Cumhuriyet Sci. J., 44(1) (2023) 106-111
DOI: https://doi.org/10.17776/csj.1228170

Cumhuriyet Science Journal

| csj.cumhuriyet.edu.tr | Founded: 2002 ISSN: 2587-2680 e-ISSN: 2587-246X Publisher: Sivas Cumhuriyet University

Development of Halloysite Loaded Polypropylene Sutures with Enhanced Mechanical and Thermal Properties

Fadime Nülüfer Kıvılcım [1,a,*]

[1] Chemistry Department, Faculty of Arts and Science, İnönü University, Malatya, 44280, Türkiye.
*Corresponding author

Research Article

History
Received: 02/01/2023
Accepted: 16/03/2023

ABSTRACT

Polypropylene is a crucial polymeric material in modern life, especially in the packaging and food industry, as well as the biomedical field. This study aimed to enhance the mechanical properties of polypropylene structures used as surgical suture material by preparing polypropylene-halloysite (PP-halloysite) composites. Halloysite was added in varying amounts (1%, 3%, 5%, and 10%) to polypropylene, and the resulting composites were passed through a double heated extruder. Structural characterization of the PP-halloysite composites was carried out using Fourier Transform Infrared Spectroscopy (FTIR), elemental analysis, Scanning Electron Microscopy-Energy Dispersive X-Ray Analysis (SEM-EDX), Differential Thermal Analysis (DTA), Thermogravimetric Analysis (TGA)), and Differential Scanning Calorimetry (DSC) techniques to determine their thermal properties and softening temperatures. Mechanical tests were conducted to examine the composite suture structures obtained and determine the effect of halloysite doping on their mechanical properties. The results of the mechanical tests showed that the mechanical strength of the fiber structure increased with the amount of halloysite added. Therefore, the PP-halloysite suture structures could be used as non-melting suture material, especially in surgeries that require high strength compared to pure polypropylene structures.

Keywords: Polypropylene, Halloysite, Polypropylene composites, Suture mechanic properties.

[a] *Nilufer.kivilcim@inonu.edu.tr* *https://orcid.org/0000-0002-6017-5326*

Introduction

Medical suture materials are of critical importance, especially in terms of surgical applications, for the healthy termination of surgical applications [1,2]. The suture materials to be used in a healthy surgical operation must be biocompatible materials with high mechanical strength, structural and thermal stability [3]. In addition, some variable properties are requested in suture materials to be used in in-body and extra-body applications [4,5]. For example, while mechanical properties come to the fore in extracorporeal applications, features such as biocompatibility and being unaffected by body fluids come to the fore in intrabody applications. However, the suture materials to be used in surgeries such as tendons and hernias must show high mechanical strength as well as structural stability [6]. Therefore, many suture materials have been used up to now. Such as nylon [7,8], polyester[9], polypropylene [10], polyvinylenedifluoride [11], polydioxanone [12] are frequently preferred suture structures. Among these suture structures, Catgut and Silk are natural compounds. Polypropylene, polyamide, polydioxane, polyglycolic acid/polylactic acid and polyglycolic acid/polytrimethylene carbomate structures are synthetically produced structures. Silk, polypropylene, polyamide and stainless steel structures are permanent structures that are not self-absorbed. Other structures are dissolved in the body after ingestion. However, polypropylene is a highly preferred suture structure due to its high biocompatibility, low toxicity, high breaking resistance and high mechanical strength as monofilament compared to multi-filament structures.

In recent years, biodegradable polymers have started to be used as suture material, as well as such polymers. Polylactic acid [13,14], polyglycolic acid [15], poly(lactic-co-glycolic acid) copolymers [16], poly(ε-caprolactone) and poly(ε-caprolactam) [17] structures are frequently used in in-body applications. Since these structures have the property of dissolving in the body, there is no need for a second intervention after the surgery. Suture structures of different diameters and lengths are used according to the place of use, the purpose of use and the size of the wound. The diameter of the suture materials varies between 0.01 and 0.799 mm. Suture structures with high mechanical strength, such as polypropylene and nylon, are still used in many surgical operations today [18,19]. It is one of the most popular surgical suture materials, especially because of its polypropylene suture structures, non-adherent properties and not being affected by body fluids. Polypropylene sutures are widely used especially in vascular surgery because they are resistant to repeated torsion and do not contain monomer residues [20]. Since polypropylene can be produced as very thin, it has a structure that does not leave traces and does not stretch the tissue, therefore it is especially preferred in sports surgeries, meniscus and tendon surgeries. For this reason, it is necessary to restrict the movement of the polypropylene structure due to stretching and increase its mechanical strength in muscle tears and menisci that require excessive movement. For this purpose, different additives were tested. Among these additives are structures such as carbon nanotubes, silica and chitosan. Within the scope of this study, the halloysite structure was used to increase the mechanical properties of polypropylene suture structures. Fiber structure in halloysite increased the secondary interactions between polypropylene chains and provided significant increases in mechanical properties. Depending on the increase in the amount of halloysite, the changes in the mechanical properties were interpreted.

Halloysite has a 2:1 structure and a tubular-wrapped clay structure showing phyllosilicate properties. The smooth tubular morphology leads to a reduction in size and an increase in efficiency in the resulting composites [21, 22]. Pure halloysite and halloysite composites are used in the production of biomedical gels and biomedical absorbents, enzyme immobilization, wound dressing materials, drug release systems and preparation of bone cement due to their biocompatibility. All of these applications are proof that halloysite structures provide the biocompatibility required for biomedical applications [23]. Halloysite has a large surface area due to its tubular structure. Depending on the increased surface area, the interaction between the matrix and the additive will increase in the composite structure, so the improvements in the mechanical properties will be quite high. Therefore, halloysite structure was preferred in this study to increase the mechanical properties of suture structures instead of organic inorganic nanomaterials with similar structures. PP-based suture structures are widely used in medical surgical operations. They have frequently preferred suture structures, especially due to their biocompatibility and low cytotoxicity. Halloysite added to the structure in this study is clay with high biocompatibility. In the study, an additional toxicity and biocompatibility test was not needed for two-component composites with high biocompatibility and low cytotoxicity. Within the scope of this study, the effect of this fairly new type of clay on polypropylene suture structures was studied in detail in terms of mechanical, thermal and morphological aspects. Its usability as a suture material has been commented on.

Materials and Methods

Materials

Halloysite structure used in this study was obtained from Sigma Aldrich Company and its metric dimensions are 30-70 nm × 1-3 µm and cation exchange capacity is 8.0 meq/g. The polypropylene was obtained from Exxon Mobil Company. The commercially available ExxonMobil™ PP3155E5 product for medical applications has a density of 0.900 g/cm³ and a melting point of 230 °C.

Characterization

Structural characterization of polypropylene-halloysite composites was determined by FTIR spectroscopy method. Perkin Elmer Spectrum 2 model FTIR spectrophotometer was used in the FTIR analysis. Analyses were performed in ATR mode, and spectra were recorded in the range of 400-4000 cm^{-1}.

DTA, DSC devices were used to analyse the thermal properties of composites. DTA measurements were carried out to determine the thermal strength of the composite structures obtained within the scope of this study. DSC analyses were performed to interpret the effects of halloysite added to the structure on the flexibility and glass transition temperature of the composite. The thermal stability of the composite structures was measured using the Shimadzu DTA-50 instrument. This analysis was performed against aluminium oxide reference material at a heating rate of 10 mg sample at 10 °C/min. The softening temperatures and glass transition temperature (Tg) of polymeric composite structures were measured with a Shimadzu DSC-60 model calorimeter. In these analyses, a heating rate of 5 °C/min and 5 mg sample were used. The samples to be analysed were studied in aluminium pans with alpha alumina reference material in a static air atmosphere at the range of 30-500 °C.

Mechanical Test

The mechanical properties of pure PP and halloysite added PP composite structures produced within the scope of the study were determined by MTS-Exceed model E42 mechanical test analyser. These analyses were performed at room temperature and at approximately 30% relative humidity. Measurement samples were used in a cylindrical geometry of 120 x 0.11 mm.

The Preparation of Polypropylene-Halloysite Composites

Polypropylene halloysite composites were obtained by adding 1%, 3, 5 and 10% halloysite into 10 g of polypropylene and passing it through a double heated extruder set at 220^{0}C.

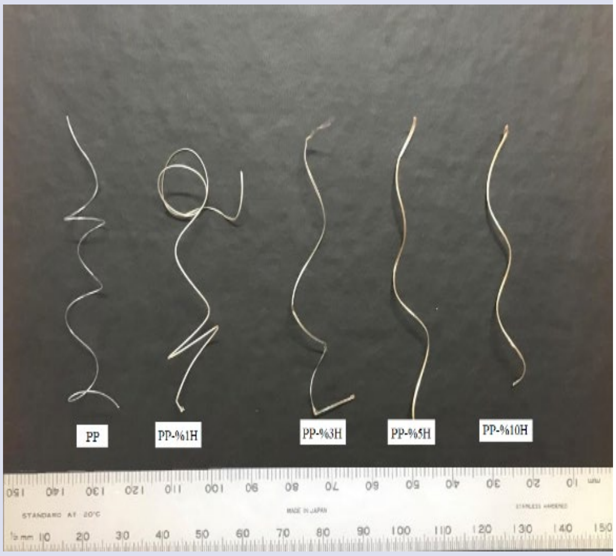

Figure 1. PP- Halloysite suture materials

Result and Discussion

Structural Characterization of Halloysite-Based PP Sutures

Structural characterization of PP-Halloysite composites obtained in this study was carried out by FTIR.

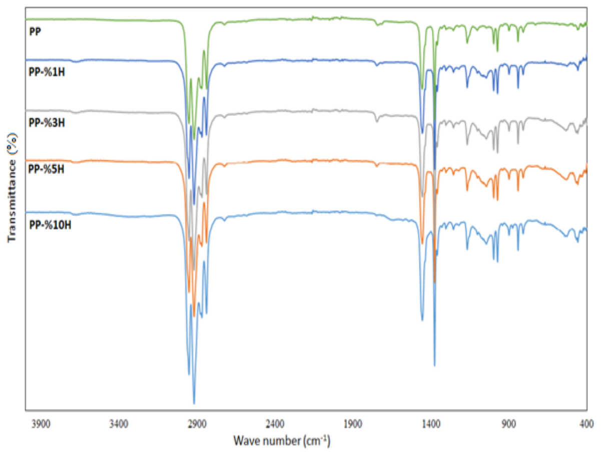

Figure 2. FTIR spectra of PP- Halloysite composites

In the FTIR spectrum given in Figure 2, the peak between 2850-2950 cm^{-1} is aliphatic C-H stretching vibrations and originates from the CH_2-CH groups on the polyprophylene main chain. The peaks at 2800-2830 cm^{-1} are the C-H aliphatic stretching vibrations of the CH_3 group in the side groups. The peak seen at 1450 cm^{-1} shows the C-C stretching vibration on the main chain, and the C-C bending vibration at 1380 cm^{-1}, C-H asymmetric stretching at 875 cm^{-1}, C-H out-of-plane bending at 825 cm^{-1} and C-H swinging peaks at 475 cm^{-1} belong to polypropylene. With the inclusion of halloysite in the structure, the Si-O-Si peak around 1000-1100 cm^{-1} appears as a band. Absorption bands at 3600 cm^{-1} in the FTIR spectrum belong to the tensile vibration originating from the inner surfaces of the O-H groups of halloysite. Furthermore, with the rise in the amount of halloysite in the composite, the peak due to Si-O at 550 cm^{-1} increases. Also, the inner Si-O stretching vibrations at 1039cm^{-1} demonstrate the increase of halloysite amount.

3.2. Thermal Properties of Halloysite- Based PP Sutures

From the DTA thermograms given in Figure 3, the classical melting peak of polypropylene at 160-180˚C is seen. Starting from 220˚C, two-stage decay is observed. It is seen that the peak area of the degradation peak decreases with the addition of halloysite to the polypropylene structure. Because while the amount of polypropylene in the structure decreases, the amount of halloysite increases.

From the DSC thermograms given in Figure 4, melting peaks of polypropylene at 180^0C are seen.

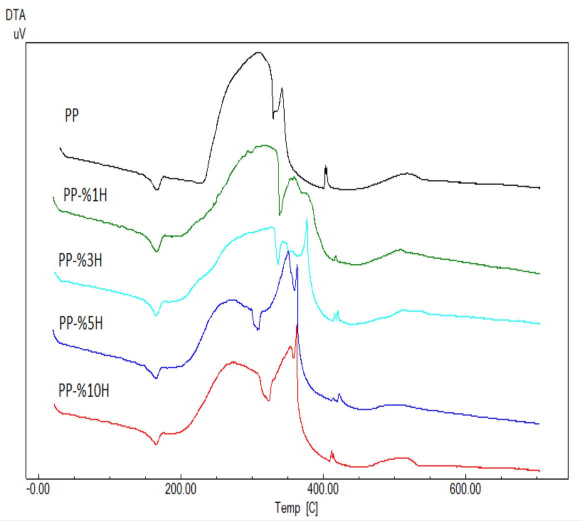

Figure 3. DTA thermograms of pure PP suture structure and sutures with PP-Halloysite composite structure.

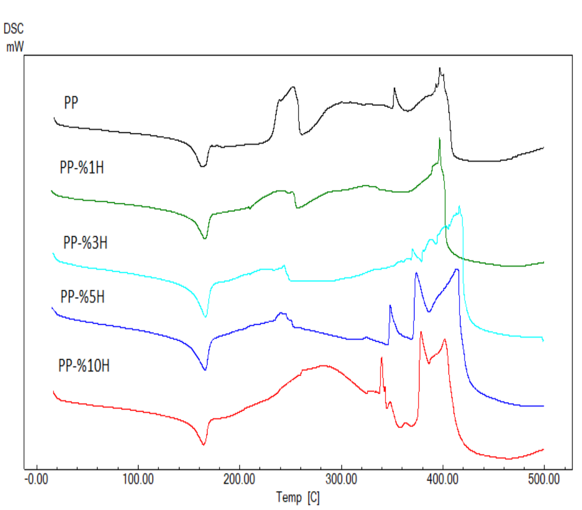

Figure 4. DSC thermograms of pure PP suture structure and sutures with PP-Halloysite composite structure.

The thermal stability of the PP-HA structures obtained within the scope of the study was confirmed by TGA analysis and the degradation steps were determined (Figure 5). In TGA analyses, a single mass loss was clearly seen in pure PP structure and all composite structures. This mass loss occurs at approximately 400 – 500°C and is seen as 100% for pure PP structure. In composite structures, the initial decomposition temperatures shift forward by about 50°C. However, the % residue amounts increase at 500°C. According to these analyses, the inclusion of halloysite groups in the PP structure partially reduces the thermal stability of the polymeric structure. This decrease is due to the inclusion of halloysite groups in the structure and the decrease in inter-chain stacking density. This leads to the formation of inter-chain spaces in composite structures and the stretching of the structure. All these findings prove to us that the desired composite structures were obtained.

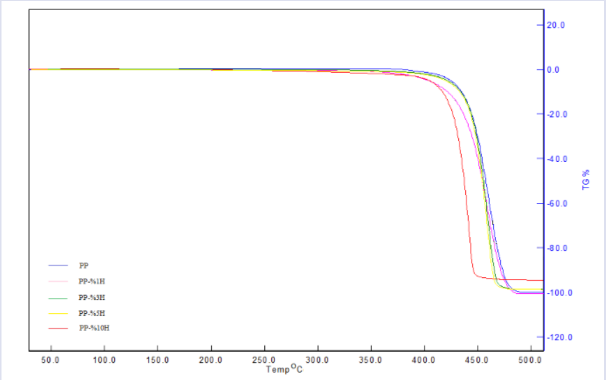

Figure 5. TGA thermograms of pure PP suture structure and sutures with PP-Halloysite composite structure.

Surface and Morphological Properties of Halloysite-Based PP Sutures

SEM images of PP-halloysite composite sutures produced within the scope of the study with different amounts of halloysite doped are given in Figure 6. When the SEM images are examined, it is seen that the pure pp structure in figure 5a has a smooth and monolithic structure. Fractal formations occur in the surface morphology of the structure with the inclusion of halloysite groups in the structure. Especially in structures with 1% and 3% halloysite additives, fractal formations are more prominent and distort the surface morphology. However, depending on the increased amount of halloysite, it is seen that the surface texture is improved again and smoother suture structures are obtained in structures containing 5% and 10% halloysite. For this reason, it can be said that the optimum 5% halloysite-containing structure has a smoother surface than other structures. In structures containing 10% halloysite, it has been determined that halloysite structures are clustered in places and there is agglomeration in the polymer.

The EDX spectra of the composite structures obtained within the scope of the study are given in Figure 6. While taking these spectra, the surfaces were coated with Au/Pd. When Figure 6 is examined, only the peak of the C atom is clearly seen in the spectrum of the pure PP structure. In addition, the peaks caused by the surface coating are evident. As halloysite is added to this structure, the peaks of O, Si and Al atoms in the halloysite structure are observed. The intensity of these peaks increases in direct proportion to the amount of halloysite. In these structures, in addition to these peaks, there are peaks originating from the 20 nm Au/Pd coating. The increase in the intensity of O, Al and Si peaks as the halloysite group's decrease in the composite structures proves that the desired composites are obtained.

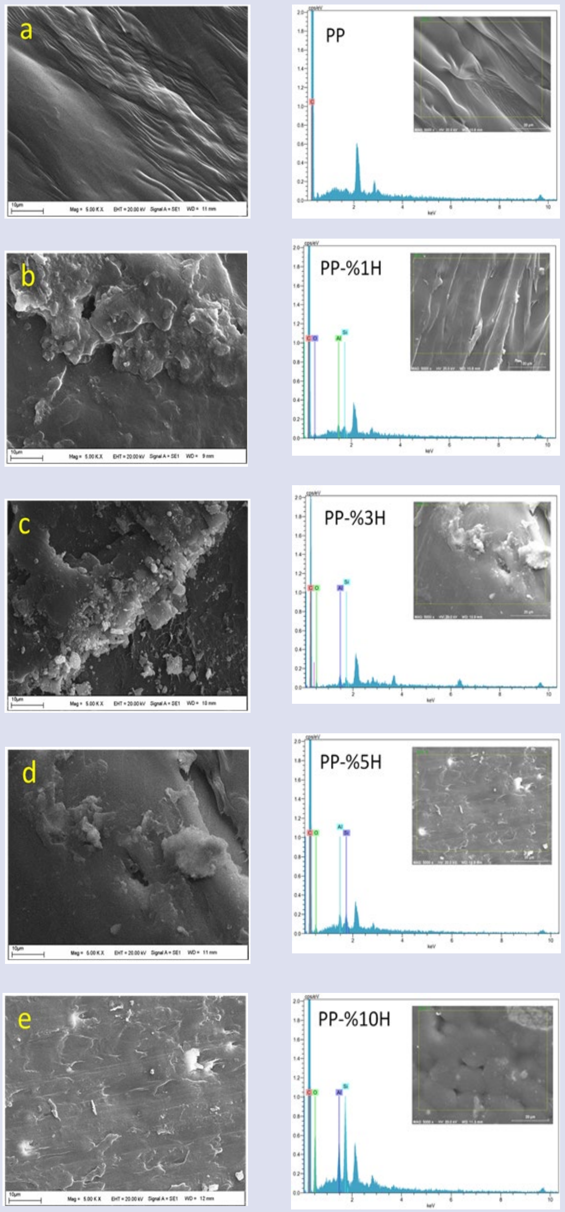

Figure6. SEM- EDX spectrum of PP-Halloysite suture structure (a); PP (b); 1%, (c); 3%, (d); 5% and (e); 10% by mass of halloysite.

Table 1. Chemical composition based on EDX analysis of the PP and the halloysite-based PP suture structures.

Sample	**Chemical composition (wt%)**			
	C	O	Si	Al
PP	95.26	4.74	-	-
PP-%1H	94.16	5.47	0.17	0.20
PP-%5H	93.58	5.54	0.42	0.45
PP-%10H	79.34	18.19	1.62	0.83

Chemical composition based on EDX analysis of the PP and the halloysite-based PP suture structures are given in Table 1. According to this table, only C and O elements are seen in the pure PP structure. Si and Al elements are also seen in halloysite-based PP suture structures. As the amount of halloysite in the structure increases, the percentages of Si and Al elements increase.

Mechanical Properties of Halloysite-Based PP Suture Structures

The most basic properties expected in suture materials used in the medical field; biocompatibility, non-toxicity, non-irritation, secure knotting and not breaking during use. In other words, its mechanical properties should be sufficient and strong. Therefore, PP-based suture materials used in this study are biocompatible and non-toxic materials. However, its mechanical properties may need to be strengthened according to the place of use. The mechanical properties of the suture structure are very important, especially in tissues and tendons with high mobility and exposed to force loads. Therefore, in this study, PP suture was doped with halloysite structure to increase the mechanical properties of the structures. The mechanical properties of the obtained halloysite-based PP suture structures were determined with a universal mechanical testing device. Each measurement was taken in triplicate and calculated as mean ± standard deviation. The mechanical test results obtained for Halloysite-based PP suture structures prepared with different halloysite ratios are given in Figure 7. According to this figure, as the amount of halloysite increased, the amount of elongation of the suture structure without breaking increased. Especially in the structure containing 10% halloysite, the highest mechanical flexibility was obtained. In this way, the tensions in the tissues and muscles after surgical operations may not cause the suture structure to break.

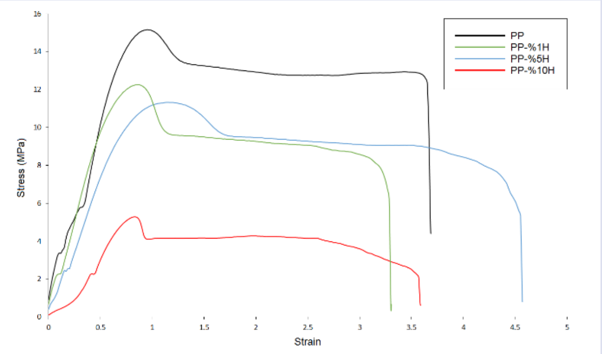

Figure 7. Mechanical test results of halloysite-based PP suture structures

Conclusion

In this study, PP-hallosite nanocomposite in the form of a series of sutures was prepared by adding halloysite into polypropylene matrix at different rates using the extrusion technique with physical interactions. These suture structures were characterized chemically, thermally and morphologically. According to morphological properties, especially homogeneous and crack-free structures were obtained. In the FTIR analysis, it was seen that the intensity of the Si-O-Si peak increased at 1000-1100 cm^{-1} as the amount of halloysite increased. As a result of thermal analysis, it was determined that the thermal stability of the composite obtained increased by 30-40 °C as the amount of halloysite increased. In terms of thermal properties, they were found to be thermally stable up to about 160°C. Therefore, they were found to be sterilizable before use. In the SEM images, it was seen that a homogeneous structure was obtained by the inclusion of halloysite in the structure. This shows that the halloysite groups are equally contributed to the whole structure. The mechanical properties of the obtained suture structures were analysed with a universal mechanical analysis system. Improvements in mechanical properties were observed as the amount of halloysite increased. It was observed that the structure containing 10% halloysite had advantages in terms of elongation and breaking strength compared to pure PP suture structures. For this reason, it is suggested that the PP-halloysite structures obtained within the study can be used as a suture.

Acknowledgments

Financial support from the İnönü University Research Fund Unit (Grant no. FBA-2022-2126) was gratefully acknowledged.

Conflicts of interest

There are no conflicts of interest in this work.

References

[1] Dennis C., Sethu S., Nayak S., Mohan L., Morsi Y., & Manivasagam G., Suture materials—Current and emerging trends, *Journal of Biomedical Materials Research*, *Part A*, 104 (6) (2016) 1544-1559.

[2] Abhari R. E., Martins J. A., Morris H., Mouthuy P. A., Carr A., Synthetic sutures: Clinical evaluation and future developments, *Journal of Biomaterials Applications*, 32 (3) (2017) 410-421.

[3] Chu C. C., Mechanical properties of suture materials: an important characterization, *Annals of Surgery*, 193 (3) (1981) 365.

[4] Zhukovskii V. A., Problems and prospects for development and production of surgical suture materials, *Fibre Chemistry*, 40 (3) (2008) 208-216.

[5] Srinivasulu K., Kumar N. D., A review on properties of surgical sutures and applications in medical field, *Int. J. Res. Eng. Technol.,* 2 (2) (2014) 85-96.

[6] Najibi S., Banglmeier R., Matta J. M., Tannast M., Material properties of common suture materials in orthopaedic surgery, *The Iowa Orthopaedic Journal*, 30 (2010) 84-88.

[7] Naleway S. E., Lear W., Kruzic J. J., Maughan C. B., Mechanical properties of suture materials in general and cutaneous surgery, *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, 103 (4) (2015) 735-742.

[8] Byrne M., Aly A., The surgical suture, *Aesthetic Surgery Journal,* 39 (2) (2019) 67-72.

[9] Bloom B. S., Goldberg D J., Suture material in cosmetic cutaneous surgery, *Journal of Cosmetic and Laser Therapy,* 9 (1) (2007) 41-45.

[10] Saxena S., Ray A. R., Kapil A., Pavon-Djavid G., Letourneur D., Gupta B., Meddahi-Pellé A., Development of a new polypropylene-based suture: plasma grafting, surface treatment, characterization, and biocompatibility studies, *Macromolecular Bioscience*, 11(3) (2011) 373-382.

[11] Sun J., Yao L., Zhao Q. L., Huang J., Song R., Ma Z., Hao Y. M., Modification on crystallization of poly (vinylidene fluoride)(PVDF) by solvent extraction of poly (methyl methacrylate)(PMMA) in PVDF/PMMA blends*, Frontiers of Materials Science,* 5 (4) (2011) 388-400.

[12] Boland E. D., Coleman B. D., Barnes C. P., Simpson D. G., Wnek G. E., Bowlin G. L., Electrospinning polydioxanone for biomedical applications, *Acta Biomaterialia*, 1 (1) (2005) 115-123.

[13] Chen Y., Geever L. M., Killion J. A., Lyons J. G., Higginbotham C. L., Devine D. M., Review of multifarious applications of poly (lactic acid), *Polymer-Plastics Technology and Engineering,* 55 (10) (2016) 1057-1075.

[14] Singhvi M. S., Zinjarde S. S., Gokhale D. V., Polylactic acid: synthesis and biomedical applications*, Journal of Applied Microbiology*, 127 (6) (2019) 1612-1626.

[15] Budak K., Sogut O., Aydemir Sezer U., A review on synthesis and biomedical applications of polyglycolic acid, *Journal of Polymer Research,* 27 (8) (2020):1-19.

[16] Chu C. C., Materials for absorbable and nonabsorbable surgical sutures, In Biotextiles as Medical Implants, *Woodhead Publishing Series in Textiles*, (2013) 275-334.

[17] Linderman S. W., Kormpakis I., Gelberman R. H., Birman V., Wegst U. G., Genin G. M., Thomopoulos S., Shear lag sutures: Improved suture repair through the use of adhesives, *Acta Biomaterialia*, 23 (2015) 229-239.

[18] Wang B., Yang W., Sherman V. R., Meyers M. A., Pangolin armor: overlapping, structure, and mechanical properties of the keratinous scales, *Acta Biomaterialia*, 41 (2016) 60-74.

[19] Javed F., Al-Askar M., Almas K., Romanos G. E., Al-Hezaimi K., Tissue reactions to various suture materials used in oral surgical interventions, *International Scholarly Research Notices*, (2012) 762095

[20] Acosta S., Björck M., Wanhainen A., Negative-pressure wound therapy for prevention and treatment of surgical-site infections after vascular surgery, *Journal of British Surgery*, 104 (2) (2017) 75-84.

[21] Joussein E., Petit S., Churchman J., Theng B., Righi D., Delvaux B., Halloysite clay minerals—a review, *Clay Minerals*, 40 (4) (2005) 383-426.

[22] Yuan P., Tan D., Annabi-Bergaya F., Properties and applications of halloysite nanotubes: recent research advances and future prospects, *Applied Clay Science*, 112 (2015) 75-93.

[23] Danyliuk N., Tomaszewska J., Tatarchuk T., Halloysite nanotubes and halloysite-based composites for environmental and biomedical applications, *Journal of Molecular Liquids*, 309 (2020) 113077.