Degradable polyurethane foams based on disaccharides

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ABSTRACT: New functional elastic polyurethane foams (PUF) degradable under environmental abiotic and biotic factors, retaining all the inherent properties of the conventional foams were synthesized using isocyanate precursors based on disaccharides (DS): lactose, maltose and saccharose. It was shown by the model reactions of monosaccharide glucose, and DS lactose and saccharose, with phenyl-isocyanate that both the primary and secondary hydroxyls of the carbohydrates reacted to form urethanes. The main properties of DS-based foams (PUF/DS) were found to be similar to PUF foam (matrix) prepared with conventional polyols. However, the new PUF/DS were found to undergo enhanced acid/alkaline hydrolysis and degradation compared with PUF matrix when incubated in soil. Mass losses of incubated PUF/DSs significantly exceeded the actual carbohydrate content 28.6%, and in 12 months reached 39.58 (PUF-4), 53.31(PUF-8), and 47.25 (PUF-12). In contrast, under the same conditions PUF matrix lost only 2–2.5%, confirming that incorporation of natural compounds into the polymer chain impacted the degradation processes. PUF/DS were characterized by FTIR, ^{1}H NMR, ebullioscopy, and exclusion chromatography (molecular masses and molecular mass distribution of the oligomeric model), physical and mechanical tests (density, tensile strength, relative elongation, moisture absorption, vapor permeability), morphology, and degradation in the soil. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42131.

INTRODUCTION

Polyurethane foams (PUFs) are a widespread class of polymer materials used in various fields of human activity. They are of great scientific and applied interest due to the complex of unique chemical and physical properties based on peculiarities of their structure.[1,2]

The main applications of PUFs' include manufacture of furniture, vehicles, packaging and isolating materials, textiles, sporting goods, biomedicine, and many others.[1]

Structure-chemical modification of the polyurethane macromolecule by incorporation of different functional groups during the PUF preparation process has been shown to affect the structure of the polyurethane products. The use of different classes of organic compounds for PUFs synthesis provides an aimed variation of structure and, therefore the macroproperties of polymer.

One of the key target applications of PUFs is its use in biomedical as a biologically active polymers.[3–5] Because of inherent structure heterogeneity both on micro- and macrolevel, PUFs posses a certain level of biocompatibility.[6–11]

The common methods used to solve the problem of plastic waste are incineration or disposal in landfields. However,

these methods have essential shortcomings and limitations.[12] During the PUFs' burning there is a risk of air pollution with toxic products of combustion (NCN, CO, NO, etc.).[13] On the other hand, during the degradation of "physical" blends of natural and synthetic polymers (the prevailing way of degradable polymer creation), primarily only a natural ingredients degrade while the synthetic components do not degrade significantly.

It was shown that incorporation of a natural component into a synthetic polymer structure can provide better mechanical properties and enhanced degradation.[14] Incorporation of so-called "weak chain" into the macromolecule architecture became a well established method to enhance the degradation and typically, natural carbohydrates serve as the "weak chain."[15–17] In our earlier studies we obtained degradable polyurethane ionomers by incorporating natural compounds such as mono-, di-, and polysaccharides into the polyurethane structure.[14,18]

Incorporation of natural carbohydrates into the macromolecule structure promotes based polymer degradation, which is one of the most effective methods to overcome the pollution of the environment with plastic wastes. These new materials were prepared in line with the principles of "green chemistry,"[19] which

is based on nontoxic principles during use and upon disposal both for person and the environment.

The present work is focused on the preparation of novel disaccharide-containing PUF with controlled structure and degradation under the influence of biotic and abiotic factors.

EXPERIMENTAL

Materials

Polyethers. Laprol 3003, L-3003 (MM 3000)–Glycerol based polyether having hydroxyl number in the range of 51.0–56.0 mg KOH/g and acid number less than 0.05 mg KOH/g. ("Vladimyr Chemical Enterprises", Russia).

Laprol 5003, L-5003 (MM 5000)–Polyatomic alcohols and copolymer of propylene and ethylene oxide based polyether having hydroxyl number in the range of 32.0–36.0 mg KOH/g and acid number less than 0.10 mg KOH/g ("Macromer Ltd", Russia).

Polyesters. Polyester P-2200 (MM 2200)–the condensation product of diethylene glycol, adipic acid, and glycerol having hydroxyl number in the range of 57.0–63.0 mg KOH/g and acid number less than 1.5 mg KOH/g ("Corundum Ltd", Russia).

Polyester P-503 (MM 500) - the condensation product of diethylene glycol, adipic acid, and glycerol having hydroxyl number in the range of 280.0–333.0 mg KOH/g and acid number less than 2.0 mg KOH/g ("Corundum Ltd.", Russia).

Diisocyanate. Toluene diisocyanate (TDI)–the mixture of 2.4 and 2.6–isomers), ("Okakhim", Russia), cleaned by vacuum distillation.

Phenylisocyanate. Phenylisocyanate (PhIC), MM = 119.12, $\rho = 1.095$ g/cm^3 («Merck», Germany), cleaned by vacuum distillation.

Catalysts. Tin octoate (TO) ("Baltic manufacture," Russia); Tris-(dimethylamino-methyl)phenol (UP-606/2) ("Khimeks Ltd.," Russia). Diazobicyclooktan (DABCO) ("Baltiyskaya manufactory," Russia).

Foam Stabilizers. KEP-2–block-copolymer of polydimethylsiloxane and alkylene oxides ("Orgsintez," Russia). Vaseline oil (VO) ("Medkhim," Russia).

Mono- and Disaccharides. Monosaccharide glucose (Gl) and the disaccharides (DS): lactose (Ls), maltose (Ms), saccharose (Sc) («Merck», Germany) were previously dried from hygroscopic moisture (and the crystallization water of lactose) to a constant weight at a temperature of 130–135°C and residual pressure of 3–4 mm Hg.

The structures of all saccharides are presented in Scheme 1:

Glucose [α(β)-D-glucopyranose]

Lactose [4-O-β-D-galactopyranosyl-D-glucopyranose]

Maltose [4-(α-D-glucosyde/o-D-glucose]

Saccharose [α-D-glucopyranosyl-(1→2)-β-D-fructofuranozide]

Synthesis

Model Systems. Model systems based on glucose, saccharose, lactose, and phenylisocyanate (PhIC) have been obtained by reaction of mono- and DS with PhIC in a minimum amount of dimethyl formamide (DMF) (molar ratio of glucose: PhIC = 1 : 1, 1 : 2; disaccharide:PhIC = 1 : 2). The reaction was carried out at 75°C for 40–60 min. The synthesized model products were washed with distilled water to remove any unreacted residual saccharides and then were dried in a vacuum oven at 60–65°C under vacuum (4.3 mm Hg) until constant weight.

The resulting products were white fine-crystalline powders, soluble in ethanol, DMF, dimethyl sulfoxide (DMSO), acetone, ethyl acetate, sulfuric ether, dioxane, methyl ethyl ketone, and insoluble in water, hexane, chloroform, and toluene. Overall yield of phenylurethane lactose was about 64.4%, phenylurethane glucose: 58.7%, phenylurethane saccharose: 62.3%.

Polymer Systems. *Disaccharide based isocyanate precursors (IPD).* The calculated amounts of DS and TDI in a molar ratio of NCO : OH = 2 : 1 or 4 : 3 were charged into a three-necked reactor. The resulting mixture was heated for 80 min at 60–62°C under argon atmosphere at constant stirring. After twice reducing the number of free NCO-groups in the reaction mixture, the reaction was stopped by cooling the reactor with cold water to 10–15°C. The experimental NCO value differed from the calculated value by no more than 0.2% wt. The resulting IPD was immediately used for the synthesis of PUF.

Polyurethane foams. Distilled water (0.32–1.03 wt %), TO (1.06–3.5 wt %), vaseline oil (0.21–0.35 wt %), KEP-2 (0.6–1.06 wt %), UP-606/2 (0.85–1.41 wt %) were charged into the wide-necked flask equipped with a mechanical stirrer at room temperature; all ingredients were mixed until a homogeneous mixture was formed. Then oligodiols L-3003 (6.65–10.7 wt %) or L-5003 (28.0–44.0 wt %), and P-503 or P-2200 (4.3–42.7 wt %) were added to the reaction mass under constant stirring. After a homogeneous product was obtained (component I), the disaccharide-based isocyanate precursor (IPD, component II) was added to the reaction mixture.

The content of the flask was stirred until a foaming was observed (start time, τ_s, was equaled 2–3 min), thereafter the mass was poured onto the molds. Foam forming was occurred due to volatilizing of carbon dioxide during the decomposition of unstable carbamic acid. Thus obtained PUFs contained in their composition of about 21 wt % of DS (NCO : OH = 2 : 1) or 28.6 wt % DS (NCO : OH = 4 : 3). Gellation time, $\tau_g = 64 \pm 3$ s, τ_g: the time from the start of stirring of components' mixture [I + II] prior the polymerization, when the thin polymer stretching threads can be obtained from the rising reaction mixture (samples PUF 2÷ PUF 12, PUF-M were obtained without DS).

The composition and codes of PUFs prepared are presented in Table I.

Methods

Fourier Transformed Infrared spectroscopy (FTIR). FTIR-measurements of PUF were performed using Tensor 37 FTIR (Bruker Optics, Germany) over the wave number ranging

Glucose [α(β)-D-glucopyranose]
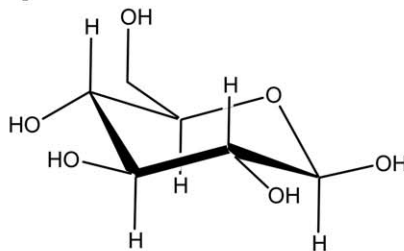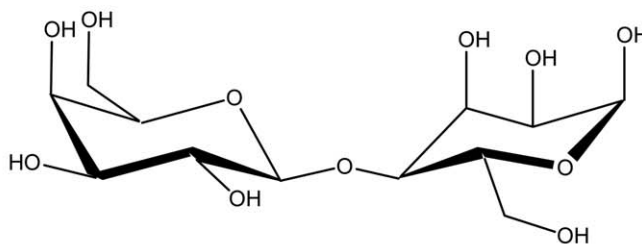
Lactose [4-O-β-D-galactopyranosyl-D-glucopyranose]

Maltose [4-(α- D-glucosyde/o-D-glucose]
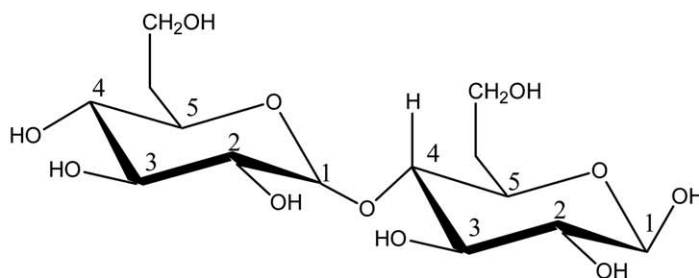
Saccharose [α- D-glucopyranosyl-(1→2)-β-D-fructofuranozide]
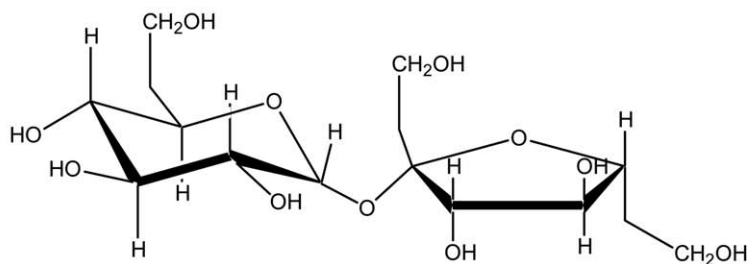
Scheme 1. The saccharides used in this study.

between 600 and 4000 cm^{-1} at the temperature of 18($\pm$1)°C. The foam samples were prepared by cryogenic mechanical grinding followed by pressing with KBr.

¹H NMR Spectroscopy. ¹H NMR spectra were obtained using «Varian VXR-500» in the solution of deuterated DMSO-d6, using tetramethylsilane as the internal standard.

Ebullioscopy (ES). Molecular weight (M_W) of the oligomeric model was determined by ebullioscopy using ebuliometr EP-68

(Chernogolovka, Russia). Phenanthrene ($M_W = 178$ g/mol) was used for calibration and dioxane was used as the solvent.

Exclusion Chromatography (EC). Studies of the molecular weight characteristics–molecular weight (MW) and molecular weight distribution (MWD) were carried out using a liquid chromatograph IS-8800 (Du Pont, USA), equipped with a bimodal column (Zorbax PSM-100 and Zorbax PSM-1000, Great Britain), suitable for MM range of 10^2-106. Silica gel with an average particle diameter of 5–6 μm (ZORBAX) was used as the stationary phase. DMF was used as the eluent for the UV detector. The

Table I. PUFs Composition and Codes

| PUF samples | Oligodiol | | | | Isocyanate precursor based on disaccharide (IPD) (% mass) | | | | | |
	Oligoether		Oligoester		TDI : Ls-2 : 1	TDI : Ls-4 : 3	TDI : Ms-2 : 1	TDI : Ms-4 : 3	TDI : Sc-2 : 1	TDI : Sc-4 : 3
PUF-1	P-2200	–	L-3003	–	41.0[a]	–	–	–	–	–
PUF-2	–	–	–	–	41.0[b]	–	–	–	–	–
PUF-3	–	–	–	–	–	64.0[a]	–	–	–	–
PUF-4	–	–	–	–	–	64.0[b]	–	–	–	–
PUF-5	–	P-503	–	L-5003	–	–	41.0[a]	–	–	–
PUF-6	–	–	–	–	–	–	41.0[b]	–	–	–
PUF-7	–	–	–	–	–	–	–	64.0[a]	–	–
PUF-8	–	–	–	–	–	–	–	64.0[b]	–	–
PUF-9	–	–	–	–	–	–	–	–	41.0[a]	–
PUF-10	–	–	–	–	–	–	–	–	41.0[b]	–
PUF-11	–	–	–	–	–	–	–	–	–	64.0[a]
PUF-12	–	–	–	–	–	–	–	–	–	64.0[b]

Reagents used in the synthesis of all samples were the follow: foaming agent–water; catalysts: TO and [a]DABCO or [b]UP-606/2; foam stabilizers–VO, KEP-2.

program «Chrome-1» was used for the analysis of gel-exclusive liquid chromatography experimental data (Insoft Group). The percentage of individual fractions with different MM was calculated using a package of free access Fityk (c).[20]

Physical and Mechanical Studies. *Density (ρ).* Three samples with the size (50.0 × 50.0 × 50.0) ± 0.5 mm, were cut from the middle part of the foam, weighed, and measured. The density of PUF was calculated according to the formula: $\rho = [M/V] \times 1000$ kg/m^3, where: M: mass of the sample (g); V: volume of the sample (cm^3).

Tensile strength (σ) and *relative elongation (ε) at break point* were evaluated using the tensile machine FU-1000 (VEB MWK "Fritz Heckert", Germany). $\sigma = P/A_0$, where P is the load at which the sample failed, kg; A_0: starting cross-section (cm^2). $\varepsilon = (\Delta l_{op}/l_o) \cdot 100$, where Δl_{op}: change of the estimated length of the sample at the time of rupture (cm); l_o: starting length of the sample (cm). Measurements were carried out in accordance with Standard 14236-81.

Moisture absorption (MA, %): the amount of moisture retained in the sample was determined gravimetrically in nonisothermal conditions. The study was carried out in the chamber (RH = 65 ± 5%, $T = 20 \pm 3°C$, $\tau = 16$ h). $MA = (m_1 - m)/m \times 100$, where m, m_1: mass of the sample before and after the measurement, g. Measurements were carried out in accordance with Standard 22900-78.
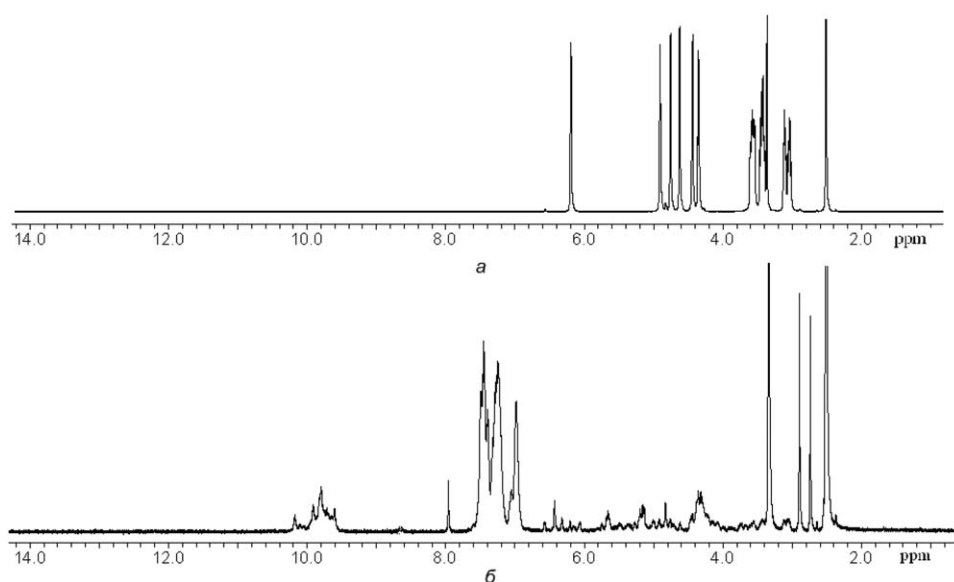
Figure 1. ^{1}H NMR-spectra of (a) Gl and of interaction product (b) Gl : PhIC.
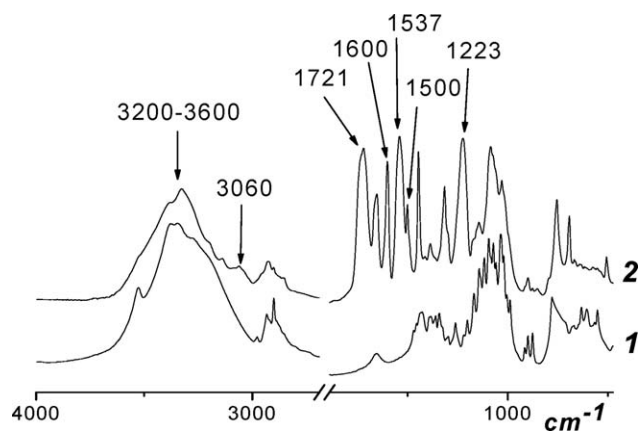
Figure 2. FTIR-spectra: 1: Lactose; 2: Phenylurethane lactose.

Vapor permeability (P_v, $mg/cm^2 \times h$): the amount of steam that passed through the sample per unit area and unit time under isothermal conditions. These studies were conducted in a chamber over sulfuric acid samples contained in a metallic beaker. P_v under the isothermal conditions ($28 \pm 1°C$) was calculated according to: $P_v = (m_1 - m_2) \times 10^3/29.4$; where m_1: is the mass of the glass with a sample after 16–18 h of thermostating (g); m_2: is the mass of the glass with the sample after 6 h of thermostating (g); 29.4: is the coefficient equal $S \times t$, where S: the working area of the sample (4, 9 cm^2); t: test period (6 h). Measurements were carried out in accordance with Standard 22900-78.

Morphological Characteristics. Quantitative characterization of PUF cells was performed using the method of image analysis with the ImageJ program.[21] The scanning of preliminary contrasted surfaces of PUF cuts were used for digital images. Statistical processing of data was performed using the statistical analysis package STATISTICA 7 (Statsoft) (Demo).

Degradation. *Abiotic factors. Hydrolysis:* The degree of hydrolysis in acid and alkaline medium was determined by mass and physic-mechanical indices.[22] Samples of known weight were immersed into $0.1N$ solution of KOH and $0.1N$ solution of HCl, respectively and were allowed to aged at the 36.6–37.00°C for 30 days.

Incubation into a soil: Investigations were carried out according to the procedure,[23] which allows to simulate the processes occurring in nature. Dried to the constant weight samples were placed into container with soil in a weight ratio of 1 : 50 and kept for 1, 3, 6, 9, 12 months at the temperature of $25 \pm 1°C$ and constant soil moisture of $60 \pm 2\%$. After this period the samples were removed from

Table II. MM and MMD of Phenylurethane Saccharides (EC)

№	Composition of model compound, mol	M_w (g/mol)	M_n (g/mol)	M_w/M_n
1	Gl : PhIC = 1 : 1	550	526	1.04
2	Gl : PhIC = 1 : 2	535	504	1.06
3	Ls : PhIC = 1 : 2	808	762	1.06
4	Sc : PhIC = 1 : 2	767	664	1.15

the soil, washed under running, then washed with distilled water and dried to constant weight at a temperature of 25°C.

Soil activity: Black earth of the fraction of 2–3 mm was used. The index of biological activity of the soil, according to a certain Standard ISO 846:1997 (E), was 34.6%

Acidity (pH) of the soil was measured in accordance with Standard 26483-85 : 30 g of Black earth and 75 mL of $0.1N$ KCl have been shaken up for 5 min. In 10–15 min after shaking the test portion was taken and pH number was controlled using "pH 150MI" (LLC "Measuring Technology," Russia). Indications were taken no earlier than in 1 min after immersion of the electrodes in the suspension. Simultaneously a blank experiment without soil samples was carried out. The soil with the solution was stirred for 1 min, pH = 7.17.

Soil microflora was determined by inoculation on culture medium with the following identification of grown microorganisms (MO) colonies (Koch's plate method).

Biotic factors. Examination of the action of the biodestructors was carried out according to Standard 9.048-9.053–75 (91). Disks of PUF samples were kept in the dampening chamber (till 87% RH, $t = 37°C$) and placed onto «Saburo» nutrient medium. Assessment of fungal growth was carried out by visual examination accordingly to Standard ISO 846:1997 (E).

RESULTS

Model Systems

Preparation. The preparation of DS based-polymers is rather laborious process requiring functionalization of the DS in order to obtain saccharide-containing monomers. Such monomers may then be polymerized or be used to modify other polymers. Obtaining of such monomers often involves a preliminary blocking of saccharide hydroxyls that is a fairly complicated process. In the absence of catalyst and under the mild conditions diisocyanate reacts with mono-, and di-, saccharides mainly on the primary hydroxyls, resulting in formation of the reaction products of linear structures.[24,25] Also, owing to the reaction of secondary carbohydrates hydroxyls, the formation of weakly branched polymers is possible.[26]

We suggest a way of preparation of Ls-, Sc-, Ms-containing PUFs by reaction of DS with diisocyanate resulting in IPD formation.

To investigate the interaction of carbohydrate and isocyanate components in terms of IPD obtaining, the synthesis of model systems on the basis of natural monosaccharide Gl and DS: Ls and Sc with monofunctional isocyanate - PhIC have been conducted. The reaction of PhIC preparation was carried out in mass until the isocyanate number, determined by reverse titration method, reached the estimated theoretical value.

The resulting products are white fine-crystalline powders, highly soluble in ethanol, dimethyl formamide, dimethyl sulfoxide, acetone, ethyl acetate, diethyl ether, dioxane, methyl ethyl ketone, and insoluble in water, hexane, chloroform, and toluene.

^{1}H NMR Spectroscopy. ^{1}H NMR spectrum of glucose [Figure 1(a)] has shown the following signals: 3.0–3.5 ppm —CH— (4H at C_2, C_3, C_4, and C_5); 3.5–3.6 ppm —CH_2— (2H); 4.35 ppm
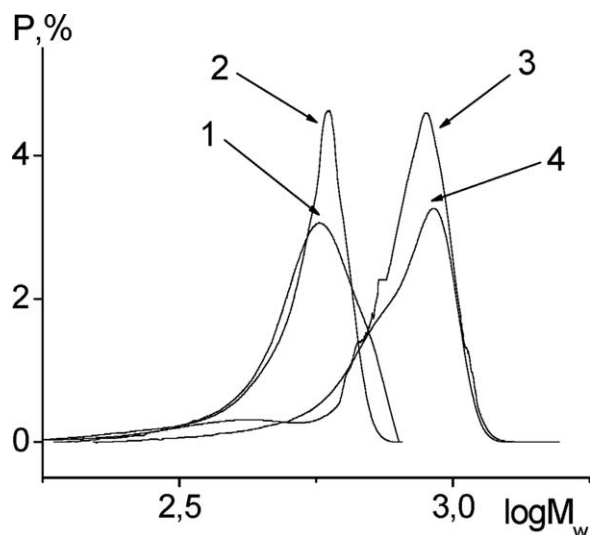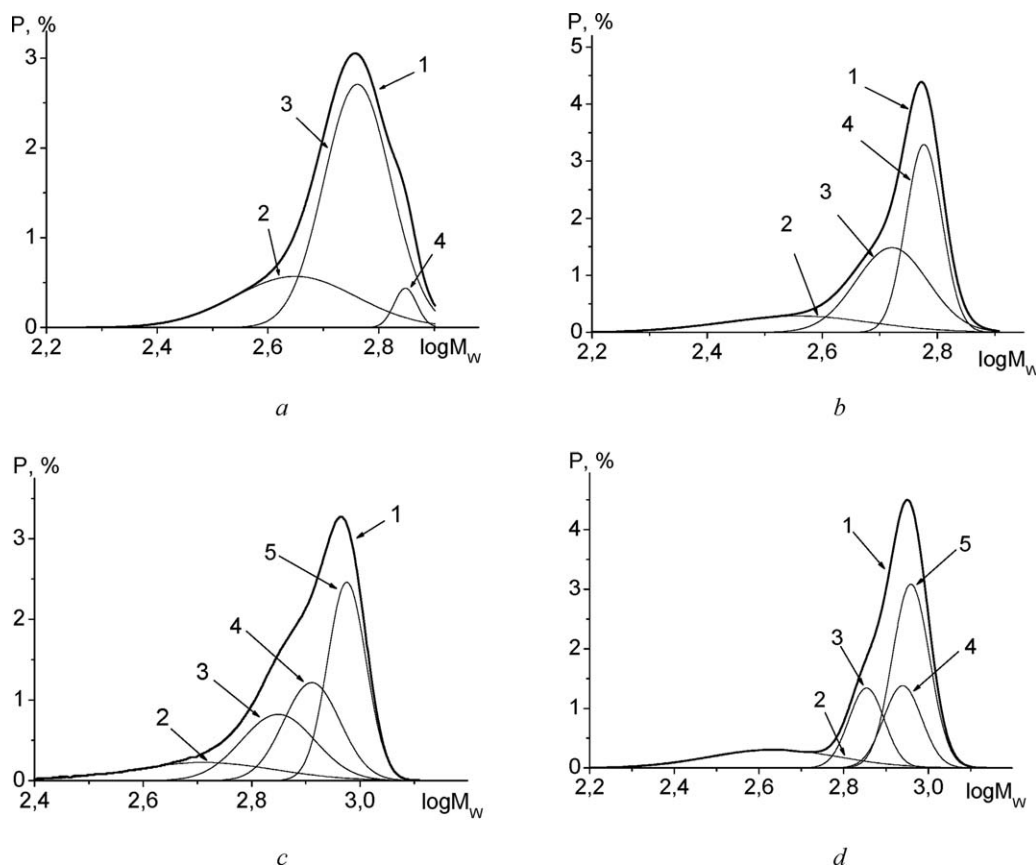
Figure 3. MMD of phenylurethane saccharides at following reagent ratios: Gl : PhIC = 1 : 1 (1), Gl : PhIC = 1 : 2 (2), Ls: PhIC = 1 : 2 (3), and Sc : PhIC = 1 : 2 (4).

—OH (1H at C_1); 4.43–4.75 ppm —OH (3H at C_2, C_3, C_4); 4.9 ppm —OH (1 H at C_6), 6.2 ppm —CH— (1H at C_1). The signals in the range of 2.5 and 3.3 ppm are attributed to residual solvent signal-dimethyl sulfoxide and water, respectively. Comparison of ^{1}H NMR spectra of Gl [Figure 1(a)] and the product

of Gl and PhIC interaction [Figure 1(b)] has shown that the spectrum of the resulting model compound–phenyluretane glucose provides clear signals that distinguishes it from the initial carbohydrate.

Signals at 7.0–7.5 ppm and 9.5–10.0 ppm correspond to the resonance of aromatic protons -Ar (5H) and protons of urethane group —O—CO—NH— (1H), respectively. Signals at 4.3–5.7 ppm correspond to protons of reaction product's OH groups. Signals at 2.7–2.9 ppm and 7.9 ppm belong to the solvent protons. ^{1}H NMR spectra of the interaction products of PhIC and Gl (PhI : Gl = 2 : 1), Sc and Ls contain the similar signals in the corresponding range, which relate to fluctuations of aromatic, hydroxyl protons, and protons of urethane groups.

FTIR Spectroscopy. Comparison of the FTIR spectra of Ls (1) and phenylurethane lactouse (2) prepared at 1 : 2 molar ratio (Figure 2) indicates the presence of intense bands of OH (3200–3600 cm^{-1}), C—H (2850–2900 cm^{-1}) and CH$_2$ (2915–2940 cm^{-1}) groups for both components. The differences are associated with the presence of two bands for the urethane group: 1721 cm^{-1} (amide I, $v_{C=O}$), 1537 cm^{-1} (amide II, the main contribution δ_{N-H}), the urethane ester group—1223 cm^{-1}, and the benzene ring vibrations (1600 cm^{-1}, 1500 cm^{-1}, 3060 cm^{-1}). Thus, IR spectroscopic study has confirmed the chemical interaction between Ls and PhIC followed by urethane group —O—CO—NH— formation.

Figure 4. MMD curves of phenylurethane saccharides 1: (Gl : PhIC = 1 : 1 (a), Gl : PhIC = 1 : 2 (b) Ls : PhIC = 1 : 2 (c), and Sc : PhIC = 1 : 2 (d) arranged in the amount of Gaussian distributions: 2: product of di-addition, 3: product of three-addition, 4: product of four-addition, 5: product of five-addition.

Table III. Structure of Model Reactions' Products

Reagent ratio	Fraction content (%)			
	Product of di-addition	Product of three-addition	Product of four-addition	Product of five-addition
Glucose : PhIC = 1 : 1	26.5	69.5	4	–
Glucose : PhIC = 1 : 2	17	39	44	–
Sucrose : PhIC = 1 : 2	15	19	21	45
Lactose : PhIC = 1 : 2	12.5	23.5	27	37

Absorption bands in the range of OH groups' vibrations (spectrum 2) suggests that at Ls : PhIC ratio 1 : 2 the resulting reaction product–phenyluretane lactose contains free OH groups. IR spectra of the reaction products of PhIC–saccharose and glucose possess similar to spectrum 2 absorption bands in the vibration range of urethane and hydroxyl groups, indicating a similar nature of carbohydrates and PhIC reaction. FTIR spectroscopy results are confirmed by ^{1}H NMR spectroscopy. Thus, FTIR and ^{1}H NMR spectroscopy analysis has confirmed the formation of phenyluretane saccharides–the products of carbohydrates and PhIC reaction.

Molecular Mass and Molecular Mass Distribution. To determine the particular functionality of carbohydrates in their reaction with isocyanates, the MM, and MMD of phenyluretane saccharides were studied by ES and EC.

According to the ES data the values of the number average MM of phenyluretane glucose studied at different reacting components ratios were found to be close to 497 g/mol (at Gl : PhIC = 1 : 2), and 515 g/mol (at Gl : PhIC = 1 : 1). MM of phenyluretane lactose is 774 g/mol, phenylurethane sucrose-669 g/mol. Defined by ES MMs of obtained model compounds were confirmed by EC (Table II).

According to ES and EC data the reaction of carbohydrates with PhIC results in formation of phenylurethane saccharide with different degree of additions.

The MMD curves have shown (Figure 3), that the product of PhIC and Gl interaction (at different reagent ratio) contains fractions with molecular masses corresponding to the two-, three-, and four addition, while the product of PhIC and Sc/Ls interaction contains fractions with molecular masses corresponding to the - two-, three-, four-, and five addition.

To determine the percentage of individual fractions the curve of molecular mass distribution was decomposed into the sum of Gaussian distributions using the least squares method (Figure 4).

Table IV. Physic-Mechanical Indices

| Sample	ρ (kg/m^3)	σ (kPa)	ε (%)	MA (%)	P_V (mg/cm$^2 \times h$)
PUF-M	48	183.0	139.3	0.027	3.53
PUF −4	52	179.3	165.0	0.,436	4.86
PUF −8	54	178.7	165.0	0.456	4.34
PUF −12	56	178.0	162.0	0.444	4.87

The averages of appropriate Gaussian distributions correspond to the common logarithm of the molecular mass of the individual fractions. Percentage content of individual fractions of different addition degrees in the reaction products of saccharides and PhIC is presented in Table III. The results indicate that both primary and secondary hydroxyl groups of saccharides participate in this reaction followed by products formation.

Thus, as the result of carried out model study of saccharide containing isocyanate precursors the glucose-, lactose-, and sucrose containing phenylurethanes have been obtained. The structure of the latter was confirmed by IR- and ^{1}H-NMR spectroscopy. The participation of both secondary and primary hydroxyl group of saccharide in the reaction of urethane formation has been confirmed by ebullioscopy and exclusive chromatography.

Polymer Systems

Physic–Mechanical Properties. Incorporation of natural compounds into the PUF's macrochain structure affects the physical and mechanical properties of the obtained PUF (Table IV).

The deformation-strength characteristics of natural compounds based PUFs are within the operational requirements for such materials. PUF-DS samples demonstrated somewhat lower values of strength (σ) and higher elongation at break (ε) versus PUF-M.
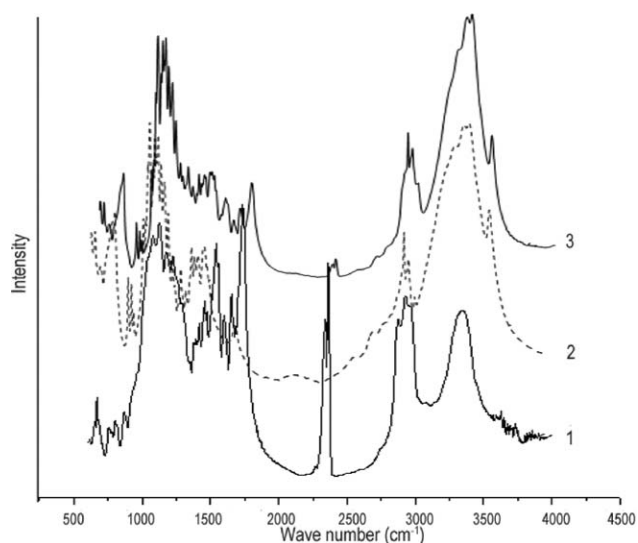
Figure 5. FTIR-spectra of synthesized PUF: 1: PUF-M, 2: Lactose, 3: PUF-4.

a   b
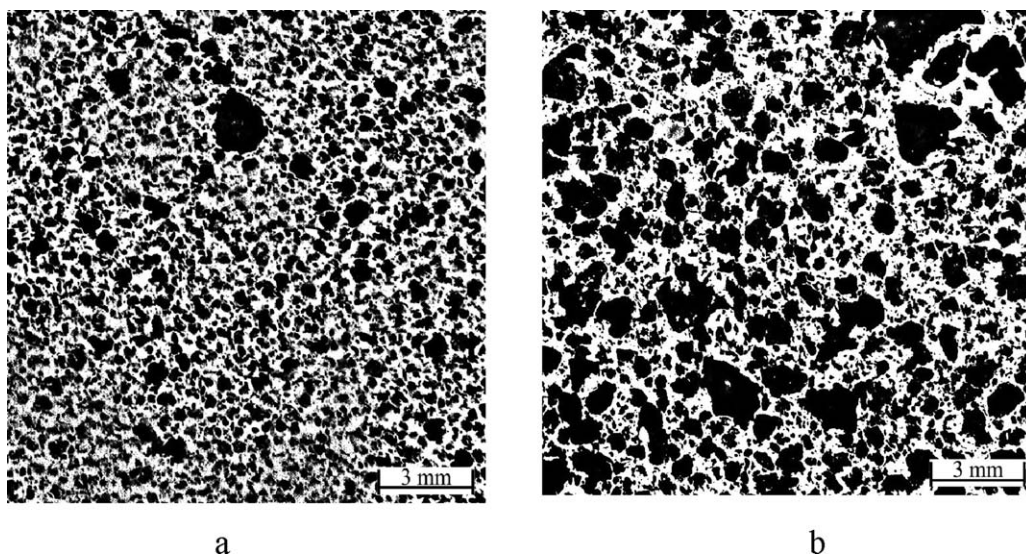
Figure 6. Images of cut surfaces of (a) PUF-M and (b) PUF-4.

All used carbohydrates are highly hydrophilic, so their incorporation into the PUF naturally increases MA of samples as compared to PUF-M. Increase of MA and, therefore, hydrophilicity will improve the adhesion of microorganisms (MO) to the polymer surface and activate the process of degradation.

FTIR Spectroscopy. FTIR-spectroscopic study of PUF-M (without DS) and PUF-4 (containing DS), has confirmed the structure of obtained foam polyurethanes (Figure 5). The bands observed for PUF-Ls in the range of 3600–3000 cm^{-1}, are not detected for PUF-M. The bands characteristic for Ls have appeared, namely, the OH-group vibrations: 3528, 3380, 3340 cm^{-1}. The superposition of the peaks of PUF-M and Ls is observed in the range of stretching vibrations of CH$_2$-group, 1800–3000 cm^{-1}. The urethane group vibrations (amide I and amide II) in the range of 1800–1500 cm^{-1} become apparent; they are similar both for PUF-M and PUF-4. The increase of their intensities confirms the reaction of urethane formation for both PUFs. Minor changes are observed in the range of CH$_2$-deformation vibrations 1500–1300 cm^{-1}, where PUF-4 bands become apparent as well as the bands of PUF-M. The increase of peaks' intensity testifies to chemical bonding of Ls in PUF-4. The characteristic bands of both PUF-M and Ls are presented in IR-spectrum of PUF-4, indicating the incorporation of Ls into the PUF structure. FTIR-spectra of Cs-, Ms-containing PUF are similar to that, described earlier.

Table V. Morphological Characteristics of the PUF Cells

Sample	Average square, S (mm^2)	Average equivalent diameter, ED (mm)	Average index of the shape
PUF-M	0.073	0.253	0.488
PUF-4	0.187	0.341	0.476

Morphology. Morphological features of cells, namely, apparent density ρ, vapor permeability P_v, and MA are important characteristics of PUF, which determine its degradation behavior. The deformation of the cells along the foaming direction observed for PUF-M, and for all obtained by free foaming method PUFs, leads to anisometric shape of the cells. Shape index, equal to the ratio of the largest to the smallest linear dimensions for PUF-M is about 0.488. Images of cut surfaces of PUF-M and PUF-4 are presented in Figure 6.

Average values of cell area (S) and the equivalent diameter (ED) are 0.073 mm^2 and 0.253 mm, respectively. Comparative analysis of the cell structure (Figure 6) of samples PUF-M and PUF-4 showed that incorporation of Ls results in increasing of all dimensional characteristics of the PUFs' cells (Table V)—S increases in 2.5 times, ED in 1.4 times (Table V). However, the decrease of form index indicates the increase of anisometric cells number. The simultaneous increase of apparent density ρ, size of cells S, and ED of PUF-4 suggests the thickening of the cell walls.

Analysis of cells' area distribution (Figure 7) has shown a little impact of Ls incorporation. Maximal part of cells (∼21–27%) corresponds to the range of 0.02–0.05 mm^2. The distribution of cells' area is characterized by a pronounced asymmetry towards the lower values. The area of the most majority of the cells (24–26%) does not exceed 0.2 mm^2.

The area of cells of PUF-M does not exceed 0.5 mm^2. Incorporation of Ls into PUF results in the increase of number of the cells which area exceeds 0.5 mm^2. The quantity of such cells reaches 11%.

Morphological characteristics of PUFs, containing sucrose and maltose are similar to those described above.

Degradation. Degradation of the polymer in the environment occurs mainly due to hydrolytic splitting, including those under the influence of MO metabolic products, namely organic acids and enzymes.[27] IR spectroscopy data of exposed to hydrolysis
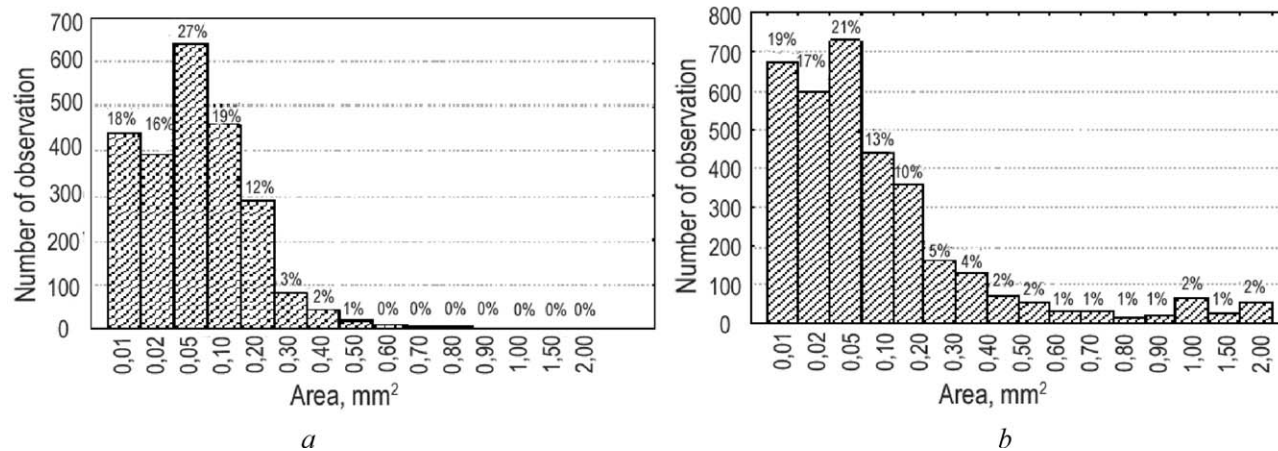
Figure 7. Histograms of cells' area distribution (a) PUF-M and (b) PUF-4.

PUF indicate that samples of PUF-DS are heavily exposed to both acid and alkaline hydrolysis.

Analysis of IR spectra showed that the sample PUF-M is more resistant to hydrolysis: the spectra of the samples before and after the tests have not changed, while the spectra of PUF-4 undergo considerable changes. Acidic and alkaline environments affect the PUF-4 structure (Figure 8). When comparing the spectra of the samples before and after hydrolysis it should be noted the decrease of the intensity of the absorption band of β-glycosidic linkages of Ls with maximum at 875 cm^{-1}. Decrease of Ls content in PUF as the result of hydrolysis provokes the redistribution of C—OH groups' absorption: the bands of 1115 and 1170 cm^{-1} have disappeared, while the intensity of the band 1142 cm^{-1} has decreased. The considerable degradation changes are confirmed by decrease of absorption intensity of C=O of urethane groups (1734 cm^{-1}) and C—O—C (1110–1170 cm^{-1}). Essential changes of the PUF-4 IR spectrum indicate the initialization of the degradation process due to DS presence.

Effect of Biodestructors. Evaluation of the natural contamination and relationship between adsorbed on the PUF surfaces mold fungi (biodestructors), air and substrate moisture have shown, that before the examination there was only one sporiferous colony of biodestructors on the sample surfaces with diameter of 1–2 mm from which *Penicillium cyclopium* was secreted and identified. During PUF keeping in a damp chamber an increase of colonies number has been observed. The viability of the mold fungi was kept up to the end of experiment, and their growth on the nutrient medium, without additional infection, was assessed at 3–4 points, in accordance with *Standard ISO 846:1997 (E)* (Table VI). First all samples overgrew with *Penicillium cyclopium,* and then with *Aspergillus niger*

Thus, the effect of biodestructors increases during the samples' keeping in the damp chamber, but the most intensive influence of biodestructors is observed on the nutrient medium. So, in terms of complex influence of the aforementioned factors, this effect is synergistic.

Study of PUF-DS degradation under the action of natural contamination in a damp chamber and nutrient medium after keeping in acid and alkaline mediums for 30 days (Table VII) has showed significant initiating effect of DS. So, incorporation of DS into the

Table VI. Assessment of the Natural Contamination by the Biodestructors
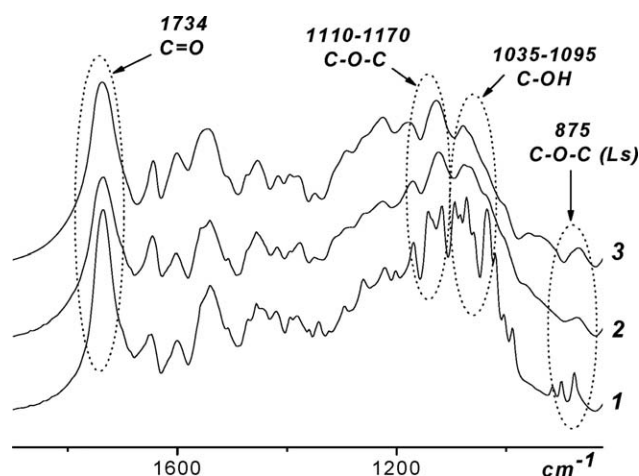
Figure 8. FTIR-Spectra fragments: PUF-4: 1: initial; 2: after acidic environment; 3: after alkaline environment.

	Assessment of fungal growth (points)		
PUF's samples	On the samples before test	In the dampening chamber	On the nutrient medium
PUF-M	1	1-2	2
PUF 1	1	2	3
PUF 2	1	2	3
PUF 3	1	2	4
PUF 4	1	2	4
PUF 5	1	2	3
PUF 6	1	2	3
PUF 7	1	2	4
PUF 8	1	2	4
PUF 9	1	2	4
PUF 10	1	2	4
PUF 11	1	2	4
PUF 12	1	2	4

Table VII. Evaluation of PUF Degradation

| | Values of PUF degradation after the keeping in different media for 30 days (% wt.) | | | | | |
| | Degradation under the influence of natural contamination | | Degradation under the influence of natural contamination and damp chamber | | Degradation under the influence of natural contamination and nutrient medium | |
PUF's samples	Solution 0.1N KOH	Solution 0.1N HCl	Solution 0.1N KOH	Solution 0.1N HCl	Solution 0.1N KOH	Solution 0.1N HCl
PUF-M	0.5	1.0	5.08	3.4	5.15	3.59
PUF-1	20.66	22.26	7.96	12.59	17.2	22.96
PUF-2	20.69	22.91	8.32	13.24	18.2	23.15
PUF-3	26.34	26.54	29.93	28.71	35.65	28.65
PUF-4	26.42	26.57	29.95	28.76	35.66	28.69
PUF-5	20.83	23.17	8.12	12.48	17.92	23.21
PUF-6	20.18	23.35	8.31	12.61	17.88	23.59
PUF-7	26.31	26.88	30.14	29.21	35.78	29.31
PUF-8	26.20	26.91	30.21	29.19	35.83	29.42
PUF-9	21.11	23.35	8.56	13.24	18.11	22.29
PUF-10	21.31	23.38	8.61	13.32	18.15	22.34
PUF-11	26.90	26.81	30.48	29.97	36.35	29.43
PUF-12	26.85	26.99	30.51	29.99	36.41	29.48

Table VIII. Results of Degradation in the Soil

| | Losses of PUF-DS during incubation, % mass/pH of the soil after experiment | | | | |
PUFs	1 month	3 months	6 months	9 months	12 months
PUF -M	2.13/7.17	2.15/7.17	2.15/7.15	2.42/7.14	2.49/7.14
PUF −4	29.20/7.11	32.11/7.10	37.32/7.08	38.36/7.06	39.58/7.03
PUF −8	37.40/7.10	39.00/7.05	46.13/7.03	50.21/7.00	53.31/6.95
PUF −12	36.27/7.09	41.66/7.06	42.37/7.02	45.82/6.99	47.25/6.95

PUF structure at molar ratio of TDI : DS = 2 : 1 results in degradation of PUF-DS up to 20.69–23.15% wt (TDI/Ls), 20.83–23.59% wt (TDI/Ms), 21.31–23.59% wt (TDI/Sc), correspondingly.

Incorporation of DS at molar ratio of TDI : DS = 4 : 3 results in following values of PUF-DS degradation: 28.76–35.66% wt (TDI/Ls), 29.42–35.83% wt (TDI/Ms), 99–36.41% wt (TDI/Sc). Under the same conditions the PUF-M degrades on 5.15% wt in alkaline and on 3.59% wt in acidic medium.

Thus, the incorporation of DS into the PUF provides the latter with ability to degradation under the action of different environmental factors, such as: (a) a long-term action of increased humidity (up to 87%) and temperature (37°C); (b) mold fungi (preferably of genera *Aspergillus* and *Penicillium* the most active biodestructors) and, (c) a solution of 0.1N KOH, and (d) a solution of 0.1N HCl.

Incubation of PUFs into a Soil. The degradation of synthesized PUF was studied according to the method simulating *in vivo* processes.[12,23] The samples were incubated into containers with soil (pH = 7.17, RH = 60%, T = 12–25°C) for a period from 1 to 12 months. Determination of soil microflora has shown the

fungi presence of the following genera: *Aspergillus, Penicillium,* and *Rhizopus*. Evaluation of the degradation results was performed by visual observation of the integrity changes of PUF samples after the experiment. Mass loss of the samples during
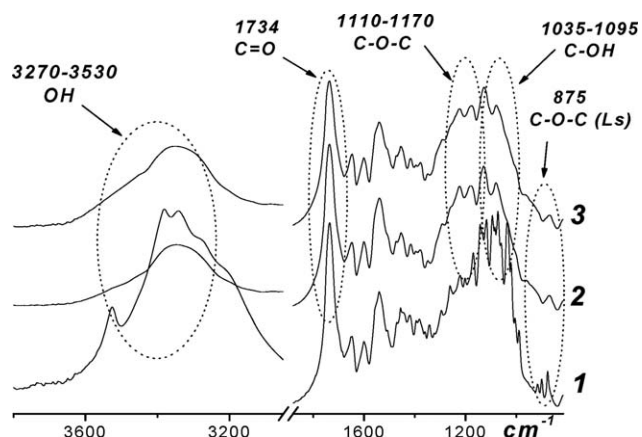
Figure 9. IR-fragments of initial PUF-Ls (28.6%) (1), after incubation into the soil for 6 months. (2) and 12 months (3).

the experiment was carried out by gravimetric method at regular time points, the structural changes were studied by IR spectroscopy. The results of PUF-Ds degradation in the soil showed (Table VIII), that in a month after incubation the mass loss of PUF-DS samples exceeded the actual DS (28.6%) content. and in 12 months reached 39.58–53.31%, that in 16–21 times exceeded the mass loss of PUF-M.

Obtained data confirmed that presence of natural component in the PUF structure promotes the degradability of PUF-DS under environmental conditions. Lowering of pH of the soil after the experiment was a result of the presence of organic acids - metabolic products of MO, which use the incubated samples as a nutrition source and testified to the increase of MO activity.

Profound changes occurred in PUF-DS samples as a result of incubation were confirmed by IR spectroscopy (Figure 9). Intensity of the band 875 cm^{-1} of β-glycosidic linkages of Ls after sample's incubation into the soil decreased compared with the original sample. The decrease of the number of physically and chemically bonded Ls in PUF samples resulted in redistribution in the absorption area of C—OH groups: the bands in the range of 1115 and 1170 cm^{-1} disappeared, the intensity of band 1142 cm^{-1} decreased.

Lowering of intensity of C=O bond of urethane group (1734 cm^{-1}) as well as C—O—C bonds in the range of 1110–1170 cm^{-1} testified to the essential changes occurred in the samples after incubation.

CONCLUSIONS

The method of synthesis of new functional elastic PUF degradable under environment destructive factors on the basis of natural DS incorporated into the isocyanate precursor has been developed.

It has been proved on model monomer systems, namely on interaction of monofunctional glucose and bifunctional lactose, and saccharose with phenylisocyanate that both primary and secondary hydroxyls of carbohydrates are involved in the reactions of urethane formation.

New foams are degradable under acidic and alkaline hydrolysis and during the incubation into the soil that has been proved by the mass losses of PUF/DS samples (40–53%), which exceeds an actual DS content in PUF (28.6%). Mass losses of PUF-M not comprising natural compounds amounts only 2–2.5% at the same conditions. So, the incorporation of natural compounds into the polymer macrochain initiates the degradation processes.

Thus, new functional elastic PUF which maintain all inherent to the PUFs' performance properties along with acquisition the ability to degrade under environmental abiotic and biotic factors at the end of term of their exploitation have been developed.

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