Synthesis of grafted polybutyl acrylate copolymer on fish collagen

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Abstract: Increasingly, scientists are turning to the study of marine, or fish, collagen, which is increasingly replacing collagen of terrestrial animals, due to the fact that it is hypoallergenic, since it is 96% identical to human protein. Materials based on fish collagen have a number of advantages over their analogue of animal origin: it is not a carrier of infectious diseases of animals transmitted to humans, it has a greater structural similarity to human collagen, which provides a higher level of biocompatibility. Materials based on collagen copolymers with synthetic monomers are promising. The use of hybrid materials also helps to reduce the consumption of non-renewable natural resources. Synthesis of grafted collagen copolymers with polybutyl acrylate was carried out at azobisisobutyronitrile initiation and triethyl borane – oxygen system initiation under comparable conditions under intensive stirring of aqueous solution dispersion of collagen and butyl acrylate. After the synthesis, the aqueous and organic phases of the reaction mixture were analyzed by composition and molecular weight parameters using infrared spectroscopy and size-exclusion chromatography. Changes indicating the formation of a copolymer are observed in the copolymer isolated from the aqueous phase, more pronounced in the triethyl borane – oxygen system. It is assumed that the formation of copolymer macromolecules for azobisisobutyronitrile and organoelement initiator takes place according to different schemes. Schemes for the formation of copolymer macromolecules for AIBN and an organoelement initiator are proposed. Only polybutyl acrylate is present in the organic phase. Biological studies were carried out for fungal resistance and bactericidal activity of the obtained copolymers.

Keywords: collagen, triethyl borane, butyl acrylate, bactericidal properties, grafted copolymerization

Acknowledgement: The work was carried out on the equipment provided by New Materials and Resource-Saving Technologies Core Facilities Centre, Lobachevsky Nizhny Novgorod State University’s R&D Chemistry Institute.

For citation: Uromicheva MA, Kuznetsova YL, Valetova NB, Mitin AV, Semenycheva LL, Smirnova ON. Synthesis of grafted polybutyl acrylate copolymer on fish collagen. Izvestiya Vuzov. Prikladnaya Khimiya i Biotehnologiya = Proceedings of Universities. Applied Chemistry and Biotechnology. 2021;11(1):16–25. (In Russian) https://doi.org/10.21285/2227-2925-2021-11-1-16-25

Синтез привитого сополимера полибутилакрилата на рыбный колллаген

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Резюме: Сегодня ученые все чаще обращаются к исследованию морского, или рыбного, колллагаена, который уверенно вытесняет колллаген наземных животных, ввиду того что он является гипоаллергенным, так как на 96% иденитичен человеческому бельку. Материалы на основе рыбного колллагаена имеют целый ряд преимуществ по сравнению с аналогом животного происхождения: он не является переносчиком инфекционных заболеваний животных, передающихся человеку; имеет большее структурное сходство с колллагеном человека, обеспечивающее более высокий уровень биосовместимости. Перспективными материалами на основе сополимеров колллагена с синтетическими мономерами. Использование гибридных материалов, кроме того, позволяет снизить потребление невозобновляемых природных ресурсов. Синтез привитого сополимера полибутилакрилата на колллаген проводили при инициировании динитрилом азокислоты и инициирующей системы триетилборан–кислород в сравнимых условиях при интенсивном перемешивании
INTRODUCTION

The use of secondary resources of the food industry is an important task. Waste from the fishing industry: skin, fins, tail contains collagen [1, 2]. Materials based on fish collagen have a number of advantages compared to the analogue of animal origin: first of all, it is a greater structural similarity with human collagen, providing a higher level of biocompatibility [1, 3-5].

Hybrid materials with the inclusion of collagen and polymers of another nature are widely used in medicine [6, 7], pharmacy [8], cosmetology [9, 10]. To obtain copolymers of collagen and its denaturant – gelatin with synthetic monomers, radical initiators of various nature are most often used [11-13], including trialkyl boranees [14-16]. Grafted copolymers [17] of polymethyl methacrylate and gelatin in aqueous dispersion were synthesized and characterized in the presence of tributyl borane and traces of oxygen. In terms of practical use, it is important that samples of the new material are biodecomposed, i.e. have the destruction prospect in the presence of microorganisms.

The aim of this work is the synthesis of grafted polybutyl acrylate (PBA) with fish collagen in the presence of various initiators: azobisisobutyronitrile (AIBN) and the initiating triethyl borane (TEB) – oxygen system. The main task of the research is to determine the composition of grafted copolymers and molecular weight characteristics.

EXPERIMENTAL PART

Preparation of initial materials for the experiment. The initial collagen was isolated from cod skin in the form of acetic dispersion by the method [18]. Butyl acrylate (BA) for purification from the inhibitor was washed with 5% soda solution and then with distilled water to a neutral medium. The washed butyl acrylate was dried with anhydrous sodium sulfate and further purified by vacuum distillation.

AIBN was purified from impurities by recrystallization of this initiator from alcohol solution. To do this, it was dissolved in ethyl alcohol at 40 °C in a water bath. The hot solution was filtered and then cooled to recrystallize AIBN. The lade-down crystals were dried in a vacuum at 25 °C.

To improve the safety of operation and storage, TEB was used in combination with hexamethylene diamine, which releases the initiator in the acidic reaction medium.

Fish collagen extraction method. Collagen was extracted from the cod skin, which was cleaned of scales, lumps of muscle tissue and fat, washed with distilled water, frozen. The raw cod skin was cleaned of scales, lumps of muscle tissue and fat, washed with water and frozen. Prepared and frozen raw material was crushed with scissors and placed in 3% acetic acid for a day at 25 °C, after which the resulting collagen dispersion was separated using a filter with a pore size of 1 μm from parts of the crushed fish skin and other impurities. We used the isolated aqueous solution of collagen in 3% acetic acid. The mass fraction of collagen in the resulting solution is 8%.

Method of butyl acrylate copolymer synthesis with collagen. Synthesis of collagen and butyl acrylate copolymers with both initiators was carried out, as follows. The mixture of aqueous 3% solution of collagen and butyl acrylate in a weight ratio of 1:1 was bubbled by argon for 15 minutes at room temperature and intensive stirring before synthesis. The initiator in amount of 1% from weight of collagen was added to mixture and quickly heated to 50 °C, without ceasing to stir intensively. The synthesis was carried out for 1 hour in an argon atmosphere. The organic phase was separated from the aqueous
layer by decantation. The copolymer is in the aqueous phase.

Method of composition determining of the aqueous phase of butyl acrylate copolymer with collagen. The composition of the obtained materials was studied using infrared (IR) spectroscopy. IR spectrophotometer "IRPrestige-21" manufactured by Shimadzu, Japan, was used to record IR spectra of absorption. Films on the KBr plate were prepared to record the IR spectrum. The spectra interpretation was carried out independently.

Method of composition determining of the organic phase of butyl acrylate copolymer with collagen. The organic layer of the synthesized copolymers was investigated in a chloroform solution by IR-Fourier-transform spectrophotometer Shimadzu FTIR-8400S in KBr cells with an optical path length of 0.26 mm in the wave number range 5500–550 cm⁻¹, the error in the determination did not exceed ±0.05 cm⁻¹. The copolymer composition was determined using a calibration graph on the characteristic peak area of the analytical band at 1726 cm⁻¹, which corresponds to the presence of a carbonyl group. The proportion of butyl acrylate was calculated according to the intensity of this band.

The calibration curve was plotted in the absorption intensity (optical density) – concentration axes (Fig. 1) by absorption of poly methyl methacrylate (PMMA) solution. This method used MMA, not BA due to polybutyl acrylate is insoluble.

$$\omega(BA) = \frac{M(BA)}{M(MMA)} \times \frac{D}{1.095} \times \frac{m(BA)}{m(CHCl_3)}$$

$D$ is the optical density of polymethyl methacrylate, $M(BA)$ is the molar mass of butyl acrylate, $m(BA)$ is the mass of butyl acrylate, $M(MMA)$ is the molar mass of methyl methacrylate, according to which the calibration graph was used, $m(CHCl_3)$ is the mass of chloroform in which the solution was prepared, 1.096 is the slope of the calibration curve.

The experiment showed that 100% PBA is formed in the organic layer when both initiators are used.

Analysis of molecular weight characteristics of the copolymer of butyl acrylate with collagen. The molecular weight characteristics of collagen and collagen-containing copolymers were studied by size-exclusion chromatography (SEC). This method is based on the molecule separation by volume sizes. Sample preparation was carried out by filtration using nozzle membranes Millipore Millex-LCR (PTFE 0.45 µm). To do this, a disposable syringe filled with a collagen aqueous solution was fitted with a nozzle membrane Millipore Millex-LCR and filtered at a rate of about 1.2 ml/min.

Method for determining fungal resistance and bactericidal activity. Tests for fungal resistance were carried out in accordance with GOST 9.049-91 “Unified system of corrosion and ageing protection. Polimer materials and their components. Methods of laboratory tests for mould resistance”. Microscopic fungi, active destructors of polymeric materials, were used as test cultures: Aspergillus niger, Aspergillus terreus, Aspergillus oryzae, Chaetomium globosum, Paecilimyces variotii, Penicillium cyclopium, Penicillium funiculosum, Trichoderma viride. Samples were placed in Petri dishes. Then the surface of the samples was inoculated with a suspension of micromycete spores and the Petri dishes with the samples were placed in a thermostat. The test duration is 28 days at a temperature of 29±2 °C and a humidity of more than 90%.

The bactericidal activity was determined in relation to the association of test cultures of bacteria: Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa, Bacillus subtilis. The presence of bactericidal properties was assessed by the size of the zone of inhibition of bacterial growth around the test object placed on an agar MPA medium. Cultivation conditions – in a thermostat at 37 °C. Exposure time – 24 hours.

RESULTS AND DISCUSSION

In connection with stated objective, the synthesis of grafted collagen copolymers with PBA was carried out at the AIBN initiation. The TEB-oxygen initiating system under comparable conditions. After the synthesis, the resulting copolymer was separated by decantation into an organic viscous layer and a liquid aqueous layer. 100% of homopolybutyl acrylate was found in the viscous organic phase.
The IR spectra of the samples isolated from the aqueous phase for the studied initiators are shown in Fig. 2 and Fig. 3 in comparison with the IR spectra of collagen and PBA. For the sample from the reaction mixture using the AIBN initiator, as in the case of the TEB initiator, a change is observed compared to the IR spectra of the original collagen and PBA.

Molecular weight (MW) characteristics of samples with different initiators isolated from the aqueous phase are presented in the form of molecular weight distribution MWD curves (Fig. 4, 5) and MW values in Table.

The MWD curves for samples obtained under different conditions are offset with respect to the collagen MWD curve. In the case of copolymerization initiation by the TEB – oxygen system, this offset is more noticeable. Presumably this indicates a greater proportion of PBA grafting to collagen when initiated by an organometallic initiator. These data are confirmed by the values of MW of grafted copolymer, obtained using the TEB – oxygen system: they are higher than the original collagen by a greater amount than in the case of AIBN.

The obtained data testify that BA grafting to collagen in the presence of the TEB – oxygen system is more visible than for AIBN. This may be due to the fact that both upon initiation with a metal-containing initiator and AIBN, grafting is carried out (2) due to the abstraction of a hydrogen atom by an active radical (R ●, RO ●) from a collagen macromolecule (1) by active radicals formed in the case of AIBN due to thermal decomposition of the initiator, or due to the oxidation of thermopile according to the known scheme [20].

Fig. 2. Infrared spectra of collagen (1), collagen and BA copolymer initiated by azobisisobutyronitrile (2), and polybutyl acrylate (3)

Рис. 2. Инфракрасные спектры коллагена (1), сополимера, инициированного динитрилом азоизомасляной кислоты (2); полибутилакрилат (3)

Fig. 3. Infrared spectra of collagen (1), collagen and BA copolymer initiated by the system triethyl borane – oxygen (2), and polybutyl acrylate (3)

Рис. 3. Инфракрасные спектры коллагена (1), сополимера, инициированного системой триэтилборан – кислород (2); и полибутилакрилат (3)
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Fig. 4. Collagen (1) weight distribution and copolymer of collagen and butyl acrylate in the presence of azobisisobutyronitrile (2)

Fig. 5. Collagen (1) weight distribution and copolymer of collagen and BA in the presence of the system triethyl borane – oxygen (2)

Collagen molecular weight characteristics and copolymers of collagen and butyl acrylate in the presence of azobisisobutyronitrile and the system triethyl borane – oxygen

| Polymer                                           | MWD     |
|---------------------------------------------------|---------|
|                                                   | Mn·10^{3} | Mw·10^{3} | Mw/Mn |
| Collagen                                          | 182     | 228       | 1.3   |
| Copolymer with azobisisobutyronitrile initiator   | 189     | 238       | 1.3   |
| Copolymer with the system triethyl borane – oxygen initiator | 239     | 291       | 1.2   |
However, when the TEB – oxygen system initiates the interaction of TEB with collagen (7) or a boroxyl radical formed according to the scheme: (6) with a growing radical, a labile bond is formed, along which the growth of the chain can pass through the mechanism of reversible inhibition (8) [21, 22].

Chain breakage by quadratic breakage of growing radicals leads to breakage of the polymer chain.

**CONCLUSION**

Grafted collagen copolymers with polybutyl acrylate were obtained in the aqueous phase of dispersion of aqueous collagen solution and butyl acrylate at initiation of AIBN and TEB – oxygen initiation system. The copolymers were characterized on the composition and molecular weight parameters using IR spectroscopy and SEC. In case of the TEB – oxygen system, butylacrylate grafting is more pronounced. The scheme for the formation of copolymer macromolecules to organoelement and AIBN initiator were proposed.

These compositions can be used as mushroom resistant and bactericidal materials.
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Contribution of the authors
The authors contributed equally to this article.

Conflict interests
The authors declare no conflict of interests regarding the publication of this article.

The final manuscript has been read and approved by all the co-authors.

The article was submitted 15.01.2021.
Approved after reviewing 26.02.2021.
Accepted for publication 28.02.2021.