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## Synthesis and characterization of poly(vinyl alcohol-*co*-aspartic acid) copolymers

**Summary** — The study presents synthesis of vinyl alcohol and L-aspartic acid copolymers (PVA-*co*-Asp), by solution polycondensation procedure using manganese acetate as a catalyst. Two copolymers were obtained with molar ratio of poly(vinyl alcohol) (PVA) structural unit to aspartic acid equal to 10/0.5 and 10/1, respectively. PVA and copolymers were investigated using Fourier transform infrared spectroscopy (FT-IR), but copolymers also with nuclear magnetic resonance (<sup>1</sup>H NMR). Molecular weight ( $\bar{M}_w$ ) and limiting viscosity numbers ( $[\eta]$ ) of these polymers were also determined. With a system for simultaneous thermogravimetric and differential scanning calorimetry analyses (TG-DSC) thermal stability of PVA and its copolymers was investigated and compared. There was also defined zeta potential of water dispersions of PVA and copolymers and also dimensions and polydispersity of copolymer particles.

**Keywords:** poly(vinyl alcohol), L-aspartic acid, crosslinked copolymers, thermal stability.

SYNTEZA I CHARAKTERYSTYKA KOPOLIMERÓW POLI[(ALKOHOL WINYLOWY)-*ko*-(KWAS ASPARAGINOWY)]

**Streszczenie** — W artykule opisano syntezę kopolimerów alkoholu winylowego i kwasu L-asparaginowego prowadzoną metodą polikondensacji rozpuszczalnikowej z zastosowaniem octanu manganu jako katalizatora. Otrzymano dwa kopolimery, w których stosunek molowy jednostki strukturalnej poli(alkoholu winylowego) (PVA) do kwasu asparaginowego wynosił 10/0,5 i 10/1 [odpowiednio, PVA-*ko*-Asp (10/0,5) i PVA-*ko*-Asp (10/1)]. PVA oraz kopolimery badano metodą spektroskopii w podczerwieni z transformacją Fouriera (FT-IR), a kopolimery także metodą magnetycznego rezonansu jądrowego (<sup>1</sup>H NMR). Wyznaczano także ciężar cząsteczkowy ( $\bar{M}_w$ ) oraz graniczne liczby lepkościowe ( $[\eta]$ ) tych polimerów. Za pomocą układu do jednoczesnej analizy termogravimetrycznej i skaningowej kalorymetrii różnicowej (TG-DSC) zbadano i porównano stabilność termiczną PVA i jego kopolimerów. Określano także potencjał elektrokinetyczny dyspersji wodnych PVA i kopolimerów oraz wymiary i polidispersyjność cząstek kopolimerów.

**Słowa kluczowe:** poli(alkohol winylowy), kwas L-asparaginowy, usieciowane kopolimery, stabilność termiczna.

Poly(vinyl alcohol) (PVA) is a polymer of great interest owing to its many desirable characteristics: biodegradability, biocompatibility, non-toxicity, that justify its utilization in various pharmaceutical and biomedical applications [1]. PVA is the only vinyl type polymer that was confirmed to be biodegradable, but its biodegradation rate is too small for practical use as a degradable polymer in environmental conditions. The most effective approach to improve its degradability is by blending it with a suitable biopolymer. There are already reported PVA/chitin-*graft*-poly(2-alkyl-2-oxazoline) and PVA/poly(sodium  $\alpha,\beta$ -D,L-aspartate) blends as miscible polymer pairs [2–5].

Although PVA is biodegradable, with good mechanical properties in dry state, its highly hydrophilic properties limit its scope of application particularly in humid

environment. PVA with an increased structural variability (different molecular weights, hydrolysis degree, tacticity), and presence of hydroxyl groups which makes feasible a number of grafting and crosslinking reactions of the polymer backbone is useful in practical investigations. These chemical modifications determine ester groups formation by grafting reactions with acid chlorides or acid anhydrides. When PVA firstly reacted with two cyclic anhydrides (phthalic or succinic anhydride) a carboxylic group was introduced in the side chain. These half-esters reacted in a second step with aromatic diglycidyl ethers (4,4'-diphenyldiglycidyl ether, 4,4'-thio-diphenyldiglycidyl ether, and 4,4'-oxydiphenyldiglycidyl ether), which caused crosslinking. Depending on the

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quantity of anhydride and hardener used, different crosslinking degrees could be obtained, resulting in products with different polarities due to remaining carboxylic and hydroxylic groups [6].

Our previous research focused on PVA grafting with acrylamide to achieve copolymers with improved properties, biodegradable and biocompatible, that would be further used as hydrogels or water absorbing copolymers [7]. PVA chemical modification was also done by grafting reactions with lactic acid or poly(lactic acid) (PLA) described in [8], or lactic acid and aspartic acid described in [9]. Poly(vinyl alcohol)-*co*-lactic acid synthesized copolymer was then crosslinked with glutaraldehyde and some conjugated copolymer/drug systems were subsequently prepared [10]. Drug release was studied by dialysis in phosphate buffer solution (pH = 7.4).

The crystalline nature of PVA is of particular interest especially for physically crosslinked hydrogels prepared by repeated cycles of freezing and thawing [11]. PVA gels achieved by freeze-thaw cycles are opaque, being consequently a major drawback for ophthalmological applications. Chemical crosslinking is a highly versatile method to prepare hydrogels with good mechanical stability. PVA was chemically crosslinked with glutaraldehyde, the gels exhibited a high swelling degree in water or biological fluids and a rubbery and elastic nature [12]. Our previous research studied synthesis and characterization of PVA hydrogels, obtained with chemical crosslinking using sodium tetraborate decahydrate as crosslinking agent, triethylenetetramine as accelerator in aqueous solution at room temperature [13].

In this paper we report synthesis and characterization of PVA copolymers using L-aspartic acid as monomer and manganese acetate as a catalyst, by solution polycondensation procedure.

## EXPERIMENTAL

### Materials

Poly(vinyl alcohol) from S.C. Romacryl SA Rasnov (Romania) of hydrolysis degree 98 % and polymerization degree 400, average molecular weights were  $\overline{M}_n = 18\ 000$  and  $M_w = 88\ 500$ , saponification index was  $140 \pm 30$  mg KOH/g.

L-aspartic acid, sodium hydroxide, ammonium hydroxide and manganese acetate, purum grade reagents from Fluka (Switzerland) were used as received.

### Copolymers syntheses

Poly(vinyl alcohol-*co*-aspartic acid) (PVA-*co*-Asp) copolymers were synthesized by solution polycondensation procedure using two molar ratios PVA/L-aspartic acid: 10/0.5 and 10/1, respectively (PVA expressed in structural units), and manganese acetate as a catalyst. PVA was dissolved under stirring at 80 °C in distilled

water and a 24 wt. % aqueous solution was obtained. L-aspartic acid was separately dissolved in NH<sub>4</sub>OH 25 wt. % aqueous solution, at room temperature and a 32 wt. % aqueous acid solution was obtained, that was gradually added to PVA solution. After adding the catalyst (CH<sub>3</sub>COO)<sub>2</sub>Mn · 4H<sub>2</sub>O (0.8 wt. % reported to the reaction components), the reaction mixture was heated to 95 °C and maintained under reflux for 3 h. In the second part of synthesis, the temperature was raised to 130–140 °C, water and secondary reaction products were collected for 2 h under vacuum using a distillation-collecting device. Then, the synthesized reaction product was precipitated in acetone, washed twice with fresh acetone and vacuum dried at 70 °C. Considering the molar ratio of the two components PVA/L-aspartic acid (10/0.5 and 10/1), we name the synthesized copolymers with 0.5 moles aspartic acid PVA-*co*-Asp (10/0.5) and with 1 mole aspartic acid PVA-*co*-Asp (10/1). The reaction yield of copolymers was approximately 86 %.

### Methods of testing

Fourier Transform Infrared Spectrometer (FT-IR) type Bruker Vertex 70 on KBr pellets was applied to investigate PVA and copolymers.

<sup>1</sup>H NMR spectra of copolymers were obtained on a Bruker Avance DRX 400 NMR spectrophotometer, equipped with 9.4 Tesla (400 MHz) UltraShield magnet. The grafted copolymers were dissolved in DMSO-*d*<sub>6</sub>, the solution concentration was about 5 w/v %. Analyses were carried out at 70 °C, all chemical shifts were reported in parts per million (ppm), using tetramethylsilane (TMS) as the internal reference.

Thermal degradation of copolymers was performed using a simultaneous thermogravimetric and differential scanning calorimetry analyses system (TG-DSC), model STA 449F1 Jupiter (Netzsch, Germany). The thermogravimetric analyzer was calibrated on temperature and sensitivity, using the melting temperatures of some standard metals (Hg, In, Sn, Bi, Zn, Al), from -38.5 °C to 600 °C. Samples with mass between 7 and 8 mg were heated from 25 °C to 600 °C, at the heating rate of 10 deg/min. Helium (of 99.999 % purity) as carrier gas with flow rate of 50 cm<sup>3</sup>/min and protective purge for thermobalance of 20 cm<sup>3</sup>/min was used. The samples were heated in an open Al<sub>2</sub>O<sub>3</sub> crucible and Al<sub>2</sub>O<sub>3</sub> as reference material was used.

Zeta potential and average particle size were measured using a Zetasizer Nano-ZS apparatus, ZEN-3500 model (Malvern Instruments, England). For measurements the copolymers were dissolved in bidistilled water at a concentration of 0.01 g/dm<sup>3</sup>. Experiments were performed in the following conditions: water as dispersant medium, medium refractive index  $n = 1.330$ , medium viscosity 0.887 cP, dielectric constant 79, temperature 25 °C. The measurements were carried out in triplicate directly after sample preparation, and the results were expressed as the mean size. Next zeta potential was measured with

the M3-PALS technique, a combination of laser Doppler velocimetry (LDV) and phase analysis light scattering (PALS). Each zeta potential measurement was performed automatically at 25 °C.

The measurement of absolute molecular weight using static light scattering (SLS) was also done with Zetasizer Nano-ZS apparatus. The intensity of scattered light that a macromolecules produce is proportional to the average molecular weight ( $\overline{M}_w$ ) and concentration of the macromolecules  $I = \overline{M}_w \cdot C$ . A common standard used in light scattering is toluene (at 633 nm the Rayleigh ratio is  $1.3522 \cdot 10^{-5} \text{ cm}^{-1}$ ). Molecular weight determination is based on Rayleigh equation:

$$K \cdot C/R_0 = (1/\overline{M}_w + 2A_2 \cdot C)P(\theta) \quad (1)$$

where:  $K$  – optical constant,  $C$  – concentration,  $\overline{M}_w$  – molecular weight,  $R_0$  – Rayleigh ratio of the sample,  $A_2$  – 2nd virial coefficient,  $P(\theta)$  – shape factor.

For Rayleigh scatterers  $P(\theta) = 1$  and the equation is simplified to  $y = mx + c$ . Therefore a plot of  $KC/R_0$  versus  $C$  should produce a straight line whose intercept at zero concentration is  $1/\overline{M}_w$  and whose gradient is  $A_2$ .

## RESULTS AND DISCUSSION

IR spectra of PVA and PVA-co-Asp copolymers are presented in Figure 1. We can notice that the copolymers have most of PVA characteristic IR absorption bands. The most representative are: at  $3412 \text{ cm}^{-1}$  ( $\nu\text{OH}$ ) characteristic to OH unmodified group from PVA chain,  $2940 \text{ cm}^{-1}$  and  $2910 \text{ cm}^{-1}$  ( $\nu\text{CH}_2$ ) and at  $850 \text{ cm}^{-1}$  ( $\gamma\text{CH}_2$ ) amorphous. Besides, other absorption bands are recorded at  $1940 \text{ cm}^{-1}$  and  $3412 \text{ cm}^{-1}$  ( $\nu\text{NH}_2$ ) characteristic to alkyl- $\text{NH}_2$  group, at  $1417 \text{ cm}^{-1}$  and  $1629 \text{ cm}^{-1}$  ( $\nu\text{C}=\text{O}$ ) characteristic to CO-NH group from amide, and at  $1234 \text{ cm}^{-1}$  characteristic to COOR ester group in the copolymer.

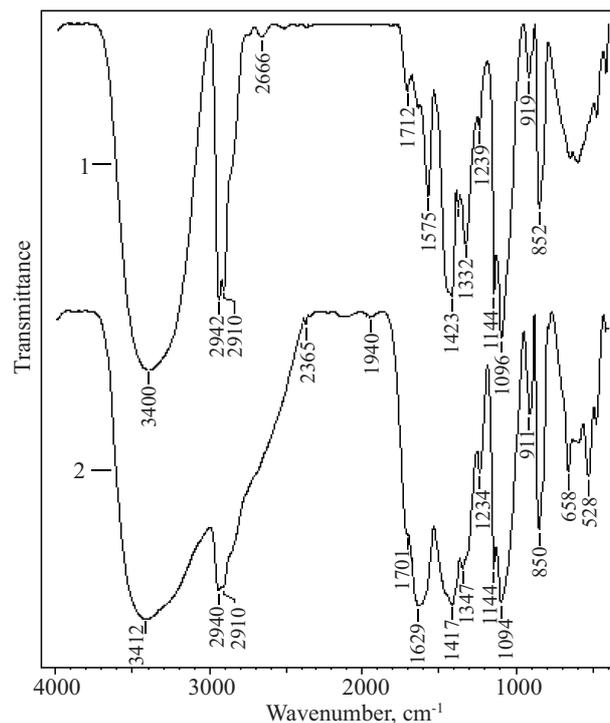


Fig. 1. FT-IR spectra of: 1 – PVA, 2 – PVA-co-Asp (10/0.5)

$^1\text{H}$  NMR spectrum of PVA-co-Asp (10/0.5) copolymer is presented in Figure 2. Based on the reports on peak assignment for proton species in PVA, polysuccinimide (PSI) and their derivatives [14–19] we attributed the proton signals in the  $^1\text{H}$  NMR spectrum of PVA-co-Asp copolymer as quoted in the figure. The resonance at  $\delta = 1.459$  ppm is assigned to  $\text{CH}_2$  groups (a–a') and at  $\delta = 2.099$  ppm to CH groups (b–b') from vinyl units existent in copolymer. In the given reaction conditions, the possibility of PSI formation as an intermediary by-product exists, then succinimide cycle can be broken and two

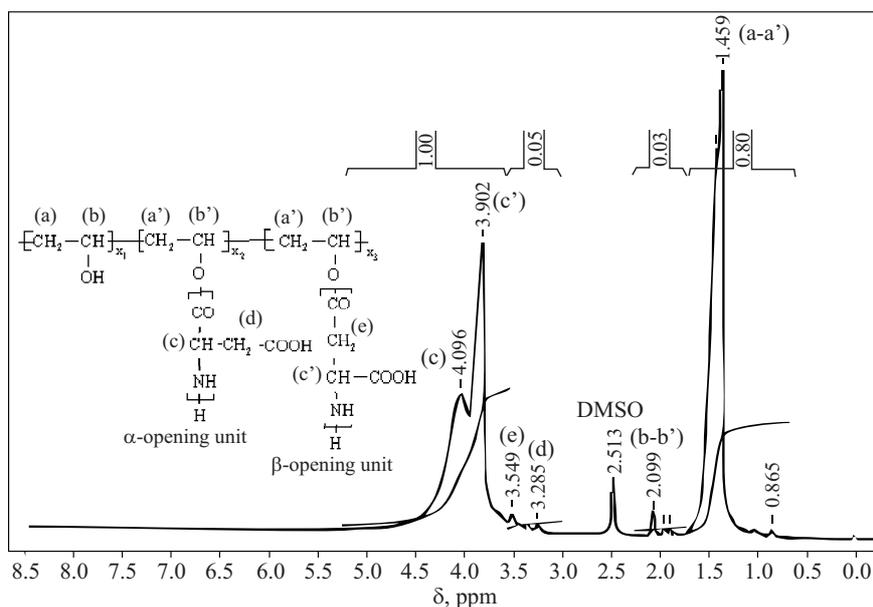


Fig. 2.  $^1\text{H}$  NMR spectrum of PVA-co-Asp (10/0.5) copolymer

structural units of  $\alpha$ - and  $\beta$ -type can be obtained [15, 16]. The protons signals of the  $\text{CH}_2$  groups from  $\alpha$  and  $\beta$  structural units of aspartic acid (d and e protons) are located at 3.285 and 3.549 ppm, respectively, and protons signals of the CH groups from  $\alpha$  and  $\beta$  units (c and c' protons) are located at 4.096 and 3.902 ppm, respectively. The shifts are influenced by the nature of the near atoms. Residual protons signal in  $\text{DMSO-d}_6$  were set at 2.513 ppm.

**Table 1.** Molecular weight and viscosity of pure PVA and copolymers

Sample	Content, mol		$\bar{M}_w$	$A_2, \text{cm}^3 \cdot \text{mol/g}^2$	$[\eta]$ dl/g
	PVA	Asp			
PVA	100	0	88 500	0.000801	1.912
PVA-co-Asp (10/0.5)	10	0.5	93 440	0.000258	2.312
PVA-co-Asp (10/1)	10	1	206 360	0.000337	2.594

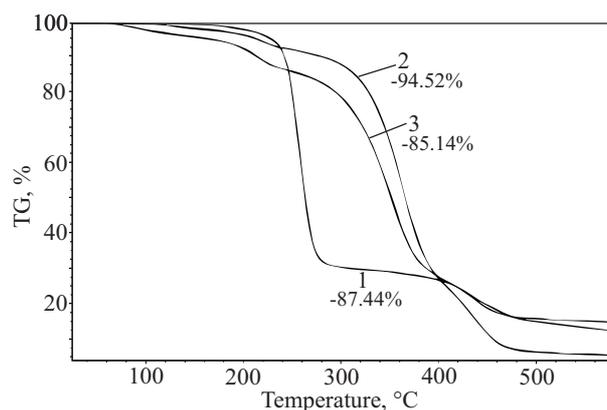
The absolute molecular weight ( $\bar{M}_w$ ) and 2nd virial coefficient ( $A_2$ ) values of PVA and PVA-co-Asp copolymers, determined with Zetasizer Nano ZS apparatus based on static light scattering, are presented in Table 1.  $\bar{M}_w$  value of PVA-co-Asp (10/0.5) copolymer equal to 93 440 is close to  $\bar{M}_w$  of PVA 88 500, while  $\bar{M}_w$  of PVA-co-Asp (10/1) has a more raised value *i.e.* 206 000.  $\bar{M}_w$  increase is due to more raised degree of branching and crosslinking reactions. The intrinsic viscosity ( $[\eta]$ ) of copolymers was determined at 25 °C using 5 g/dm<sup>3</sup> solutions in DMSO, the obtained values were in accord with ones measured on the Zetasizer apparatus.

**Table 2.** Characteristic temperatures of thermal degradation of pure PVA and PVA-co-Asp copolymers

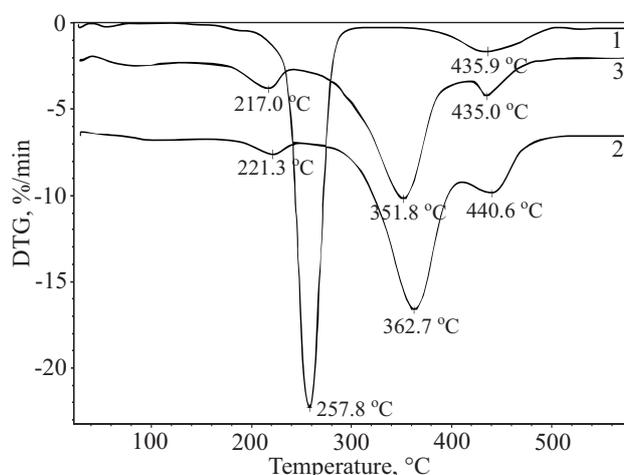
Sample	Temp. range °C	Mass loss %	DTG peak °C	$T_{10}^*)$ °C	$T_{50}^*)$ °C	Ash %
PVA	188–305	67.87	257.8	242	263	12.56
	360–510	14.00	435.9			
PVA-co-Asp (10/0.5)	180–257	5.57	221.3	278	366	5.48
	257–410	67.00	362.7			
	410–510	18.20	440.6			
PVA-co-Asp (10/1)	168–243	8.45	217.0	214	352	14.86
	243–412	60.50	351.8			
	412–510	10.12	435.0			

\*)  $T_{10}$ ,  $T_{50}$  – temperature corresponding to 10 % and 50 % weight loss.

In Figures 3 and 4 TG and DTG curves of the synthesized copolymers and PVA are presented, and in Table 2 some data concerning thermal behavior. The thermal stability of copolymers modified with L-aspartic acid is superior to PVA. From the data presented in the Table 2 we



**Fig. 3.** TG curves of: 1 – PVA, 2 – PVA-co-Asp (10/0.5), 3 – PVA-co-Asp (10/1)



**Fig. 4.** DTG curves of: 1 – PVA, 2 – PVA-co-Asp (10/0.5), 3 – PVA-co-Asp (10/1)

notice that PVA modified with L-aspartic acid presents a higher thermal stability compared to pure PVA. In the case of PVA-co-Asp (10/1) copolymer, weight losses of 50 % are recorded at 352 °C, and for PVA-co-Asp (10/0.5) copolymer at 366 °C, while for pure PVA are recorded at 263 °C. It is known that cyclic poly(aspartic acid) is thermally stable up to 340 °C. Thermogravimetric analysis of obtained copolymers confirms this assumption. Insertion of aspartic acid fragments into PVA structure causes an increase of copolymer thermal stability. PVA-co-Asp (10/0.5) copolymer presents more raised thermal stability than PVA-co-Asp (10/1) until 400 °C temperature, and at higher temperatures the thermal stability is slightly changed, this aspect is also noticed from the content of final residue. By thermal decomposition process of PVA-co-Asp (10/1) copolymer ash is 14.86 %, compared to 5.48 % in the case of PVA-co-Asp (10/0.5). This aspect can also be explained by the greater number of branches obtained when higher content of aspartic acid is used. These branches contain more unbound  $\text{NH}_2$  or  $\text{COOH}$  functional groups that can participate at other branching and/or crosslinking reactions, causing consequently thermal stability increase. In the case of thermal decompo-

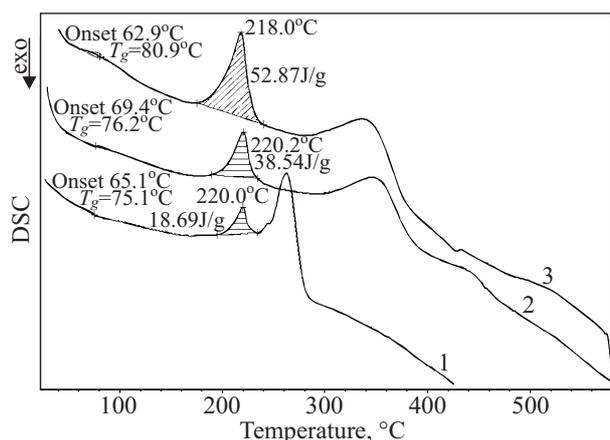


Fig. 5. DSC curves of: 1 – PVA, 2 – PVA-co-Asp (10/0.5), 3 – PVA-co-Asp (10/1)

sition of copolymers there exists a main decomposition process situated in 243–412 °C temperature interval where weight losses are between 60 and 67 %, and other two secondary processes where weight losses are lower. The appearance of the third thermal decomposition process in the case of copolymers is caused by aspartic acid units grafted on PVA chains. On the other hand, PVA presents a main thermal decomposition process in 188–305 °C interval with weight losses of almost 67 %, and a single secondary process with weight losses of 14 %.

Table 3. DSC characteristics of pure PVA and copolymers

Sample	$T_g$ °C	$\Delta C_p$ J/(g·deg)	$T_m$ °C	$\Delta H_f$ J/g	$\chi_c$ %
PVA	75.1	0.118	220.0	18.69	11.98
PVA-co-Asp (10/0.5)	76.2	0.169	220.2	38.54	24.71
PVA-co-Asp (10/1)	80.9	0.174	218.0	52.87	33.89

In Figure 5 and Table 3 thermal characteristics of copolymers and PVA determined by DSC are presented. Glass transition temperature ( $T_g$ ) is influenced by aspartic acid ratio and grafting or crosslinking degree of copolymers. At higher crosslinking degrees, the polymer chains are constrained to remain close to each other in the crosslinking sites and the free volume decreases. The decrease of the free volume determines  $T_g$  increase.  $T_g$  value of the copolymer PVA-co-Asp (10/1) has a more raised value (80.9 °C), compared to PVA (75.1 °C) than value of PVA-co-Asp (10/0.5) which is 76.2 °C. This fact suggests that the crosslinking and branching reactions took place. The copolymers crystallinity is modified with aspartic acid percent raise in their structure. On the basis of enthalpy of fusion ( $\Delta H_f$ ) of copolymers, calculated from the melting peak area of crystalline phase and enthalpy of fusion of completely crystalline PVA ( $\Delta H_f^0 = 156$  J/g) [20], the degree of crystallinity ( $\chi_c$ ) (listed in Table 3) was de-

termined.  $\chi_c$  values of copolymers are much more raised compared to PVA utilized in the synthesis. In general, for copolymers and copolymer blends containing a crystalline component, the variation of melting temperature ( $T_m$ ) and  $\chi_c$  values are attributed either to interactions between components or hydrogen-bonding interactions [21]. The degree of crystallinity was determined with the formula:

$$\chi_c = \frac{\Delta H_f}{\Delta H_f^0} \cdot 100 \quad (2)$$

The values of the specific thermal capacities ( $\Delta C_p$ ) of the copolymers  $\Delta C_p = 0.174$  J/(g · °C) for PVA-co-Asp (10/1) and  $\Delta C_p = 0.169$  J/(g · °C) [for PVA-co-Asp (10/0.5)] present slightly raised value compared to the value for PVA  $\Delta C_p = 0.118$  J/(g · °C) suggesting that the amorphous/crystalline ratio is also modified.

The presence of aspartic acid units in the synthesized copolymer structure, was emphasized by nitrogen content using Kjeldahl method [22]. In the case of PVA-co-Asp (10/0.5) copolymer, nitrogen is found in proportion of 1.30 % and in copolymer PVA-co-Asp (10/1), approximately 3.04 %. The higher nitrogen value in PVA-co-Asp (10/1) demonstrates a raised grafting and crosslinking degree. Also the solubility of copolymers in water and DMSO at 80 °C temperature was modified compared to PVA. PVA-co-Asp (10/0.5) copolymer and PVA are totally soluble in both solvents, while PVA-co-Asp (10/1) copolymer is soluble only in DMSO.

Size distribution of aqueous dispersions of the two copolymers is presented in Figure 6. Z-average diameter was determined with a Zetasizer Nano ZS equipment, at 25 °C. The particles diameter for both copolymers was 215 nm and the polydispersity index was 0.608 in the case of PVA-co-Asp (10/0.5) copolymer and 0.469 in the case of PVA-co-Asp (10/1), respectively. Also other dimensional species with Z-average diameter outside the domain 215 nm exist, but their presence in the total particles volume is not significant.

Zeta potential and electrical conductivity were studied as temperature function in 25–40 °C interval and variations of these parameters are presented in Figu-

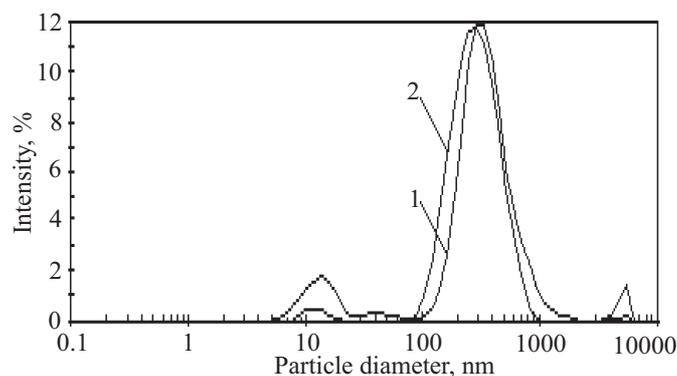


Fig. 6. Particle size distribution for: 1- PVA-co-Asp (10/0.5), 2 – PVA-co-Asp (10/1)

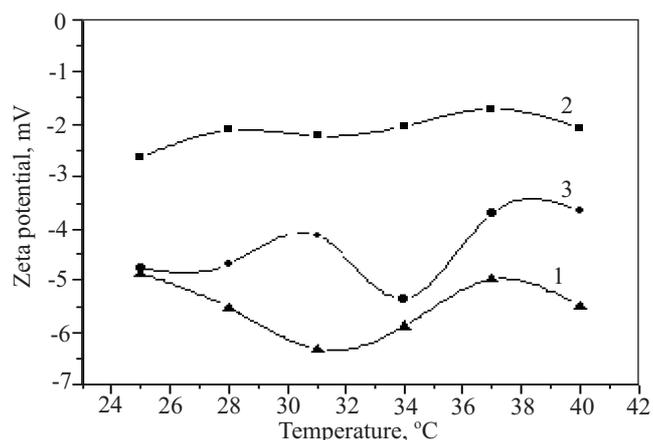


Fig. 7. Zeta potential versus temperature for: 1 – PVA, 2 – PVA-co-Asp (10/0.5), 3 – PVA-co-Asp (10/1)

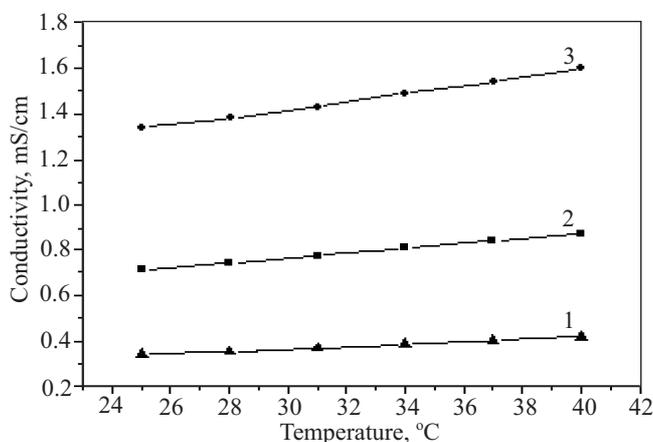


Fig. 8. Conductivity variation versus temperature for: 1 – PVA, 2 – PVA-co-Asp (10/0.5), 3 – PVA-co-Asp (10/1)

res 7 and 8. pH value of the solutions was 4.72 in the case of PVA-co-Asp (10/0.5) copolymer and 4.82 in the case of PVA-co-Asp (10/1) copolymer. Zeta potential presents negative values in both cases, lower values are recorded in the case of the copolymer with higher content of aspartic acid. As absolute zeta potential values are included inside the domain  $\pm 30$  mV, the stability of the solutions is reduced, therefore the possibility of particles sedimentation exists. The electrical conductivity variation with temperature exhibits a linear growth in the whole range 25–40 °C, higher values are recorded in the case of PVA-co-Asp (10/1) copolymer.

### CONCLUSIONS

By grafting aspartic acid in PVA, its thermal stability and humidity resistance were improved, due to changes of hydrophilic/hydrophobic ratio and of possible cross-linking reactions. Although PVA modification was achieved by grafting with small amounts of aspartic acid,

the solubility of both copolymers in water and DMSO was raised in comparison to PVA. The copolymer PVA-co-Asp (10/0.5) dissolves in water and DMSO at 80 °C, while PVA-co-Asp (10/1) copolymer only in DMSO. The thermal stability of copolymers modified with aspartic acid is superior to PVA. In the case of PVA-co-Asp (10/1) copolymer, weight losses of 50 % are recorded at 352 °C, for PVA-co-Asp (10/0.5) copolymer at 366 °C, while for PVA at 263 °C. Copolymers crystallinity is modified with aspartic acid percent raise in their structure. Taking into account the nature of the reactants used in the synthesis we can appreciate that biodegradable copolymers are obtained, which can be used as matrices for controlled delivery systems of active ingredients, with possible application in medicine or agriculture.

### REFERENCES

1. Finch C. A.: "Polyvinyl Alcohol", John Wiley & Sons, Bristol, Great Britain 1973.
2. Aoi K., Takasu A., Okada M.: *Macromol. Rapid Commun.* 1975, **16**, 757.
3. Aoi K., Takasu A., Okada M.: *Macromolecules* 1997, **30**, 6134.
4. Aoi K., Takasu A., Tsuchiya M., Okada M.: *Macromol. Chem. Phys.* 1998, **199**, 2805.
5. Takasu A., Aoi K., Okada M.: *Macromol. Rapid Commun.* 1997, **18**, 497.
6. Gimenez A., Mantecon A., Ronda J. C., Cadiz V.: *J. Appl. Polym. Sci.* 1997, **65**, 1643.
7. Tudorachi N., Lipsa R.: *J. Optoelectron. Adv. Mater.* 2006, **8**, 659.
8. Tudorachi N., Lipsa R.: *Materiale Plastice* 2004, **41**, No. 2, 99.
9. Tudorachi N., Lipsa R.: *e-Polymers* 2009, No. 122.
10. Tudorachi N., Lipsa R., Chiriac A.: COFrRoCA – Bacau, Romania, 22–26 September 2004, 141.
11. Hassan C. M., Peppas A.: *Adv. Polym. Sci.* 2000, **153**, No. 41, 38.
12. Peppas N. A., Benner R. E.: *Biomaterials* 1980, **1**, 158.
13. Tudorachi N., Lipsa R.: *J. Optoelectron. Adv. Mater.* 2007, **9**, 952.
14. Elisseeff J., Anseth K., Langer R., Hrkach J. S.: *Macromolecules* 1997, **30**, 2182.
15. Tomida M., Nakato T., Kuramochi M., Shibata M., Matsunami S., Kakuchi T.: *Polymer* 1996, **37**, 4435.
16. Tomida M., Nakato T., Matsunami S., Kakuchi T.: *Polymer* 1997, **38**, 4733.
17. Feng Y., Klee D., Höcker H.: *Macromol. Chem. Phys.* 2002, **203**, 819.
18. Polaczek J., Dziki E., Pielichowski J.: *Polimery* 2003, **48**, 61.
19. Tylek E., Polaczek J., Pielichowski J.: *Polimery* 2005, **50**, 341.
20. Tubbs R. K.: *J. Polym. Sci. A* 1965, **3**, 4181.
21. Koyama N., Doi Y.: *Polymer* 1997, **38**, 1598.
22. Dumitru F.: "Practical Working of Biochemistry", Romania, Bucharest 1977, p. 76.

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