both types of fibres heated to 300°C that is close to the temperature corresponding to the maximal temperature of the exothermic transition rate under consideration. In the spectrum of the alginic acid fibre one can observe considerable decreases in the band height of –OH stretching vibration at 3440 $cm^{-1}$ and that of –CH at 2926 $cm^{-1}$. There is no change in the band at 2926 $cm^{-1}$ corresponding to the

**Table 3** Results of thermal analysis of alginate fibres

| Sample symbol | Water desorption | | Dehydration | | Decomposition with formation of carbon structures | | Oxidation | | Decomposition of oxidation products | | Residue at $T$=800°C/% | Thermal stability indicator | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\Delta T$/°C | $\Delta m$/% | $\Delta T$/°C | $\Delta m$/% | $\Delta T$/°C | $\Delta m$/% | $\Delta T$/°C | $\Delta m$/% | $\Delta T$/°C | $\Delta m$/% | | $T_5$/°C | $T_{50}$/°C |
| Alg.Ca | 40–150 | 21.67 | 190–320 | 56.67 | 320–440 | 64.16 | 440–510 | 79.16 | 580–660 | 87.50 | $12.50^1$<br>$15.95^2$ | $70^1$<br>$210^2$ | $275^1$<br>$400^2$ |
| Alg.$Ca_{3\%SiO_2}$ | 40–150 | 23.33 | 190–350 | 56.67 | 350–440 | 63.33 | 440–510 | 80.00 | 590–670 | 86.67 | $13.33^1$<br>$17.39^2$ | $60^1$<br>$220^2$ | $280^1$<br>$450^2$ |
| Alg.$Ca_{5\%SiO_2}$ | 40–150 | 21.67 | 190–350 | 56.67 | 350–440 | 61.67 | 440–510 | 80.00 | 600–670 | 86.67 | $13.33^1$<br>$17.02^2$ | $60^1$<br>$225^2$ | $290^1$<br>$440^2$ |
| Alg.acid | 40–150 | 12.50 | 150–280 | 58.33 | 280–360 | 74.17 | 360–470 | 95.00 | – | – | $5.00^1$<br>$5.66^2$ | $80^1$<br>$180^2$ | $250^1$<br>$265^2$ |
| Alg.Na | 40–150 | 18.33 | 220–310 | 56.67 | 310–510 | 64.16 | 510–570 | 78.33 | 750–800 | 83.33 | $16.67^1$<br>$20.41^2$ | $60^1$<br>$185^2$ | $210^1$<br>$330^2$ |
| Alg.Zn | 40–150 | 20.00 | 200–300 | 52.5 | 300–370 | 61.67 | 370–500 | 85.00 | 570–660 | 88.33 | $11.67^1$<br>$14.89^2$ | $70^1$<br>$210^2$ | $285^1$<br>$370^2$ |
| Alg.Cu | 40–150 | 20.00 | 170–260 | 60.00 | 260–320 | 70.00 | 320–400 | 85.00 | – | – | $15.00^1$<br>$18.75^2$ | $60^1$<br>$180^2$ | $240^1$<br>$285^2$ |

$\Delta m$ – calculated in relation to the initial sample mass. $m_0$=60 mg, [1]in relation to the initial sample mass, [2]in relation to the fibre-forming material in the initial sample mass, $T_5$ – temperature corresponding to a 5% mass loss, $T_{50}$ – temperature corresponding to a 50% mass loss stretching vibration of the –CH group of calcium alginate fibres. The two strong bands appearing at 1718 and 1600 $cm^{-1}$ are absent in the spectra of unheated and heated fibres of alginic acid up to 170°C (Fig. 4, curves 1 and 2). At the slope of the first of them, from the higher wavelength end, one can observed two shoulders at 1836 and 1774 $cm^{-1}$. These are the wave numbers ascribed to carbonyl groups in acid anhydrides, while the previously mentioned bands appearing at 1718 and 1600 $cm^{-1}$ can be ascribed to new structures being formed, among which conjugated systems (wavenumber 1600 $cm^{-1}$) are the most probable to possess double bonds C=C and the cyclic and conjugated systems (wavenumber 1718 $cm^{-1}$) to have carbonyl groups. A clearly marked band at 1600 $cm^{-1}$ is also observed in the spectrum of calcium alginate fibres heated up to 300°C. In this spectrum one can also observed a clear band at 1408 $cm^{-1}$ that can be ascribed to carbonyl groups (Fig. 5).

The cleavage of C=O and C–C bonds is accelerated at 260–510°C, which is accompanied by the formation of carbon structures and a slight, slow mass loss. These processes are reflected in the DTA curves of the examined fibres in the form of a small exothermic peak at $T$=410°C (Fig. 1), while in the case of alginic acid they occur at considerably lower temperatures, with a maximum of transition recorded at $T$=320°C (Fig. 2).

In the DTA curves of the examined samples, within the temperature range 320–570°C, is recorded a high exothermic peak that is connected with the oxidation of the previously formed carbon structures (Figs 1 and 2). Maximal rates of this process in the case of calcium alginate fibres, regardless of the content of silica nano-particles, are observed at $T$= 480°C (Fig. 1). These processes resulting from heating fibres of copper and zinc alginates and alginic acid takes place at a considerably lower temperature (Table 3).

Once the oxidation process is completed, the examined samples contain, in addition to a low quantity of carbon, inorganic salts of corresponding metals that are decomposed to oxides at 580–670°C, as reflected by low endothermic peaks in the DTA curves (Fig. 1). This process is particularly visible in the thermal curves of the fibres made from calcium alginate regardless of the included silica nanoparticles (Fig. 1). This is due to a partial decomposition of calcium carbonate resulting in the formation of carbon dioxide and calcium oxide that shows a high thermal stability [11]. These changes are not observed in samples marked with Alg.acid and AlgCu symbols. This is obvious in the case of alginic acid sample. With the Alg.Cu sample the transition into oxide takes place within the range of considerably lower temperatures, which is due to the presence of the metal with a variable valence. At temperatures higher than 400°C we deal with a residue consisting of 18.75% of the fibre-forming material in relation to the initial sample mass (Table 3). Theoretically calculated mass of the mentioned CuO residue is 19.23% assuming a complete substitution of carboxylic groups with copper ions.

The thermal stability of the fibres under investigation was assessed on the basis of indicators $T_5$ and $T_{50}$ [10, 12, 13]. Regardless of the fact whether they are determined in relation to the initial sample mass or to the fibre-forming material contained in the initial sample mass, the highest thermal stability is shown by the calcium alginate fibres containing silica nano-particles despite their slightly higher total pore volume in comparison to the fibres with no $SiO_2$ (Tables 2 and 3). The increased thermal stability is thus connected with the presence of silica nano-particles in the fibre-forming material, which is consistent with the literature reports concerning other fibre-forming polymers [14].

The effect of fibre-forming material structure and silica nanoparticles content is clearly visible in the thermal stability of alginate fibres. Considering the value of the thermal stability indicator $T_{50}$ various types of alginate fibres can be arranged in the following series:

$T_{50}$:Alg.$Ca_{SiO_2}$>Alg.Ca>Alg.Zn>Alg.Cu>Alg.Na>Alg.acid

The fibres of sodium alginate and alginic acids show also the lowest thermal stability defined by $T_5$, which may be connected with the fact that in this case only secondary bonds occur between macromolecules. On the other hand, in Alg.Cu fibres the metal with variable valence facilitates decomposition processes.

The chemical composition of fibre-forming material of the fibres under investigation affects the temperature range of particular thermal changes. Despite the substantial similarity between the chemical compositions of alginate and cellulose fibres, their thermal decompositions are different. Cellulose fibres undergo quite a violent destruction, which causes their inflammability as indicated by the value of LOI amounting to 18.0 [15]. The stage-wise thermal decomposition processes of alginate fibres, as reflected in the TG curves, as well as the wide temperature range of these processes and the formation of $CO_2$ and $H_2O$ during dehydration decidedly make their combustion difficult. According to the standard PN-EN-ISO6940 cellulose fibres are classificated as combustible but alginate fibres are flame resistance, glowing is observed under influence of the flame. Glowing stopped after removal of the flame [16].

## Conclusions

- The incorporation of silica nanoparticles into calcium alginate fibres cause significant increases their thermal stability as defined by indicator $T_{50}$.
- The chemical composition of fibre-forming material affects the thermal stability of alginate fibres.

The order of $T_{50}$ values of fibres substituted with various divalent metals corresponds to the positions of these metals in the electrochemical series.

- The resulting from thermogarvimetric curves stage-wise thermal processes of alginate fibres and the wide temperature range of these processes, especially desorption and dehydration, followed by the formation of carbon dioxide and water, make their combustion difficult.

## References

1 P. Hertman, Proceedings of the MEDTEX'99 Conference, Łódź 10–11th May, 1999.
2 S. Tokura and H. Tamura, Proceedings of the MEDTEX'99 Conference as above.
3 B. Kneafsey, M. O'Shaughnessy and K. C. Condon, Burns, 22 (1996) 40.
4 G. Klöck, A. Pfeffermann, Ch. Ryser, P. Gröhn, B. Kuttler, H. J. Hahn and U. Zimmermann, Biomaterials, 18 (1997) 707.
5 K. J. Draget, G. Skjak-Break and O. Smidsrød, Int. J. Biolog. Macrom., 21 (1997) 47.
6 T. Mikołajczyk, Fibres and Textiles in Eastern Europe, 3 (2001) 9.
7 Y. Qin, Ch. Agboh and X. Wang, Gilding Chemical Fiber International, 46 (1996) 272.
8 M. Iijima, T. Hatakeyama, K. Nakamura and H. Hatakeyama, J. Therm. Anal. Cal., 70 (2002) 807.
9 T. Mikołajczyk, D. Wołowska-Czapnik and M. Boguń, Fibres and Textiles in Eastern Europe, 12 (2004) 18.
10 G. Janowska and T. Mikołajczyk, J. Therm. Anal. Cal., 71 (2003) 549.
11 G. Janowska, Scientific Bulletin of Technical University, Nr. 801, Łódź 1998.
12 G. Janowska and T. Mikołajczyk, J. Therm. Anal. Cal., 63 (2001) 815.
13 G. Janowska, J. Therm. Anal. Cal., 53 (1998) 309.
14 M. Kacperski, Polimery, 2 (2003) 85.
15 C. M. Tian, Z. H. Shi, H. Y. Xu, J. R. Shi and H. Z. Guo, J. Therm. Anal. Cal., 55 (1999) 93.
16 Unpublished performance research of Department of Man-Made Fibres.

Received: January 24, 2005
In revised form: March 15, 2005

DOI: 10.1007/s10973-005-6800-y