

DUAL RESPONSIVE MODIFIED CELLULOSE/CHITIN MIXED FIBERS

ANAMARIA SDROBIŞ, GHIOCEL EMIL IOANID, CRISTIAN-DRAGOŞ VARGANICI
and CORNELIA VASILE*Romanian Academy, "Petru Poni" Institute of Macromolecular Chemistry,
41A, Grigore Ghica Voda Alley, Iasi, Romania
✉ Corresponding author: Cornelia Vasile, cvasile@icmpp.ro*

Received December 6, 2013

Dual responsiveness to temperature and pH of textile fibers constituted of cellulose/chitin mixture modified with N-isopropylacrylamide (NIPAAm) or poly(N-isopropylacrylamide) (PNIPAAm) has been demonstrated, by investigating their swelling behavior and by optical microscopy. It has been established that the fibers exhibit a critical temperature of 32-33 °C and a critical pH around 4.5, and that the swelling kinetics reveal Fickian behaviour.

Keywords: cellulose, chitin, dual responsiveness, smart polymers, thermal properties

INTRODUCTION

The properties and interactions of cellulose surfaces are of great interest for a wide variety of applications including paper, textiles, medical and pharmaceutical products.^{1,2} In contact with aqueous solutions or humid environments, the formation of electric charges determines swelling and adsorption phenomena at the polymer/solution interface, as occurring in paper making/recycling, textile production or washing.³

Chitin and modified chitins as raw materials for man-made fibers can be useful as absorbable sutures and wound dressing materials,⁴ as well as anti-bacterial sponges and hospital dressings, artificial blood vessels, contact lenses, tumor inhibition, dental plaque inhibition, and blood cholesterol control.

Smart textiles have been developed by grafting/copolymerization of environment-responsive polymers (ERP), such as poly(N-isopropyl acrylamide) (PNIPAAm) onto the surfaces of fabrics.^{5,6} PNIPAAm is an intensively investigated temperature-sensitive polymer, which exhibits a hydrophilic/hydrophobic balance and a lower critical solution temperature (LCST) at about 32 °C, which is close to body temperature. PNIPAAm and its copolymers or hydrogels can be applied to obtain temperature-sensitive hygroscopic fabrics, environment-sensitive deodorant fibers and stimuli-sensitive nutrient delivery fabrics. When such materials are exposed to external stimuli, they display swelling/shrinkage or hydration/dehydration

properties, and cause changes in the water vapor transmission rates and permeability of the fabrics.

In our previous work, the cold plasma activation followed by the coupling reaction with N-isopropylamide (NIPAAm) and poly(N-isopropylamide) (PNIPAAm) has been applied to modify the cellulose/chitin mix fibers.⁷ Because the mixed fibers could combine properties of mix fibers with those of thermoresponsive polymer PNIPAAm, such fibers are expected to exhibit multi responsiveness to external factors, such as temperature, pH, ionic strength, etc. The objective of this work is to demonstrate the dual responsiveness of modified cellulose-chitin mix fibers.

EXPERIMENTAL**Materials**

Unwoven cellulose-chitin mix fibers (CC) were delivered under the trade name of Chitcel by Shandong Helon Textile Sci. & Tech. Co. Ltd, China (Mainland). From elemental analysis, it was found that the content of nitrogen was between 0.75 and 1.06 wt%, which indicated 11-15 wt% chitin content in Chitcel.⁷

The Chitcel fibers modified with N-isopropylacrylamide (CC/NIPAAm) and poly(N-isopropylacrylamide) (CC/PNIPAAm) were obtained according to the procedure described in our previous paper.⁷ In brief, the cellulose/chitin mix fibers (CC) have been activated for 15 minutes in high frequency plasma of 1.3 MHz and in a plasma discharge device of 100 W power at a pressure of 0.4 mbar, which was created inside of a glass reactor. After cold plasma activation, the fibers were removed from the treatment

chamber and then immersed in the aqueous solution (10 wt%) of NIPAAm or PNIPAAm, for 30 minutes. These solutions were previously activated with a mixture of two chemical coupling agents, NHS (N-hydroxysuccinimide) and EDC (1-(3-dimethylaminopropyl)-3-ethylcarbodiimide) in the 1:7 molar ratio. After that, the fibers dried at 60 °C were extracted with methanol for 25 hours in a Soxhlet extractor in order to remove the physically absorbed chemicals. After extraction, about 80-85% of reagent remained attached to the fiber surface. The purified and modified fibers (CC/NIPAAm and CC/PNIPAAm) were dried under vacuum for 24 h and further analyzed.⁷ Functional groups, such as carbonyl and carboxyl, which can be linked to the amino groups of NIPAAm, were introduced on the CC fibers by plasma activation. EDC was used as coupling agent of the amine groups with the carboxyl groups incorporated by plasma activation in order to yield amide bonds, while the NHS increased coupling efficiency by creating an amine-reactive intermediary compound.

It was also estimated from XPS data that surface modification/grafting degrees were of about 23% for CC/NIPAAm and 13% for CC/PNIPAAm, respectively.

Investigation methods

Swelling degree determination

The temperature and pH responsiveness were observed by allowing the cellulose/chitin mix fibers to swell in double distilled water. The temperature range varied from 25 °C to 40 °C, being maintained by a thermostat with a precision of ± 0.2 °C. Several phosphate buffer solutions of different pH (1.2, 2.2, 3.2, 4.3, 5.5, 6.2 and 7.4) were used. The pH was determined with a C835 multi-parameter analyzer from CONSORT, Belgium. In order to obtain pH variation, a 7.4 phosphate buffer solution was prepared and then the pH was adjusted by dropping a HCl solution (37 wt%). The temperature range was chosen around the LCST of PNIPAAm (~ 32 °C) and the pH range around the pKa of cellulose (4.3).

Swelling studies were carried out by direct immersion of the fibers (unmodified and modified) in the above mentioned solutions, at pre-determined time intervals. Then, the samples were removed from the solution, gently wiped with a soft tissue to remove the excess of surface solution, weighed and placed back into the vessel as quickly as possible.

Swelling degree (Q) was determined by the weighing method using equation (1):

$$Q_{\max} = \frac{(m - m_0)}{m_0} * 100(\%) \quad (1)$$

where: m_0 – weight of dry sample (g), m – weight of wet sample (g). At least two measurements were done for each experimental condition and the average was given.

The swelling kinetics was analyzed for the portion of the water absorption curve with linear variation of the fractional water uptake (M_t/M_{eq}) up to 60%, using equation (2):⁸

$$\frac{M_t}{M_{eq}} = kt^n \quad (2)$$

where: M_t is the mass of water absorbed at time t , M_{eq} is the mass of water absorbed at equilibrium, k (min^{-n}) is the characteristic constant of the material describing the rate of swelling, and n is the characteristic exponent describing the mode of the penetrant transport mechanism.

Optical microscopy

Optical microscopy images were obtained on a LEICA DM 2500M microscope – Leica microsystems, in polarized light, at 500X magnification. Average diameter was determined by the LAS AF software of the instrument, both for dry and swollen unmodified and modified fibers.

Thermogravimetric analysis and differential thermal analysis

Thermogravimetric analysis and differential thermal analysis were carried out under constant nitrogen flow (200 mL/min) at a heating rate of 10 °C/min, on a DTA/TG coupled instrument, model STA 449 F1 Jupiter (Netzsch, Germany). Heating and cooling runs were performed at a 10 °C/min rate. The kinetic parameters were evaluated by integral methods, using a VERSATILE program (Dragoe, license: 1012-9716-400058, Bucharest, Romania), which provides the kinetic parameters by various methods. The thermogravimetric characteristics of CC fibers can be quantified by several parameters, related to the temperature ranges of the different steps (errors ± 1 °C) of the mass loss (errors $\pm 2\%$) and also to the yield of residues.

RESULTS AND DISCUSSION

Temperature responsiveness

Swelling degree of both CC/NIPAAm and CC/PNIPAAm samples increases with an increase of temperature (Figure 1) for the first 130-160 minutes, after that the equilibrium is reached. The time to reach equilibrium is equal with that to reach maximum Q . The swelling profiles of the CC fibers at different temperatures are similar, but the maximum swelling degree increases with the rise of temperature – Figure 1. In the case of the modified fibers, the dependence of temperature is different from that of unmodified CC, the curves being overlapped at $T > 35$ °C. The variation of the swelling degree with temperature was evaluated; it has been found that modified fibers swelled at least two times faster ($dQ/dT =$

4.7%/°C) than the unmodified ones ($dQ/dT = 2.2\%/^{\circ}\text{C}$).

For the untreated fibers, the swelling degree increases with increasing the temperature up to around 35 °C, then the increase of the swelling degree is slowed down.

For pH values between 1.2 and 7.4, the swelling degree vs. temperature curves were similar with those measured in doubled distilled water. The swelling degree increased with the rise of temperature, reaching a maximum, and then decreased.

The LCST was determined with good accuracy by the graphical method. The maximum swelling degree vs. temperature curves were fitted by a Boltzmann function (y) – equation (3) (using the Origin program):

$$y = \frac{A_1 - A_2}{1 + e^{\frac{(x-x_0)}{dx}}} + A_2 \quad (3)$$

where: A_1 is the minimum value of the function; A_2 is the maximum value of the function; x_0 represents the value on the x axis corresponding to the inflection of the curve, equivalent to the transition temperature, and dx is the domain over which this value is found.

The critical temperature rises with an increase in the solution pH for both samples, the values of the critical temperature being higher for fibers modified with PNIPAAm compared to those modified with NIPAAm (Table 1).

The variation of the equilibrium swelling degree with temperature is observed for the sample modified with NIPAAm, (Figure 1), the swelling degree increased linearly with temperature up to around 32 °C and then the fibers contracted. As already known, only PNIPAAm chains exhibit LCST and temperature responsive character,⁹ so it is possible that during the modification a part of NIPAAm monomer was polymerized and grafted like short chains under the action of the active species created under cold plasma conditions. That is why, even for CC modified with NIPAAm, a volume transition was

found as a sudden variation of the swelling degree with temperature around 32 °C.

For the sample modified with PNIPAAm (Figure 1), the variation of the equilibrium swelling degree is similar with that of NIPAAm modified fibers, but the transition was observed at a higher temperature (~33 °C). Therefore, the CC fibers modified with PNIPAAm according to the procedure presented here displayed notable temperature-sensitive behavior.

pH Responsive character

Since hydrolysis of chitin by chitinase treatment leads to the release of glucosamine in addition to *N*-acetylglucosamine, it was concluded that glucosamine might be a significant part of the chitin polymer. Chitin samples contain a low amount of 2-amino-2-deoxy-D-glucose units.¹⁰ A combination of these properties in Chitcel fibers could impart antimicrobial properties and pH responsiveness to the fibers.

In order to demonstrate this pH responsiveness, the swelling of the fibers was followed in several phosphate buffer solutions of different pH of 1.2, 4.3, 5.5 and 7.4 and constant temperatures of 25 °C and 36 °C.

In Figure 2, the maximum swelling degrees are plotted as a function of pH, at room temperature (25 °C), for the samples modified with NIPAAm and PNIPAAm.

For both CC/NIPAAm and CC/PNIPAAm, the swelling degrees increase as a function of time at all pH values for the first 130-160 minutes, after that the samples reach equilibrium – Figure 2. The maximum swelling degree increases with pH, from 67.1% and 55.3% at pH 1.2 to 89.5% and 84.6% at pH 7.4 in the case of NIPAAm and PNIPAAm modified fibers, respectively. A sudden variation of the swelling degree can be observed around pH = 4.5, this revealing the pH-responsive character of the fibers. The curves show similar patterns at 36 °C, as may be also noted from the data in Table 2.

Table 1
Critical temperature of cellulose/chitin mix fibers modified with NIPAAm and PNIPAAm in different pH solutions

pH	Tc (°C)	
	CC/NIPAAm	CC/PNIPAAm
1.2	31.6	32.6
4.3	31.8	32.9
5.5	32.5	33.2
7.4	32.6	33.4

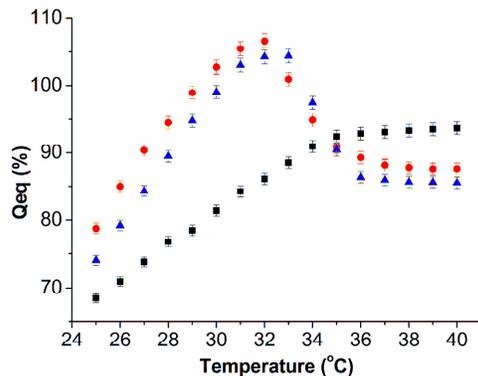


Figure 1: Equilibrium swelling degree versus temperature in double distilled water (pH ~5.5) for unmodified CC (■), NIPAAm-modified fibers (●) and PNIPAAm-modified fibers (▲)

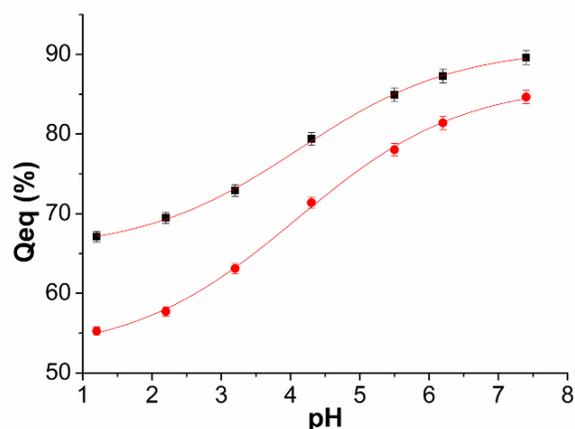


Figure 2: Maximum swelling degree versus pH of solutions, at room temperature (25 °C) for NIPAAm grafted samples (■) and PNIPAAm grafted samples (●)

Table 2
Parameters n and k for CC/NIPAAm and CC/PNIPAAm at different pH and temperature

CC/NIPAAm										
pH	25 °C		30 °C		32 °C		33 °C		36 °C	
	n	k , (min ⁻ⁿ)								
1.2	0.08	0.68	0.08	0.69	0.08	0.69	0.08	0.69	0.08	0.68
4.3	0.07	0.71	0.07	0.73	0.07	0.73	0.07	0.73	0.07	0.71
5.5	0.06	0.74	0.06	0.77	0.06	0.77	0.07	0.75	0.07	0.74
7.4	0.05	0.77	0.05	0.78	0.05	0.79	0.06	0.78	0.06	0.77
CC/PNIPAAm										
pH	25 °C		30 °C		32 °C		33 °C		36 °C	
	n	k , (min ⁻ⁿ)								
1.2	0.07	0.72	0.07	0.73	0.06	0.76	0.06	0.76	0.07	0.74
4.3	0.06	0.75	0.06	0.76	0.06	0.77	0.05	0.78	0.06	0.77
5.5	0.06	0.76	0.06	0.78	0.05	0.79	0.05	0.79	0.06	0.78
7.4	0.05	0.78	0.05	0.79	0.05	0.79	0.04	0.80	0.05	0.79

Swelling kinetics

The n and k values in eq. 3 were calculated from the slopes and intercepts of the plots of $\ln(M_t/M_{eq})$ vs. $\ln t$ for different pH solutions at different temperatures (Table 2).

The n values decrease, while rate constant k slightly increases until the critical temperature is reached, and then decreases, while k increases with the rise of the pH for NIPAAm and PNIPAAm treated CC fibers.

Since the increase of n means relaxation of the fiber structure,¹¹ by rising the pH value, the

maximum swelling degree decreases and the fibers undergo contraction – Table 2. The values of n for all pH solutions and at all temperatures, both for CC/NIPAAm and CC/PNIPAAm, were between 0.04 and 0.08, which indicated that the transport mechanism was Fickian diffusion,¹² although very low values of n are still controversial.

To confirm the assessment of the Fickian mechanism of swelling, the process kinetics were calculated by using various models, followed by the selection of the most suitable one.¹³ Common

kinetics reaction models were used to analyze the swelling kinetics.¹³⁻¹⁵

The choice of the model is based on the so-called “model-fitting method”, which is widely used to establish the reaction models for reactions occurring in solid state.

The normalized swelling degree, α , is defined as the ratio between the degree of swelling, Q , at time, t , and the equilibrium swelling degree, Q_{eq} – equation (4):

$$\alpha = \frac{Q}{Q_{eq}} \tag{4}$$

When the kinetics of swelling is determined by the kinetics of molecules penetration in the swelling medium, Fick’s law of diffusion: $Q = kt^{1/2}$ could be used to describe the kinetics of the isothermal swelling.

If the kinetics of swelling is determined by the diffusion of the network, the isothermal swelling kinetics of the fibers could be described by equation (5). The plots of $\ln(Q_{eq}/(Q_{eq}-Q))$ vs. t give straight lines.

$$\ln \frac{Q_{eq}}{Q_{eq} - Q} = kt \tag{5}$$

According to this procedure, the best choice of the approximate reaction model of the swelling process is achieved by comparing (both graphically and analytically) the shapes of the function: $\alpha_e = f(t^*_{e,red})$ of the investigated systems to the shape of the function $\alpha = f(t^*_{red})$ of common reaction kinetic models for heterogeneous processes, where α is the normalized degree of swelling and t^*_{red} is the reduced time – equation (6):

$$t^*_{red} = \frac{t_{\alpha}}{t_{0.9}} \tag{6}$$

where: t_{α} is the swelling time, which corresponds to the normalized degree of swelling α , while $t_{0.9}$ is the swelling time, which corresponds to $Q = 0.9Q_{eq}$.

Figure 3 shows the experimental plots $\alpha_e = f(t^*_{e,red})$ according to different reaction models.

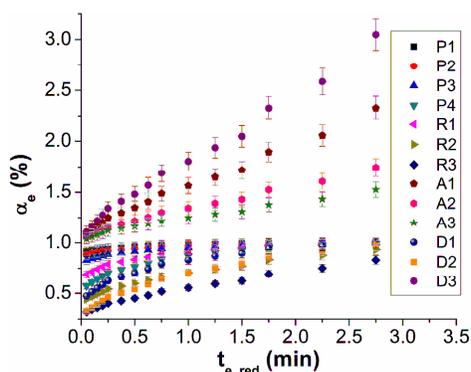


Figure 3: Plot of $\alpha_e = f(t^*_{e,red})$

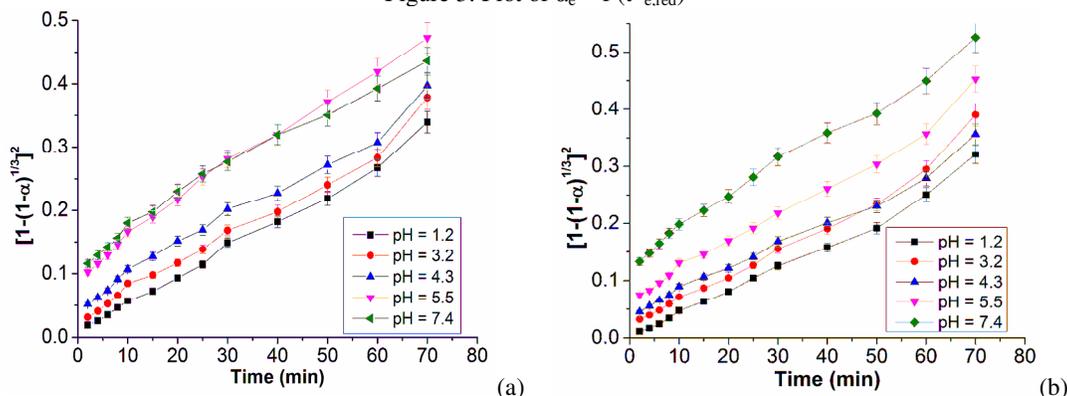


Figure 4: Plot of $[1-(1-\alpha)^{1/3}]^2$ as a function of time for swelling of (a) CC/NIPAAm and (b) CC/PNIPAAm fibers in different pH solutions at 25 °C

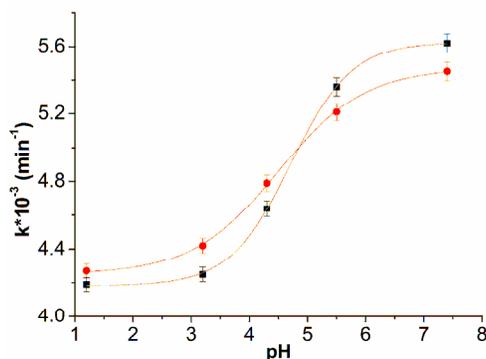


Figure 5: Swelling rate constant (k) vs pH for the swelling of CC/NIPAAm (■) and CC/PNIPAAm (●)

Based on the results presented in Figure 3, it may be concluded that the isothermal swelling kinetics of CC mix fibers could be described with the so-called kinetic model of “three-dimensional diffusion” ($n \sim 0.33$). This means that the following expression is valid – equation (7):

$$[1 - (1 - \alpha)^{1/3}]^2 = kt \quad (7)$$

where k is the model rate constant.

Figure 4 presents the dependence of $[1 - (1 - \alpha)^{1/3}]^2$ as a function of time for the swelling of CC/NIPAAm mix fibers in different pH solutions at 25 °C.

The values of the model swelling rate constants (k) were determined from the slopes of the lines obtained according to equation (7) – Figure 4. These plots are shown in Figure 5.

Based on the results presented in Figure 5, a critical pH was found around $\text{pH} = 4.67$ for NIPAAm modified samples and around $\text{pH} = 4.5$ for PNIPAAm modified samples, in accordance

with the values obtained from equilibrium swelling degree variation.

Optical microscopy

The swelling behavior has been also evidenced by optical microscopy. The average diameter of unmodified CC fibers after swelling continuously increases with the rise of temperature and pH, while in the case of CC plasma activated and NIPAAm (PNIPAAm) modified fibers, the variation of the average diameter shows a decrease after the LCST of PNIPAAm is exceeded ($T > 32$ °C) from around 34 μm at 32 °C to about 29 μm at 36 °C, due to the collapse of the thermoresponsive polymer chains (Figure 6). These results are in accordance with those obtained by investigating the swelling of the fibers using weight measurements.

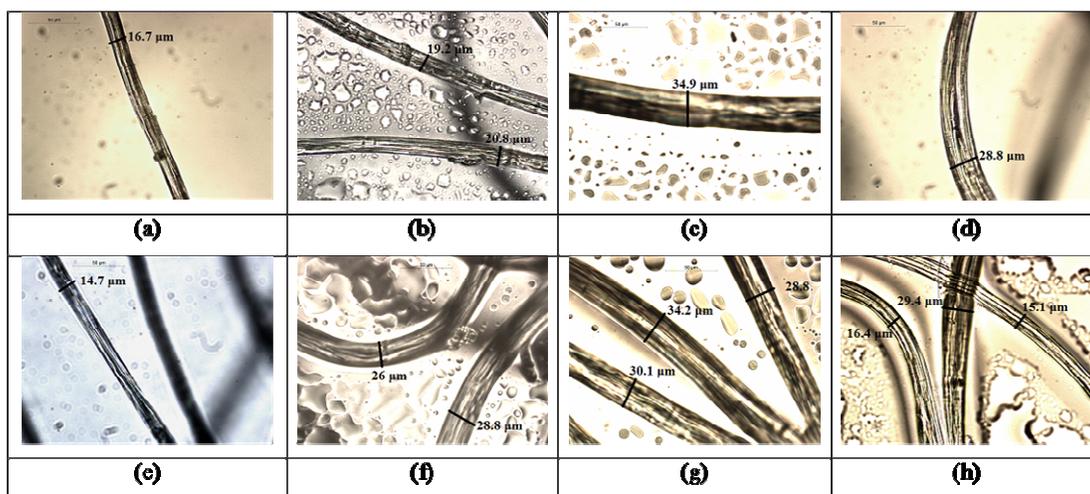


Figure 6: Optical microscopy images of the cellulose/chitin mix fibers treated with NIPAAm – (a) dry and swollen at different temperatures (b) 30 °C, (c) 32 °C, (d) 36 °C; and with PNIPAAm – (e) dry and swollen at different temperatures (f) 30 °C, (g) 32 °C, (h) 36 °C

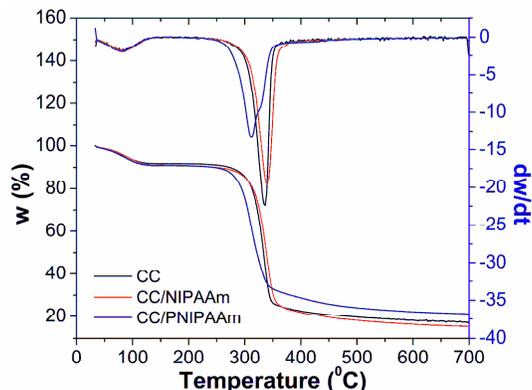


Figure 7: TG/DTG curves for untreated and modified cellulose/chitin mix fibers

Table 3
Thermogravimetric data of untreated and modified CC fibers

Step no.	TG data	CC	CC/NIPAAm	CC/PNIPAAm
Step 1	T_i (°C)	47.0	49.1	48.1
	T_m (°C)	80.1	83.9	82.7
	T_f (°C)	115.9	114.8	114.5
	W (wt%)	8.3	9.2	9.1
Step 2	T_i (°C)	280.4	263.5	244.0
	T_m (°C)	335.5	339.6	311.9
	T_f (°C)	346.4	354.7	342.6
	W (wt%)	74.5	75.4	68.9

Note: T_i – onset temperature, T_m – temperature corresponding to the maximum rate of mass loss, T_f – end temperature; W – mass loss

Thermogravimetric analysis

The mass loss (TG) and derivative mass loss (DTG) curves of the analyzed unmodified and modified cellulose/chitin mix fibers are shown in Figure 7, while the characteristic parameters of devolatilization are listed in Table 3.

The thermograms show two steps of mass loss in the DTG curves. The differences between samples appear in characteristic temperatures and mass losses. The first step corresponds to the (physically or chemically bonded) water loss and to the evaporation of some volatile substances. The second step can be associated with the volatilization/decomposition of different compounds (hemicelluloses, amorphous and crystalline cellulose, residual compounds and lignin). Below 120 °C, about 8% mass loss was found for the unmodified CC fibers. Mass loss begins at a higher temperature for modified fibers compared with untreated ones, the mass loss being also higher (about 9%), indicating that the cellulose/chitin mix fibers absorb more moisture after modification. This tendency of modified fibers to release moisture at higher temperature

may be due to the incorporation of NIPAAm and PNIPAAm chains on the fiber surface.

The overall kinetic parameters have been evaluated (Table 4) by the Coats Redfern (C-R),¹⁶ Flynn–Wall (F-W),¹⁷ and Urbanovici–Segal (U-S) integral methods.¹⁸ The agreement among the values obtained by the three methods is satisfactory, thus the results may be considered reliable.

The overall activation energy of the first thermogravimetric step increases for CC/NIPAAm, while for PNIPAAm modified sample a slight decrease can be observed. The reaction orders recorded values around 1.5-1.6 for both untreated and modified fibers.

The major thermogravimetric step assigned to degradation occurred between 240 °C and 360 °C for all samples. In the second thermogravimetric step, the onset temperatures for modified fibers are lower than those of the unmodified ones. Furthermore, the modified samples yielded residual mass values that decreased from 17.2 wt% for CC to 15.4 wt% for CC/NIPAAm, and

increased from 17.2 wt% for CC to 22.0 wt% for CC/PNIPAAm fibers.

The analysis of the activation energy of decomposition can be also helpful in determining the thermal stability of the fibers. The higher the value of the activation energy, the greater will be the thermal stability. In the second thermogravimetric step, the activation energies decreased significantly for NIPAAm and

PNIPAAm modified fibers, indicating that the thermal stability of the cellulose/chitin mix fibers decreased after modification. This can be attributed to the increase in the amorphous or disordered regions in the cellulose, which are more easily decomposed than the crystalline part. The improved swelling ability of the treated fibers support this statement.

Table 4
Kinetic parameters of untreated and modified CC fibers

Method used	Sample	CC	CC/NIPAAm	CC/PNIPAAm
Step I				
C-R	E _A (kJ/mol)	79.6	85.1	79.4
	n	1.5	1.6	1.5
F-W	E _A (kJ/mol)	81.3	83.7	81.0
	n	1.5	1.5	1.5
U-S	E _A (kJ/mol)	81.1	83.7	80.8
	n	1.5	1.5	1.5
Step II				
C-R	E _A (kJ/mol)	228.4	196.5	204.4
	n	0.9	0.8	1.3
F-W	E _A (kJ/mol)	226.2	195.9	203.3
	n	0.9	0.8	1.3
U-S	E _A (kJ/mol)	230.2	198.0	205.9
	n	0.9	0.8	1.3

Note: C-R: Coats-Redfern, F-W: Flynn-Wall, U-S: Urbanovici-Segal

Table 5
DTA results for untreated and plasma treated samples

Characteristic	CC	CC/NIPAAm	CC/PNIPAAm
T _w (°C)	92.8	96.2	91.8
T _d (°C)	338.3	334.1	329.1
ΔH _d (J/g)	-112.1	-94.4	-58.5

Differential thermal analysis

Two distinct endothermic peaks were found for all samples in the DTA curves. The broad endothermic peak observed in the temperature range of 50-150 °C corresponds to the heat of vaporization of water absorbed in the fibers and/or evolution of some volatile compounds, while the second peak between 290 and 370 °C corresponds to degradation. The maximum water loss temperatures (T_w), decomposition temperatures (T_d), and enthalpies of decomposition processes (ΔH_d) are given in Table 5 for all the samples. The characteristic temperatures and the enthalpies vary with the nature of the grafts.

The enthalpy associated with decomposition decreases for modified cellulose/chitin mix fibers

from 112.14 J/g to 94.35 J/g in the case of CC/NIPAAm and to 58.54 J/g for CC/PNIPAAm. The obtained results show that the thermal stability decreases after modification.

CONCLUSION

The dual responsiveness of the cellulose/chitin mix fibers to temperature and pH was evidenced after swelling in double distilled water by the gravimetric method and by optical microscopy.

It has been found that the fibers exhibit a LCST of 32.4 °C for CC/NIPAAm and 33.1 °C for CC/PNIPAAm, and a critical pH around 4.5 for both treated samples.

The results obtained by TG and DTA analyses showed a decrease in the thermal stability of NIPAAm and PNIPAAm treated samples.

The research results may be applied to develop intelligent fabrics, which could be useful for *in vivo* applications in cosmetic or pharmaceutical fields.

ACKNOWLEDGEMENTS: This work was financially supported by the Romanian UEFISCDI in the framework of Applied Research Projects PN-II-PT-PCCA-2011-3, by project BIONANOMED 164/2012.

REFERENCES

- ¹ D. Klemm, B. Heublein, H. P. Fink and A. Bohn, *Angew. Chem. Int. Edit.*, **44**, 3358 (2005).
- ² W. Czaja, A. Krystynowicz, S. Bielecki and R. M. Brown Jr., *Biomaterials*, **27**, 145 (2006).
- ³ U. Freudenberg, R. Zimmermann, K. Schmidt, S. Holger Behrens and C. Werner, *J. Colloid. Interf. Sci.*, **309**, 360 (2007).
- ⁴ B. K. Park and M. M. Kim, *Int. J. Mol. Sci.*, **11**, 5152 (2010).
- ⁵ L. Jianqin, Z. Maolin and H. Hongfei, *Radiat. Phys. Chem.*, **55**, 55 (1999).
- ⁶ B. Liu and J. Hu, *Fibres Text. East. Eur.*, **13**, 45 (2005).

- ⁷ A. Sdrobiş, G. E. Ioanid, T. Stevanovic and C. Vasile, *Polym. Int.*, **61**, 1767 (2012).
- ⁸ P. L. Rittgerand and N. A. Peppas, *J. Control. Release*, **5**, 37 (1987).
- ⁹ Y. Vickie Pan, R. A. Wesley, R. Luginbuhl, D. D. Denton and B. D. Ratner, *Biomacromolecules*, **2**, 32 (2001).
- ¹⁰ I. Aranaz, M. Mengibar, R. Harris, I. Paños, B. Miralles *et al.*, *Curr. Opin. Chem. Biol.*, **3**, 203 (2009).
- ¹¹ S. Murata, T. Sako, T. Yokoyama, H. Gao, K. Kidena *et al.*, *Fuel Process. Technol.*, **89**, 434 (2008).
- ¹² A. Hekmat, A. Barati, E. V. Frahani and A. Afraz, *W.A.S.E.T.*, **56**, 96 (2009).
- ¹³ A. Kostić, B. Adnadjević, A. Popović and J. Jovanović, *J. Serb. Chem. Soc.*, **72**, 1139 (2007).
- ¹⁴ J. Cai and R. Liu, *Ind. Eng. Chem. Res.*, **48**, 3249 (2009).
- ¹⁵ A. K. Gatwey and M. E. Brown, in "Handbook of Thermal Analysis and Calorimetry: Principles and Practice" edited by P. K. Gallagher and R. B. Kemp, Elsevier Sci BV, Amsterdam, 1998, pp. 147-214.
- ¹⁶ A. W. Coats and J. T. Redfern, *Nature*, **201**, 68 (1964).
- ¹⁷ J. H. Flynn and L. A. Wall, *J. Polym. Sci. Pol. Lett.*, **4**, 323 (1966).
- ¹⁸ E. Urbanovici and E. Segal, *Thermochim. Acta*, **80**, 389 (1984).