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# THE EFFECT OF THE FILLER NATURE ON THE PROPERTIES OF HYDROGELS BASED ON POLYVINYLPYRROLIDONE COPOLYMERS

*The influence of nature and amount of filler on technological and performance properties of polymer hydrogels based on copolymers of 2-hydroxyethylmethacrylate (HEMA) with polyvinylpyrrolidone (PVP) have been investigated. The synthesis of composite copolymers was carried out by the method of polymerization with simultaneous filling, which consists in the mechanical mixing of the original composition with the filler and its subsequent curing under the action of initiators or catalysts. To obtain filled hydrogels, a copolymerization of HEMA with PVP in the presence of iron sulfate (II) was used, which occurs at high rate, at room temperature, in air, which greatly simplifies and reduces the cost of the process, reduces its duration and expands the areas of application. For research, fillers of organic nature – wood flour, grinded waste of hydrogel material and mineral – aerosil, crushed glass, amorphous silica $SiO_2$ were used. Test samples based on filled hydrogels were obtained in polymerization mold by pouring method. In order to combine the stages of synthesis of the hydrophilic polymer and its subsequent swelling to provide elastic properties, the polymerization was carried out in the presence of water. To improve the mechanical properties and reduce the shrinkage of the hydrogel materials, small amounts of triethylene glycol dimethacrylate were introduced into the formulation of the initial polymer-monomer composition, which promotes the increase of crosslinking degree and hardness of the copolymer.*

*The influence of nature and the amount of filler on the performance properties of the material, namely – shrinkage, hardness, resilience, plasticity have been studied.*

*It was established that the presence of filler has a positive impact on the physico-mechanical properties of copolymers – there is a regular increase in the hardness of the compositions with the addition of filler, although the resilience thereby decreases slightly. In particular, the addition of fillers has a sharp effect on the shrinkage, which decreases in each case, regardless of its nature.*

***Key words:*** *polyvinylpyrrolidone, 2-hydroxyethylmethacrylate, copolymers, composite hydrogels, filled hydrogels, fillers.*

**Formulation of the problem.** Quick-setting materials with high resilience-deformation properties and high accuracy of reproduction of the duplicated surface, as well as low-tonnage technologies of obtaining products, which can be carried out directly in an outpatient or clinical setting, are currently needed as duplicate materials for clasp prosthetics in dentistry.

The main properties that assess the suitability of polymer material for the manufacture of duplicate molds are shrinkage and quality of reproduction of the purity and sizes of the surfaces of duplicate objects, also they must be characterized by corresponding resilience and hardness [1, p. 327]. The first characteristics determine the accuracy and purity of reproduction of the dimensions, and the hardness with resilience – the reliability and durability of the mold during operation.

For these purposes in orthopedic dentistry are used materials and technologies for duplicate molds, which are characterized by durability and multi-stage [1, p. 327]. However, such materials do not always meet modern requirements for the accuracy of the size and quality of reproduction of the duplicated surface. Existing molding methods are mainly technologically complex and are characterized by limited ability to control the structure and properties of the polymer.

In this regard, the problem of searching for new polymers and simple technologies for molding precise products is extremely relevant.

The possibility of obtaining quick-setting polymer-oligomer compositions based on 2-hydroxyethylmethacrylate (HEMA) and polyvinylpyrrolidone (PVP) has been proved. They possess high reactivity and can be cured in air at room temperature for 2–30 min depending on the original composition formulation [2, p. 59; 3, p. 236; 4, p. 82] and can be used to obtain duplicate molds. However, the obtained materials require an improvement in the strength and resilience properties, as well as reduction of the shrinkage impact on dimensional accuracy. One of the methods of modifying polymer hydrogels and improving their physico-mechanical properties is the use of fillers. The addition of fillers opens up new ways to influence the formation of the structure and significantly expands the range of properties and, consequently, the use of polymer materials, which is why the study of filled hydrogels is of both scientific and practical importance.

**Analysis of recent research and publications.** Polymer hydrogels find a wide practical use in the biomedical field [5, p. 18; 6, p. 197] as hydrogel medical dressings [7, c. 1569], contact lenses [8, c. 52], hydrogel membranes [9, c.889], materials for regeneration of damaged tissues [10, c. 14976], as enzyme immobilization systems [11, c. 1666], drug delivery systems [12, c. 1993], vascular prostheses [13, c. 1537]. They swell but do not dissolve in water and saline. Due to their structure, which resembles the structure of living tissues, hydrogels are characterized by good biocompatibility, which allows them to be used in a direct contact with a living organism.

Among the wide range of hydrogel polymers known today, HEMA with PVP copolymers have a number of valuable performance properties [5, p. 18; 6, p. 197]. Preliminary studies conducted in the Department of Chemical Technology of Plastics Processing at Lviv Polytechnic National University developed compositions based on PVP, mono- and dimethacrylic esters of glycols, which polymerize under the action of metal ions with variable oxidation state [2, p. 59; 3, p. 236; 4, p. 118]. PVP affects the course of polymerization of HEMA (polymerization of HEMA in the presence of PVP occurs by a matrix mechanism), the formation of the structure and the properties of the final product. “Matrix effect” [14, p. 136], when monomer molecules are solvated on a polymer matrix, promotes the increase of polymerization rate, the course of the reaction with the transfer of the kinetic chain on the PVP macromolecule and the formation of grafted cross-linked copolymer (pHEMA-gr-PVP). The kinetics of polymerization has been studied, the optimal composite formulations were selected, the ways of practical application of such copolymers in the biomedical field are found [9, p. 52; 15, p. 6; 16, p. 187]. The obtained hydrogels based on pHEMA-gr-PVP copolymers attract attention with their elasticity, resilience, high chemical and biological inertness, which provides the prospect of their use as technological materials for dental practice, in particular, as duplicating masses in prosthetics [17, p. 39].

**Formulation of the article goals.** The aim of the work was to investigate the influence of nature and amount of filler on the main technological and operational properties of hydrogel copolymers based on HEMA with PVP compositions and to identify possible ways to improve these properties and to reduce the cost of the original composition.

**Presentation of the main material**

**Materials and methods of research.** The following substances were used: 2-hydroxyethylmethacrylate (Sigma Chemical Co), which was purified and distilled under vacuum (residual pressure = 130 N/m$^2$, $T_B$=351K); polyvinylpyrrolidone (AppliChem GmbH) of high purity with MM = 28000 was dried at 338 K in vacuum for 2-3 hours before use; iron (II) sulfate was used of p.a. grades.

For research, fillers of organic nature were used – wood flour (particle size 0,15–2,5 mm), grinded waste of hydrogel material (particle size 0,25–0,8 mm) and mineral – aerosil, crushed glass (fraction 0,05–0,16), amorphous silica $SiO_2$ (CP). Shrinkage of the material (S, %) was determined by the difference between the size of the template and the hydrogel imprint using a cathetometer KM-8 with a measurement accuracy of ± 0,005 mm, strain-resilience properties – on the hardness meter TShR according to the procedure described in [18, p. 429].

**Results and discussion**

Polymer-monomer compositions (PMC) based on HEMA with PVP, especially in the presence of solvent (e.g., water, dimethyl sulfoxide) are characterized by high fluidity, which ensures their ability to process into products by pouring method to obtain quality products of various shapes. The prototypes were obtained in polymerization mold, the main elements of which are the matrix and the sign (Fig. 1). The outer molding surface (matrix) was made from polypropylene, because the adhesion of pHEMA-gr-PVP copolymers to it is the lowest, the sign (duplicate object) – from polytetrafluoroethylene.

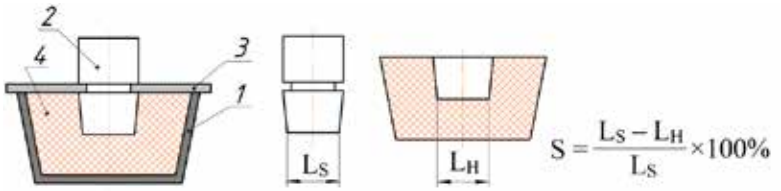
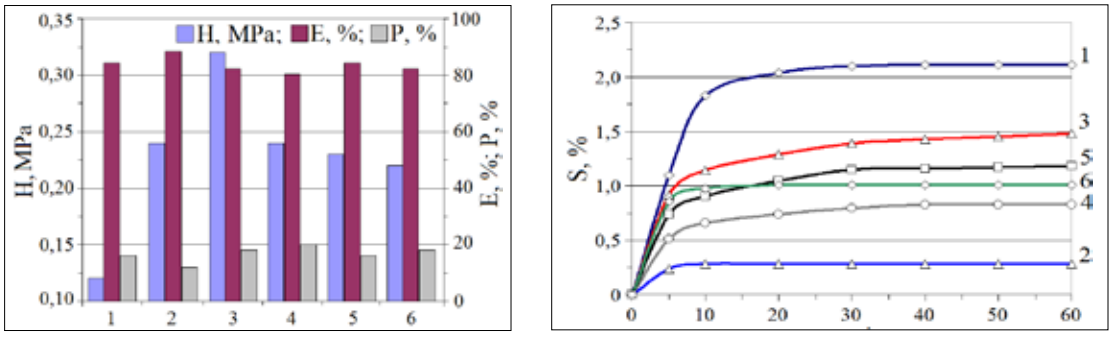



**Fig.1. Mold for the manufacture of prototypes from pHEMA-gr-PVP copolymers by pouring method:**
1 – matrix; 2 – sign; 3 – cover-holder of the sign; 4 – hydrogel

Synthesis of composite pHEMA-gr-PVP copolymers was carried out by the method of polymerization with simultaneous filling, which consists in mechanical mixing of the original composition with the filler and its subsequent curing under the action of initiators or catalysts. On the basis of the results of previous studies [2, p. 59; 3, p. 236; 4, p. 118], copolymerization of HEMA with PVP in the presence of iron sulfate (II) was used to obtain imprinted masses. Polymerization occurs at high rate, at room temperature, in air, which greatly simplifies and reduces the cost of the process, reduces its duration and expands the areas of application. Based on previous studies, a following polymer-monomer composition was chosen with the formulation HEMA:PVP=80:20 mass parts with 100 mass parts of solvent ($H_2O$). The choice of such formulation of the original composition arise due to the fact that the lower PVP content significantly increases the curing time of the compositions, the higher PVP content increases the duration of its dissolution in HEMA, hence the viscosity of the composition increases, which becomes difficult to dose and deaerate. In order to combine the stages of synthesis of the hydrophilic polymer and its subsequent swelling to provide elastic properties, the polymerization was performed in water. At the same time, solution polymerization helps to avoid or minimize the exothermic effect that accompanies block polymerization of methacrylates [14, p. 136; 19, p. 1109]. To improve the mechanical properties and reproducibility of duplicate objects, triethylene glycol dimethacrylate (TEGDMA) was added to the original PMC, which promotes the increase of crosslinking degree and hardness of the copolymer [17, p. 39].

The influence of nature and the filler amount on the performance properties of the material were studied, namely shrinkage, as well as hardness, resilience, plasticity, which were characterized by the hardness number (H, MPa), elasticity index (E, %) and plasticity index (P, %) respectively.

The study results of the obtained composite hydrogels on the basis of compositions with the maximum possible filler content at which the composition retained the necessary technological properties (fluidity and viability) are shown in Fig. 2. For aerosil this amount is 10 wt.% by weight of the composition, for wood flour – 15 wt.%, for $SiO_2$ – 23 wt.%, for grinded hydrogel – 40 wt.%, for crushed glass – 100 wt.%. Figure 3 presents the study results of the influence of the filler nature with its same content on the properties and changes in the deviation of the size (S) of duplicate molds over time. According to the analysis of the obtained results, the addition of




*a* *b*

**Fig. 2. Dependence of properties (a) and changes in size deviation (S) of duplicate molds over time (b) from the maximum content of filler (PMC:$H_2O$ =1:1 mass parts; T=298 K. PMC formulation, mass parts: HEMA:PVP:TEGDMA=70:29:1):**
1 – unfilled hydrogel; 2 – crushed glass (100 wt.%); 3 – wood flour (15 wt.%); 4 – amorphous silica (23 wt.%); 5 – grinded material (40 wt.%); 6 – aerosil (10 wt.%)

filler mostly has a positive impact on the physico-mechanical properties of copolymers. In particular, the filler has a sharp effect on the shrinkage, which decreases in each case, regardless of its nature.

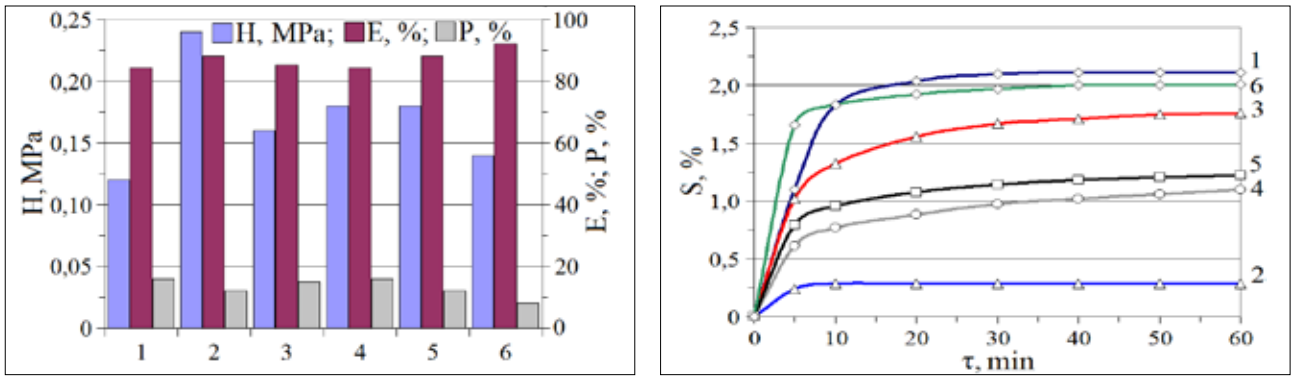
In the case of aerosil use (10 %) shrinkage equals 0,28 % and remains unaltered within 24 hours, which is four times less than the shrinkage of the hydrogel material without filler in 5 minutes and 7,5 times in an hour. Besides, a significant reduction in shrinkage is characteristic to the composition with $SiO_2$ and wood flour. Compositions containing as a filler – grinded waste of hydrogel material and aerosil have dimensional stability of the elastogel imprint over time and even after 24 hours.

Since shrinkage occurs due to the formation of a crosslinked polymer because of the reduction of the distance between the macrochains, it is obvious that the filler particles promote to maintain distances between macromolecules, and crosslinking occurs between particles with the inclusion of the latter into crosslinked structure.

To detect the effect of the filler amount on the properties of the filled hydrogel, the samples were made with different content of crushed glass (Fig. 4). The extreme dependence of the hydrogel imprint size change on the filler content was established. The best results were obtained for the content of crused glass in the amount of 50 % by weight of the composition.

Regarding the physico-mechanical properties, there is a natural increase in the hardness of the compositions with the addition of a filler, although the resilience is slightly reduced.

**Conclusions.** As a result, conducted studies of the performance properties of filled hydrogel materials showed a positive effect of filling on the shrinkage




*a* *b*

**Fig. 3. The effect of filler nature on the properties (a) and the changes in the deviation of the size (S) of duplicate forms in time (b) (PMC:$H_2O$=1:1 mass parts; T=298 K. PMC formulation, mass parts: HEMA:PVP:TEGDMA=70:29:1; filler content – 10 wt.%):**
1 – unfilled hydrogel; 2 – crushed glass; 3 – wood flour; 4 – amorphous silica; 5 – grinded material; 6 – aerosil.

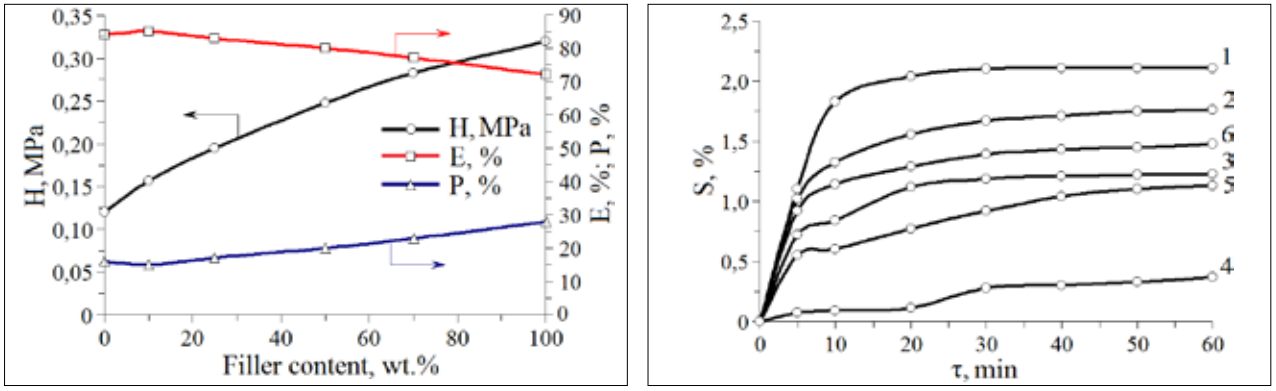



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**Fig. 4. Effect of filler content (crushed glass) on properties (a) and change of size deviation (S) of duplicating molds in time (b) (PMC:$H_2O$=1:1; T=298 K; PMC formulation, mass parts: HEMA:PVP:TEGDMA=70:29:1): Filler content, wt.%:**
1 – 0; 2 – 10; 3 – 25; 4 – 50; 5 – 70; 6 – 100.

and hardness of hydrogels and the possibility of using fillers not only for economic purposes – to reduce the cost of polymeric materials, but to improve physico-mechanical properties.

The following research will be aimed at studying the influence of the filling process on the kinetics of polymer-monomer compositions curing, as well as on the structure of the obtained composite hydrogels.

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**ВПЛИВ ПРИРОДИ НАПОВНЮВАЧА НА ВЛАСТИВОСТІ ГІДРОГЕЛІВ НА ОСНОВІ КОПОЛІМЕРІВ ПОЛІВІНІЛПІРОЛІДОНУ**

*В роботі досліджено вплив природи та кількості наповнювача на технологічні та експлуатаційні властивості полімерних гідрогелів на основі кополімерів 2-гідроксіетилметакрилату (ГЕМА)*

*з полівінілпіролідоном (ПВП). Синтез композиційних кополімерів здійснювали методом полімеризації з одночасним наповненням, який полягає у механічному змішуванні вихідної композиції з наповнювачем та подальшого її затвердження під дією ініціаторів чи каталізаторів. Для одержання наповнених гідрогелів використали кополімеризацію ГЕМА з ПВП в присутності феруму сульфату (II), яка відбувається з високою швидкістю за кімнатної температури, на повітрі, що дає можливість значно спростити та здешевити процес, скоротити його тривалість і розширити можливості його використання. Для досліджень використовували наповнювачі органічної природи – деревна мука, перемелені відходи гідрогельного матеріалу та мінеральні – аеросил, мелене скло, аморфний кремнезем $SiO_2$. Дослідні зразки на основі наповнених гідрогелів одержували у полімеризаційній формі методом заливання. З метою суміщення стадій синтезу гідрофільного полімеру і подальшого його набрякання для надання еластичних властивостей, полімеризацію здійснювали у присутності води. Для покращення механічних властивостей та зменшення усадки гідрогелевих матеріалів до складу вихідної полімер-мономерної композиції вводили невеликі кількості диметакрилату триетиленгліколю, який сприяє зростанню ступеня зшивання і підвищенню твердості кополімеру.*

*Вивчали вплив природи та кількості наповнювача на експлуатаційні властивості матеріалу, а саме – усадку, твердість, пружність, пластичність.*

*Встановлено, що присутність наповнювача позитивно впливає на фізико-механічні властивості кополімерів – простежується закономірне зростання твердості композицій, хоча пружність при цьому дещо зменшується. Зокрема, додавання наповнювачів різко впливає на усадку, яка зменшується в кожному випадку незалежно від його природи.*

***Ключові слова:*** *полівінілпіролідон, 2-гідроксіетилметакрилат, кополімери, композиційні гідрогелі, наповнені гідрогелі, наповнювачі.*