

HSP for biomedical polymers - application of inverse gas chromatography

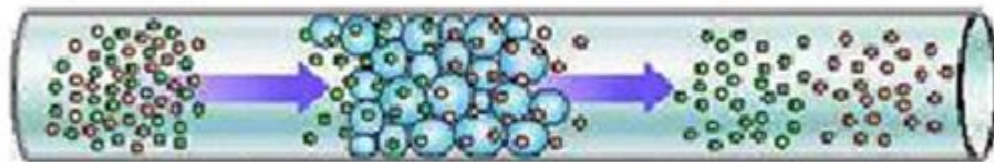
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Solubility parameter

Biomedical field

- pharmacy
- dentine bonding systems
- polymer miscibility/solubility
- biological materials

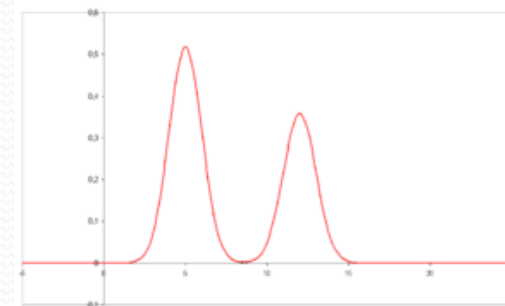
ANALYTICAL CHROMATOGRAPHY



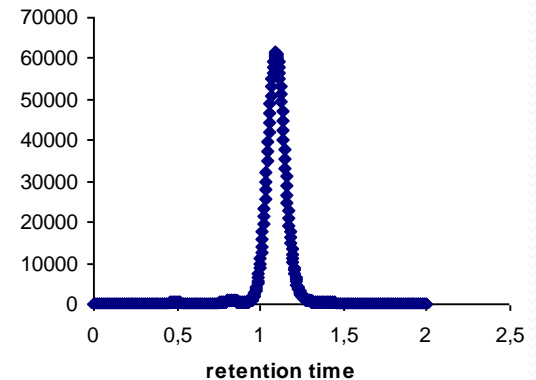
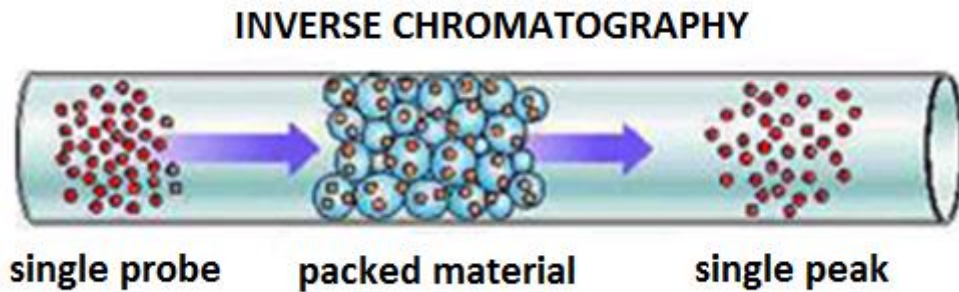
sample mixture

standard analytical
column packing

separated sample peaks



- technique of mixture separation on the individual components
- chromatographed substance is divided between the mobile phase (gas/liquid) and stationary phase (solid, liquid)
- components of the mixture interact with the stationary phase with a different strength and with different speed migrate along the column - separation of the mixture



- a stationary phase (investigated material) is immobilized within a column,
- probes (test solutes) of known physicochemical properties are injected and passed through the column with mobile phase,
- the retention time of probes reflects interactions between the test solute and stationary phase (investigated material)
- retention parameters are used for calculation of different thermodynamic parameters - materials characteristics

IGC- applications

- Surface energy
- Acid/base functionality of surfaces
- Adsorption isotherms
- Solubility parameter
- Glass transition and crystallinity of polymer stationary phases

Solubility parameter/IGC

- The Flory-Huggins interaction parameter

$$\chi_{1,2}^{\infty} = \chi_H^{\infty} + \chi_s^{\infty}$$

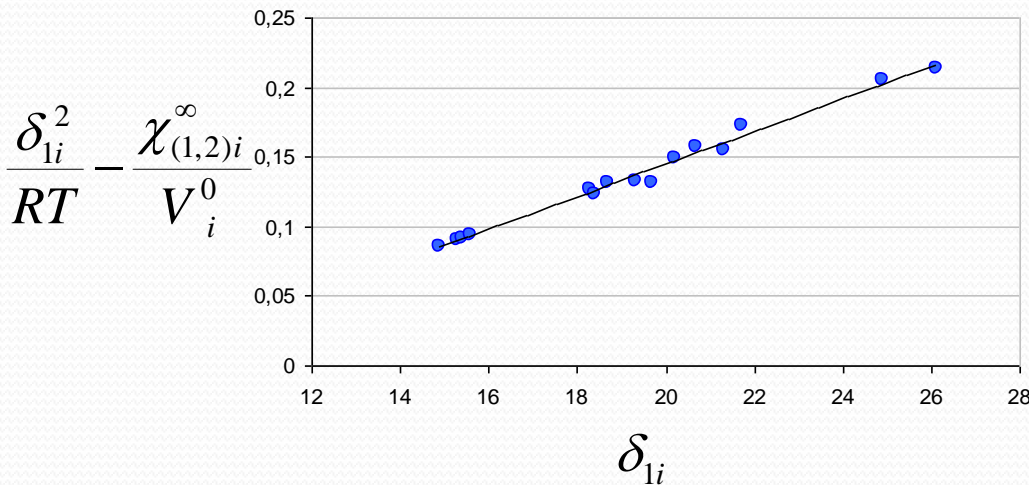
$$\chi_{1,2}^{\infty} = (V_1 / RT)(\delta_1 - \delta_2)^2 + \chi_s^{\infty}$$

$$\chi = \ln\left(\frac{273,15R}{p_1^0 V_g M_1}\right) - \frac{p_1^0}{RT} (B_{11} - V_1) + \ln\left(\frac{\rho_1}{\rho_2}\right) - \left(1 - \frac{V_1}{V_2}\right)$$

Solubility parameter/IGC

- Smidsrod and Guillet

$$\frac{\delta_{1i}^2}{RT} - \frac{\chi_{(1,2)i}^\infty}{V_i^0} = (2\delta_2 / RT)\delta_{1i} - \left(\frac{\delta_2^2}{RT} + \frac{\chi_{si}^\infty}{V_i^0} \right)$$



Solubility parameter can be calculated from:

the slope

$$\frac{2\delta_2}{RT}$$

the intercept

$$\left(\frac{\delta_2^2}{RT} + \frac{\chi_{si}^\infty}{V_i^0} \right)$$

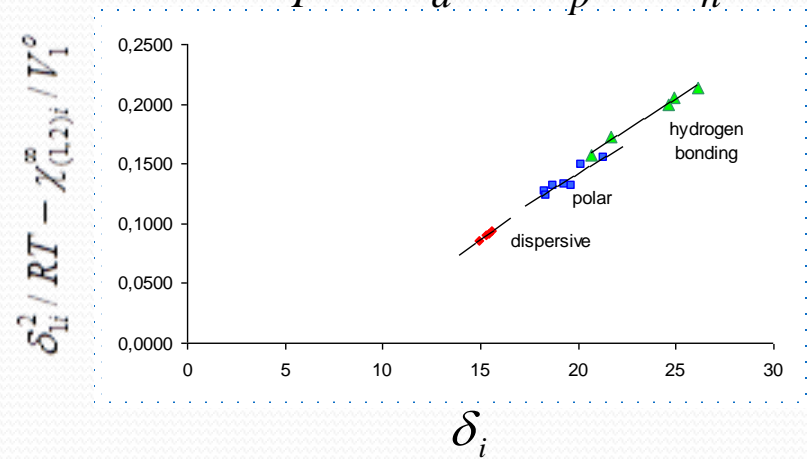
HSP/IGC

- Price

$$\delta_T^2 = \delta_d^2 + \delta_p^2$$

- Voelkel, Janas

$$\delta_T^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$



$$\delta_d = \frac{m_{n-alkanes} \times RT}{2}$$

$$\delta_p = \frac{(m_1 - m_{n-alkanes}) \times RT}{2}$$

$$\delta_h = \frac{(m_2 - m_{n-alkanes}) \times RT}{2}$$

m_1 - value of the slope for aromatic hydrocarbons, ketones, 1-nitropropane

m_2 - value of the slope for alcohols and pyridine

Test solute selection

Test solute	δ_p [MPa] ^{1/2}		δ_h [MPa] ^{1/2}		ratio δ_p / δ_h	
	Data 1*	Data 2*	Data 1*	Data 2*	Data 1*	Data 2*
acetonitrile	11.1	18	19.6	6.1	0.57	2.9
toluene	8.0	1.4	1.6	2.0	5.0	0.7
1,2-dichloroethane	11.2	8.2	9.1	0.4	1.2	20.5
butan-2-one	9.5	9.0	9.5	5.1	1.0	1.8
					ratio δ_h / δ_p	
ethanol	11.2	8.8	20	19.4	1.78	2.20
propan-1-ol	10.5	6.8	17.7	17.4	1.68	2.56
butan-1-ol	10.0	5.7	15.4	15.8	1.54	2.77
1,4-dioxane	10.1	1.8	7.0	7.4	0.69	4.11
chloroform	13.7	3.1	6.3	5.7	0.46	1.84

*Data from A.F.M. Barton. CRC Handbook of Solubility Parameters and Other Cohesion Parameters. CRC Press, Boca Raton, Florida, 2000: [1] – Table 2, p. 94, [2] – Table 5, p. 153.

Hansen/ Flory-Huggins interaction parameter

- Lindvig et al. proposed to use the modified Hansen relationship correlating experimentally determined values of the Flory-Huggins interaction parameter and the differences between HSP values of the examined material and respective test solutes:

$$\chi = \alpha \frac{V_1}{RT} \left((\delta_{1,d} - \delta_{2,d})^2 + 0.25(\delta_{1,p} - \delta_{2,p})^2 + 0.25(\delta_{1,hb} - \delta_{2,hb})^2 \right)$$

Lindvig/ABV procedure

- Experimental $\chi_{1,2}^{\infty}$ data for series test solutes were taken to calculate HSP parameters of the examined material by finding of minimum of the function:

$$G^2 = \frac{4\chi_{12}^{\infty}RT}{\alpha V_1} \left((\varepsilon_{1,d} - \varepsilon_{2,d})^2 + (\delta_{1,p} - \delta_{2,p})^2 + (\delta_{1,p} - \delta_{2,p})^2 \right)$$

where: $\varepsilon_{1,d} = 2\delta_{1,d}$

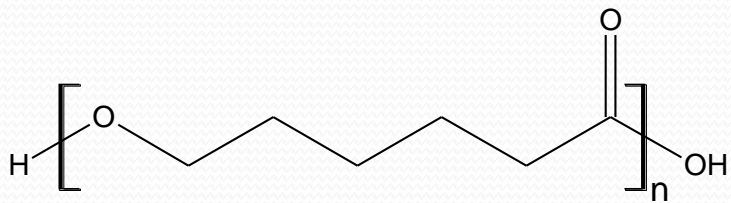
Optimization was carried out in two ways:

OPT_A taking into account the difference - $\left(G_{\text{exp}}^2 - G_{\text{act}}^2 \right)^2$

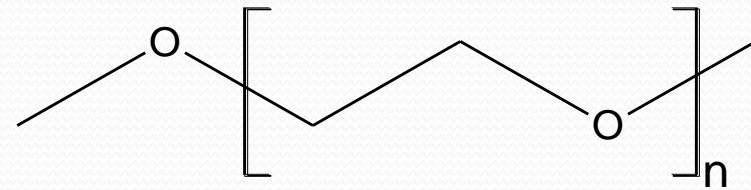
OPT_B taking into account the difference - $\left(\frac{G_{\text{exp}}^2 - G_{\text{act}}^2}{\min(G_{\text{act}}^2)} \right)^2$

Experimental

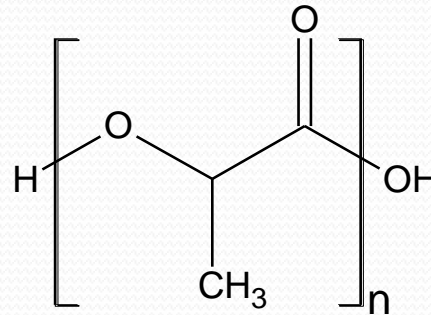
- Biopolymers



poly(ε-caprolactone) (PCL)
Mw = 70 000-90 000



poly(ethylene glycol) (PEG)
Mw=10 000



polylactide (PLA)

Experimental

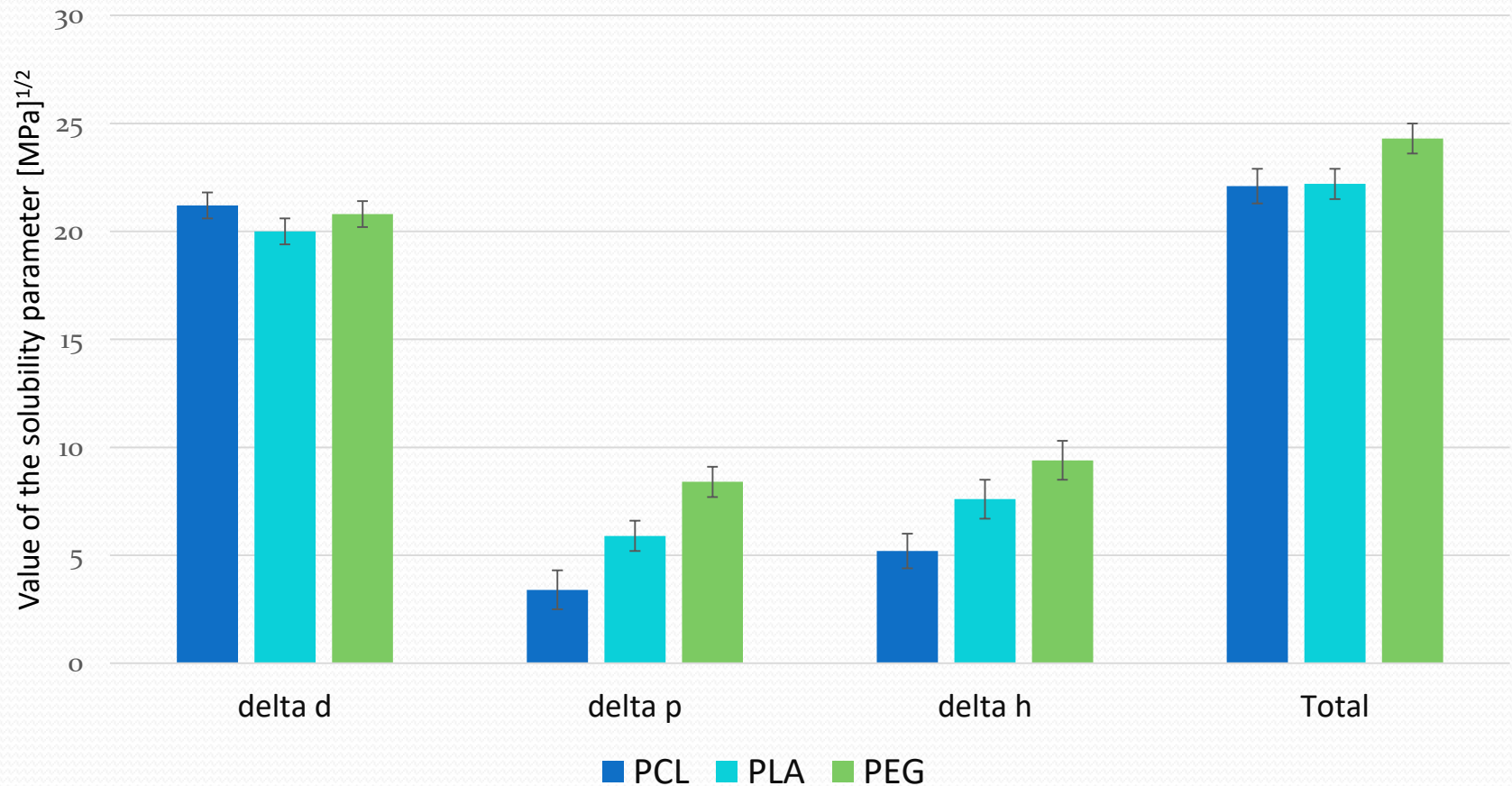
Solid support	Chromosorb P AW / DMDCS 100/120 mesh
Glass column	30 cm length, 2 mm i.d.
Loading of the column	20% of liquid stationary phase
Carrier gas	Helium, flow 10 ml/min
Temperature of measurements	75°C
Temperature of detector	180°C

Test solutes

- dispersive - (n-alkanes)
- polar - acetonitrile, toluene, 2-butanone, 2-pentanone, 1,2-dichloroethane, 1-nitropropane
- hydrogen bonding – ethanol, 1-propanol, 1-butanol, 1,4-dioxane, pyridine

Equipment - SEA (Surface Energy Analyzer, Surface Measurement System Ltd., UK) equipped with a flame ionization detector, FID.

Results

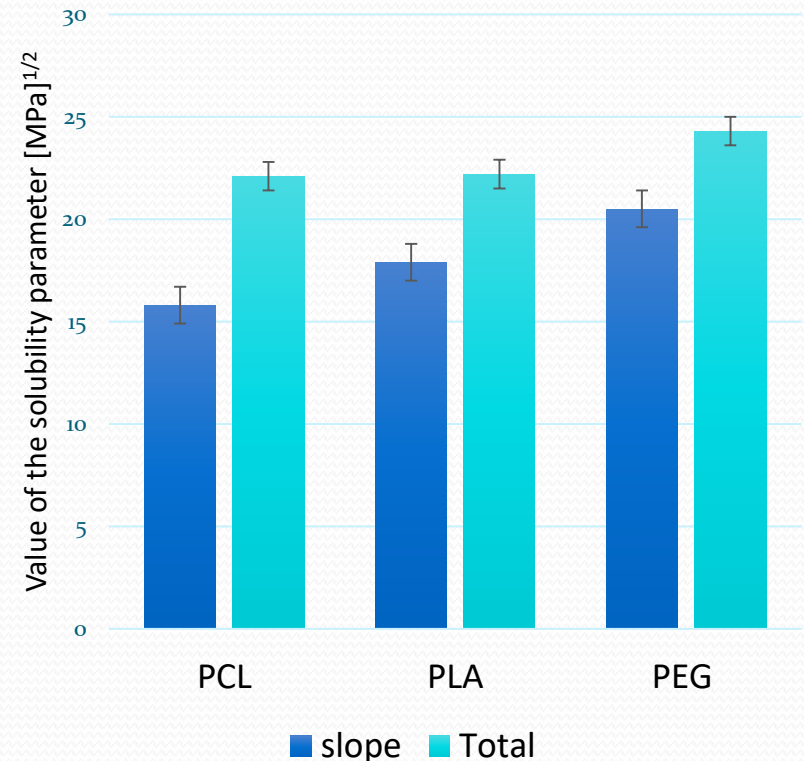


Results

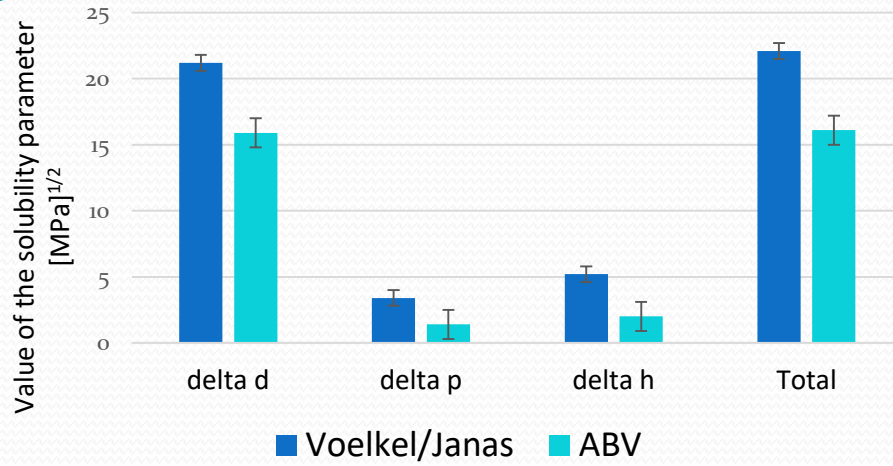
The solubility parameter of blood components*

Blood component	Solubility parameter (MPa) ^{1/2}
Cholesterol and esters	17.2-17.6
Triglycerides	16.4-17.0
Lipid-soluble vitamins	17.6-22.3
Phospholipids	>32

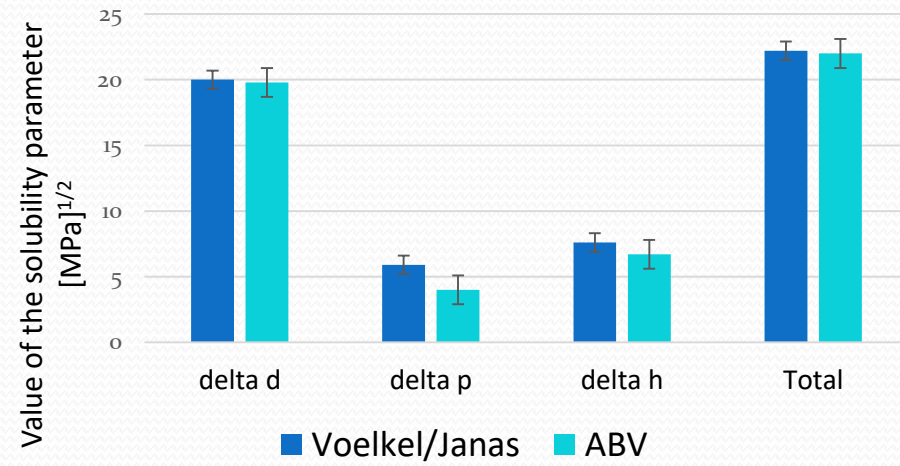
* S. D. Bruck, *Calcification of glutaraldehyde-treated xenografts and blood-contacting synthetic elastomers*, *Bioengineering: Proceedings of the Ninth Northeast Conference*, Pergamon Press 1981



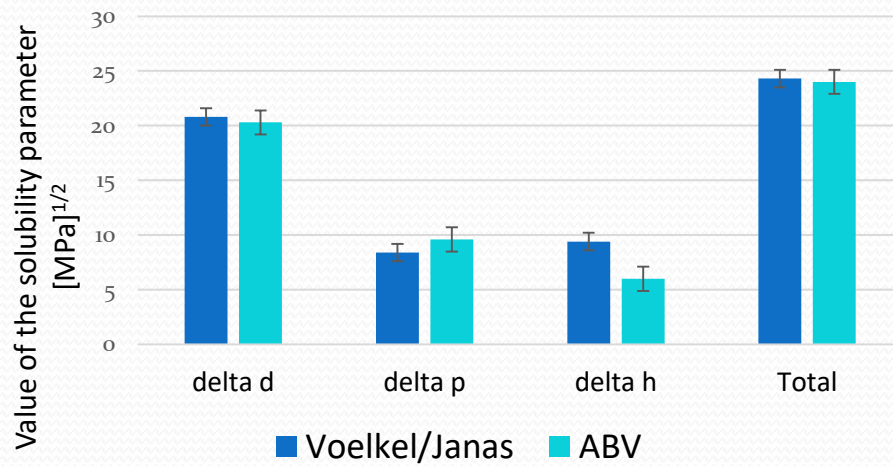
PCL



PLA



PEG 10000



Conclusions

- Inverse gas chromatography is useful in HSP determination for biopolymers.
- The Hansen solubility parameters data vary depending on the procedure of calculation – important test solutes selection.
- The value of the total solubility parameter for all biopolymers is higher than value obtained from the Guillet procedure.
- The values of dispersive component for all the materials are very close, but slight differences are observed for the polar and the hydrogen bonding components.
- PEG addition to the PCL-PLA mixture influenced the hydrogen bonding ability of PCL/PLA/PEG blend (what is evidenced by using HSP) and the increase of the hydrophilicity of such system.



Thank you for your attention