Evaluation of the Physico – chemical Characteristics of Leather Samples of Some Historical Objects from Kiev

VICTORYA PLAVAN[1], MARIA GIURGINCA[2*], PETRU BUDRUGEAC[3], MIHAELA VILSAN[4], LUCRETIA MIU[4]

[1]Kiev National University of Technologies & Design, 2, Nemirovich-Danchensko Str., Kiev, 02011, Ukraine

[2] University Politechnica of Bucharest, 011061, 1 Polizu, Bucharest, Romania

[3]National Institute for Research and Development in Electrical Engineering ICPE-CA, Splaiul Unirii 313, 030138, Bucharest, Romania

[4]National Research and Development Institute for Textile and Leather, 93 Ion Minulescu, 031215 Bucharest, Romania

Ukrainian museum and monasteries preserve a large number of parchment and leather documents dated from the 14th to the 19th centuries. As any organic structure, these materials are subjected to the destructive processes due to physico-chemical (light, humidity, temperature, pollutants, etc), biological and microbiological factors that lead to change in the polypeptide chain structure. The change resulting from the oxidation, hydrolysis and gelatinization processes in the collagen, can be identified in the IR (middle and NIR), UV-VIS spectra based on some characteristic bands, thermal analysis (DSC) and MHT techniques. These techniques were applied to point out the different kinds of degradation at the microsopic, mesoscopic and molecular levels of the collagen materials.

Keywords: leather, DSC, FTIR and UV-VIS-NIR spectra

Ukrainian museums and monasteries preserve a large number of parchment and leather documents dated from the 14th to the 19th centuries, whose deterioration must be evaluated for selection of the suitable treatment for preservation and restoration.

As any organic structure, these materials are subjected to the destructive processes due to physico-chemical (light, humidity, temperature, pollutants, etc.), biological and microbiological factors that lead to changes in the polypeptide chain structure. The change resulting from the oxidation, hydrolysis and gelatinization processes in the collagen can be identified in the IR (middle and NIR), UV-VIS spectra based on some characteristic bands, thermal analysis (DSC) and shrinkage temperature by MHT method (Micro Hot Table) [1 – 4].

Based on experience gathered by analyzing the collagen support (leather and parchment) by varied investigation techniques [5 – 10], our paper presents data regarding the study of leather samples coming from Ukrainian patrimony objects.

Experimental part
Devices
- FT-IR 100 Spectrometer, Perkin-Elmer with vertical ATR, with diamond head;
- UV-VIS-NIR-V670 Spectrometer, Jasco with diffuse reflectance accessory ILN-725; both techniques are non-destructive;
- The DSC curves were recorded using DSC 204 F1 Phoenix apparatus produced by Netzsch – Germany. The following kind of DSC measurements were performed:
· DSC analysis of the sample (1.12-1.71 mg) in nitrogen flow (purity of gas is higher than 99.999%; 20 mL.min-1), in an open aluminium pan, at the heating rate of 10 K.min-1, and in the temperature range 25^{0}C … 280^{0}C;
·DSC analysis of the sample (0.93-2.50 mg) immersed in water (35µL deionised water), hermetically sealed in an aluminium pan and stocked for 24 h. Each sample was heated from 25^{0}C to 110^{0}C, at a heating rate of 10 K.min-1;

- MHT with Caloric equipment (Stereomicroscope Leica), hot table, webcam, computer and software to acquire the image correlated with the shrinkage temperature.

Materials
- P1 book leather, Lvov;
- P2 book leather, Lvov;
- P3 archaeological leather (XV century);
- P4 carriage leather – Historical Museum (Kiev).
- P5 calf leather tanned with quebracho (ICPI, Bucharest)

Results and discussions
Spectral characteristics
In order to identify the degradation types, we selected some IR spectral characteristics:
3450 – 3200 cm-1 for $\nu OH + \nu NH$
1660 – 1630 cm-1 for $\nu C=O$ (amide I)
1550 – 1530 cm-1 for δNH (amide II)
1750 – 1700 cm-1 for $\nu C=O$ (oxygenated structures)
We have computed:
- A_I/A_{II} for information regarding the hydrolysis degree of the collagen support;
- $\Delta \nu = \nu_1 - \nu_2$ for information on the denaturation of the polypeptide chain [4, 9, 11].
The main spectral characteristics of the investigated samples are presented in table 1.

In comparison with the standard – calf leather tanned with quebracho – all the historical leathers present a 10 – 30% higher degree of hydrolysis and oxidation groups coming from the tanning agent (at P5) as well as from oxidative processes taking place in time (P1 - P4) proved by the presence of the free acids (ν 1730 cm-1) and the ketones (ν 1750 cm-1) (fig. 1) [8].

For the UV-VIS-NIR domain, the main bands are:
- bands from the 250 – 500 nm domain, attributed to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ like the extended conjugation structure from the tannants;

* Tel.: 0213154193

Table 1
CHARACTERISTICS OF THE LEATHERS

Sample code	FT-IR, cm^{-1}			NIR, nm	Chromatic characteristics			
	A_I / A_{II}	Δv	v_{CO}		L^*, %	C^*	H^0	ΔL^*
Historical samples P1	1.30	102	1730	1480; 1905	44.15	11.10	58.10	-32.57
P2	1.05	107	1730	1480; 1900	53.74	11.60	58.07	-22.98
P3	1.16	95	1750	1500; 1900	41.60	5.19	51.51	-35.12
P4	1.14	104	1710 / 1730	1480; 1900	55.60	9.14	70.23	21.12
Standard sample P5	1.03	102	1700	1490; 1920	76.72	24.93	67.54	-

L^* - luminosity; C^* - chroma; H^0 – color angle.

- the 1470 – 1510 nm band given by the valence harmonic vibrations of the hydroxyl groups (vOH) from the water absorbed into the collagen structure and which allows the identification of the types and the strength of the hydrogen bond from the peptide chain;

- the 1900 – 1920 nm bands are given by the valence and deformation vibrations (vOH + δOH) of the hydroxyl groups from the peptide chain.

In the UV-VIS domain, all the samples present a wide band at 250 – 500 nm due to the – CONH – group and the tanning agent color. In the NIR domain, the bands from 1480 – 1500 and 1900 – 1920 nm point to the presence of the hydroxyl structures associated inter/intra molecular by hydrogen bonds (fig. 2) [12, 13].

The absorbance of the 1480 – 1500 nm band is partially correlated with the shrinkage temperature (ST) pointing to changes in the hydrogen bonds structure.

The main chromatic characteristics are the luminosity (L^*) and chroma (C^*), while for the differentiation of the samples, we selected the value $\Delta L^* = L^*_{st} - L^*_s$ (st – standard, s – sample).

The change in luminosity varies between 21 – 35%, suggesting an increase of the luminosity but the nuance angle remains in the same domain (50 – 70%).
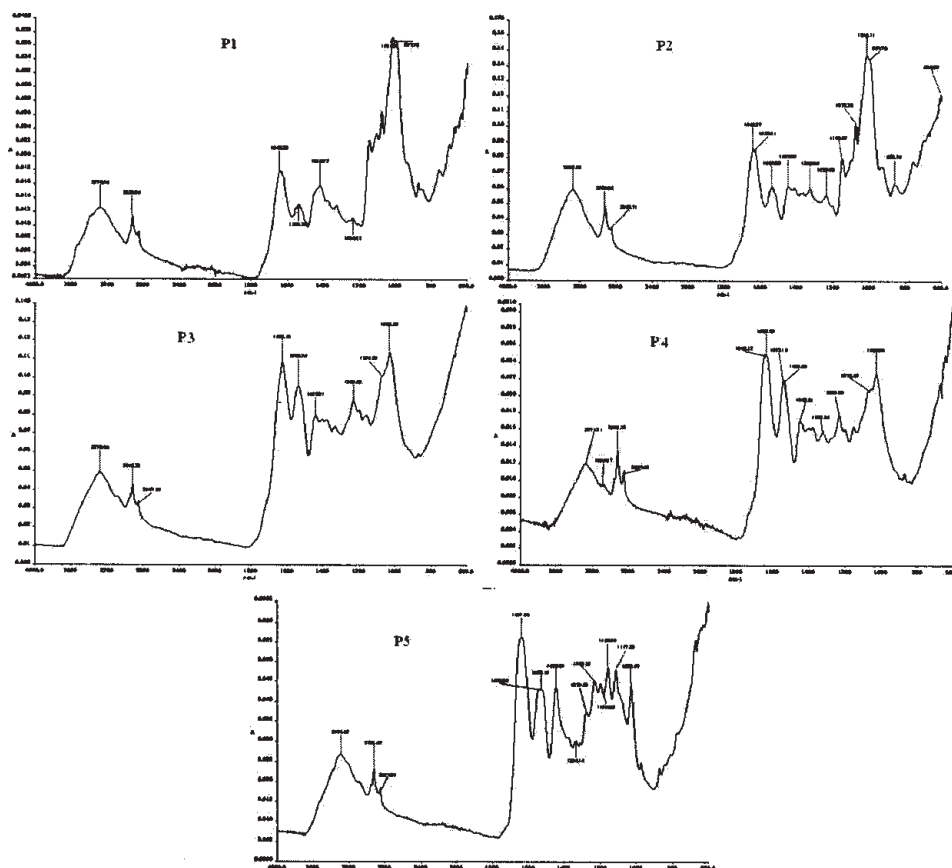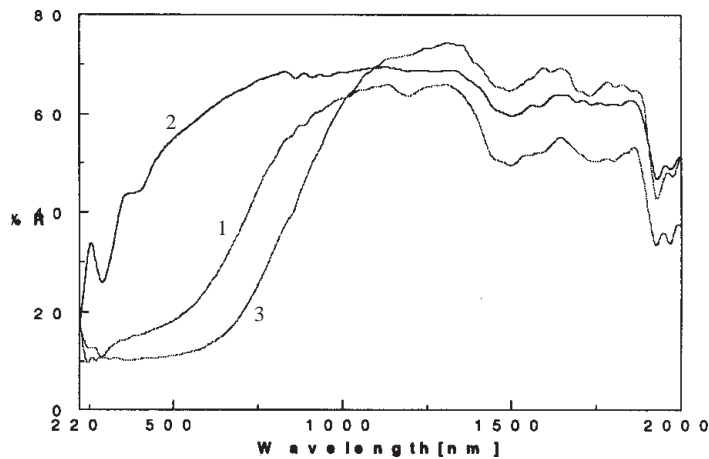

Fig. 1. FT-IR spectra of the samples

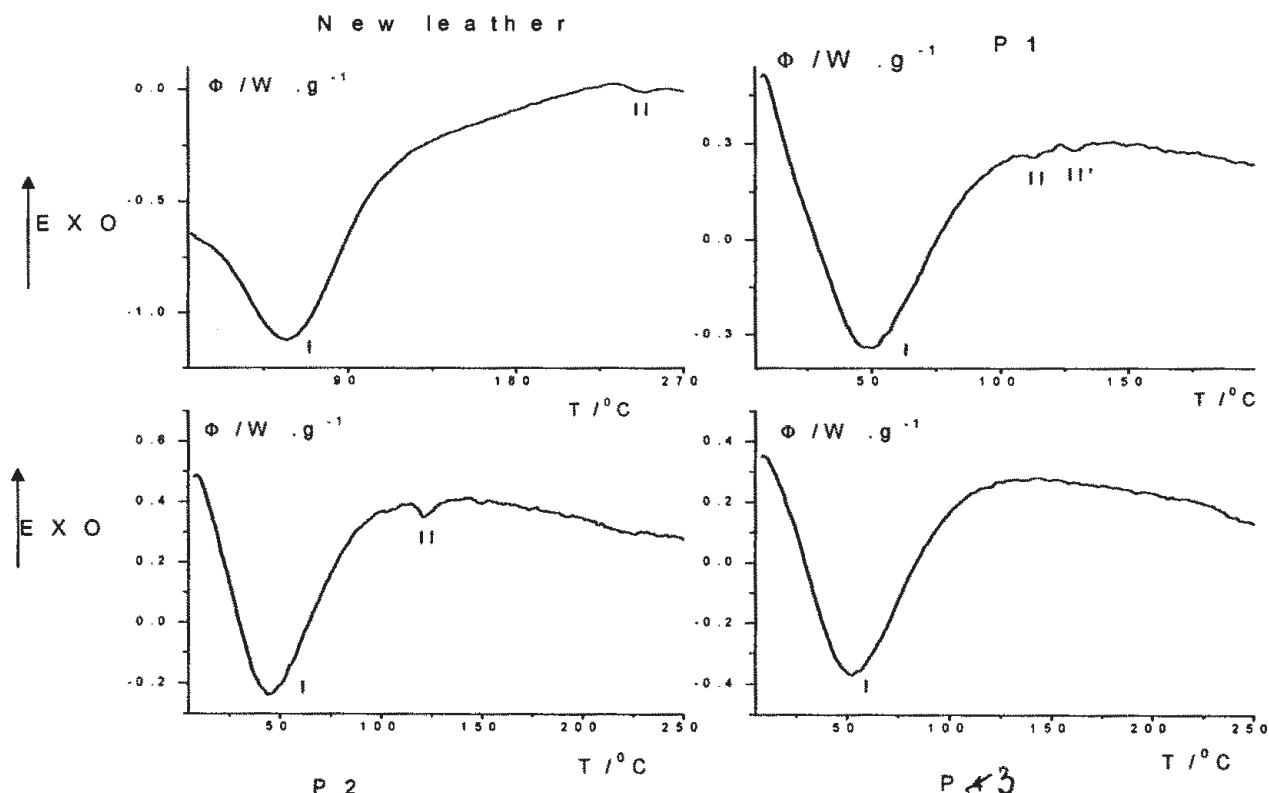Fig. 2.UV-VIS-NIR spectra of the samples P1 (1), P2 (2) and P3 (3)

Fig. 3. DSC curves obtained by analysis for samples in N_2 flow

Thermal characteristics
DSC analysis in N_2 flow

Figure 3 shows the DSC curves obtained by analysis in N_2 flow for the investigated samples; similar DSC curves were obtained for many new and old collagen-based materials [5,14]. At a relative low temperature, each investigated material has exhibited an endothermic peak, denoted by I, corresponding to the loss of material humidity. For the samples P1, P2 and P5, this process is followed by one or two endothermic processes, denoted by II. This process, earlier detected by Okamoto and Saeki [15, 16], and recently [5, 14] put in evidence for pure collagen and collagen-based materials, could be explained by the biphasic amorphous-crystalline structure of collagen-based materials according to which the crystalline triple-helix is embedded into a amorphous matrix [5]. Very recently [14], the data from Proton solid-state NMR, obtained for pure collagen, parchments and leathers, have lead to a three-phase model (rigid, inter-face, and mobile phase). Consequently, the process II might be related to softening (melting) of the rigid (crystalline) part of parchment.

The characteristic parameters put in evidence in the DSC curves –N_2 flow are listed in table 2.

According to the curves shown in figure 4 the data listed in table 2:

(a) the standard sample exhibit a single melting process having the parameters in the ranges previously reported [14] for many new leathers manufactured by vegetable tanning ($240^0C \le T_m \le 252^0C$; 0.9 J.$g^{-1} \le -\Delta H \le 2.2$ J.g^{-1});

(b) the samples P1 and P2 exhibit melting points in the temperature range $113^0C \ldots 121^0C$;

(c) the sample P1 exhibits two melting processes;

(d) in the temperature range in which the analyses were performed, the sample P4 has not a melting process.

The statement (b) could be explained by the results obtained in our previous DSC study of the thermal behavior of leathers and parchments [14]. It was observed that at the heating in both O_2 and synthetic air flows, all investigated new leathers manufactured by vegetable tanning and old leathers exhibit a softening process at lower temperatures ($118^0C \ldots 135^0C$). This means that a thermo-oxidation of new and old leathers occurs when these materials are heated in oxidative atmosphere. It was also

Table 2
THE CHARACTERISTIC PARAMETERS OF THE PROCESSES PUT IN EVIDENCE IN DSC CURVES

| | DSC in N_2 flow | | | | DSC of samples immersed in water | | | | |
| | Dehydration | | "Melting" | | | | | | |
Sample code	T_m °C	$-\Delta H$ J.g^{-1}	T_m °C	$-\Delta H$ J.g^{-1}	N	Process	T_{onset} °C	T_m °C	$-\Delta H$ J.g^{-1}
P1	49.6	196.5	113.4	1.00	5	I	35.2	38.5	2.83
			128.1	0.87		II+II'	55.1	59.5; 61.7	8.02
						III+III'	67.0	68.8; 71.3	1.15
P2	44.1	184.7	120.8	2.01	4	I	34.6	38.3	0.63
						II	46.6	47.9	0.58
						II	54.3	56.8	0.62
						IV	61.4	65.4	5.17
P3	52.4	211.5	-	-	4	I	34.3	38.1	0.18
						II	43.8	46.9	0.12
						III+III'	51.1	57.4; 61.7	12.54
Standard sample P5	67.3	218.8	249.4	1.91	1	I	72.7	78.0	27.61

T_m = temperature corresponding to the peak minimum; ΔH = process enthalpy; N = number of processes put in evidence in the temperature range 30°C ... 95°C; X' is the process overlapped with process X
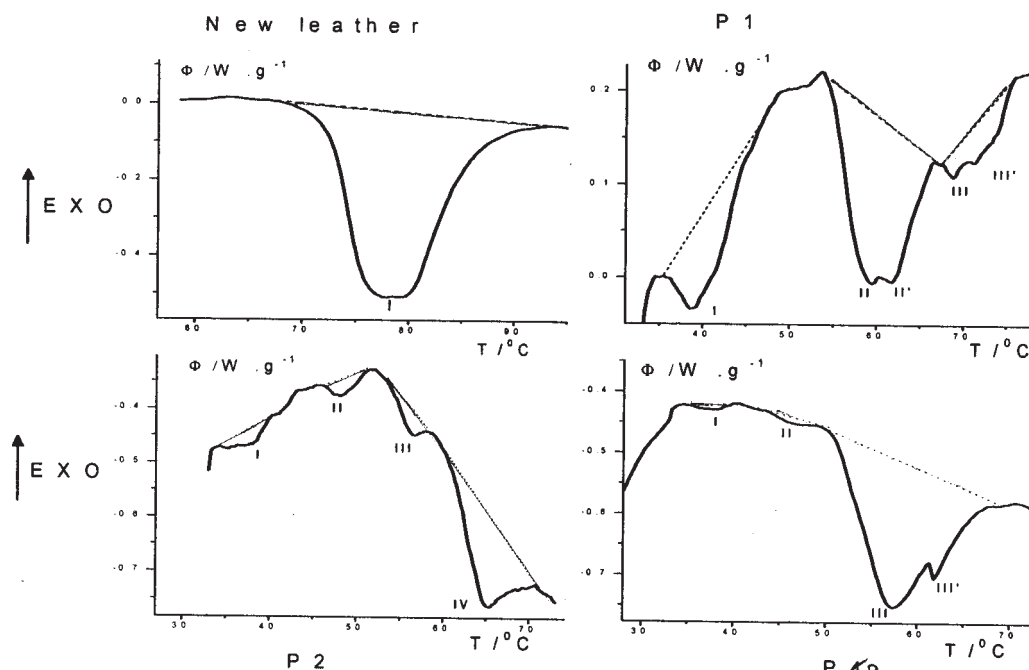

Fig. 4.DSC curves for the investigated leathers immersed in water

noted that at the heating in N_2 flow, some sorts of old leathers have also exhibited a softening process around 133° C. This means that the thermo-oxidation process also has taken place during the naturally ageing of leathers. Our results show that such a process occurred at the natural aging of leathers P1 and P2.

The statement (c) could be explained by heterogeneity of the sample P1, while the statement (d) shows that the leather P3 looses its crystalline part by natural ageing [15].

DSC analysis of the sample immersed in water

Figure 4 shows the DSC curves obtained by analysis of the investigated samples immersed in water.

The DSC analysis of the samples immersed in waters show that in the temperature range 20°C...95°C only the recent manufactured leather exhibit a single endothermic peak. The characteristic parameters put in evidence in the DSC curves –water are listed in table 2.

It was pointed out by several authors [16] that the value of the shrinkage temperature determined by classical or MHT methods for a given collagen based material is closed to the extrapolated onset temperature (T_{onset} in table 2) corresponding to the main process of denaturation put in evidence in DSC curve recorded for the sample immersed in water. The existence of many peaks in the DSC curve

Table 3
THE VALUES OF SHRINKAGE TEMPERATURE

Sample code	Initial temp. °C	A1 °C	B1 °C	C °C	B2 °C	A2 °C	Final temp. °C
Historical sample: P1	24,4	37,4	42,4	45,3	52,7	57,8	58,1
P2	23,8	35,7	37,7	48,5	62,7	64,6	68,4
P3	21,5	42,8	45,6	46,9	49,4	51,4	60,5
P4	24,3	27,3	35,2	44,1	61,6	65,2	70,0
Standard sample P5 (ICPI)	24,3	29,6	50,8	69,0	76,2	78,8	82,9

A1, B1 – initial shrinkage and the following one; A2, B2 – shrinkage of the last individual

fibres; C – shrinkage temperature (simultaneous and consecutive shrinkages).

(fig. 5 and table 2) indicates a high degree of material heterogeneity. On the other hand, the DSC investigation of many collagen based materials [5] leads to the following values of T_{onset}: 77.1±8.0⁰C for recent leathers manufactured by vegetal tanning, 67.0±12.0⁰C for middle age leathers, 58.0±7.0⁰C for new and old (middle age) parchments, and 40.1±2.2⁰C for fresh collagen extracted from animal skins. The data listed in table 2 allow making some similarities between the hydrothermal stabilities of the investigated leathers and the above mentioned collagen based materials. The low values of T_{onset} and/or the existence of many DSC peaks indicate a high degree of deterioration of all investigated leathers.

Shrinkage temperature

By using the MHT method (Micro Hot Table) the results obtained are shown in the table 3.

The samples P1 – P4 have 30 % lower shrinkage temperature in comparison with the standard (P5).

Conclusion

The samples from Ukraine present a moderate degree of degradation, 20 – 35% losses in the initial luminosity and, on average, a 23% diminishing in the contraction temperature. The shrinkage temperature is semi-quantitatively correlated with the absorbance of the 1480 – 1500 nm bands, pointing to changes in the hydroxyl structures associated by hydrogen bonds.

The DSC analyses of some patrimony leathers were performed in the following conditions: samples immersed in water, hermetically sealed in an aluminum pan and stocked for 24 h; samples in open crucible, under N₂ flow. The DSC plots recorded in gas flow show two different processes occurring, namely, the loss of water (dehydration) and the softening (melting). Focusing on the second process observed when the analysis is performed in N2 flow, it was pointed out that unlike the new leathers, and the naturally aged ones exhibit an advanced degree of oxidation.

The results obtained by DSC analyses of sample immersed in water show a high heterogeneity of the old leathers, which could be assigned as a mixture of untanned collagen and sorts of leathers with different degree of cross-linking.

References

1. LARSEN, R. STEP, Leather project. Evaluation of the correlation between natural and artificial ageing of vegetable tanned leather and determination of parameters for standardization of an artificial ageing method. European Commission, Research Report No. 1, 1994
2. LARSEN, R., ENVIRONMENT Leather project. Deterioration and conservation of vegetable tanned leather, European Commission, Research Report No. 6, 1996
3. DELLAGATTA, G., BADEA, E.,CECCARELLI, R., USACHEVA, T., MASIC, A., COLLUCIA, S., J. Therm, Anal. Calorim., 82 (2005) 637
4.BADEA, E., MIU, L., BUDRUGEAC, P., GIURGINCA, M., MAŠIC, A., BADEA, N., DELLA GATTA, G., J. Thermal anal. Calorim., **91**, nr. 1, 2008, p.17
5.BUDRUGEAC, P., MIU, L, J. Cult. Heritage, **9**, 2008, p. 146.
6.BUDRUGEAC, P., MIU, L., SOUCKOVA, M., J. Therm. Anal. Calorim., **88** (2007) 693
7.BUDRUGEAC, P., MIU, L., BOCU, V., WORTMANN, F.J., POPESCU, C., J. Therm. Anal. Calorim., **72** (2003) 1057
8.MIU, L., GIURGINCA M., Rev. Chim.(Bucharest), **57**, no. 1, 2006, p. 42
9.TIDE, T., MIU, L., GIURGINCA, M., MEGHEA, A., Rev. Chim. (Bucharest), **57,** no.5, 2006, p. 466
10. BUDRUGEAC, P., MIU,L., POPESCU,C., WORTMANN, F.J., J. Therm. Anal. Calorim., **79** , 2004, 975
11.DERRICK M., Annual of the Book and Paper Group, the American Institute for Conservation, **10**, 1991
12.EGAWA, M., FURUHARA,T., TAKAHASHI, M., OZAKI, Y., Applied Spectroscopy **57**, 4 (2003) p.473
13.SEGTMAN, W.H., ŠAŠC, S. , ISSAKSSOU, T., Y. OZAKI , Y., Anal. Chem **73** (2001) p. 3153
14.POPESCU, C., BUDRUGEAC, P., WORTMANN, F. J., MIU, L., DEMCO, D. E., BAIAS, M., Polym. Degrad. Stab., **93**, 2008, p. 976
15.LOKE, W. K., KHOR, E, Biomaterials, **16**, 1995, p. 251
16. OKAMOTO, Y., SAEKI, K., Kolloid-Zeitscrift. Zeitschrift fur Polymere, **194**, 1964, p. 124