

Conservation-restoration of Textile Materials from Romanian Medieval Art Collections

I. Spectral characteristics of the naturally aged silk

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The most representative pieces belonging to the thesaurus-collection of Putna Monastery – most of them donations from the part of Prince Stephan the Great and the Holly – have been selected. Some of these cultural heritage objects are dated, while others have been only written down in the documents of their time (XVth – XVIth centuries). Analysis and characterization of the micro-samples taken over for experiments aim at elucidating of the mechanisms of natural ageing. To this end, the micro-samples have been analysed by FTIR spectrometry, for the identification of the materials and of their extent of damage. The destructive, hydrolysis – and denaturation – type processes have been evidenced by the spectral characteristics specific to amides I and II, and also to the hydroxylic groups. An important observation was that the samples taken over from objects with pronounced functional wear and tear have suffered processes of hydrolysis and denaturation of the polypeptidic chain. A correlation has been established between the degradation of the polypeptidic chain and the manner in which the object had been utilized.

Keywords: textile materials, IR spectral analysis, natural ageing, silk

The medieval art collections organized in Romania in the second half of the XXth century contain unique objects of inestimable artistic value. Most of these textile treasures, gathering an important number of pieces, have been preserved along the centuries by the Orthodox Church in its monasteries, known as having played an especially important part over the whole history of our nation. The constant concern for their safe preservation and transmission from generation to generation necessarily involves a scientific approach both from a historical artistic perspective and equally from a practical one, namely their conservation and possible restoration.

Investigations on the historical textiles may contribute to create an as faithful as possible image with the respective epoch.

At present, the researches devoted to the physico-chemical characterisation of the textile materials from old art collections are scarce; generally, only an approximate, descriptive visual analysis being made. [1].

Recent studies on the characterisation and conservation assessment of the cultural heritage objects are based on complex investigation systems, among which special mention should be made of: special photographic techniques, radiographic techniques, IR spectroscopy, UV – Vis absorption spectrometry, chromatographic techniques, differential thermal and thermogravimetric analyses, X ray fluorescence, mass spectrometry, microscopic techniques [2-9].

Considering all the above-mentioned aspects, the present paper is devoted to the scientific investigation of

the historical textile materials from the collection of Romanian medieval art treasured at Putna Monastery, the district of Suceava.

Experimental part

Silk samples, taken over from various cultural heritage textile goods, have been employed for IR spectral characterization.

Materials

From the art collection of Putna Monastery, micro-samples, the codes and significance of which are listed in table 1, have been taken over.

Figure 1 illustrates the textile objects considered for the study.

Equipment

FTIR spectrometer, Jasco (Japan) (4000 – 400 cm⁻¹ domain)

Reactives: Spectral potassium bromide (Merck, Germany) for inclusion of the suitable broken up fibers

Results and discussions

Analysis and characterization of the micro-samples permitted a correlation between the conservation condition and the results of the investigations, for better understanding of the mechanisms governing the process of natural ageing.

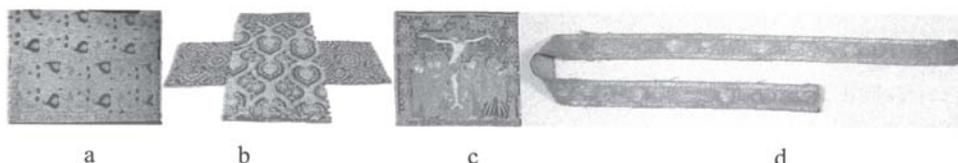


Fig. 1. Cultural heritage objects considered for the study:
a – cover for tomb;
b – *Catasarghion*; c – iconostasis veil *Crucifixion*; d – deacon stole

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Sample Code	Code significance
P2-AV	Deacon stole (Fig. 1 d) – green thread
P2_AR	Deacon stole – red thread
P2_AG	Deacon stole – yellow thread
P3AFG	Bishop's garment <i>Epigonat</i> – silky, yellow sewing thread
P3_AFR	Bishop's garment <i>Epigonat</i> – silky red thread
P3ATV	Bishop's garment <i>Epigonat</i> – decorative pattern lining – green fabric
P4-CR	Cover for the tomb of Prince Stephan the Great and the Holly, manufactured by order of Princes Bogdan for the tomb of his father – red threads from the basic fabric (Fig 1.a)
P4_CG	Cover for the tomb of Prince Stephan the Great and the Holly, manufactured by order of Princes Bogdan for the tomb of his father – yellow threads from the basic fabric
P4-CA	Cover for the tomb of Prince Stephan the Great and the Holly, manufactured by order of Princes Bogdan for the tomb of his father – blue threads from the basic fabric
P4_BR	Cover for the tomb of Prince Stephan the Great and the Holly, manufactured by order of Princes Bogdan for the tomb of his father – red sewing threads
P5_BRF	Cover for the altar (<i>Catasarghion</i>) – red thread for fabric sewing, zone 1
P5-BG	Cover for the altar (<i>Catasarghion</i>) – pale yellow thread for fabric sewing
P5-DR	Cover for the altar (<i>Catasarghion</i>) – red threads for sewing, zone 2
P5_BR	Cover for the altar (<i>Catasarghion</i>) – red fabric (Fig 1. b)
P6_R	Multi – coloured voided velvet – red threads
P6_V	Multi – coloured voided velvet – green threads
P6A	Multi – coloured voided velvet – white threads
P7-B	Iconostasis veil (<i>Dvera</i>) <i>Assumption</i> – white threads
P8R	Iconostasis veil (<i>Dvera</i>) <i>Crucifixion</i> – red fabric (Fig 1. c)
P9AM	Iconostasis veil (<i>Dvera</i>) <i>Annunciation</i> – white threads from upper part
P9FV	Iconostasis veil (<i>Dvera</i>) <i>Annunciation</i> – greenish blue threads for sewing from upper part
P9_MV	Iconostasis veil (<i>Dvera</i>) <i>Annunciation</i> – greenish blue threads from upper part

Table 1
MICRO-SAMPLES TAKEN OVER FROM
CULTURAL HERITAGE OBJECTS OF
PUTNA MONASTERY

Characteristic bands ν, cm^{-1}	Assignment of bands
3420	$\nu \text{ NH} + \nu \text{ OH}$
3306	$\nu \text{ NH} + \nu \text{ OH}$
3050	$\nu \text{ CH} = \text{CH}$
2977	$\nu \text{ CH}$ (valence vibration)
2925	$\nu \text{ CH}_2$ (asymmetrical valence vibration)
2860	$\nu \text{ CH}_2$ (symmetrical valence vibration)
1707	$\nu \text{ C=O}$ (valence vibration)
1650	$\nu \text{ C=O}$ (amide I)
1530	$\delta \text{ NH}$ (amide II)
1448	$\delta \text{ CH}$
1230	$\nu \text{ C-N} + \nu \text{ N-H}$
1160	$\nu \text{ C-O}$
1065	$\nu \text{ C-C}$
675 - 420	$\gamma \text{ CH}_2 + \gamma \text{ CH} + \gamma \text{ NH}$

Table 2
SPECTRAL CHARACTERISTICS OF NATURAL SILK
(REFERENCE)

All samples have been qualitatively characterized for the identification of the type of material used by artisans who weaved or embroidered the objects, comparatively with the traditional materials (silk, cotton, hemp) viewed as reference.

Spectral characteristics of the reference sample

Natural silk is a proteic fibre, mainly including in its structure the following amino-acids: glycine, alanine, serine and tyrosine, with β -arrangement quite close to that of polyglycine, and an identity period of 7.0 Å, which indicates a slight wrinkle, as due to the inter – and intra – molecular hydrogen bonds among chains. The polypeptidic chains are constituted of units of the – RCH-CO-NH- type,

connected head – to – head, and differing among them by the nature of the R radical from the lateral chain.

On the basis of such general information, the main bands occurring in the IR spectrum of a natural silk reference sample have been assigned. The characteristics bands and their assignment in the IR spectrum (fig. 2) of natural silk are presented in table 2.

Consequently, in the 3450 – 3050 cm^{-1} domain, the NH group evidences characteristic bands, attributed to the valency vibration of the NH and OH groups, both associated and non-associated through hydrogen bonds. The aspect of the bands from 3420 and 3306 cm^{-1} indicates an advanced association among chains, the higher intensity of the band from 3306 cm^{-1} representing also a characteristic of the wrinkled conformation [10-12].

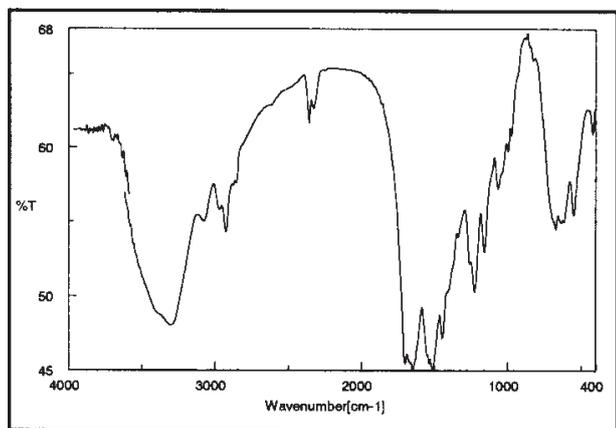


Fig 2. IR spectrum of reference silk

The carbonyl group (C = O) generates typical vibrations at 1707 cm⁻¹ (valency vibration) and at 1650 cm⁻¹ (amide I). The band from 1707 cm⁻¹ is a low intensity one, probably resulting from a marginal acid rest.

The NH group evidences deformation vibrations at 1530 cm⁻¹ similar to those of the secondary amides (amide II), as well as rocking-type vibrations (γ NH) over the 675 – 420 cm⁻¹ domain, included together with those of the CH₂ groups, and attributed to the whole skeleton.

The CH, CH₂ and CH₃ alkylic groups, of both asymmetrical and symmetrical type, show valence vibrations over the 3000 – 2800 cm⁻¹ domain.

The band from 1230 cm⁻¹ is attributed to the C-N structure from the skeleton of the polypeptide [11].

Characterisation of the silk samples from Putna collection

The IR spectral analysis of the silk samples taken over from Putna collection was performed in the same conditions applied for the reference. The spectra obtained are plotted in figure 3.

Examination of the spectra showed that the main bands are similar to those of the reference. However, certain differences were noticed in the aspect of the bands from 3420 and 3300 cm⁻¹ [14], namely three different situations of the ratio in which they occur, as follows:

- a higher intensity of the band from 3420 cm⁻¹ (P2-AV, P4-CR, P4-CA, P5-BG, P5-DR, P6A, P9FV), indicating the presence of some structures with NH groups, partially associated through hydrogen bonds, which may be due either to the breaking of some transversal bonds along chains, as result of some slow destructive processes, or to a treatment in which the molecule had adopted the preponderantly extended configuration, with the marginal NH group

- a higher intensity of the band from 3300 cm⁻¹ (P3AFG, P3ATV, P9FV), indicating an association through inter- and intramolecular hydrogen bonds [12]

- an equal intensity of the two absorption bands (P7-B, P8R, P9AM), indicating the simultaneous presence of the two types of structures, associated through transversal hydrogen bonds – in different ways.

Also, some low intensity additional bands may occur in the 1550 – 1670 cm⁻¹ region, as due to the succession of some aminoacids with certain structural peculiarities in the macromolecule; it is the case of some samples (P2_AR, P2_AG, P5_BRF, P6_V) not considered in the present study, whose additional bands from 1670 and 1570 cm⁻¹ might result from an aromatic group present in tyrosine and / or phenylalanine.

The polypeptidic chain of silk suffers a degradation process during its processing, utilization and prolonged storing, induced by physico-chemical (light, temperature, humidity, atmospheric pollutants), biological and microbiological (bacteria fungi, microorganisms) factors which contribute to the occurrence of certain structural modifications.

In the case of cultural heritage objects, all such modifications are produced over long periods of time, being part into evidence by spectral data.

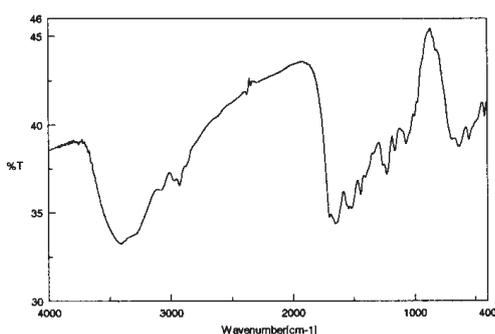
The transformation of the polypeptidic chain results from processes of oxidation, hydrolysis and / or denaturation of the amidic structure.

Knowledge of the main spectral characteristics of silk from the IR domain permitted selection of a few bands that might turn to good account the structural modification produced during degradation.

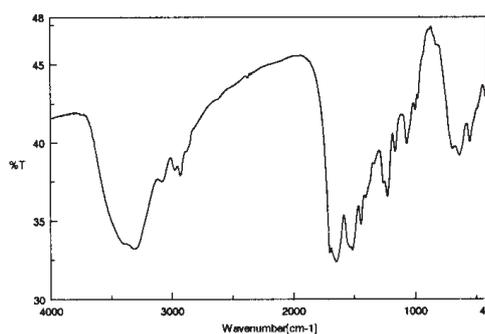
Thus, in the IR domain, there have been considered the bands from 1650 – 1630 cm⁻¹ (amide I) and 1550 – 1530 cm⁻¹ (amide II), as well as the wide band from 3450 – 3300 cm⁻¹ (ν OH + ν NH), and the distance between the two amidic structures ($\Delta\nu = \nu A_1 - \nu A_{II}$). There have been also followed the evolution of the band from 1230 cm⁻¹ (amide III), responsible for the ν C-N + ν N-H vibrations produced in the main chain.

Knowing the absorbency value of each absorption band, there have been calculated:

- the A_{ν}/A_{II} ratio, providing information on the hydrolysis degree of the peptide chain [13];
- the $\Delta\nu$ difference between the wavenumbers specific to amidic structures, offering information on chain denaturation;
- the A_{OH}/A_I ratio, granting additional data on the hydrolysis degree of the chain;
- the shifting of the band from 1230 cm⁻¹ provides information on the stability of the main chain, as it refers to the elongation of the C-N link from amides;
- the presence of a band at $\nu = 1700 - 1740$ cm⁻¹ indicates the formation of carbonylic / carboxylic structures during the oxidative process [11].



P2-AV



P3AFG

Fig. 3. IR spectra of the micro – samples under analysis

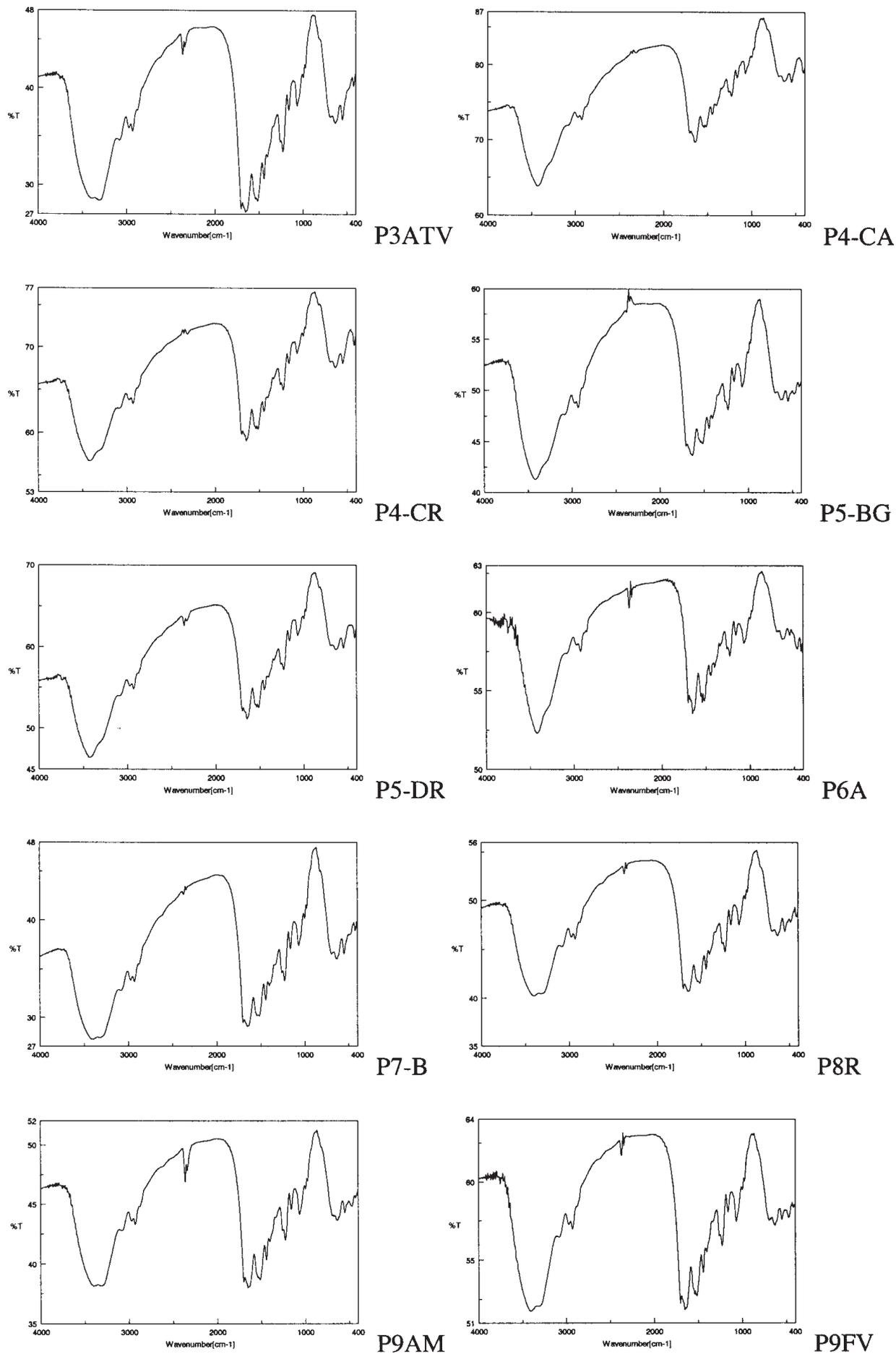


Fig. 3. IR spectra of the micro - samples under analysis

Table 3
CHARACTERISTICS OF THE SILK SAMPLES UNDER ANALYSIS

Sample Code	Characteristics		
	A_1/A_{II}	Δv	A_{OH}/A_I
Reference Natural silk	1,00	99	0,91
Sample Putna			
P2-AV	1,04	100	1,02
P3AFG	1,02	101	0,98
P3ATV	1,04	100	0,96
P4-CA	1,07	103	1,19
P4-CR	1,05	102	1,00
P5-BG	1,06	104	1,05
P5-DR	1,00	108	1,17
P6A	1,00	101	1,00
P7-B	1,04	101	1,04
P8R	1,03	101	1,03
P9AM	1,05	103	0,98
P9FV	1,00	101	1,00
P9_MV	1,03	102	0,95

The main data provided by the IR spectra are listed in table 3.

A comparative analysis between these characteristics and those of natural silk permits the following observations:

- the (A_1/A_{II}) hydrolysis degree of the cultural heritage samples is 2 – 7 % higher than that of the reference, with the exception of samples P5-DR, P6A si P9FV;

- the hydrolysis degree considering the band from 3450 – 3300 cm^{-1} is also higher than in the reference, the highest value being recorded in samples P4-CA and P5-DR;

- the denaturation degree (Δv) shows a 1 – 8 % increase, the highest value being evidenced by sample P5-DR;

- all samples have been evidenced a low intensity band at 1705 – 1710 cm^{-1} , coming from the carbonylic / carboxylic groups formed during the destructive process and / or from the pigments / dyers with which the materials had been dyed.

- the band from 1230 cm^{-1} suffered no sensible shifting ($\pm 1 \text{ cm}^{-1}$), so that one may appreciate that no breakings of the C – N bond from the main chain had occurred in time.

Corroboration of all data obtained shows that the cultural heritage samples under analysis had suffered a weak hydrolysis of the polypeptidic chain. Special mention should be made of sample P5-DR which, besides hydrolysis, has also suffered a denaturation process. Such an intense degradation may be attributed to the wear-and-tear resulted from a prolonged utilization of the textile object. Sample P9AM has also suffered, apart from chemical degradation, some depreciation caused by physico-mechanical stresses, which is of the manner in

which the object (*divera*) has been utilized and exposed as early as its manufacturing, being vertically suspended.

Conclusions

Nine textile treasury pieces from collection of Putna Monastery have been selected for analysis. The microsamples taken over were analysed by IR spectrometry, for the identification of the materials and of their extent of damage. It has been observed that the samples from objects with prolonged functional wear-and-tear have suffered processes of hydrolysis and denaturation of the polypeptidic chain. A correlation has been established between the degradation of the polypeptidic chain and the manner in which the object had been utilized in time.

The degradation signs are more pronounced when the large-size textiles are vertically suspended, which leads to the conclusion that, for conservation purposes, the horizontal or oblique exposure is recommended.

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Intre 19 și 20 iunie 2008, la Institutul de Chimie Macromoleculară "Petru Poni" din Iași, a avut loc FIRST SYMPOSIUM - CRISTOFOR I. SIMIONESCU - FRONTIERS IN MACROMOLECULAR SCIENCE. Aceasta primă sesiune a unei manifestări prevăzute a fi reeditată și în anii următori a fost inițiată de către profesorul Virgil Percec, de la University of Pennsylvania, membru de onoare al Academiei Române. Simpozionul s-a desfășurat sub auspiciile Academiei Române, ale Institutului de Chimie Macromoleculară "Petru Poni", ale University of Pennsylvania (UPenn) - Philadelphia, The Laboratory for Research on the Structure of Matter (LRSM), Materials Research Science and Engineering Center at UPenn și a fost finanțat din grantul NSF-1MR-05.20020 și parțial de către ANCS. Profesorul Percec a fost cercetător în cadrul Institutului de Chimie Macromoleculară "Petru Poni" și și-a susținut doctoratul sub conducerea acad. Cristofor I. Simionescu.

Coorganizator al reuniunii din partea institutului a fost dr. Virgil Bărboiu. Institutul urmărește ca, prin manifestări de înalt nivel științific, să promoveze cele mai noi descoperiri și idei din domeniul științei polimerilor și, totodată, să mențină vie amintirea unui eminent profesor și om de știință, academicianul Cristofor I. Simionescu, promotorul cercetărilor de chimie macromoleculară din țara noastră și recunoscute internațional.

Deschiderea lucrărilor a fost făcută de prof. Virgil Percec, care a salutat prezența participanților și a evocat personalitatea academicianului Cristofor I. Simionescu. A vorbit, cu acest prilej, despre harul didactic al profesorului Simionescu apreciat de multe generații de studenți, atrași de noutățile din domeniu, nelipsite din cursurile sale, doctoranzii care au avut privilegiul să se bucure de competența și generozitatea sa intelectuală, de îndrumarea unui mare specialist ale cărui lucrări, foarte numeroase, au fost publicate timp de decenii în reviste internaționale cu puternic impact în lumea științifică. Recunoașterea meritelor științifice ale acestui mare profesor s-a concretizat în titluri onorifice ale unor academii străine și ale unor societăți științifice, precum și în cooptarea sa în comitetele de redacție ale unor periodice de la noi și din alte țări.

Detalii despre relația personală a profesorului Percec cu cel evocat și elogiat au introdus trăsături suplimentare unui portret complex, trăsături la care auditoriul a fost vădit sensibil.

Celelalte expuneri în plen (cca o oră fiecare), desfășurate pe parcursul a doua zile, s-au succedat astfel:

- Prof. Michael I. Klein (FRS Hepburn Professor of Physical Science and Director of Laboratory for Research on the Structure of Matter, Univ. of Pennsylvania, USA), COMPUTATIONAL STUDIES OF SOFT MATTER & BIOMATERIALS: THE CHALLENGE OF BRIDGING LENGTH & TIME-SCALES TO PROBE NATURE'S DESIGN;

- Prof. Roeland J. M. Nolte (Royal Netherlands Academy of Arts and Science, Professor of Molecular Chemistry, Director of Institute of Molecules and Materials, Radboud University of Nijmegen, Netherlands), MACROMOLECULAR ARCHITECTURES INSPIRED BY NATURE;

- Prof. Hans Spiess (Max-Planck-Institut für Polymerforschung, Mainz, Germany), INTERPLAY OF STRUCTURE AND DYNAMICS IN MACROMOLECULAR AND SUPRAMOLECULAR SYSTEMS; - Prof. Virgil Percec (PRoy Vágelos Chair and Professor of Chemistry, Department of Chemistry, University of Pennsylvania, USA), BIOINSPIRED SYNTHESIS OF COMPLEX SYSTEMS WITH BIOLOGICAL FUNCTIONS;

- Prof. Bert Meijer (Distinguished University Professor in Molecular Sciences and Professor of Organic and Macromolecular Chemistry, Eindhoven University of Technology, Netherlands), SUPRAMOLECULAR POLYMERS; A MODULAR APPROACH TO FUNCTIONAL MATERIALS;

- Prof. Jos Put (Chief Technology Officer, DSM Innovation Center, Netherlands), SUSTAINABILITY IN POLYMERS, A PROBLEM OR AN OPPORTUNITY?;

- Prof. David A. Tirrell (Roos McCollum-William H. Corcovan Professor and Professor of Chemistry and Chemical Engineering, Chair of the Division of Chemistry and Chemical Engineering, California Institute of Technology, Caltech USA), REINTERPRETING THE GENETIC CODE: NON-CANONICAL AMINO ACIDS IN MACROMOLECULAR DESIGN, EVOLUTION AND ANALYSIS;

- Prof. Martin Moeller (Chair of Textile and Macromolecular Chemistry and Director of the German Wool Research Institute DWI, Rheinisch-Westfälisch Technical University RWTH, Aachen, Germany), BIOMIMETIC AND BIOACTIVE POLYMERS AND INTERFACES;

- Prof. Bogdan C. Simionescu (Universitatea Tehnică "Gh. Asachi" și Institutul de Chimie Macromoleculară "Petru Poni", Iași), FUNCTIONAL POLYMERS-BUILDING BLOCKS FOR MACROMOLECULAR AND SUPRAMOLECULAR ARCHITECTURES.

Conferențiarilor străini - mari personalități științifice, au tratat aspecte de evidentă actualitate în cercetările de vârf al căror obiect este relația dintre știința polimerilor și științele biologice (științele vieții) sau din domeniul materialelor funcționale, aducând astfel elemente de certă originalitate și real interes.

Departate de a fi o simplă înșiruire de date din literatura de specialitate, conferințele au prezentat concepții inovatoare și noi direcții de investigare pentru viitor. Subiecte ca polimerii biomimetici și bioactivi, reinterpretarea codului genetic și utilizarea aminoacizilor necanonicii sau studiile prin modelare pe calculator a materiei moi (soft matter) și a biomaterialelor pot induce noi progrese în bionanotehnologie și în bioingineria medicală. Recurgerea la sisteme inspirate din biologie și în general din natură permite obținerea unor materiale și dispozitive fundamentale noi, care pot revoluționa știința și tehnologia materialelor și a nanostructurilor. Trei dintre conferențiarii și-au axat expunerile pe noi aspecte și interpretări ale sistemelor supramoleculare destinate obținerii de materiale funcționale sau multifuncționale.

Prima zi s-a încheiat cu o prezentare de comunicări de tip poster. Au fost expuse 31 de lucrări originale ale cercetătorilor din institut. De semnalat faptul că nouă dintre lucrări au avut drept coautori cercetători din Franța, Germania, Italia, Polonia și Turcia.

Sesiunea poster s-a bucurat de interes real din partea oaspeților, o analiză realistă a acestei prime întâlniri justifică, fără excese de optimism, organizarea edițiilor viitoare.

Adrian CARPOV