Physical and Mechanical Properties of Films Based on Graft Copolymers of Chitosan with N,N-Dimethylaminoethyl Methacrylate

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Abstract. The graft-polymerization of N,N-dimethylaminoethylmethacrylate (DMAEMA) on chitosan (CTS) was performed in the presence of ammonium persulfate (PSA) at a temperature of 323K. The effect of the DMAEM concentration in the reaction mixture on the copolymer yield, the degree and effectiveness of grafting, as well as on the physical-mechanical properties of films obtained on the basis of synthesized copolymers was studied. The copolymers formation was proven by gravimetric method, extraction, and IR spectroscopy. Chitosan-graft-DMAEM copolymers of various compositions were obtained. The grafting degree reached ~ 350 wt. % with the ratio [DMAEMA]/[CTS] = 5 (mol/(base-mol), the grafting effectiveness was ~ 86 wt. % with the ratio [DMAEMA]/[CTS] = 1 (mol/(base-mol). It was established that the changing the copolymers composition lead to variation of tencile strength and deformation characteristics of films widely from 1.4 MPa to 25.7 MPa and from 34% to 413%, correspondingly.

1. Introduction
In the last decades an increased interest of researchers has been observed to renewable natural polymers. Among such polymers chitin and its deacetylated derivative – chitosan (CTS) hold a peculiar place [1-3]. The unique properties of chitosan, such as biocompatibility, physiological activity in the absence of toxicity and biodegradation determine a relatively narrow range of its applications - in medicine, pharmacy and cosmetology primarily [4]. At the same time chitosan's organic solvent resistance and low physical-mechanical properties constrain its large-scale application in other industries. The presence of reactive amino and hydroxy groups in the polysaccharide macromolecules enables its chemical modification by graft and block copolymerization and allows to combine it with synthetic polymers with the preservation of homopolymers useful properties or their strengthening in some cases [2]. Numerous literature data indicate the prospects of chitosan and its derivatives using as a film and fiber products, medical and protective coatings, as well as in the separation membranes form, in medicine, biotechnology, pharmaceuticals, and the food industry.

Other promising polymer to create materials for bio-medical purposes is synthetic poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA) and its derivatives. They have been already actively studied for the development of drug delivery systems [5, 6], as effective dispersants [7] and emulsifiers [8, 9]. Molecular polymer brushes with PDMAEMA as side chains have been successfully
used for nanocapsules’ producing [10]. PDMAEM copolymers have proposed for obtaining a new class of effective stationary phases in liquid chromatography [11], for coating silicon capillaries in capillary electrochromatography [12], and so on. The noble metals nanoparticles (NPs) obtaining is one of the important applications of PDMAEMA copolymers. Such NPs are widely used in optics, analytical chemistry, biology, and medicine because of their highly-developed surface and unique optical and biological properties. PDMAEMA grafted to various surfaces (cellulose single crystals [13], lignin nanofibers [14]) is effective for producing hybrid conjugates containing gold, palladium, platinum NPs, as well as bimetallic nanoparticles (Pd/Pt, Pd/Au) and for their use in teranostics [13], for catalysis [15], and for producing metal-modified carbon nanofibers [14]. However, the literature review shows that the issues of polymerization kinetics and physical-mechanical properties of copolymers containing PDMAEMA chains remain less studied still. Taking into account the importance of in-depth study of these problems this work aimed to obtaining of chitosan derivatives by graft-copolymerization with N,N-dimethylaminoethyl methacrylate and investigation the physical and mechanical properties of films based on them.

2. Materials and methods

The chitosan (LLC "Bioprogress", Moscow) with a molecular weight of 1.5×10⁶ and a deacetylation degree of 82% obtained from crab shells were used without additional purification for copolymers’ synthesis. Chitosan was dissolved in dilute solutions of analytically pure hydrochloric acid. N,N-dimethylaminoethyl methacrylate («Sigma Aldrich», with purity 98%) was distilled in vacuum before use (pressure 0.1 MPa); desired cut collected at temperature 335 – 338 K. Ammonium persulfate (PSA, analytically pure) was used as the initiator of radical copolymerization.

Graft polymerization of DMAEMA to chitosan was performed in a three-necked round-bottomed flask placed in a temperature-controlled thermostat with continuous stirring. The concentration of chitosan in water-acetic acid solutions was 3 wt. % in all experiments; pH of the medium was ~ 5.4 and 3.8; the reaction temperature was 323 K. The [glucosamine]/[monomer] ratio was 1:1, 1:3, 1:5 (base-mol)/mol, respectively. The polysaccharide-monomer system was purged with argon before starting synthesis, then the reactor temperature was raised to 323 K and an initiator (1.4×10⁻³ mol/l) dissolved in water was introduced into the reaction mixture. Synthesis was performed for 4 hours.

The DMAEMA conversion during copolymerization with chitosan was determined by gravimetric method. For this purpose samples were taken at certain intervals, the resulting product was precipitated with acetone and dried to a constant mass in a vacuum drier. The conversion (C) was calculated by the formula (1):

\[
C = \frac{m_{PL} - m_{CTS}}{m_{DMAEM}}
\]

where C – DMAEMA conversion, \( m_{PL} \) – mass of the polymer extracted from the test portion, \( m_{CTS} \), \( m_{DMAEMA} \) – mass of CTS and DMAEMA, correspondingly.

The formation of copolymers CTS-graft-DMAEMA had been proven by IR spectroscopy (Perkin-Elmer spectrophotometer). For analysis we used reaction products’ samples subjected to extraction using Soxhlet apparatus for removing of DMAEMA homopolymer. PDMAEMA extraction had been performing with toluene during 48 h. In preliminary experiments on mixtures of chitosan with PDMAEMA it has been shown that the specified time is sufficient for complete extraction of the latter. The solvent from the Soxlet apparatus and the filtrate obtained by 2recipitating the reaction product from the solution were analyzed for the homopolymer presence. The grafting efficiency (GE) (the ratio of the mass of the grafted polymer to the mass of the entire polymerized monomer) (formula 2) and the grafting degree (GD) (the ratio of the mass of the graft polymer to the mass of chitosan) (formula 3) of monomers per chitosan were calculated based on the extraction results:

\[
GE = \frac{m_{PL} - m_{CTS}}{m_{PL} - m_{CTS} + m_{EXM}} \times 100
\]

\[
GD = \frac{m_{PL} - m_{CTS}}{m_{PL} - m_{CTS} + m_{EXMPL}} \times 100
\]
where \( m_{\text{GPL}} \) – copolymer mass in the test portion, \( m_{\text{CTS}} \) – chitosan mass in the test portion, \( m_{\text{HOMOPOL}} \) – PDMAEMA mass extracted from the test portion.

Films based on CTS and its copolymers with DMAEM were prepared by irrigation on a Teflon substrate under equilibrium evaporation of water at room temperature conditions. After drying samples were vacuuming at 30 °C to a constant mass. The physical-mechanical properties of the films (tensile strength (\( \sigma \)) and elongation (\( \varepsilon \))) were determined using a test machine ZWICK ROELL Z005 (Germany) at a tensile speed of 50 mm/min.

3. Results and discussion

Copolymerization of vinyl monomers with chitosan is a promising method of chemical polysaccharide modification for obtaining multi-purpose derivatives. Literature analysis shows that PSA is an effective initiator of polymerization of vinyl monomers in polysaccharide solutions. This is probably due to the formation of several active centers on chitosan chains simultaneously because of the separation of mobile hydrogen atoms from unprotonated amino groups in the C2 or C6 atom of the pyranose ring by primary anion radicals SO\(_4^2-\) [2, 16, 17]. However, a significant disadvantage of PSA as an initiator is the destruction of polysaccharide chains as a result of the primary radicals generation on the C2 carbon atom of the pyranose ring (bound to the amino group), with subsequent conversion leading to the glycoside bond destruction [18]. Authors [2, 19, 20] selected optimal conditions for the graft-polymerization of vinyl monomers on chitosan (initiator concentration [PSA] = 1.4×10\(^{-3}\) mol/l, temperature 323-333 K), which provide a high yield of the target product – the graft-copolymer. Therefore, in this work, all experiments were performed at these values of temperature and PSA concentration.

Figure 1 shows the dependences of the DMAEMA conversion in the chitosan solutions during graft-copolymerization under condition of different reagents’ ratios in the reaction mixture.

\[
GD = \frac{m_{\text{GPL}} - m_{\text{CTS}}}{m_{\text{CTS}}} \times 100
\]

\(GD\) is the conversion of DMAEMA. The optimal ratio of reactants was determined using the graph and the formula for the conversion of DMAEMA. For example, for the conversion of DMAEMA of 75%, the ratio of [DMAEMA]/[CTS] = 3 mol/(base-mol).

**Figure 1.** Dependence of the DMAEMA conversion in chitosan solutions during graft-copolymerization: 1 – [DMAEMA]/[CTS] = 1 mol/(base-mol), 2 – [DMAEMA]/[CTS] = 5 mol/(base-mol), 3 – [DMAEMA]/[CTS] = 3 mol/(base-mol), [CTS] = 0.186 (base-mol)/l, [acetic acid] = 1 mol/l, pH = 3.5, \( T = 323 \) K
The graft-polymerization of DMAEMA to chitosan in the presence of PSA was characterized by a high rate. The monomer conversion was not less than 55% in 1 h; the maximum conversion reached 80-90%.

The polymerization product could be either a mixture of CTS and PDMAEMA, or a graft-copolymer, or a mixture of graft-copolymer and PDMAEMA homopolymer. The synthesis products were analyzed by IR spectroscopy and extraction methods. The degree and effectiveness of DMAEMA grafting on chitosan were calculated depending on the ratio of reagents in the reaction mixture after PDMAEM extraction from the synthesis products using Soxlet apparatus (table 1). Table 1 shows that the polymerization of DMAEMA in chitosan solutions lead to graft-copolymer’s formation mainly. The yield of the resulting homopolymer does not exceed 17%. GE and GD depend on the DMAEMA concentration in the reaction mixture. The grafting degree reaches ~350 wt. % at the ratio [DMAEMA]/[CTS] = 5 (in mol/(base-mol)), the grafting effectiveness reaches ~86 wt. % with the ratio [DMAEMA]/[CTS] = 1 (in mol/(base-mol)).

Table 1. Grafting effectiveness and grafting degree of DMAEMA on CTS at different components ratios ([CTS] = 0.186 (base-mol)/l, T = 323 K).

| [DMAEMA]/[CTS], mol/(base-mol) | DMAEMA conversion, % | Grafting degree, % | Grafting effectiveness, % |
|-------------------------------|----------------------|--------------------|--------------------------|
| 1                             | 91                   | 76,6               | 86,4                     |
| 3                             | 83                   | 202,7              | 83,2                     |
| 5                             | 86                   | 350,6              | 83,6                     |

The IR spectra of synthesis products washed from the PDMAEMA homopolymer contain absorption bands corresponding to the valence vibrations of chitosan functional groups and the C=O vibrations of aliphatic esters (1730 cm⁻¹), which indicates the formation of copolymers CTS-graft-DMAEM.

The physical-mechanical properties of CTS-graft-DMAEMA film were studied (table 2). The table shows that variation of CTS-graft-DMAEM copolymer composition allows to change the film’s deformation from 34% to 413%, which is 17-200 times higher than the original polysaccharide is characterized (Table 2). At the same time, the copolymer films’ tensile strength vary in wide range from 1.4 to 25.7 MPa. This characteristics are attributable to the requirements for mesh implants that are used for surgical treatment of abdominal hernias (deformation is not less than 125%, strength is not less than 0.75 MPa).

Table 2. Physical-mechanical properties of CTS-graft-DMAEMA copolymers’ films.

| [DMAEMA]/[CTS], mol/(base-mol) | σ, MPa | ε, % |
|-------------------------------|--------|------|
| CTS                           | 27,0   | 1,9  |
| 1                             | 25,7   | 34,8 |
| 3                             | 2,7    | 246,8|
| 5                             | 1,4    | 413,4|

Thus, the modification of CTS by graft-copolymerization with DMAEMA, the change of the copolymers’ composition have a significant influence with the physical-mechanical properties of materials based on them.
4. References

[1] Ahmad M, Manzoor K, Ikram S 2017 Versatile nature of hetero-chitosan based derivatives as biodegradable adsorbent for heavy metal ions; a review Iner. J. of Biol. Macromol. 105 190-203

[2] Mochalova E, Smirnova L A 2018 State of the art in the targeted modification of chitosan Polim. Science Ser. B, 60 131-161

[3] Rostami E 2020 Progresses in targeted drug delivery systems using chitosan nanoparticles in cancer therapy: A mini-review J. of Drug Delivery Science and Technol 58

[4] Detsi E, Kavetsou I, Kostopoulos 2020 Nanosystems for the encapsulation of natural products: the case of chitosan biopolymer as a matrix Pharmaceutics 12

[5] Yoncheva K, Kamenova K, Perperieva T, Hadjimitova V, Donchev P, Kaloyanov K, Konstantinov S, Kondeva-Burdina M, Tzankova V, Petrov P 2015 Cationic triblock copolymer micelles enhance antioxidant activity, intracellular uptake and cytotoxicity of curcumin Int. J. Pharm. 298–307

[6] Tzankova V, Gorinova C, Kondeva-Burdina M, Simeonova R, Philippov S, Konstantinov S, Petrov P, Galabov D, Yoncheva K 2016 In vitro and in vivo toxicity evaluation of cationic PDMAEMA-PCL-PDMAEMA micelles as a carrier of curcumin Food and Chemical Toxicology 97 1–10

[7] Protat M, Bodin N, Gobeaux F, Malloggi F, Daillan J 2016 Biocompatible Stimuli-Responsive W/O/W Multiple Emulsions Prepared by One-Step Mixing with a Single Diblock Copolymer Emulsifier Langmum 32 10912–10919

[8] Han G, Ju Y, Zhao H 2016 Synthesis of amphiphilic block-type macromolecular brushes with cleavable pendant chains and fabrication of micelle-templated polymer nanocapsules Polym. Chem. 7 1197–1206

[9] Sepehrifar R, Boysen R I, Danylec B, Yang Y 2017 Design, synthesis and application of a new class of stimuli-responsive separation materials Anal. Chim. Acta. 963 153–163

[10] Sepehrifar R, Boysen R I, Danylec B, Yang Y 2016 Application of pH-responsive poly (2-dimethyl-aminooethylmethacrylate)-block-poly (acrylic acid) coatings for the open-tubular capillary electrochromatographic Anal. Chim. Acta. 917 117–125

[11] Hu H, Hou X J, Wang X C, Nie J J, Cai Q, Xu F J 2016 Gold nanoparticle-conjugated heterogeneous polymer brush-wrapped cellulose nanocrystals prepared by combining different controllable polymerization techniques Polym. Chem. 7 3107–3116

[12] Gao G, Ko F, Kadla J F 2015 Synthesis of noble monometal and bimetal-modified lignin nanofibers and carbon nanofibers through surface-grafted poly (2-(Dimethylamino) ethyl methacrylate) brushes Macromolecular Materials and Engineering 300 836–847

[13] Mogha N K, Gosain S, Masram D T 2017 Gold nanoworms immobilized graphene oxide polymer brush nanohybrid for catalytic degradation studies of organic dyes Appl. Surf. Sci. 1427–1434

[14] Shvedchenko D O, Nekrasova T N, Nazarova O V, Buffat P A, Suvorova E I 2015 Mechanism of formation of silver nanoparticles in MAG–DMAEM copolymer aqueous solutions J. Nanopart. Res. 17 275–288

[15] Trandafilović L V, Luyt A S, Bibić N, Dimitrijević-Branković S, Georges M K, Radhakrishnan T, Djoković V 2012 Formation of nano-plate silver particles in the presence of polyampholyte copolymer Colloids and Surfaces A: Physicochem. Eng. Aspects 414 17–25

[16] Retuert J, Yazdani-Pedram M 1993 Cocatalyst effect in potassium persulfate initiated grafting onto chitosan Polymer Bulletin 31 559–562

[17] Najjar Abduel Majid K, Wan Md Zin Wan Yunus, Mansor Ahmad B, Mohamad Zaki Rahman Ab 2000 Preparation and characterization of poly(2-acrylamido-2-methylpropane-sulfonic acid) grafted chitosan using potassium persulfate as redox initiator J. Appl. Polym. Sci. 77 2314 - 2318
[18] Tatarinov P V, Mochalova A E, Belysheva I V 2010 Induced degradation of chitosan, conjugated with block copolymerization with acrylamide *Russian J. of Appl. Chem.* *83* 1294-1298

[19] Mochalova E, Smirnova L A, Semchikov Y D 2005 Structure and properties of vinylpyrrolidone-chitosan graft copolymers and homopolymer mixtures *Polym. Science. Ser. B.* *47* 614-618

[20] Mochalova E, Zaborshchikova N V, Knyazev A A 2006 Graft polymerization of acrylamide on chitosan: Copolymer structure and properties *Polym. Science. Ser. B.* *48* 918-922

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