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MODIFICATION OF POLYMERS IN JOINT ARTHROPLASTY

Abstract: *The review describes the known and most common modifications to various polymers in surgical applications. A short history of the plastics used as sliding materials in endoprostheses is presented. The unsuccessful attempts of using materials in joint alloplastic, such as PMMA, POM, PTFE and PEEK, as well as their modifications, were analyzed. Many polymers with excellent sliding properties cannot be used in joint arthroplasty due to allergic, toxicological reactions or technological problems. Attention was focused on PE-UHMW polyethylene, and also its modifications that increase its wear resistance and mechanical strength. The paper summarizes the wear rates of polyethylene subjected to various types of modification, such as plastic working, crosslinking, or carbon fiber reinforcement. The latest trends for improving polyethylene are also described. Modification of polymers in joint arthroplasty. A significant advance would be to obtain PEEK that is suitable for use in arthroplasty without negative consequences. An important direction of development in the area of sliding biomaterials may also concern materials obtained by incremental methods (3D printing).*

Key words: *biotribology, joint arthroplasty, PE-UHMW, selective cross-linking, polymers.*

Introduction

In modern medicine, endoprosthetic surgery is the only and best way to restore the lost motor function of the hip joint. It allows you to forget about pain and return to normal daily life. The vector of modern scientific research in the field of treatment of severe arthrosis of the hip joints is directed towards the improvement of technologies and materials for endoprosthetics. Today, this is the most progressive and fastest growing field of orthopedics. In order to increase the service life of endoprostheses, the latest innovative materials and technologies are used: titanium (as the main component metal), metal-ceramics, hydroxyapatite sputtering, porous metals and high-solid polymers.

The history of the development of sliding biomaterials has a rather specific course. Polyethylene (PE-UHMW) was first used in the 50s of the previous century, and despite the search for other polymers it is still a leading and irreplaceable material in endoprostheses. New trends related to the working of plastic and selective crosslinking indicate the possibility of obtaining very good mechanical and tribological properties. However, despite the fact that it is not free from imperfections, there is still no alternative to this material.

Directions of application and conditions of functioning of implants and endoprostheses, which are in contact with living tissues, determine the requirements to the nature and quality of materials intended for implant manufacturing, as well as to the technologies of their manufacturing. The general requirement related to the properties of materials for implants is the presence of osteoplastic, osteoconductive properties – the ability to act as conductors for blood vessels sprouting with the subsequent resorption and replacement by bone tissue. Osteoconductive materials serve as a matrix for the formation of new bone during reparative osteogenesis and have the ability to guide the growth of bone tissue. Hydrophilic properties are required for implants. Surgical interventions in bone surgery are often associated with pre-infected pathologic foci, and surgical treatment is often performed due to the development of inflammatory complications. An important problem is the choice of resistant (resistant to infection) materials, as well as materials that do not cause thrombosis.

Scientists are searching for materials and compositions that would have an osteoplastic effect and at the same time be resistant to bacterial influences. Recently, the range of materials with the above properties has been greatly expanded by the use of synthetic materials, including biopolymers and biodegradable compositions. Biopolymeric materials are most often completely nonimmunogenic, can be sterilized by modern medical methods, are relatively inexpensive to produce with few exceptions and, their most valuable advantage, can have a wide range of physical, mechanical and biochemical properties due to the regulation of the supramolecular and molecular structure of the polymers.

The successful clinical efficacy of total joint endoprosthetics can be determined by many factors, including biomedical, biomechanical, and tribological considerations. Wear and biological response to wear have been found to play an important role in implant longevity. The choice of implant material is made based on its mechanical, technological, physical and chemical properties.

The article presents the most important achievements in the development of sliding polymers used in orthopedics. Much attention has been paid to the latest trends in the development of the polymers used for the sliding elements of endoprostheses.

Review of sliding polymers

The evolution of subsequent generations of endoprostheses gave reason for the application of newer materials. In the 20th century, a broad spectrum of completely different materials was used as the sliding components of endoprostheses, e.g. rubber [29], glass, celluloid, pyrex glass, bakelite [22], or polymethyl methacrylate (PMMA) [8]. The rapid growth of interest in polymers in the 1950s also influenced the development of biomaterials. At the end of the 50s and start of the 60s, sliding components made of polytetraethylene (PTFE) were very common. The huge wear and the allergic reactions on debris quickly ended the role of this material in arthroplasty [4]. Polyethylene was also used at this time, and Sir John Charney first used it in 1962 as an insert made of ultra-high molecular weight grade (PE-UHMW) [9, 12].

Apart from ultra-high molecular weight polyethylene, polyoxymethylene (POM) was also used for the sliding components of endoprostheses [1, 19]. Laboratory studies [3] later revealed, however, that the process of polyacetale wear is associated with the destruction of polymer chains with the dissipation of formaldehyde - a highly carcinogenic agent – which excluded the use of POM as a sliding biomaterial.

Another material with excellent mechanical and tribological properties, the use of which was tried in arthroplasty, was PEEK. Attempts have been made to use it in an unmodified and reinforced with carbon fiber form (CFR-PEEK) [15,26] as a material for the acetabulum of the hip joint. Despite the excellent results obtained in in vitro studies [17], and also the fact that it has 10 times less wear than PE-UHMW, it has been proved that there is a significant influence of wear particles on cytotoxic reactions [24,27]. Currently, in the area of sliding biopolymers, this material is only used for the coating on friction surfaces [6, 28].

Unsuccessful attempts (in orthopedics) to apply various polymers on the elements of working friction resulted in a return to the proven material polyethylene [10]. Interestingly, at the end of the 20-th century there were 10 varieties of PE-UHMW. They differed, among others, with regards to their molecular mass and content of calcium stearate (added to reduce oxidisation during gamma sterilisation), and also with regards to the method of machining [13]. At the beginning of the current century, the number of polymer varieties dropped to three [13]. Efforts to improve the properties of PE-UHMW have been undertaken for many years. The objective was to reduce the quite high value of the rate of wear, and also to improve its resistance to cracking under impact loading.

Reinforcement of PE-UHMW by the addition of carbon fibres increased its resistance to creep and better reduced its wear rate [13], however, some technological issues appeared. The material Poly II® was withdrawn from the market 7 years after its introduction due to manufacturing problems involved with compression moulding [11, 13].

The next interesting modification of PE-UHMWPE was Hylamer®, a material produced with a strict control of its crystalline structure. The production process consisted in the application of a very high pressure (above 280 MPa), high temperature (above 250°C), and a slow cooling of the ready-made product. The material had a markedly higher rate of crystallinity (80%) and an elevated Young’s modulus value [14]. On the basis of numerous laboratory and clinical tests, it was found that the production method has a great impact on the tribological properties of polyethylene [16]. Components manufactured by the direct moulding method are two times more resistant to wear then those manufactured by machining methods [13].

However, the most important modification in the use of polyethylene for an endoprosthesis element was cross-linking treatment, which is a natural consequence of radiation sterilization. The main chemical transformations driven by ion radiation in polyethylene, besides cross-linking, is degradation and oxidation [21]. Cross-linking consists of the creation of C-C links between molecules. The degradation of elements made of polyethylene involves the disruption of chemical bonds between the macromolecules of the polymer. Oxidation developing at the surface, or just below the surface [13], consists of the creation of oxides and hydroxides [30]. A considerable decrease in the wear of elements made of PE-HD, which are subjected to 100 Mrad radiation, was observed when compared to radiation free PE-UHMW [13]. This increase in the resistance to wear is due to a better cross-linking of polyethylene molecules. Restriction in the access of oxygen during radiation by the use of neutral gas or a vacuum atmosphere significantly reduces negative chemical transformations in the upper layer of the material (oxidation). A considerable improvement of tribological performance, which is as a result of ion radiation and the limitation of the negative impacts of this process, resulted in its widespread and successful application to the present day. Table 1 contains a summary of approximate wear data for different types of polyethylene.

Table 1 – Wear of polymer materials used for hip endoprostheses

Material	Wear of socket of THR
Non-modified PE-UHMW	0.12 – 0.25 mm/year – metal head 0.098 – 0.03 mm/year – ceramic head
Crosslinked PE-UHMW	0.022 – 0.15 mm/year – metallic head
Highly crosslinked PE-HD	0.076 mm/year – metallic head 0.072 mm/year – ceramic head
Direct compression moulding PE-UHMW	0.05 mm/year – metallic head
Reinforced by CF PE-UHMW (20% CF) Poly II®	$4.89 \cdot 10^{-9}$ g/cycle – metallic head
Specific manufacturing conditions PE-UHMW Hylamer®	0.13 – 0,4 mm/year – metallic head 0.15 – 0.33 mg/mln. cycles – ceramic head

It should be noted that excessive cross-linking, in addition to generating a large amount of free radicals, reduces the impact toughness of the material [2, 23]. The optimal dose of radiation increases the wear resistance, while at the same time maintaining the required mechanical properties [5, 7]. The use of selective cross-linking can be seen to be interesting, the idea of which is to radiate only some areas of the polyethylene [18]. This allows the material matrix to remain flexible, while also reducing tribological wear [18].

There have been many different polymers in the history of alloplastic. Many polymers with excellent sliding properties cannot be used in joint arthroplasty due to allergic, toxicological reactions or technological problems. The polymers applied in joint arthroplasty are subjected to various modifications, such as plastic deformation, cross-linking or carbon fiber reinforcement. New modification methods, such as selective crosslinking, allow tribological properties to be improved without decreasing mechanical properties.

Figure 1 graphically presents all materials used in joint arthroplasty along with their possible modifications and tribological properties.

With the current development of new technology and material engineering, it seems bizarre that one base material is still used for the sliding elements of endoprostheses. Everything indicates that the further development of sliding materials in joint arthroplasty will involve modification of the material that has been used for the past 70 years - polyethylene. A significant advance would be to obtain PEEK that is suitable for use in arthroplasty without negative consequences. An important direction of development in the area of sliding biomaterials may also concern materials obtained by incremental methods (3D printing) [25].

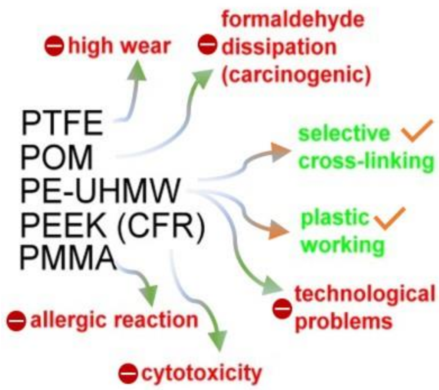

Figure 1 – List of materials used in joint arthroplasty, their tribological features and modification possibilities

Conclusion

In this review the approaches to achieving the material properties required for perfect implants have been considered. Polymeric implants have been produced for more than 15 years and are widely used in medicine not only in our country. They turned out to be very reliable, compatible with biological tissues and there are reasons to say that they have high durability. The role of polymeric material is to be a carrier of various growth factors and not to cause rejection by the body.

The introduction of a new generation of polymer implants will allow to significantly expand the range of patients who can be provided with surgical assistance, reduce the number of recurrences, improve the results of surgical interventions, and as a result - to restore the ability to work and improve the quality of life of patients. The success of using bone materials based on biodegradable polymers is based on an accurate understanding of the mechanism of action of various components of the implant composition and strict compliance with the increasingly stringent regulatory requirements of implant technology.

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БУЫН АРТРОПЛАСТИКАСЫНДАҒЫ ПОЛИМЕРЛЕРДІҢ МОДИФИКАЦИЯСЫ

Шолуда хирургиялық қолдануға арналған әртүрлі полимерлердің белгілі және кең таралған модификациялары сипатталған. Эндопротезде жылжымалы материалдар ретінде қолданылатын пластмассалардың қысқаша тарихы ұсынылған. PMMA, POM, PTFE және PEEK сияқты аллопластикалық материалдарды, сондай-ақ олардың модификацияларын біріктіруде қолданудың сәтсіз әрекеттері талданды. Аллергиялық, токсикологиялық реакцияларға немесе технологиялық мәселелерге байланысты буындарды эндопротездеу кезінде тамаша жылжымалы қасиеттері бар көптеген полимерлерді пайдалану мүмкін емес. PE-UHMW полиэтиленіне, сондай-ақ оның тозуға төзімділігі мен механикалық беріктігін арттыруға арналған модификацияларына назар аударылды. Мақалада пластмассамен өңдеу, тігу немесе көміртекті талшықты арматуралау сияқты әртүрлі түрлендірулерге ұшыраған полиэтиленнің тозу көрсеткіштері жинақталған. Полиэтиленді жетілдірудің соңғы тенденциялары да сипатталған. Буындарды эндопротездеу кезінде полимерлердің модификациясы. Маңызды жетістік теріс салдарсыз эндопротездеуге жарамды PEEK алу болар еді. Сырғанау биоматериалдары саласындағы дамудың маңызды бағыты кезең-кезеңмен алынған материалдарға да қатысты болуы мүмкін (3D басып шығару).

Түйін сөздер: *биотрибология, буын артропластикасы, PE-UHMW, селективті тігу, полимерлер.*

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МОДИФИКАЦИЯ ПОЛИМЕРОВ ПРИ АРТРОПЛАСТИКЕ СУСТАВОВ

В обзоре описаны известные и наиболее распространенные модификации различных полимеров для применения в хирургии. Краткая история пластмасс, используемых в качестве скользящих материалов в эндопротезах. Проанализированы неудачные попытки использования в соединении аллопластических материалов, таких как PMMA, POM, PTFE и PEEK, а также их модификаций. Многие полимеры с отличными скользящими свойствами не могут быть использованы при эндопротезировании суставов из-за аллергических, токсикологических реакций или технологических проблем. Внимание было сосредоточено на полиэтилене PE-UHMW, а также его модификациях, повышающих износостойкость и механическую прочность. В статье приводится краткая информация об интенсивности износа полиэтилена, подвергнутого различным видам модификации, таким как пластическая обработка, сшивание или армирование углеродными волокнами. Также описаны последние тенденции в области совершенствования полиэтилена. Модификация полимеров в артропластике суставов. Значительным достижением было бы получение PEEK, пригодного для использования в эндопротезировании без негативных последствий. Важное направление развития в области биоматериалов скольжения может также касаться материалов, полученных поэтапными методами (3D-печать).

Ключевые слова: *биотрибология, артропластика суставов, PE-UHMW, селективное сшивание, полимеры.*

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