

## Composite materials based on dental acrylic plastic and chitosan

L.A. Yakovishin \* , E.V. Tkachenko 

Sevastopol State University, 299053 University st., 33, Sevastopol, Russia

\* Corresponding authors: [chemseventu@rambler.ru](mailto:chemseventu@rambler.ru)

This short communication (letter) belongs to the MOSM2021 Special Issue.

© 2021, The Authors. This article is published in open access form under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).



### Abstract

Chitosan and poly(methyl methacrylate) (PMMA) composites were synthesized by polymerization with heating and mechanochemical method. The obtained polymer composites were analyzed by the ATR FT-IR spectroscopy method. The presence of intermolecular hydrogen bonds and hydrophobic interactions in formation of PMMA and chitosan polymer composites was shown.

### Keywords

polymer composites  
poly(methyl methacrylate)  
chitosan  
FT-IR spectroscopy

Received: 03.11.2021

Revised: 16.12.2021

Accepted: 16.12.2021

Available online: 17.12.2021

## 1. Introduction

New composites are currently being actively studied [1–3]. Such materials may be promising for use in various fields of medicine. For example, composite materials are widely used in modern dentistry [1].

Poly(methyl methacrylate) or poly(methyl 2-methylpropenoate) (PMMA) is one of the most important polymers in industry and medicine [1, 4]. PMMA is widely used in dentistry practice for the fabrication of dentures [4]. On the basis of PMMA, heat-curing acrylic resins for removable prostheses, cold-curing resins for frameworks and self-curing resins for denture repairs and for custom trays have been developed [5, 6]. However, PMMA can have a toxic effect on the human body, which is accompanied by allergic reactions and impaired oral microflora [7].

Polysaccharide chitosan is used for obtaining new biomedical materials [8, 9]. Chitosan has antitumoral, antioxidative, bacteriostatic and fungistatic properties [8]. Earlier, various composites of chitosan with gelatin [10], clay [9] and other substances were prepared. In addition, a block copolymer of chitosan with PMMA was obtained [11]. This article is devoted to the preparation of composite materials based on PMMA and chitosan.

## 2. Experimental

Low-molecular water-soluble chitosan (freeze-dried powder; purity 88.4%; molecular weight 1–30 kDa) was pur-

chased from Bioprogress (Russia). The source of PMMA was the Villacryl H Plus (Zhermack S.p.A., Poland).

### 2.1. Preparation of composites

Preparation of composite 1. 1 g of chitosan and 1 g of Villacryl H Plus were stirred for 1 min, 0.44 ml of PMMA monomer was added to the resulting mixture, stirred for 10 min at room temperature, and heated at 60 °C for 60 min.

Preparation of composite 2. 1 g of chitosan and 1 g of Villacryl H Plus were stirred for 1 min, 0.44 ml of PMMA monomer was added to the resulting mixture, stirred for 10 min at room temperature and heated at 60 °C for 30 min. Then the temperature was raised to 100 °C and the mixture was heated for another 30 min.

Preparation of composite 3. 1 g of chitosan and 1 g of Villacryl H Plus were grinded in an agate mortar for 120 min. To the resulting mixture was added 0.44 ml of PMMA monomer, stirred for 10 min at room temperature and heated at 60 °C for 30 min. Then the temperature was raised to 100 °C and the mixture was heated for another 30 min.

The powders of the obtained composites were cooled to room temperature and investigated by the FT-IR spectroscopy method. The IR spectra were recorded on the Simex FT-801 IR-Fourier spectrometer (Russia) in the 4000–550 cm<sup>-1</sup> region (spectral resolution 4 cm<sup>-1</sup>; 25 scans) using the ATR accessory with diamante crystal plate. Photos of the composites were obtained using the ATR accessory with built-in lens (Simex, Russia) at 60x magnification.

## 2.2. IR spectra

IR spectrum of PMMA ( $\nu$ ,  $\text{cm}^{-1}$ ): 2998 (CH), 2948 (CH), 2853 (CH), 1719 (C=O), 1474 (CH), 1458 (CH), 1432 (CH), 1387 (CH), 1364 (CH), 1322 (CH), 1268 (C-O-C), 1237 (C-O-C), 1188 (CO-O-CH<sub>3</sub>, CH), 1140 (C-O-C), 1059 (C-O-C), 984 (C-C), 962 (C-C), 912 (CH), 839 (CH), 809 (C=O), 747 (C=O, CH), 692 (CH).

IR spectrum of chitosan ( $\nu$ ,  $\text{cm}^{-1}$ ): 3310 (OH, NH), 2869 (CH), 2836 (CH), 1655 (C=O<sub>Amid I</sub>), 1619 (NH<sub>2</sub>), 1609 (NH<sub>2</sub>), 1602 (NH<sub>2</sub>), 1543 (N-H+C-N<sub>Amid II</sub>), 1516 (N-H+C-N<sub>Amid II</sub>), 1509 (N-H+C-N<sub>Amid II</sub>), 1501 (N-H+C-N<sub>Amid II</sub>), 1489 (CH), 1474 (CH), 1418 (CH), 1379 (CH), 1339 (CH), 1317 (N-H+C-N<sub>Amid III</sub>, CH), 1260 (C-O-C, OH, C-N), 1244 (C-O-C, C-OH), 1149 (C-O-C, C-OH), 1057 (C-O-C, C-OH), 1015 (C-O-C, C-OH), 995 (C-O-C, C-OH, C-C), 889 (CH), 720 (NH<sub>Amid V</sub>), 679 (NH<sub>2</sub>), 661 (OH), 635 (CH), 617 (O=C-N<sub>Amid IV</sub>), 603 (CH), 567 (NH, CO).

IR spectrum of composite 1 ( $\nu$ ,  $\text{cm}^{-1}$ ): 3297 (OH, NH), 2989 (CH), 2948 (CH), 2888 (CH), 2836 (CH), 1731 (C=O<sub>PMMA</sub>), 1715 (C=O<sub>PMMA</sub>), 1654 (C=O<sub>Amid I</sub>), 1636 (NH<sub>2</sub>), 1623 (NH<sub>2</sub>), 1610 (NH<sub>2</sub>), 1558 (NH<sub>2</sub>), 1542 (N-H+C-N<sub>Amid II</sub>), 1517 (N-H+C-N<sub>Amid II</sub>), 1508 (N-H+C-N<sub>Amid II</sub>), 1488 (CH), 1474 (CH), 1451 (CH), 1433 (CH), 1418 (CH), 1397 (CH), 1387 (CH), 1379 (CH), 1363 (CH), 1339 (CH), 1318 (N-H+C-N<sub>Amid III</sub>, CH), 1296 (CH), 1268 (C-O-C, OH, C-N), 1239 (C-O-C, C-OH), 1188 (CO-O-CH<sub>3</sub>, CH), 1145 (C-O-C, C-OH), 1086 (C-O-C, C-OH), 1060 (C-O-C, C-OH), 1034 (C-O-C, C-OH), 1012 (C-O-C, C-OH), 991 (C-O-C, C-OH, C-C), 966 (C-C), 943 (CH), 838 (CH), 812 (C=O), 747 (C=O, CH), 720 (NH<sub>Amid V</sub>), 686 (CH), 679 (NH<sub>2</sub>), 660 (OH), 636 (CH), 618 (O=C-N<sub>Amid IV</sub>), 602 (CH), 572 (CH), 558 (NH, CO).

IR spectrum of composite 2 ( $\nu$ ,  $\text{cm}^{-1}$ ): 3247 (OH, NH), 2996 (CH), 2947 (CH), 2865 (CH), 1732 (C=O<sub>PMMA</sub>), 1716 (C=O<sub>PMMA</sub>), 1698 (C=O<sub>PMMA</sub>), 1647 (C=O<sub>Amid I</sub>), 1636 (NH<sub>2</sub>), 1623 (NH<sub>2</sub>), 1617 (NH<sub>2</sub>), 1609 (NH<sub>2</sub>), 1557 (NH<sub>2</sub>), 1541 (N-H+C-N<sub>Amid II</sub>), 1522 (N-H+C-N<sub>Amid II</sub>),

1507 (N-H+C-N<sub>Amid II</sub>), 1497 (N-H+C-N<sub>Amid II</sub>), 1489 (CH), 1473 (CH), 1456 (CH), 1435 (CH), 1419 (CH), 1396 (CH), 1387 (CH), 1374 (CH), 1362 (CH), 1339 (CH), 1319 (N-H+C-N<sub>Amid III</sub>, CH), 1268 (C-O-C, OH, C-N), 1241 (C-O-C, C-OH), 1186 (CO-O-CH<sub>3</sub>, CH), 1141 (C-O-C, C-OH), 1090 (C-O-C, C-OH), 1060 (C-O-C, C-OH), 1028 (C-O-C, C-OH), 1012 (C-O-C, C-OH), 985 (C-O-C, C-OH, C-C), 968 (C-C), 905 (CH), 839 (CH), 807 (C=O), 747 (C=O, CH), 720 (NH<sub>Amid V</sub>), 696 (CH), 681 (NH<sub>2</sub>), 650 (OH), 617 (O=C-N<sub>Amid IV</sub>), 601 (CH), 572 (CH), 562 (NH, CO).

IR spectrum of composite 3 ( $\nu$ ,  $\text{cm}^{-1}$ ): 3239 (OH, NH), 3031 (CH), 2993 (CH), 2951 (CH), 2801 (CH), 1720 (C=O<sub>PMMA</sub>), 1655 (C=O<sub>Amid I</sub>), 1638 (NH<sub>2</sub>), 1627 (NH<sub>2</sub>), 1619 (NH<sub>2</sub>), 1610 (NH<sub>2</sub>), 1561 (NH<sub>2</sub>), 1542 (N-H+C-N<sub>Amid II</sub>), 1523 (N-H+C-N<sub>Amid II</sub>), 1509 (N-H+C-N<sub>Amid II</sub>), 1499 (N-H+C-N<sub>Amid II</sub>), 1474 (CH), 1458 (CH), 1449 (CH), 1432 (CH), 1419 (CH), 1396 (CH), 1387 (CH), 1376 (CH), 1365 (CH), 1338 (CH), 1323 (N-H+C-N<sub>Amid III</sub>, CH), 1297 (CH), 1267 (C-O-C, OH, C-N), 1239 (C-O-C, C-OH), 1185 (CO-O-CH<sub>3</sub>, CH), 1139 (C-O-C, C-OH), 1102 (C-O-C, C-OH), 1082 (C-O-C, C-OH), 1062 (C-O-C, C-OH), 1029 (C-O-C, C-OH), 1016 (C-O-C, C-OH), 987 (C-O-C, C-OH, C-C), 961 (C-C), 917 (CH), 838 (CH), 814 (C=O), 798 (CH), 780 (CH), 747 (C=O, CH), 723 (NH<sub>Amid V</sub>), 694 (CH), 684 (NH<sub>2</sub>), 654 (OH), 620 (O=C-N<sub>Amid IV</sub>), 607 (CH), 573 (CH), 561 (NH, CO).

## 3. Results and discussion

Composites of chitosan and PMMA were obtained by *in situ* polymerization with heating at different temperatures (Fig. 1). To obtain composite 3, mechanochemical activation was preliminarily carried out by grinding chitosan and PMMA powders for 120 min. The source of PMMA was the Villacryl H Plus heat-curing acrylic resin for denture bases [6].

The resulting composites were analyzed by ATR FT-IR spectroscopy. It is often used to research composite materials [10].

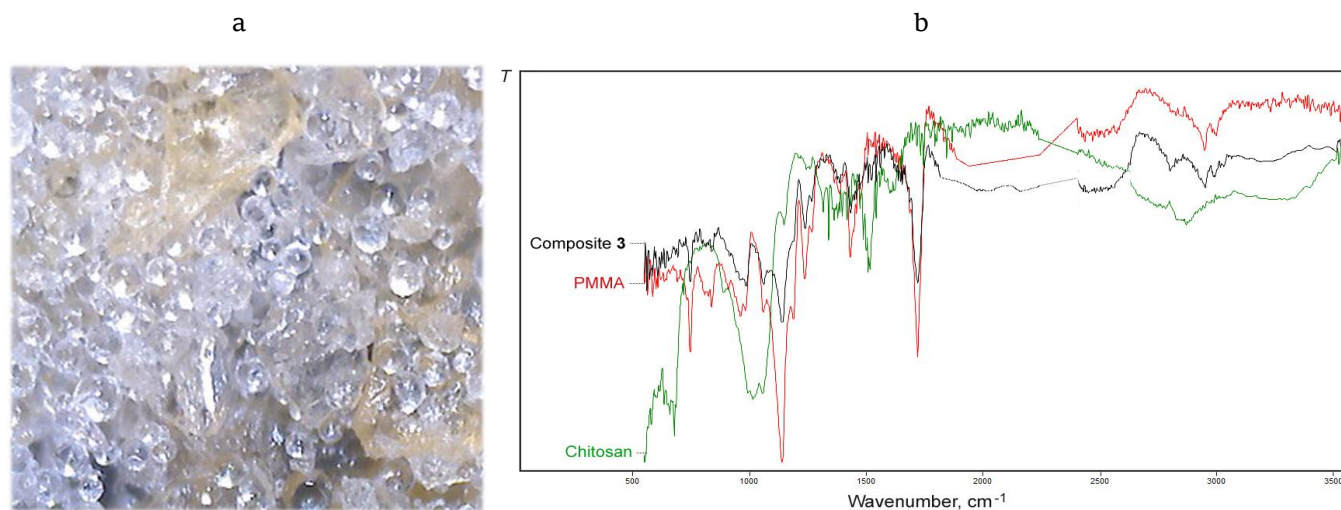


Fig. 1 Photo of the PMMA-chitosan composite 3 (a) and ATR FT-IR spectra of PMMA, chitosan and PMMA-chitosan composite 3 (b)

The IR spectra of chitosan and PMMA composites show low-frequency shifts of the absorption band of stretching vibrations of O–H and N–H bonds in chitosan from 3310  $\text{cm}^{-1}$  to 3297  $\text{cm}^{-1}$  (for composite 1), to 3247  $\text{cm}^{-1}$  (for composite 2) and to 3239  $\text{cm}^{-1}$  (for composite 3; Fig. 1). Such changes in the spectra confirm the formation of hydrogen bonds.

In addition, IR spectra of composites 1–3 show certain changes related to the absorption bands of stretching vibrations of C–O bonds in C–O–C and C–OH groups, as well as to the in-plane bending vibrations of O–H bonds in chitosan: 1260→1268, 1244→1239, 1149→1145, 1057→1060, 1015→1012, 995→991  $\text{cm}^{-1}$  (for composite 1), 1260→1268, 1244→1241, 1149→1141, 1057→1060, 1015→1012, 995→985  $\text{cm}^{-1}$  (for composite 2), and 1260→1267, 1244→1239, 1149→1139, 1057→1062, 995→987  $\text{cm}^{-1}$  (for composite 3). In this case, the most significant shifts were noted for the composites 2 and 3.

The main absorption band of C=O stretching vibrations in PMMA ester bond was found at 1715  $\text{cm}^{-1}$  (composite 1), at 1716  $\text{cm}^{-1}$  (composite 2) and at 1720  $\text{cm}^{-1}$  (composite 3). Moreover, additional bands are observed at 1698 and 1732  $\text{cm}^{-1}$  (for composite 1), and at 1731  $\text{cm}^{-1}$  (for composite 2). The presence of low-frequency shifts in the IR spectra is indicative of involving C=O group of PMMA in hydrogen bonding with chitosan.

High-frequency shifts of some absorption bands of in-plane bending vibrations of N–H bonds in the chitosan molecule are observed in the spectra of composites: 1602→1610  $\text{cm}^{-1}$  (for composite 1), 1602→1609  $\text{cm}^{-1}$  (for composite 2), 1623→1627  $\text{cm}^{-1}$  (for composite 3). In addition, the IR spectra show shifts of the main absorption bands of stretching vibrations of CH bonds, which can be caused by hydrophobic interactions during the formation of composites.

#### 4. Conclusions

Polymer composites of PMMA and chitosan were obtained by polymerization with heating and mechanochemical method. The composites 1–3 are formed due to hydrogen bonds ( $\text{C}=\text{O}_{\text{PMMA}}\dots\text{H}-\text{O}_{\text{Chitosan}}$  and  $\text{C}=\text{O}_{\text{PMMA}}\dots\text{H}-\text{NH}_{\text{Chitosan}}$ ) and hydrophobic interactions. It is possible that the presence of chitosan in composite materials can change some of their mechanical properties and eliminate the toxicity of PMMA.

#### Acknowledgements

This study was carried out on the experimental equipment of the Sevastopol State University (project PR/807-42/2017).

#### References

- Stein PS, Sullivan J, Haubenreich JE, Osborne PB. Composite resin in medicine and dentistry. *J Long Term Eff Med Implants*. 2005;15(6):641–654. doi:[10.1615/jlongtermeffmedimplants.v15.i6.70](https://doi.org/10.1615/jlongtermeffmedimplants.v15.i6.70)
- Scharf F, Mikhnevich E, Safronov A. Interaction of iron oxide nanoparticles synthesized by laser target evaporation with polyacrylamide in composites and ferrogels. *Chimica Techno Acta*. 2017;4(2):128–139. doi:[10.15826/chimtech/2017.4.2.028](https://doi.org/10.15826/chimtech/2017.4.2.028)
- Mikhnevich EA, Safronov AP, Beketov IV, Medvedev AI. Carbon coated nickel nanoparticles in polyacrylamide ferrogels: interaction with polymeric network and impact on swelling. *Chimica Techno Acta*. 2020;7(3):116–127. doi:[10.15826/chimtech.2020.7.3.04](https://doi.org/10.15826/chimtech.2020.7.3.04)
- Frazer RQ, Byron RT, Osborne PB, West KP. PMMA: an essential material in medicine and dentistry. *J Long Term Eff Med Implants*. 2005;15(6):629–639. doi:[10.1615/jlongtermeffmedimplants.v15.i6.60](https://doi.org/10.1615/jlongtermeffmedimplants.v15.i6.60)
- Liber-Kneč A, Lagan S. Surface testing of dental biomaterials—determination of contact angle and surface free energy. *Materials (Basel)*. 2021;14(11):2716. doi:[10.3390/ma14112716](https://doi.org/10.3390/ma14112716)
- Solutions for the dental laboratory. Catalogue [Internet]. Zhermack S.p.A., 2019. p. 72–79. Available from: [https://www.zhermack.com/public/uploads/F300072\\_19-07\\_Catalogo\\_LABO\\_EN\\_low.pdf](https://www.zhermack.com/public/uploads/F300072_19-07_Catalogo_LABO_EN_low.pdf)
- Leggat PA, Kedjarune U. Toxicity of methyl methacrylate in dentistry. *Int Dent J*. 2003;53(3):126–131. doi:[10.1111/j.1875-595x.2003.tb00736.x](https://doi.org/10.1111/j.1875-595x.2003.tb00736.x)
- Zargar V, Asghari M, Dashti A. A review on chitin and chitosan polymers: structure, chemistry, solubility, derivatives and applications. *Chem Bio Eng Rev*. 2015;2(3):204–226. doi:[10.1002/cben.201400025](https://doi.org/10.1002/cben.201400025)
- Kusmono, Abdurrahim I. Water sorption, antimicrobial activity, and thermal and mechanical properties of chitosan/clay/glycerol nanocomposite films. *Heliyon*. 2019;5(8):e02342. doi:[10.1016/j.heliyon.2019.e02342](https://doi.org/10.1016/j.heliyon.2019.e02342)
- Voron'ko N, Sokolan N, Kuchina Y, Berestova G. Formation of polyelectrolyte complexes from chitosan and alkaline gelatin. *KnE Life Sciences*. 2020;5(1):109–119. doi:[10.18502/kls.v5i1.6031](https://doi.org/10.18502/kls.v5i1.6031)
- Smirnova NN, Markin AV, Smirnova ON, Smirnov VF, Knyazev AV. Effect of technogenic factors and biodestructive agents on the thermal behavior of chitosan and poly(methyl acrylate) block copolymer. *Russ J Phys Chem*. 2020;94(6):1262–1267. doi:[10.1134/S0036024420060254](https://doi.org/10.1134/S0036024420060254)