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Preparation of Polymer Composites on the Base of Polyurethanes and Natural Polysaccharides

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SUMMARY: A series of composites based on segmented polyurethanes (PU) as polymer matrices and natural polysaccharides – cellulose and starch - as fillers have been synthesized. Using IR method and Differential Scanning Calorimetry the peculiarities of the structure of composites and their behavior in the buffer solutions in conditions imitating natural soil environment have been investigated.

Introduction

Investigations and development of special composites based on renewable polymer materials are of intense interest due to the ecological and economic aspects of manufacturing a novel modified polymers for industrial needs. The main efforts to be directed in this field, on the one hand, focuses on elaboration of environmentally friendly production technologies of above composites and, on the other hand, these products should possess biodegradability together with defined physico-chemical and processing characteristics.

Several reviews deal with the study of biodegradable polymers [1,2]. According to the IUPAC recommendations of 1996 [3], for definitions and terms of degradation, aging, and other related processes for polymers, the term "polymer biodegradability" can be defined as a polymer being degraded under natural conditions, i.e., in the environment. It has also been stressed that after polymer degradation no contaminants are formed.

At present there exists several different ways to create biodegradable polymeric materials, one of them is mixing of commercial synthetic polymers with natural polymers (preparation of polymer mixtures) which have good biodegradable properties; another option is the synthesis of polymers with use of products from natural sources[1-4].

For example, chemical and physical modification of polyurethanes (PU) and their combination with natural polymers is an effective path for preparation of composites which are able to degrade in natural conditions. The properties of these composites are strongly dependent on the chemical components being used, and on physical and chemical interactions between the matrix and the filler on the phase interface.

The present research is devoted to the synthesis of polymeric composites based on synthetic and natural polymers, which tend to be decomposed under environmental conditions. For preparation of polymeric composites we applied segmented polyurethanes as polymer matrices because their chemical bonds are similar to those of natural products, such as proteins, lipids, polysaccharides, etc. Moreover, while synthesizing a PU, it is possible to introduce into the polymer backbones various biodegradable blocks with different chemical structures and to regulate their biodegradable characteristics in different ways. Polymers from renewable resources - powder microcrystalline cellulose (MCC) and starch - were used as

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fillers for PU matrices. These fillers have reactive functional groups, are able to degrade in the environment, and are easily available at low prices. Introduction of above fillers into the polyurethane matrices may lead to re-arrangement of physical and chemical bonds existing in the neat polyurethane, thus resulting in changes of structural parameters (crystallinity, microheterogeneity) of polymer composites obtained.

Therefore, structural peculiarities, character of intermolecular interactions in the PU-natural polysaccharides, their physico-mechanical properties, thermal characteristics and the ability to hydrolize in the neutral, acid and alkali medium have been studied.

Experimental

Synthesis of composites

Totally, three types of PUs based composites were obtained as follows: At first stage, polyurethane based on poly(oxytetramethylene)glycol (PTMG) with molecular weight (Mw) 1000, TDI (mixture of 2,4- and 2,6- tolylene diisocyanate (65/35) and 1,4 butanediol (BD) in the following molar ratio - PTMG: TDI: BD = 1:2:1 (PU-1) was synthesized. Then, microcrystalline cellulose (MCC) being introduced ranges from 10 to 40%, while the PU formation occurred.

Microcrystalline cotton cellulose had particle size < 0.05 mm and was bone-dried up to moisture content not exceeding 1.0 wt %. The DP_v of MCC was 170. This corresponds to its MM 27500 [5)].

Composite II has analogue components for PU matrix – PTMG: TDI: BD =1:2:1 (PU-II), but, in this case, natural starch was used as filler (starch contents are 10, 20 and 60%, respectively). Starch was of technical grade (moisture content ~5.5 wt %).

Composition III was obtained by mixing of water dispersed anionic PU ionomer being synthesized using the following components: PTMG Mw 1000, 4,4' – MDI (diphenylmethane diisocyanate) and N-methyldiethanolamine, and BD at molar ratio 1:3:1:1, respectively and, finally quaternized by appropriate amount of hydrochloric acid [6-7)], with aqueous dispersion of starch as filling agent. Starch content in PU ionomer matrix ranges from 10% to 60% by weight.

The reactive composite formation were carried out in heterogeneous conditions at 90°C. Before testing composites obtained were vacuum dried at 60°C to the constant weight. The samples based on MCC appeared to be films. and foamed materials, if starch is used.

Methods

IR investigations of composites during their formation and their ability to subsequent biodegradation have been carried out at UR-20 spectrophotometer, as described elsewhere[6)].

Surface structure of samples was studied using the method of attenuated total inner reflectance (ATIR) with UR-20 spectrometer at room temperature. As the inner reflection element, the prism with reflection angle is equal to 45° and KRS-element has been used. Structural testing of samples' surface both segmented PU I (neat) and its composite filled with MCC obtained as films, have been studied after specimens being treated in aqueous solutions as model experiment (see below). IR spectra were recorded every two weeks. Weight loss of samples were monitored every two weeks as well.

Thermal characteristics of polymeric compositions (sample feeds were $0{,}2\text{-}0{,}4\cdot10^{-3}$ kg) were investigated by Differential Scanning Calorimetry (as described in Ref. 8) in the temperature interval between –100 and 200°C at heat rate 2,0 (plus-minus 0,5) degree/min. For getting degradable characteristics in different solutions, composites obtained were placed into the

buffer solutions at pH 4,0, 7,0 and 8,5, respectively, for 4 months at 25^{0}C. Above pH range was chosen in order to simulate the one, occurring in the natural soil environment.
Buffer solutions were replaced for fresh ones every 48 hours.

Results and Discussion

Effect of starch and MCC on some properties of composites in model and real experiments

To evaluate reactivity of hydroxyl groups of filler macromolecules relative to isocyanate groups the model experiments have been carried out. Equal quantities (by weight) of filler and TDI were mixed together, and, then, mixture was heated up to 90^{0}C.

The reaction was controlled by following the changes in absorption intensity of spectral bands at 2280 cm^{-1} (ν NCO) in the IR spectrum. After keeping TDI-starch mixture for 1 hour at 90^{0}C the intensity of ν NCO bands decreased by half.

In contrast, during experiment with neat TDI (without starch) this spectral band is reduced for 10% only. This decreasing of intensity is due to interaction of isocyanate groups with moisture containing in the air. Taking into account the other transformations in the IR spectrum, in particular, increasing intensity of absorption bands at 1670 cm^{-1} (ν C=O urea groups) and no absorption in the area at 1720-1740 cm^{-1} (ν C=O urethane groups), it may be concluded, that OH-groups of starch do not interact with isocyanate under above conditions of experiment, but reaction taking place with traces of water permanently incorporated in the natural starch to form urea groups. It is known, while reaction between isocyanate and water occurs, it leads to the release of carbon dioxide, thus forming foamed materials. Actually, during preparing composition on the base of PU I and starch, foamed materials have been obtained.

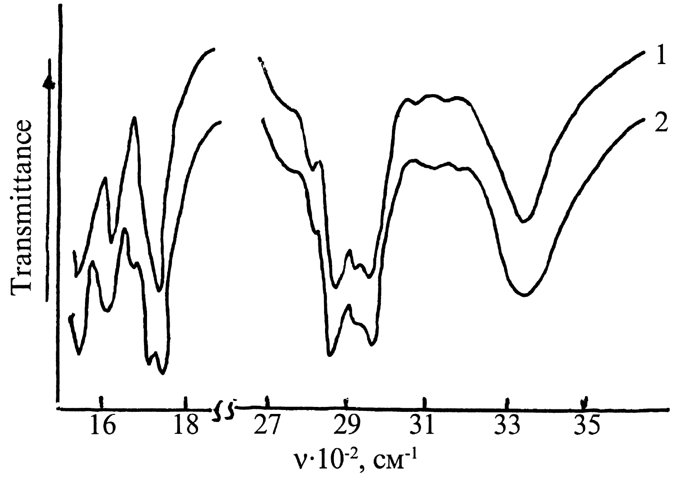

Fig.1. Infrared spectra of PU in the NH and C=O stretching regions: 1.neat PU 2. PU + 60% starch

The specimens having filler content 10% and 20% could be dissolved in dimethylformamide (DMF), but at high degree of starch filling (more than 20%) the samples are no longer soluble in DMF. IR spectrum of these compositions (Fig.1) have crisp spectral bands, attributing to fluctuation of C=O-, NH- groups for urethane fragment. Moreover, there appear band in the region at 1670 cm^{-1} (valent vibration of carbonyl in urea group). The network formed by hydrogen bonds is non-homogeneous, as it is seen from shifting of spectral bands of valent vibrations of N-H- groups at 3300 cm^{-1} in the neat PU up to 3320 cm^{-1} in the PU-starch composite. Emerging of spectral bands at 1720 cm^{-1} in samples having high level of starch filling could be explained by vibrations of C=O-groups, which form hydrogen bonds with OH-groups of starch.

In contrast, when model experiments were carried out with the TDI-MCC mixtures only the intensity of absorption bands ν NCO in IR spectrum decreased for 10%. It was shown, additionally, that reaction between isocyanate prepolymer with Mw 1360 (prepared by reaction of 1 mole PTMG and 2 mole of TDI) and MCC did not occur because the NCO-group intensity does not change, thus confirming the fact that hydroxyl groups of the MCC did not interact with isocyanate groups under the above described conditions.

DSC method

Thermal properties of PU I - MCC compositions have been studied by DSC method as well. From the results obtained, one can conclude that neat MCC exhibits a homogeneous crystalline phase with melting temperature at 120^0C (which is a rather low temperature with respect to cellulose).

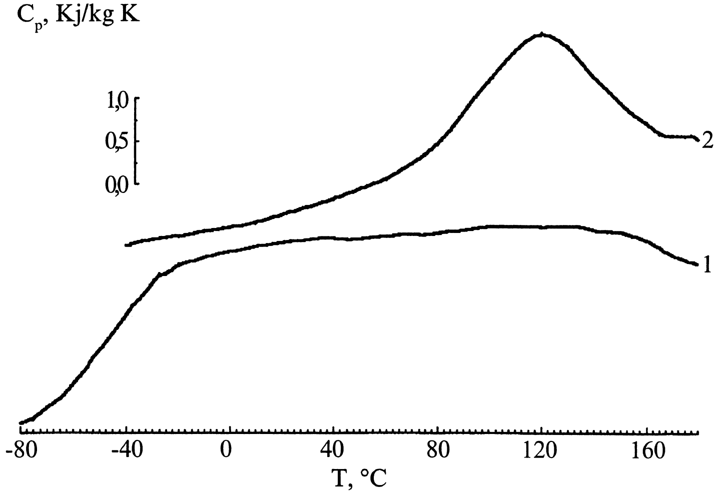

Fig.2.Temperature dependence of thermal capacity of samples: 1. neat PU 2. MCC

According to the thermogram of neat PU (Fig.2, curve 1), there is no well-segregated structure. This is seen due to the lack of any high-temperature transitions in the curve Cp = f(T) and the presence of an extended glass transition interval (34^0 C) for the flexible matrix (see Table 1). These data confirm the fact that the system shows a homogenous phase behavior.

Various contents of MCC (as a filler) in the PU matrix result in different effects (Fig.3). Thus, addition of 10 weight % of the MCC weakly affects glass transition interval, but ΔCp strongly decreases at glass transition. In contrast, glass transition interval decreases when 20 weight % of MCC was added. This decrease is accompanied by a leap of thermal capacity and an endothermic peak in the Cp = f(T) curve emerges and confirms the MCC phase melting.

However, the most outstanding changes were established when 40 weight % of the MCC being incorporated into the polymer matrix. A crisp glass transition of the PU flexible blocks and also the melting of the MCC crystalline phase were detected in the thermogram of this sample. Moreover, the melting point of the MCC in composition with PU is 15^0 C higher than that for the neat MCC. This fact could be explained by an plasticizing role of PU flexible chains in this composition which promotes the formation of a more regular MCC structure with increased melting point.

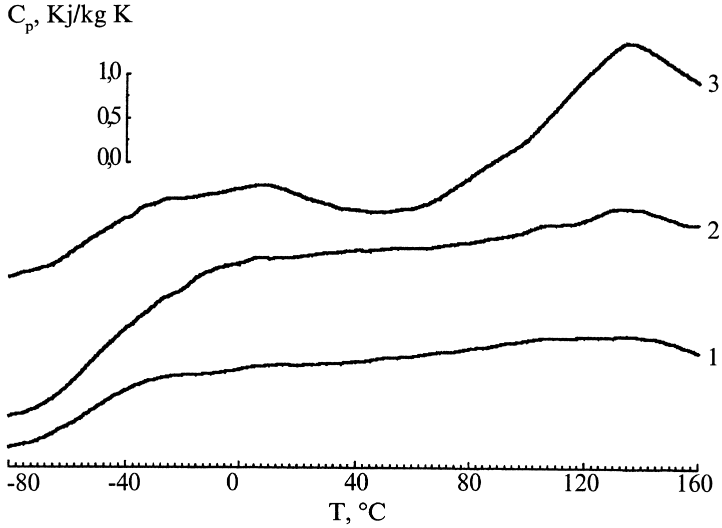

Fig.3.Temperature dependence of thermal capacity of samples: 1. PU+10% MCC 2. PU+20% MCC 3. PU+40% MCC

Table 1:Thermal characteristics of PU based compositions

Sample	$T_{glass\ transition}$, ^{0}C			ΔC_p, Kj/kg K		Melting point, ^{0}C (for MCC)
	start	end	interval	for 1 kg of composition	for 1 kg of neat PU	
PU neat	- 62	- 28	34	---	1,420	---
PU + 10% MCC	- 65	- 30	35	0,720	0,800	---
PU + 20% MCC	- 62	- 35	27	0,750	0,930	130
PU + 40% MCC	- 65	- 32	33	0,780	1,300	135
MCC neat	---	---	---	---	---	120

Thus, by varying the filler content in compositions, it is possible, one the one hand, to obtain materials (PU+10% MCC) with properties to be determined mainly by flexible blocks of PU, and on the other hand, materials (PU+40% MCC) whose behavior is governed by filler, and finally, (PU+20% MCC) sample, also material is available which shows characteristics inherent to both flexible matrix and hard chain filler. Exactly, the latter was chosen for assessing its behavior in a different aqueous solutions.

DEGRADATION OF COMPOSITES IN AQUEOUS SOLUTIONS AT DIFFERENT PH

It is known, that polymer degradation in nature could be affected by many environmental factors$^{9)}$. Polymer degradation may proceed in the following ways: biodegradation, photodegradation, oxidation, and hydrolysis. Biodegradability of polymers could be regulated by varying their structure in different ways $^{10)}$. Here we studied the behavior of PU based composites in buffer solutions, modeling the pH range of natural soils.

Composites PU-MCC: IR study

IR- spectra of surface of neat PU samples and those filled with MCC after being subjected to model solutions at pH 4.0, 7.0, and 8.5 are shown in Fig.4.

As it can be seen, PU I samples are stable against action of model solutions, but at the same time, polyurethanes filled by MCC exhibit considerable transformations according to their IR spectra. Thus, after keeping these specimens in above model solutions for two weeks there was considerable decrease of intensity of the absorption band at ν=1560 cm^{-1}, which relates to deformation vibrations of NH–groups for urethane fragments. For comparison, the absorption band at ν=1603 cm^{-1} as inner standard was selected, characterizing the C=O fluctuations of phenolic groups in urethane fragments, which tend to be influenced by the environment to a lesser extent.

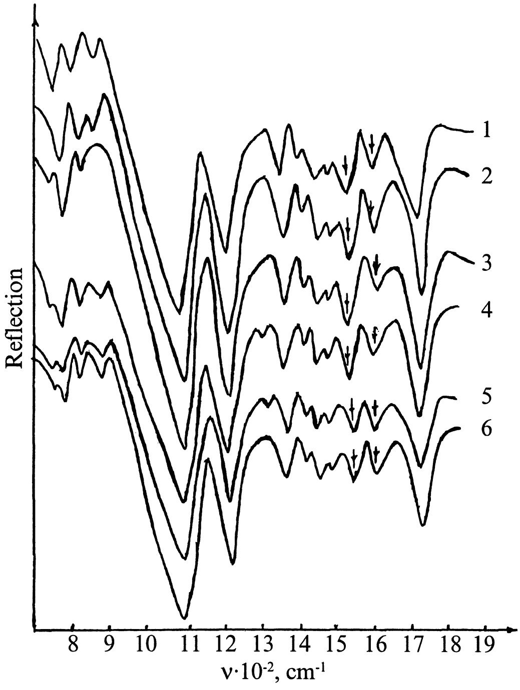

Fig.4. Reflection IR spectra of PU compositions being kept in the buffer solutions:
1. neat PU in the neutral solution 2. neat PU in the alkali solution 3. neat PU in the acid solution 4. PU+20% MCC in the neutral solution 5. PU+20% MCC in the alkali solution 6. PU+20%MCC in the acid solution

Probably, MCC being integrated into segmented polyurethanes results in formation of composites possessing a loose structure, compared with the starting materials. This fact, in its turn, promotes intensive penetration of solution molecules into the deep layers of the polymer and enhances interaction with urethane fragments, thus improving surface hydrophilicity of urethane associates. Thereby, apparently, in contrast to their non-filled urethane analogues these filled, film-forming segmented polyurethanes are attacked by model soil which should lead to a degradation in the environment.

After keeping specimens for more than one month in the model solutions, one can see, that above stated band (Fig.4) declined even more, which indicates that urethane bonds break off under influence both acid and alkali medium. In the neutral medium no changes in absorption were observed. The weight loss of the samples is equal to 3 % which was evaluated by several parallel tests.

The most crucial changes in the intensity of the spectral bands of the NH-groups of both, the neat samples and filled ones, could be seen after the composite films have been treated in alkali solution. But, in this case the above mentioned tendency is more pronounced in the filled materials.

Composites PU-starch: Effect of temperature

After being kept in water at room temperature for 2 months the composite III having 60% of filled starch lost 50% of its weight and steam absorption was increased from 2% to 17%. When the water temperature was increased up to 80^0C, degradation of filled PU was enhanced. The specimen with 20% of starch content lost his tensile strength just after 50 hours under such condition.

The results obtained during these experiments will be published soon.

Conclusions

Composites obtained on the base of polyurethanes (PU) and natural polysaccharides – microcrystalline cellulose (MCC) and starch - have been studied by IR and DSC method.

It has been shown, that incorporating of MCC into PU matrix leads to film-forming PU-MCC composites. Their microstructure is strongly dependent on MCC content. Introduction of starch into PU matrix leads to foamed composites with structure being defined by emerging a new hydrogen bonds between PU and starch.

PU-polysaccharides composites exhibit increasing biodegradable characteristics in model solutions with pH ranges from 4 to 8,5.

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