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# Polyglucanurethanes: Cross-Linked Polyurethanes Based on Microbial Exopolysaccharide Xanthan

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Additional information is available at the end of the chapter

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## 1. Introduction

Considering environmental protection and resolution a number of ecological problems (including problem of recourses for chemical synthesis depletion) synthesis of the biodegradable polymer materials becomes one of the most actual tasks of modern polymer chemistry. Among ways of environmental protection from polymer waste (keeping on waste deposits, burials, incineration, pyrolysis, recycling) there can be distinguished the method of minimization of ecological pollution due to creation of polymers able to be destructed under influence of natural factors such – chemical (oxygen, air, water), physical (sun light, heat), biological (bacteria, fungi) etc. These factors are very effective and lead to fragmentation of polymer as a result of macromolecule degradation and turning it into low-molecular compounds which become part of natural circuit of substance. In other words biodestruction is reliable and comparatively fast method of utilization. Usually it can be achieved by implication of natural compounds fragments into polymer structure. Other promising method is biopolymers modification with further creation of new synthetic polymers able for degradation under biological factors. Development of this method in future allows to resolve one of the most actual modern problems and to substitute petroleum refining products as the base of chemical synthesis with renewable source. It is also relevant using as reagents economically effective products which are cheaper than oil refining raw materials.

Purpose of our study was to create new polymerizing systems possessing above mentioned attractive features. Therefore new polyglucanurethane (PGU) networks were obtained on the base of microbial polysaccharide xanthan and blocked polyisocyanate (PIC) using environment friendly method. Biopolymer application as reagent provides both preserving advantages of initial materials and developing new advanced properties of obtained biodegradable materials due to chemical modification. Replacement of toxic compounds

with latent isocyanate-containing reagent blocked polyisocyanate is also a prominent advantage of developed technique. PGU were obtained via interaction of xanthan hydroxyl groups and isocyanate groups of deblocked above 125°C PIC (Kozak & Nizelskii, 2002).

Microbial polysaccharide xanthan is produced by *xanthomonas campestris* pv. *Campestris* bacteria (Gzozdyak et al., 1989). Xantan is well known and most widely used microbial exopolysaccharide. It is used in light industry (textile), heavy industry (drilling and oil production) and food industry as well as in agriculture, forestry, pharmaceuticals, medicine and cosmetics. The water solutions of xantane have unique rheological properties due to metal cation complexing ability and formation of primary, secondary and higher levels of structure. The main chain of the polysaccharide is alike to cellulose and its side-chains (pendants) consist of glucose, mannose and glucuronic acid residues.

Blocked polyisocyanate is latent reagent which is able to produce reactive isocyanate groups under elevated temperature. It is multifunctional latent reagent that can consist of 40 to 70 % of dimeric compound, 20 to 60 % of tetramer and 1 to 5 % of trimer and hexamer. Melting temperature interval of blocked PIC is from 80 to 95 °C, NCO-group unblocking temperature ranges from 125 to 130 °C. PIC is soluble in most of organic solvents and can be used both in powder and liquid form.

## 2. Synthesis

The reaction was provided in solid. Fig. 1 describes the scheme of PGU synthesis. There occur both deblocking of polyisocyanate groups and urethane bonds formation.

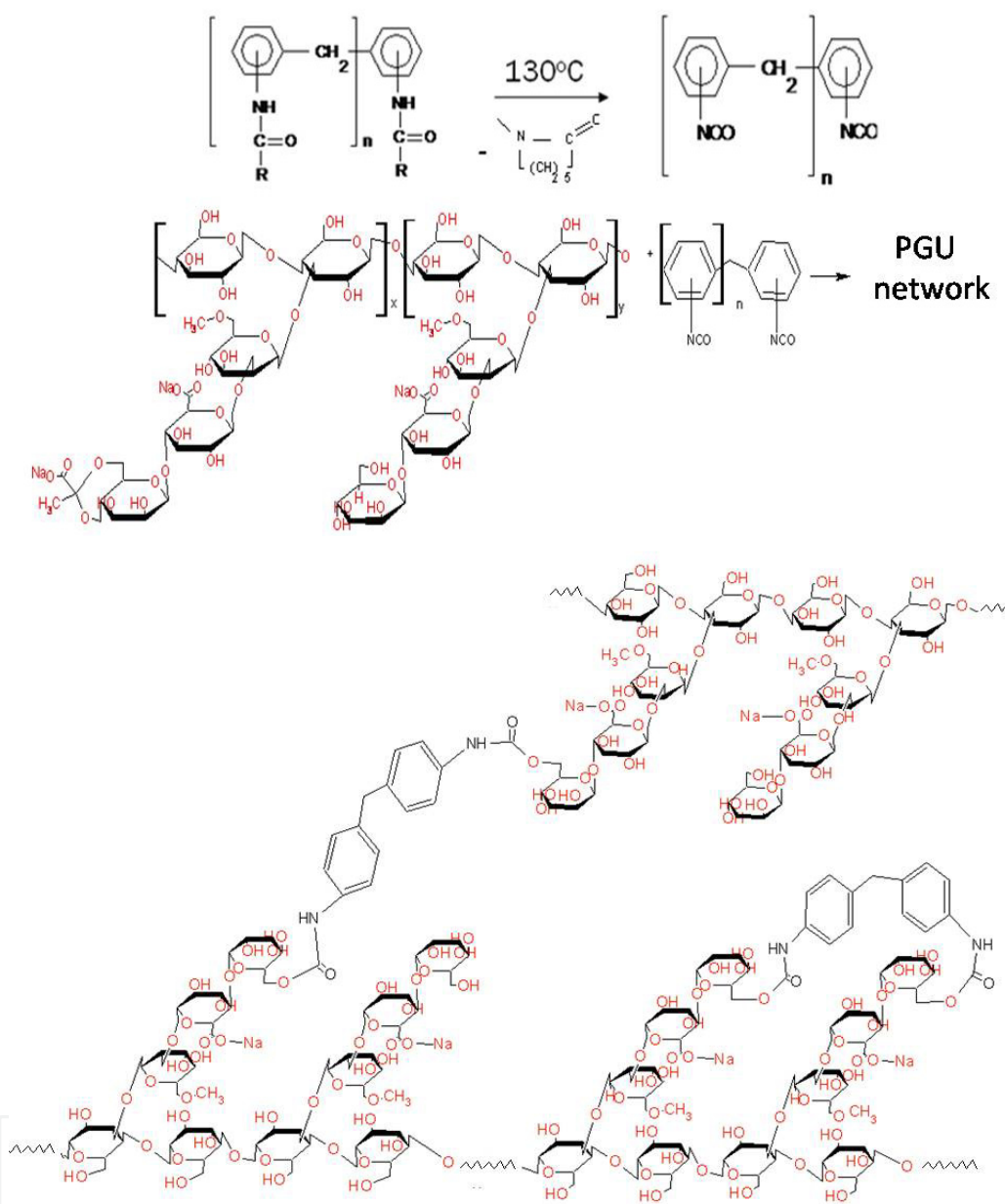
There were obtained powdered PGU, hot-pressed samples and reinforced PGU with calculated degree of polysaccharide hydroxyl group substitution of 20, 40, 60, 80 and 100%. As far as obtained polymer is quite new and unexplored polymer material, not full range of the hydroxyl/urethane ratio was studied by methods presented in this Chapter. The obtained materials are acid-, alkali- and thermo resistant.

The reaction path was controlled using sampling procedure and sample analysis with FTIR spectroscopy.

Characteristic band at 2276  $\text{cm}^{-1}$  which appears after heating the reactive mixture up to 130°C demonstrates the process of isocyanate groups deblocking. On the initial stages of reaction all of PGU samples show increasing intensity of this band due to active isocyanate group formation.

Interaction of  $\text{N}=\text{C}=\text{O}$  groups with the nearest primary and secondary hydroxyl groups of polysaccharide leads to decreasing intensity of characteristic band 2276  $\text{cm}^{-1}$  during next 10 min. Diffusion limitations of this reaction are determined by heterogeneity of reactive mixture and results in retarding of urethane bonds formation. Mechanic stirring of reactive mixture allows improve reactive centers contact and leads to total disappearance of isocyanate groups in the system. (Fig 2.a). Consumption of hydroxyl groups is accompanied by disappearance of the band at 3165  $\text{cm}^{-1}$  and decreasing of intensity band at 1209  $\text{cm}^{-1}$  (valence vibrations and deformation vibrations of O-H bond in glucuronic acid residue

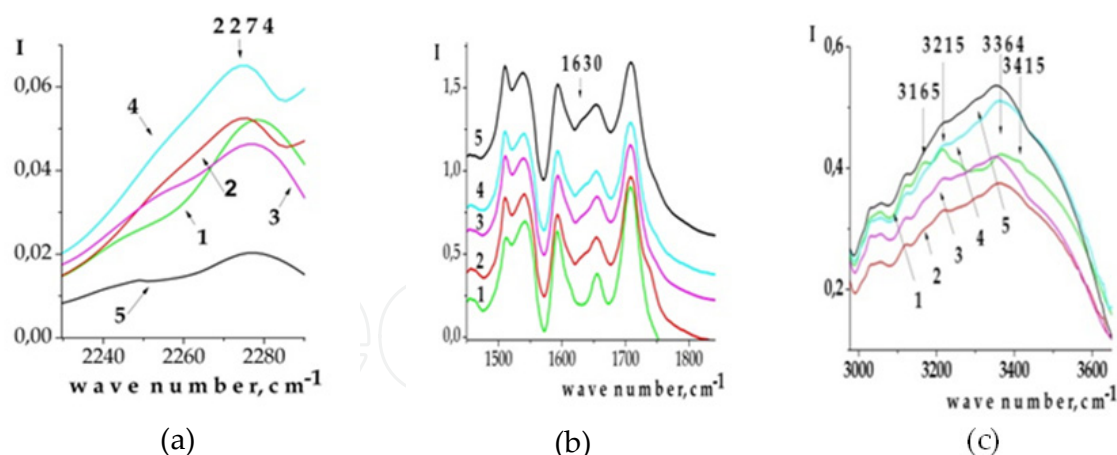
respectively) and by intensity reduction of the band at  $3215\text{ cm}^{-1}$  (valence vibrations of primary OH-groups in mannopyranose cycles) (Fig 2 c).



**Figure 1.** Scheme of PGU synthesis

Increasing intensity of the band at  $3364\text{ cm}^{-1}$  (in characteristic doublet of N-H valence vibrations), appearance of the  $1635\text{ cm}^{-1}$  band in the region of NH deformation vibrations (amide II) and changes of intensity of  $1650$  and  $1590\text{ cm}^{-1}$  bands respond to formation of urethane bonds and releasing of blocking agent (Fig 2b).

In the wave numbers range from  $3000$  to  $3500\text{ cm}^{-1}$  redistribution is observed of the intensities of absorption bands corresponding to hydrogen linked OH-groups. That points on redistribution of intermolecular bonds in the system during polysaccharide cross-linkage and PGU formation.



**Figure 2.** IR spectra of reactive mixture for PGU60 at temperature 130°C(1), 150°C (2), at 150°C after 10 min (3), after 20 min (4) after 30 min(5)

According to FTIR spectra of various PGU (PGU40, PGU80 and PGU100) the number of isocyanate groups released at the initial stage of reaction correlates with the polyisocyanate content in the system. During the first 10 min the process of polyisocyanate deblocking dominates. At the same time the urethane group formation occurs via interaction of NCO groups and polysaccharide hydroxyl groups in acid residue of glucuronic acid and/or hydroxyl groups of mannose. The time when the urethane group formation begins to dominate depends on balance of the reagents in reaction mixture.

### 3. Polyglucanurethane chemical and thermal resistance

Obtained PGU networks possess advanced thermal and chemical (both alkali and acid) resistance. Chemical resistance of PGU was analyzed using standard method...[State Standart 12020-72]. Thermal resistance of initial reagents and PGU of various composition were studied with the thermogravimetry. Table 1 shows the results of PGU20 exposure in water, acid- and alkali media. Fig 4. illustrates the TGA curves: mass loss (TG), differential mass loss (DTG) and differential thermal analysis (DTA) that characterize the dependence of thermooxidative destruction character of PGU on the degree of substitution of xanthan hydroxyl groups.

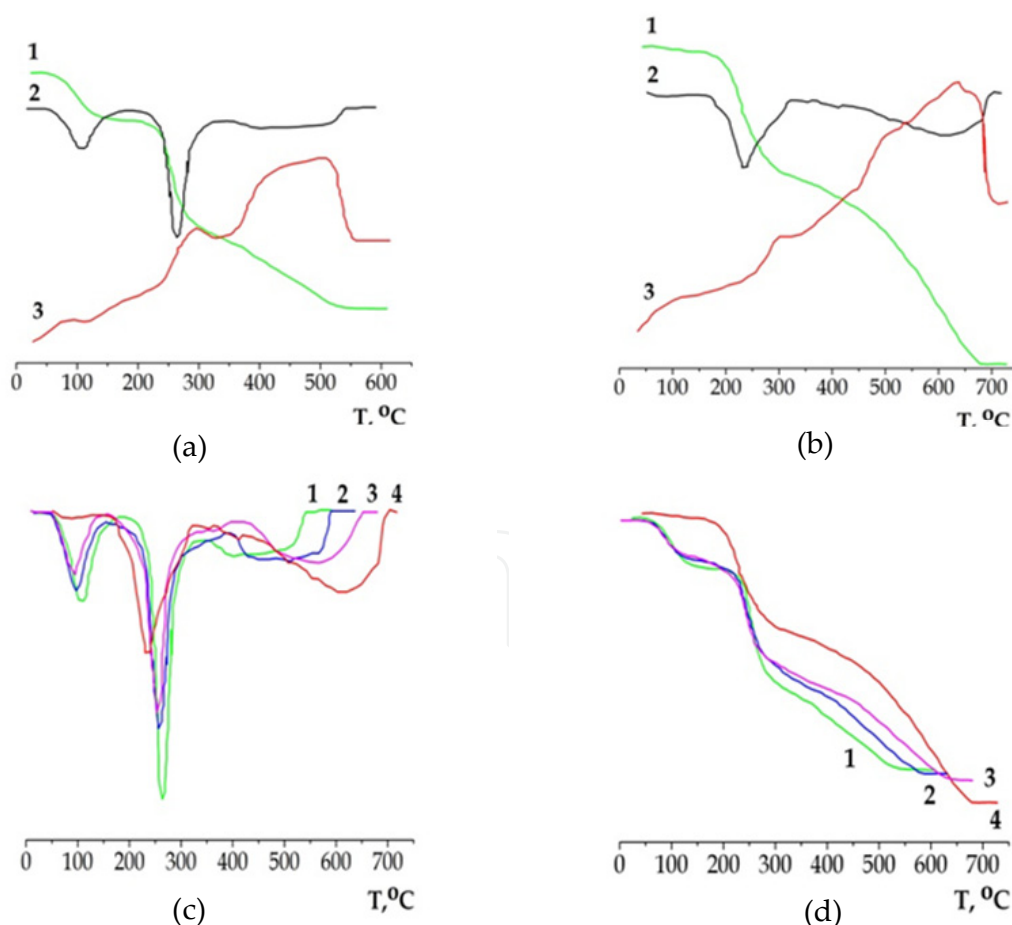
As it can be seen from table 1 data the mass of PGU20 samples remains practically unchanged after the 7 and 13 days exposure in aggressive alkali and acid medium. The initial stages of PGU interaction with water, alkali- and acid media are characterized with significant swelling of polysaccharide component.

According to TGA data thermooxidative destruction of the systems analyzed consists of several stages. TGA curves of xanthan are typical for polysaccharides. TGA curves character for PGU networks and number of stages in temperature interval from 20 to 700°C depend on the balance of hydroxyl and urethane groups in PGU. Stage of weight loss in temperature interval 60-140°C is accompanied with endothermal peak on DTA curve and responds to absorbed water removal.

Time, day	Sample weight, g		
	$H_2O$	$H_2SO_4$	$NaOH$
1	0,081	0,085	0,081
2	0,213	0,205	0,431
3	0,217	0,213	0,489
7	0,250	0,224	0,485
13	0,425	0,241	0,489

**Table 1.** The weight change of PGU20 exposed in deionized water, concentrated sulphuric acid ( $V=20$  ml, 30% wt.) and concentrate alkali solution ( $V=20$  ml, 40% NaOH).

Presenting mass of absorbed water in modified and non-modified samples of exopolysaccharide as mass loss at the first stage (temperature interval 45 – 150°C) we can see that amount of absorbed water correlates with balance of hydroxyl and urethane groups in the system (Fig.3). It corresponds with the fact that system hydrophilic properties correlate with amount of hydroxyl groups. Weight loss at this stage is 1,5; 2,5; 8,5 % wt. for PGU80, PGU40, PGU20, respectively.



**Figure 3.** TGA curves - TG (1), DTG (2), DTA (3) of initial reagents: xanthan (a), blocked PIC (b); curves DTG (c) and TG (d) for initial reagents and PGU of various composition: xanthan (1), 2- PGU20 (2), PGU40, PIC (4)



Intensive thermal-oxidative destruction is observed in 200 – 400°C temperature interval. The characteristic temperature responding to maximum speed of weight loss at the stage shifts toward the higher temperatures with increasing of urethane groups amount in the system. Weight loss at this stage is 35, 30, 35 % wt. for PGU80, PGU40, PGU20, respectively.

Wide peak on DTG curves in temperature interval from 500 to 700°C mainly corresponds to destruction of carbon base of polymer. With growth of urethane group content in the system the carbon residual decreases.

As it can be seen thermal resistance of PGU grows with increasing of urethane group amount. For instance, for PGU40 high temperature stage is allocated 40°C lower than for the PGU 80. The degree of hydroxyl substitution also influences the system capacity of water absorbance. With growth of urethane group content in the system the amount of absorbed water declines

#### **4. PGU interaction with water solutions of phenol and transition metal salts**

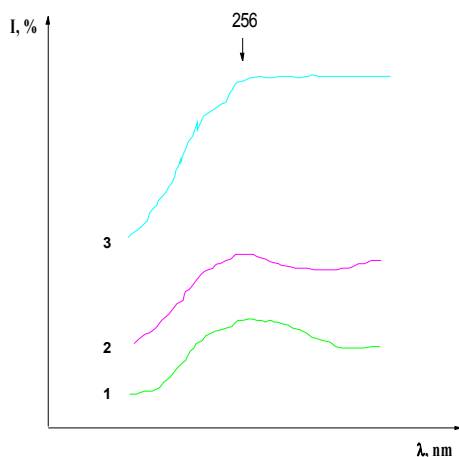
It is known that microbial polysaccharides are considered as prospective raw materials for obtaining effective sorbents for extracting organic compounds and metal ions from water solution (Crini, 2005). Application of water-soluble polysaccharides (eg. xanthan) as sorbents is difficult. Using of PGU allows both keep sorption properties of polysaccharide and eliminate a number of disadvantages (water solubility, low chemical resistance etc.). Study of properties of cross-linked PGU (Hubina, 2009) revealed its ability to quantitative extraction of phenol and bivalent metal ions from water solution, while controlling capacity of the material with cross-linking degree.

To analyze ability of PGU to phenol sorption from its water solution the pollutant concentration was controlled before and after exposure of PGU20 and PGU60 films in  $10^{-4}$ M phenol water solution during 24, 48 and 120 hours. Phenol concentration was monitored using UV electron spectroscopy by the change of band intensity near 256 nm. Experiment conditions were as follows:  $T=18^{\circ}\text{C}$ ,  $m_{\text{sorbent}}=7\text{ g}$ ,  $V_{\text{solution}}=50\text{ ml}$ . Calibration curve was plotted for 0,05; 0,075; 0,1; 0,15 and 0,2 M phenol water solutions.

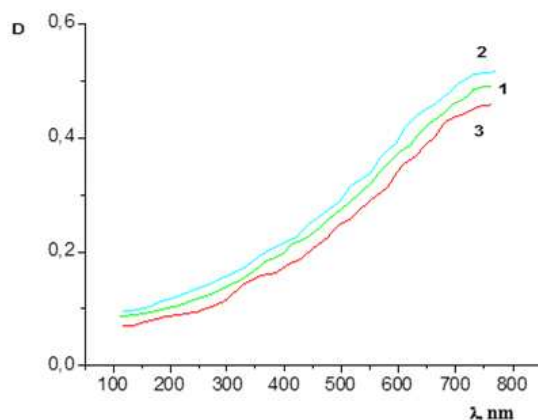
According to UV-spectroscopy data after 24 hours of exposure PGU in phenol solution increasing of phenol concentration is observed both for PGU20 and PGU60 (Fig.4). Further exposure of PGU in solution leads to essential decreasing of phenol concentration. Such phenol concentrating during PGU interaction with phenol solution can be explained by the preferable swelling of polysaccharide component of the polymer in water.

The same character of concentration change is observed while extracting  $\text{Cu}^{2+}$  ions from copper sulfate solution. (Fig.5). Its concentration change was controlled using electron spectroscopy in Vis-region by the change in band intensity near 810 nm. That band corresponds to d-d transitions in  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  aqua ion. Exposure of PGU60 sample in copper sulfate water solution during 10 min. is accompanied by sufficient growth of

solution absorbance and shows copper ions concentrating. Increasing time of interaction with sorbent to 60 min leads to absorbance reduction.



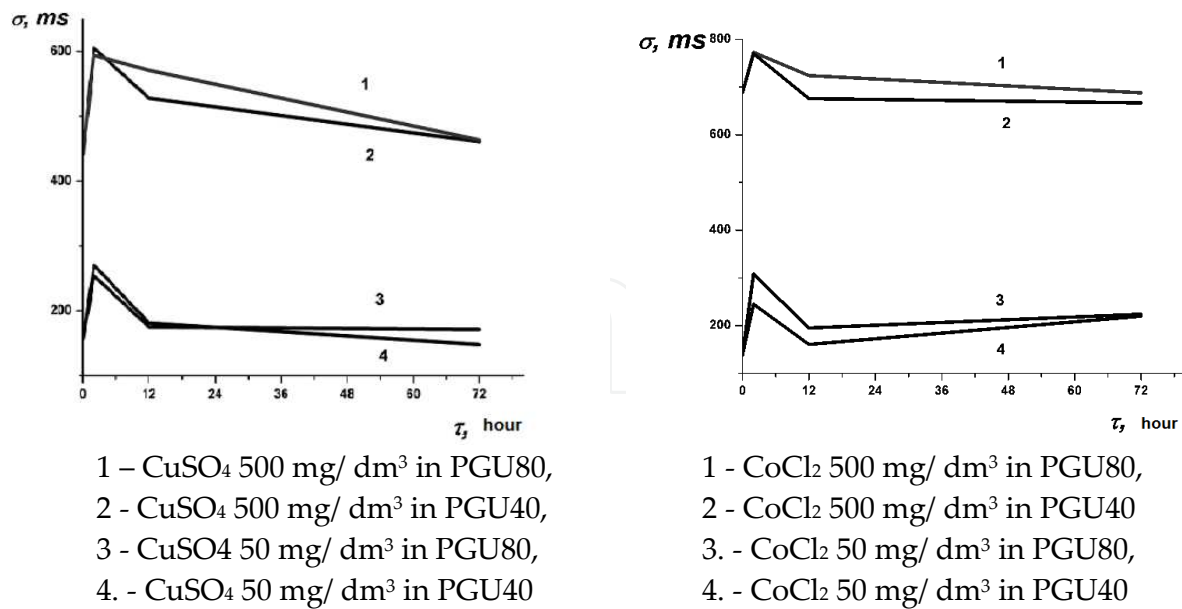
**Figure 4.** The electron spectra of phenol water solutions: 1 – initial; 2 – PGU60 after 10 min exposure; 3 – PGU20 after 10 min exposure



**Figure 5.** The electron spectra of copper salt water solutions: 1 - initial, 2 - after 10 min of PGU exposure and 3 - after 60 min of PGU exposure

Interaction of PGU40 and PGU80 with water solution of  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  salts with concentration of 50 and 500  $\text{mg/dm}^3$  was studied in static conditions using conductometry. Solution conductivity was fixed after 2, 12 and 74 hours of PGU exposure. Experiment conditions were as follows  $m_{\text{PGU}}=1,25 \text{ g}$ ;  $V_{\text{solution}}=50 \text{ cm}^3$ ; permanent stirring frequency=2 Hz; room temperature. Intermediate and final concentrations were calculated from calibration curve. Fig 7 demonstrates conductivities of cobalt and copper salt solutions of various concentrations (50 and 500  $\text{mg/dm}^3$ ) depending on the time of interaction with PGU40 and PGU80. In the table 2 there are the results of concentration changes of copper(2+) sulfate and cobalt(2+) chloride solutions respectively *vs* time of exposure PGU40 and PGU80. Fig 6 shows that conductivity of cobalt chloride and copper sulfate solutions grows on the initial stages of sorbent exposure for both high (500  $\text{mg/dm}$ ) and low (50  $\text{mg/dm}$ ) concentrations.





**Figure 6.** Dependence of solution conductivity *vs* time of sorbent exposure

Similar effect was observed for hot-pressed samples of PGU while interacting with water solutions of phenol and transition metal salts due to predominant swelling of polysaccharide component on the initial stages. Next 12 and 74 hours of PGU exposure result in sufficient solution concentration decreasing due to metal ions capture by the functional groups of sorbent. Equilibrium was achieved both for PGU40 and PGU80 in solutions of high cobalt salt concentration (500 mg/ dm<sup>3</sup>) while for copper salt solutions equilibrium was achieved for low concentration (50 mg/ dm<sup>3</sup>).

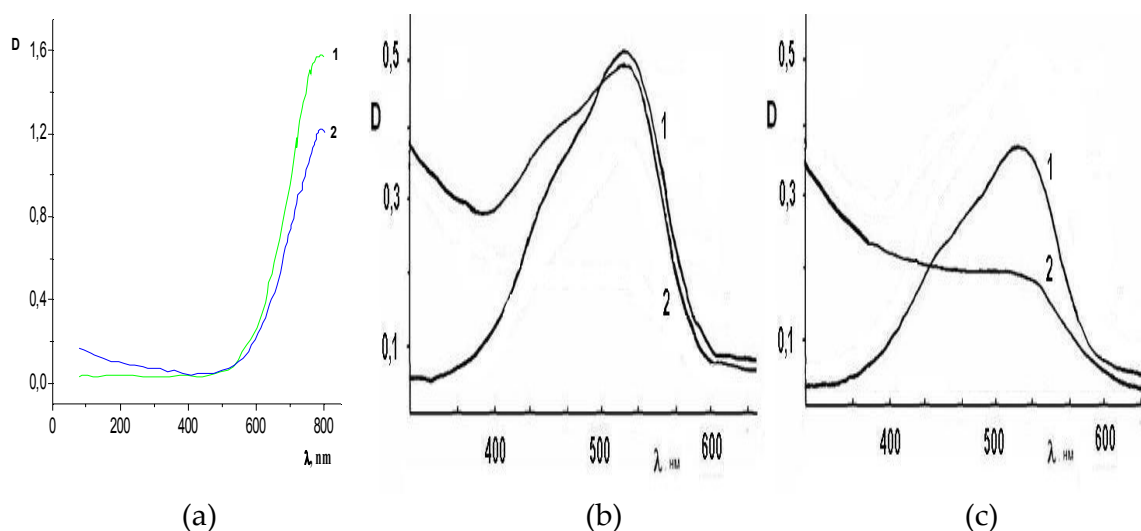
As table 2 and Fig 6 show the efficiency of metal ions extraction depends on both concentration of solution and the balance of hydroxyl and urethane groups in PGU. The highest concentration fall was observed for PGU80. The solutions of low concentration aren't sensible to hydroxyl and urethane balance in PGU. Besides, the best ion extraction of cobalt ions from low concentration solutions is achieved with short-time exhibition of sorbent. For cobalt salts solutions of high concentration and copper salts solutions of low concentration the best effect is achieved during 74 hours of exhibition.

PGU	C, mg/dm <sup>3</sup>	Cu SO <sub>4</sub>			CoCl <sub>2</sub>		
		ΔC <sub>2h</sub> , %	ΔC <sub>12h</sub> , %	ΔC <sub>74h</sub> , %	ΔC <sub>2h</sub> , %	ΔC <sub>12h</sub> , %	ΔC <sub>74h</sub> , %
40	50	20,0	45,3	55,0	11,2	43,4	33,1
80	50	24,2	47,2	48,3	29,2	53,6	36,4
40	500	73,2	84,7	86,4	55,0	58,0	60,0
80	500	63,2	83,2	86,3	55,2	60,7	61,2

**Table 2.** Concentration change of cobalt chloride and copper sulfate solutions.

The results of PGU sorptive properties research in static conditions correspond with the research results obtained under dynamic conditions. Ability of synthesized powdered PGU materials to sorb metal ions in dynamic conditions was examined for  $\text{CoCl}_2$  and  $\text{CuSO}_4$  water solutions of various concentration. PGU60 sorbent was used. Concentration of initial and final solutions was controlled using electron spectroscopy in Vis-region by the change of band intensity responding to d-d transitions in aqua ion  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  and d-d transitions in aquaion  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  (near 510 nm and 810 nm respectively). Calibration graphs were plotted for 0,05; 0,075; 0,1; 0,15; 0,2 M concentrations of  $\text{CoCl}_2 \times 6\text{H}_2\text{O}$  and  $\text{CuSO}_4 \times 5\text{H}_2\text{O}$ . Experiment was carried out at 18 °C. Solutions of copper and cobalt salts with initial concentrations of 0,1 M and 0,05 M were pumped through the column filled with the sorbent powder.  $m_{\text{PGU}}=7 \text{ g}$ ;  $V_{\text{solution}}=50 \text{ cm}^3$ . Under dynamic conditions the time of interaction ranged from 60 to 120 seconds. Fig. 7 illustrates the character of  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  ion sorption.

After dynamic contact of copper salt with sorbent during 60 seconds absorbance of filtrate (D) falls to 1,08 in comparison with the initial solution absorbance value of 1,4. It responds to 40% decreasing of copper ions in solution. For 0,1M solution of cobalt chloride after dynamic contact with PGU40 there is observed absorbance fall from 0,52 to 0,48 that responds to extracting of 20% metal ions. For 0,05M solution of cobalt chloride is achieved 40% decreasing of cobalt ion concentration after 60 sec contact. Calculated concentration of cobalt ions in final solutions was 0,08M for initial 0,1M and 0,03M for initial 0,05M. The dynamic sorption of metal ions with PGU40 sorbent is more effective for solutions with lower concentration.



**Figure 7.** The electron spectra of water solutions of metal salts before (1) and after (2) passing through the column filled with powdered PGU40

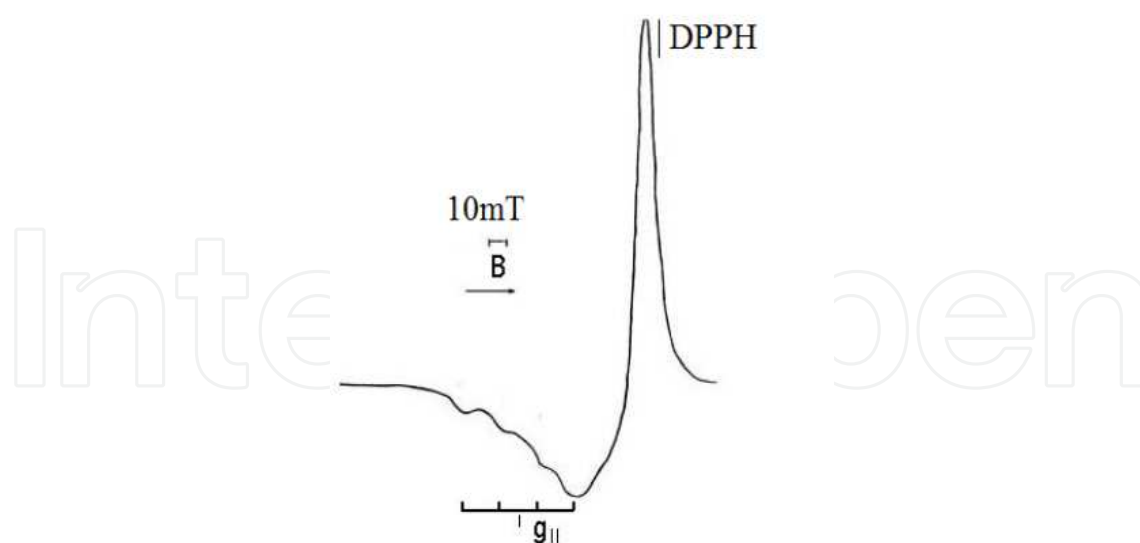
According to (Bergmann et al., 2008) the mechanism of ion capture by water soluble polysaccharides mainly related to formation of complexes of chelate structure. Research of complex formation of PGU with metal ions allows conclude of chelate structure of formed

complexes. In particular chelate structure of copper ion (2+) complexes with PGU is confirmed in (Hubina et al., 2010). Using results of (Bergman et al., 2008; Hubina et al., 2010) we can assume that cobalt ions also form chelate structures with PGU.

Analysis influence of cross-linking degree of PGU on complexing metal ions with functional groups of PGU demonstrated that variation of hydroxyl and urethane groups balance in the system allows to achieve effective control over holding metal ions in PGU matrix.

Peculiarities of “PGU-copper ion” complex formation were studied using electron paramagnetic resonance method (EPR). Copper ions were introduced into PGU matrix via pumping of 0,1M water solution of  $\text{CuSO}_4$  through column filled with PGU60 (the way it described above for dynamic sorption conditions). Then metal-containing PGU sample was dried and the EPR spectra of bivalent copper were recorded. Fig. 8 demonstrates EPR spectrum of dried PGU60 after interaction with copper sulfate water solution.

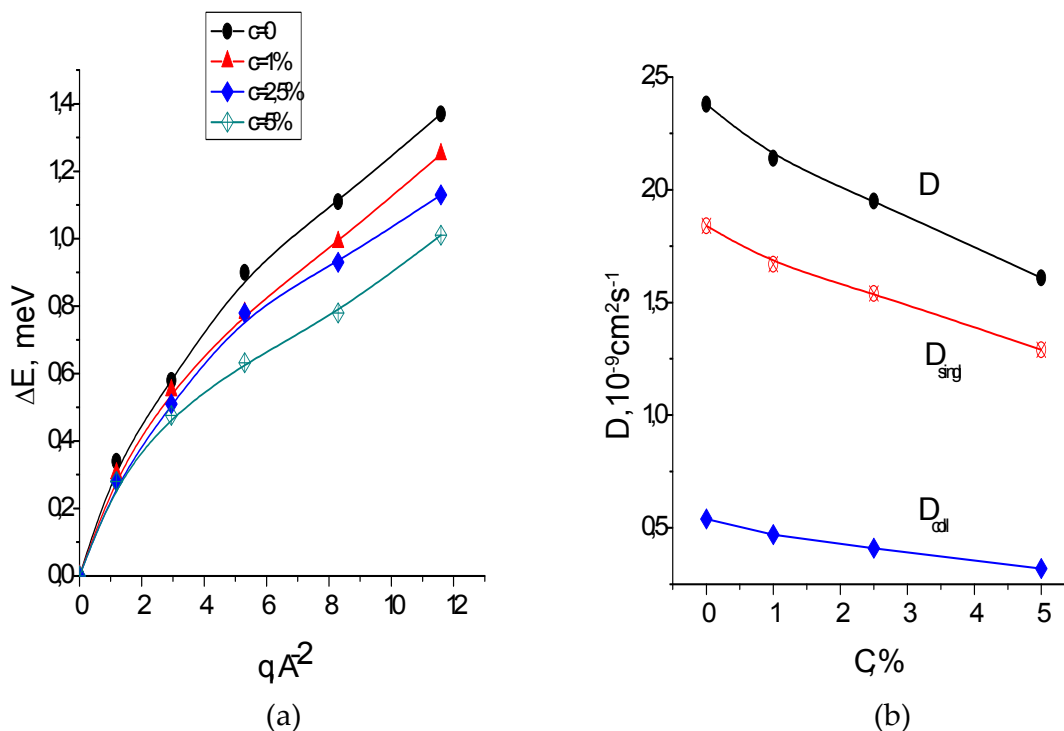
Recorded spectra are characterized with anisotropy of g-factor and appearance of hyperfine structure in the region of  $g_{\parallel}$  that is usually concerned to tetragonal chelate complexes of bivalent copper. Hyperfine structure components are broadened as a result of superposition of signals from tetragonal copper complexes which can differ both in symmetry distortion and in nearest chemical surrounding. Integral intensity of obtained EPR spectra depends on the balance of hydroxyl and urethane group in PGU while electron spin parameters are almost unchanged. That points on preferable interaction of metal cation with one of the components of PGU. This conclusion corresponds with the regularities of bivalent copper ion complexing with mono saccharides.



**Figure 8.** The representative EPR spectrum of copper containing PGU

Experimental analysis of influence of metal ions on water molecules self diffusion process in swelled polysaccharide gel was carried out by the method of quasi-elastic neutron scattering.

For description of experimental dependences there was calculated the values of general coefficient of water self diffusion in swelled gel  $D = D_{\text{singl}} + D_{\text{col}}$  as well as values of its  $D_{\text{singl}}$  (single particle) component and  $D_{\text{col}}$  (collective) component. (Fig 9b).



**Figure 9.** Dependence of energy broadening of quasi-elastic peak  $\Delta E$  vs squared transferred kinetic moment  $q$  for various polymer-metal salt ratio (a) and concentration dependencies of  $D$ ,  $D_{\text{singl}}$  and  $D_{\text{col}}$  (b).

Obtained data demonstrate that addition of metal salt to water and increasing of solution concentration decreases the coefficient of water molecules self diffusion in swelled xanthan gel both for general coefficient and for its components.

That indicates the swelled polymer density growth in presence of metal ions. Such condensation effect can be explained taking into account ability of transition metal chelates to form charge-transfer complexes with electron-donor centers of polymer resulting in creation of additional 'coordination juncs' both in swelled linear polysaccharide and in chemically cross-linked PGU.

Thus, polyglucanurethanes based on water soluble polysaccharide xanthan and blocked polyisocyanate are able to extract heavy metal ions from their salt water solutions. Variation of hydroxyl and urethane groups balance at the cross-linking stage provides effective regulation of complexing and capturing of metal ions with polyglucanurethanes.

## 5. Biodestruction

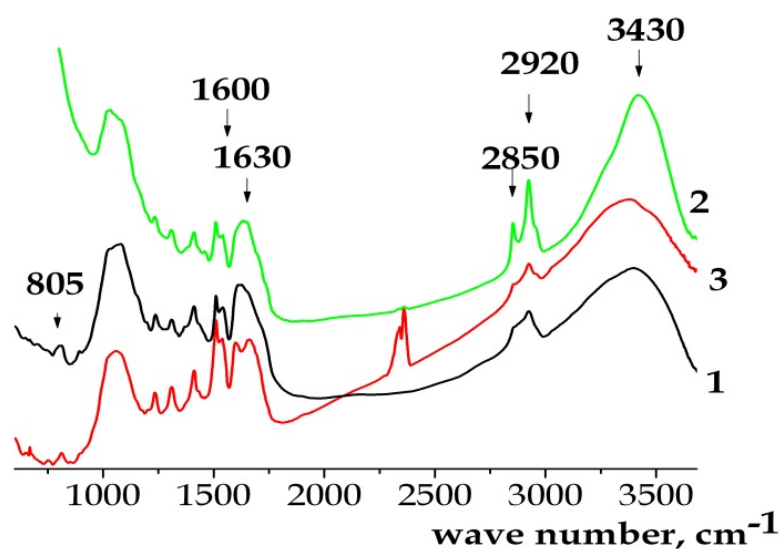
Used plastics utilization had become an important problem. One of the ways of polymer and in particular of polyurethane waste reclamation is biodegradation of plastic. The ability

to biodegradation was analyzed on the PGU exposed in the medium of common soil microorganisms association as well as into the medium of resistive microbial association isolated from soils polluted by chlorine-organic pesticides. (Hubina et al., 2009). There were explored biodegradable properties of two types of PGU20: based on microbial polysaccharide xanthan (PGU20) and methylcellulose (PGU20-cellulose).

The resistant microbial association with working name "Micros" was isolated from soil polluted by chlorine-organic pesticides. This association has high destructive activity with respect to chlorine-organic, organic-phosphorous, simm-triazine and other pesticide groups. It was supposed, that "Micros" is able to specialize to exotic substratum and could decompose polyglukanurethane systems due to utilization of this polymer as carbon or nitrogen source. To compare destruction of the PGU by common soil microorganisms the soil native-born microbial association was isolated from pollution-free chernozem soil. It has never contacted with pollutants in soil.

Changes in polymer structure after exposure in microbial medium were analyzed by FTIR spectroscopy, optical microscopy and thermogravimetry. Fig presents IR – spectra of PGU20 after contact with aggressive and natural microbial medium. Evaluation of redistribution of bonds in destructed PGU was provided by analysis of the location, width and intensity of valence vibrations band of C-O-C intercycle group of polysaccharide ( $805\text{ cm}^{-1}$ ) and also by analysis of location and intensity of band amide II) in PGU urethane bridges ( $1600 \div 1660\text{ cm}^{-1}$ ).

In PGU spectrum after the sample contact with aggressive medium (spectrum 3 fig 10) it is seen resolving of complex band at  $1600 - 1660\text{ cm}^{-1}$  (N-H vibrations) comparing to initial PGU20 spectrum (Fig.10 spectrum 1). This may be caused by destruction of essential part of urethane bonds of PGU in aggressive medium.



**Figure 10.** IR spectra of PGU20 based on xanthan 1 – initial PGU, 2 – PGU after contact with natural microbial medium, 3 – PGU after contact with aggressive microbial medium



Other type of PGU destruction is observed in natural medium (fig. 10 Spectrum 2). It is approved by redistribution of intensities of valence vibrations of C-O-C groups comparing with initial PGU and by absence of prominent changes in area of amide II. The band at 805 cm<sup>-1</sup> responding to intercycle C-O-C bonds disappears. It is accompanied by increasing of intensity of the band responding to free OH-group (3430 cm<sup>-1</sup>) and C-H bonds (2850 and 2920 cm<sup>-1</sup>).

Another evidence of sufficient urethane bonds destruction in PGU20 in aggressive medium is seen on microphoto of PGU films after aggressive destruction (Fig. 11). There can be distinguished fibrous polymer elements, usual for fibrous of initial polysaccharide xanthan, which formed after urethane destruction. This effect is absent on the micro photos of PGU sample after destruction in natural microbial medium.



1 – initial polysaccharide fibers; 2 - effect of aggressive microbial medium; 3 – effect of natural microbial medium.

**Figure 11.** Micro images of PGU films after contact with natural and aggressive microbial mediums

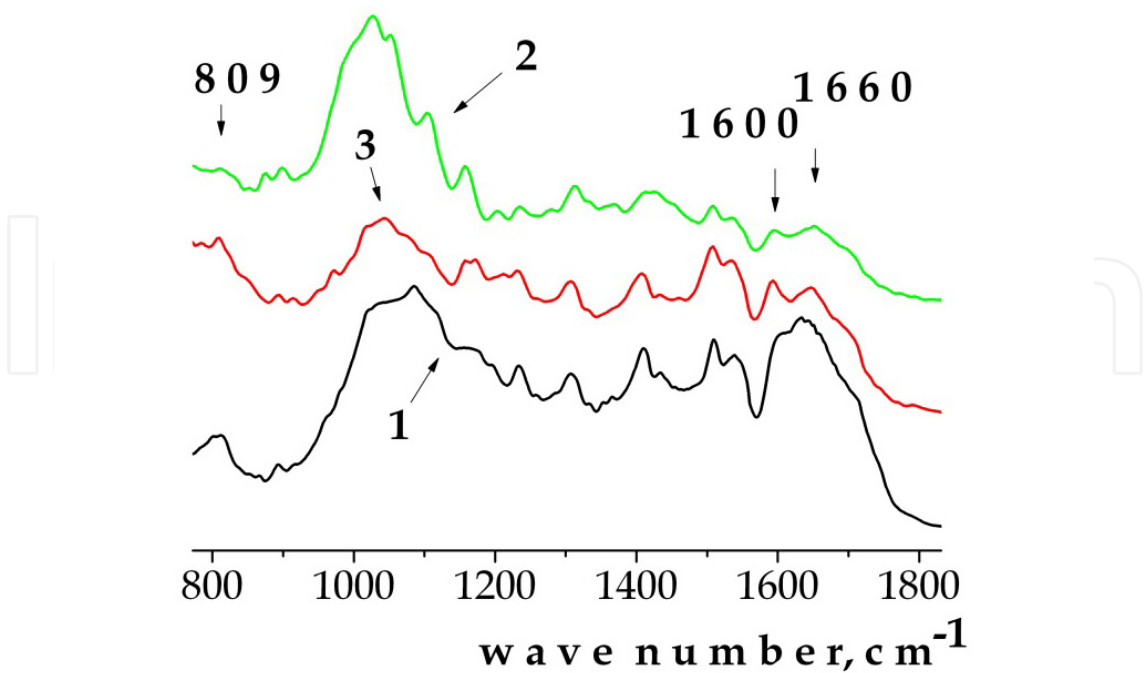
IR spectra of PGU20-cellulose present the difference between this polymer biodestruction and biodestruction of PGU20-xanthan (Fig. 12)

In particular, the intensity of the band in area 1600 – 1660 cm<sup>-1</sup> falls both for natural medium and aggressive one. (Fig.13 spectra 2 and 3). Intensity of 809 cm<sup>-1</sup> band decreases (valence vibrations of intercycle bonds C-O-C) after exposure of PGU20-cellulose in natural microbial medium (Fig.12 spectrum 2) differing from intensity of this band in PGU20-cellulose spectrum after contact with aggressive medium. Bands corresponding to symmetric and asymmetric vibrations of saccharide groups C-O-C are nearly unchanged.

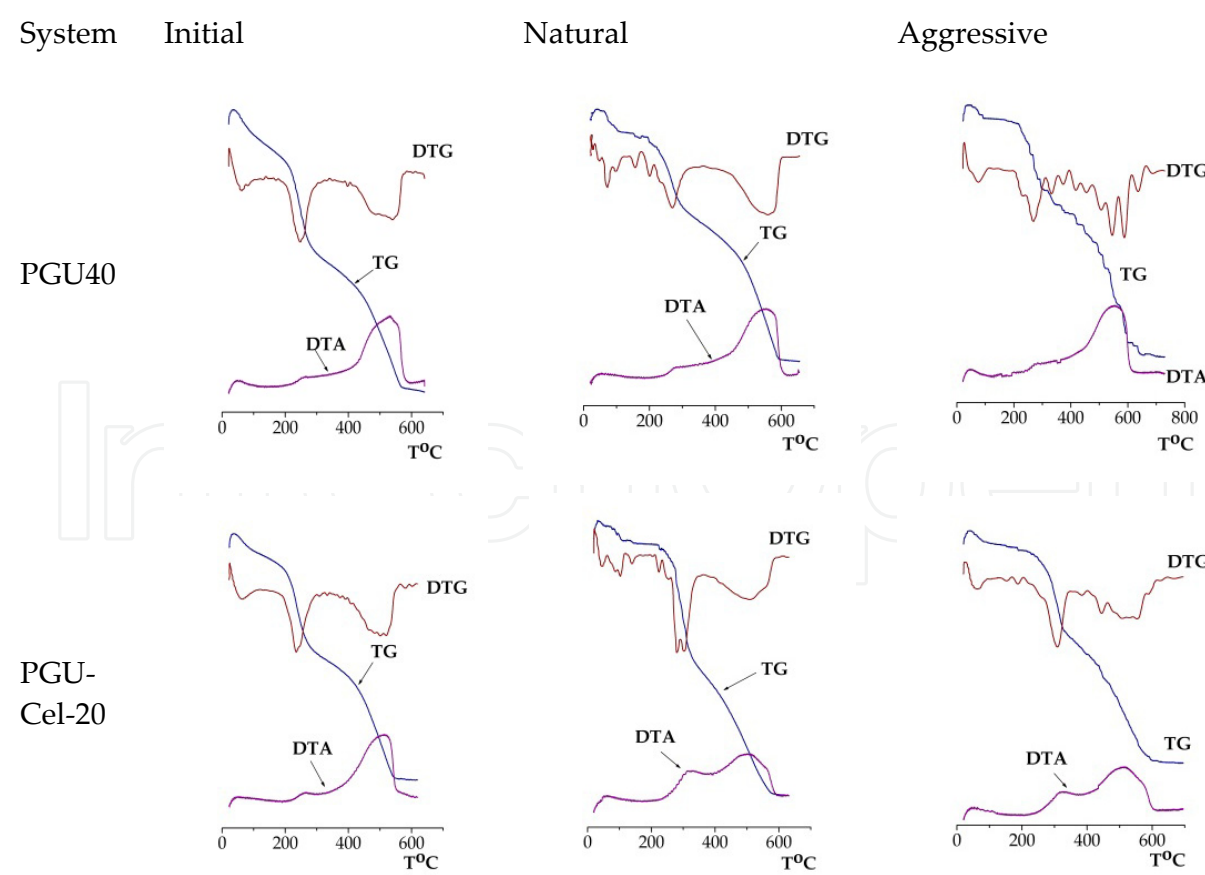
Efficient difference in biodestruction character of PGU20-xanthan and PGU20-cellulose allows conclude that xanthan based PGU is destroyed mainly in its saccharide side-chains (containing D-mannose, D- glucuronic acid and D-glucose).

IR data correlate with results of TGA analysis. Table 3 shows difference in character of TG, DTG and DTA curves for PGU20-cellulose after contact with aggressive and natural medium. On DTG curves of PGU20-cellulose after natural and aggressive medium it is seen that stage of thermal destruction in temperature interval 200 – 300 oC is moved into district of higher temperatures while in PGU40-xanthan this stage is splitted and differs for natural and aggressive medium.





**Figure 12.** IR spectra PGU20-cellulose 1 – initial PGU20-cellulose; 2 – PGU after contact with natural microbial medium, 3 – PGU after contact with aggressive microbial medium.



**Table 3.** IR spectra of PGU40 and PGU-cellulose-20 after biodestruction

## 6. Conclusions

New hydroxylcontaining polyurethane networks (polyglucanurethane) with various urethane group content were obtained based on microbial exopolysaccharide xanthan and latent blocked polyisocyanate using environment friendly technique. Obtained polyglucanurethanes possess advanced thermal and chemical (both alkali and acid) resistance. Thermal resistance of PGU grows with increasing of urethane group amount. Were as with growth of urethane group content in the system the amount of absorbed water declines.

Study of properties of polyglucanurethanes reveals their ability to quantitative extraction of phenol and bivalent metal ions from water solution, while controlling sorption properties of the material with polysaccharide cross-linking degree. According to electron spectroscopy and EPR data the main mechanism of ion capture by polyglucanurethane consists in formation of "polymer-metal ion" chelate complexes.

Biodestruction research demonstrate that polyglucanurethane degradation in aggressive microbial media occurs via polysaccharide fragmentation due to urethane bonds cleavage. On the contrary microbial association that was isolated from pollution-free chernozem disintegrate the polysaccharide chains predominantly.

But both in aggressive microbial association and in natural microbial association that was isolated from pollution-free soil the direct relation was observed between destruction process intensity and percentage of polysaccharide OH-group substitution in PGU. The lower percentage of OH-groups was substituted, the more intensive destruction process was observed.

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## 7. Acknowledgement

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