Thermal stability of polymer mixtures based on oxidized cellulose and polyguanidine hydrochloride

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Abstract. Thermal stability data of the polymer mixtures based on oxidized cellulose and polyguanidine hydrochloride were obtained by dynamic thermogravimetric analysis (TGA). It was established that the obtained compositions have a lower decomposition temperature than the initial components of the mixture, that can lead to an increase in the degree of biodegradability of the composition. It was shown that photoirradiation does not affect the thermal stability of the studied compositions.

1. Introduction

In the past few decades, polymers from renewable sources have attracted increasing attention, mainly for two main reasons: environmental problems and awareness of the limited availability of hydrocarbon resources.

In this regard, special attention is drawn to natural biopolymers from renewable raw materials - cellulose, starch, chitin, etc. [1-5], which are the basis for biodegradable and biocompatible materials, which can be an alternative to synthetic polymers obtained from oil and gas raw materials. Among the various ways to create polymer composite materials capable of biodegradation under the influence of various environmental factors, the most effective and cost-effective is to create them by obtaining mixtures of natural and synthetic polymers for tissue and cell engineering, while creating hemostatic agents, implants, long-acting drug carriers, scaffold technology, etc. [6-8].

Materials based on mixtures of polysaccharides and synthetic polymers should retain their performance characteristics during the entire period of use, and then under the influence of physico-chemical, biological environmental factors be incorporated into the metabolic processes of natural biosystems.

Biodegradation of most such polymer composites is initiated, as a rule, by non-biological processes (thermal and photo-oxidation, mechanical destruction, etc.), which leads to a decrease in the molecular weight of the polymer components and an increase in the biodegradability of the compositions.

In this regard, it is necessary to note some features of the used polymer components for biomedical purposes. Thus, monocarboxycellulose (oxidized cellulose, OC) is of great interest as a hemostatic preparation [9, 10]. Synthetic polyguanidine hydrochloride has antibacterial properties, aqueous solutions of which are used to disinfect medical instruments and premises [11, 12].
Polymer compounds with various biomedical characteristics can be used to create new polyfunctional polymer composites for use in medical practice. The study of the processes patterns, that occurring in mixtures of synthetic and natural polymers under the influence of environmental factors is of great importance in the development of innovative biomedical materials that combine the hemostatic and antibacterial properties to the maximum.

The purpose of this work is to study the thermal properties of mixtures based on polyguanidine hydrochloride (PGHC) and oxidized cellulose (OC), as well as the effect of photoirradiation on the thermal stability of the compositions.

2. Models and Methods

Water-soluble PGHC obtained by polycondensation of diamines and guanidine hydrochloride [13] in accordance with the scheme:

\[
\begin{align*}
RHN \quad & \quad C^\Phi \quad NHR \\
\times & \quad (CH_2)_n \quad NH_2 \\
\end{align*}
\]

The interaction of the reagents is of equilibrium nature, so polymer formation begins with the attack of the lone electron pair (LEP) of the amino group on the GHC cation center, followed by proton transfer and release of NH\textsubscript{3}. At the initial stage of the synthesis, a similar mechanism prevails and is accompanied by an increase in molecular weight (MW). However, even with an equivalent ratio of monomers, a partially branched polymer is formed, which is confirmed by the GPC data of the sample synthesized at 150 °C for 9 hours, since MWD has a bimodal character, corresponding to polymer fractions with M\textsubscript{w} = 49,500 and 1,000 Da. The presence of the high molecular weight fraction can be explained by the formation of branched macromolecules, but this does not lead to the formation of a gel fraction and loss of solubility. The structure of the resulting PGGH is confirmed by IR spectroscopy data. In the region of 3270 and 3160 cm\textsuperscript{-1}, stretching vibrations of free amino groups are observed. Two bands in the region of 2930 and 2855 cm\textsuperscript{-1} correspond to the valent asymmetric and symmetric vibrations of the methylene groups. The band at 1630 cm\textsuperscript{-1} is the characteristic band of guanidine salts.

Monocarboxycellulose (OC) is obtained by oxidation of cellulose powder with a solution of nitrogen dioxide in an inert solvent, at room temperature [14, 15]:

\[
\text{An increase in the oxidation rate and an increase in the content of carboxyl groups was achieved by carrying out the synthesis in a microwave reactor, with a radiation power of 80 W, a temperature of 27–28 °C, and constantly stirring for 4 hours. The content of carboxyl groups in the obtained samples was 20–21 %, the content of fixed nitrogen did not exceed 0.5 %. The molecular mass of the OC was 31.8 ± 6.1 kDa.}
\]

Samples are characterized by IR and NMR spectroscopy. In the IR spectrum of the OC obtained, absorption of carboxyl groups is observed at 1735 cm\textsuperscript{-1}, in the NMR spectrum, a signal of carboxyl carbon is observed in a weak field with a chemical shift at δ 173 ppm.

The mixture of polymers was performed by dispersing the OC in a 2 % aqueous solution of PGHC (OC/PGHC = 50/50 by dry matter) for 24 hours at 20–25 °C. After decantation and filtration, the composition was dried in a vacuum closet at 20–30 °C/5 mm Hg.
IR spectroscopic studies were performed on an ALPHA FT-IR spectrometer (Bruker, Germany) in the range of wave numbers 4000–550 cm⁻¹. Samples were prepared by pressing with KBr. ¹³C NMR spectra were recorded on a Varian VXR-500S spectrometer at 500 MHz, in DMSO-d₆.

Thermal studies were performed on a synchronous thermal analyzer STA 449C (Netzsch, Germany) in the temperature range 25–1000 °C at a heating rate of 10 °C/min. The mass of the samples was 10–15 mg.

30 ml of the aqueous suspension of the composite were subjected to photoirradiation with KrCl excilamp, a UV wavelength of 222 nm for 20 min at an intensity of I = 0.97 mJ/cm².

3. Results and Discussion

Thermal destruction of OC, PGGH and their compositions was investigated by the method of dynamic thermogravimetric analysis (TGA) in order to determine the effect of synthetic PGGH on the heat resistance of their compositions with OC and to determine the temperature range of their use.)

The temperature of the onset of thermal decomposition was determined by the standard method of ISO 7111 from the point of intersection of tangents, carried out to the mass loss curve in the area with no mass loss and at the point of maximum mass loss rate of the sample. Experimental data for TGA for PHH, OC, and their compositions before and after UV irradiation are shown in Figure 1. Table 1 presents the main characteristics of the TGA samples.

![Figure 1. Curves TG for PGHC, OC and compositions based on them: 1 - PGHC; 2 - OC; 3 - PGHC/OC (50/50 wt.%); 4 - PGHC/OC (50/50 wt.%) (after UV irradiation).](image)

The values given in this table show that under anaerobic conditions PGHC begins to decompose at 337 °C, while thermal decomposition of the OC and its compositions with PGHC begins in the region of 160-180 °C due to the initial stages of OC destruction.

The thermal destruction of PGHC occurs, apparently, in two stages. At the first stage, the macromolecular chain is depolymerized with the elimination of the guanidine fragment of the macromolecule. In the second stage, thermal decomposition of the remaining hydrocarbon portion of the macromolecule occurs with the formation of a carbonized residue.

Thermal destruction of OC is accompanied by desorption of physically bound water [16]. The destruction of OC proceeds very quickly and even at very low temperatures (Tₜₐₓ. 181.5 °C, Table 1), obviously, oxidation of the hydroxyl group at the sixth carbon atom of cellulose leads to a decrease in
the strength of carbon-carbon bonds. The destruction products are mainly volatile products (H₂O, CO₂, CO) and a small amount of resin.

Table 1. Characteristics of the processes of thermal destruction PGGH, OC and their compositions.

| Sample         | T_{b,d.}, °C | T_{max}¹, °C | T_{max}², °C | Solid carbonated residue, at 1000 °C, wt.% |
|----------------|--------------|--------------|--------------|------------------------------------------|
| PGHC           | 337.4        | 355          | 480          | 1.8                                      |
| OC             | 181.5        | 255          | -            | 20.0                                     |
| PGHC/OC (50/50 wt.%) | 155.8      | 228          | 450          | 26.5                                     |
| PGHC/OC (50/50 wt.%) after UV irradiation | 165.2 | 215          | 420          | 24.0                                     |

¹ The temperature of the maximum decomposition rate in the second stage.

The study of the thermal degradation of the PGHC/OC polymer compositions showed a slight decrease in their thermal stability as compared to the initial OC (Figure 1, Table 1). Photoirradiation of a mixture of PGHC/OC (in the given dose of radiation) practically does not lead to a change in the thermal stability of the compositions.

In the studied polymer composition PGHC/OC, the formation of a donor-acceptor bond is possible, due to the overlapping of molecular orbitals due to LEP of PGHC heteroatoms and carbonyl groups that accept an electron to the p-orbital. This is evidenced by a shift in the carbonyl absorption at 1735 cm⁻¹ to the shortwave region of the IR spectrum. The magnitude of the hypsochromic shift is small, because the energy of intermolecular interaction is comparable with the energy of the van der Waals interaction. However, this can lead to additional steric hindrances and, as a result, weakening of the OC ring bonds, which can lead to an increase in the degree of biodegradability of the composite with a slight deterioration in thermal indicators.

4. Conclusion
Polymer mixtures were obtained by dispersing OC in an aqueous solution of PGHC. Using IR spectroscopy and TGA, it was shown that the formation of a donor-acceptor interaction between the carbonyl carbon atom and the LEP of nitrogen PHGH in the polymer mixture is possible. This interaction can lead to an increase in the degree of biodegradability of the composition.

Acknowledgments
This work was financially supported by the Russian Foundation for Basic Research (project No. 18-43-030004).

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