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EFFECT OF HYDROXYAPATITE ON THE GLUE LINE STRENGTH OF THE COMPOSITIONS CONTAINING POLYVINYLPIRROLIDONE

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Abstract. The influence of nature and mineral filler amount on adhesive ability of composite materials based on 2-hydroxyethylmethacrylate and polyvinylpyrrolidone modified by the low-molecular additives has been determined. The hydroxyapatite effect on the value of adhesive strength of the glued seam composites has been researched.

Keywords: polyvinylpyrrolidone, hydroxyapatite, adhesive strength, glue line, low-molecular additives.

1. Introduction

The needs of modern medicine lead to the creation of biologically inert and bioactive polymer materials that would be highly resistant to biologically active environments. The quest for the relevant material for use in orthopedic applications of synthetic replacement and regeneration of bone tissue has been of vital importance for the last 90 years. The use of calcium phosphate materials such as hydroxyapatite (HA) captivates the researchers' attention in its ability to be utilized in reconstructive surgery, dentistry as far as a vital component of toothpastes and gels, cosmetics, hygiene products and food additives [1-5].

Among the new generation of implants the materials based on hydroxyapatite (HA), 77 % of which forms the human bone tissue, present the most practical interest. Hydroxyapatite is a structural analogue of the mineral component of bone material. It has the same chemical composition, similar chemical, physical and mechanical quality, and what is more, it has a high biocompatibility index and ability to create a matrix for the formation of new bone and fibrous tissue *via* direct biochemical binding. But we also know that biological and mechanical properties of pure powder are deficient. One of the ways of the deficiencies elimination of calcium phosphate material is a combination of the polymer matrix which would play the role of coherent and contribute to the bone growth.

The previous studies have determined the regularities of obtaining HA filled porous composite materials based on 2-hydroxyethylmethacrylate (HEMA) with polyvinylpyrrolidone (PVP) [7].

The influence of the nature and amount of pore-formers, the number of HA, the ratio of monomer:polymer matrix in the original composition on the porosity of composites and their mechanical properties have been studied. It has been also established that the optimal pore-former is cyclohexane, however the porous material obtaining without hydroxyapatite is impossible. It is well- known about the effective use of polymer materials implants production based on polylactides, polyglycolides [8, 9] and polymethylmethacrylate [10]. The injection of mineral fillers in polymer matrix allows us to control and regulate surface properties, increase their compatibility with the polymer matrix and consequently improve the strength characteristics of composites. Compositions of 2-hydroxyethylmethacrylate and polyvinylpyrrolidone which are able to react with the mineral surfaces open up new prospects for polymer composite formation in the biomedical field.

The aim of the given work is to investigate the influence of the nature and amount of hydroxyapatite on adhesive strength of composite materials based on 2-hydroxyethylmethacrylate and polyvinylpyrrolidone which are modified by low-molecular additives.

2. Experimental

2.1. Materials

Polyvinylpyrrolidone (PVP) of molecular weight $28 \cdot 10^3$ g/mol is the powder of white or white with a slightly yellowish color and a weak specific smell; hygroscopic; easily soluble in water, alcohol, chloroform, practically insoluble in diethyl ether. Before using it was dried under vacuum at 338 K for 2–3 h.

2-Hydroxyethylmethacrylate (HEMA) used for research (r_{20} = 1079 kg/m^3, n = 1.4520) was purified and distilled under vacuum (residual pressure of 14 N/m^2, boiling point of 351 K).

Phosphoric acid (H_3PO_4) under normal conditions is the colorless hygroscopic crystals. We used 80 % aqueous solution of phosphoric acid – the colorless, odorless liquid with a slight odor.

Lecithin – a general term for any group of yellow-brown fatty substances that are found in the tissues of animals and plants, egg yolks. We used lecithin capsules produced by Pharmetics Inc., Canada.

Isopropanol ($CH_3CH(OH)CH_3$) is a colorless transparent liquid with a characteristic pungent odor and density of 0.7851 g/cm^3 (at 293 K).

Hydroxyapatite (HA) was synthesized at the Department of Chemical Technology of Silicates of Lviv Polytechnic National University [11]. Hydroxyapatite powder was obtained *via* deposition reaction occurred in the aqueous solution containing ions of Ca^{2+} and PO_4^{3-} at pH ≥ 7 at the stoichiometric ratio of Ca/P = 1.67. As a source of Ca^{2+} the ions of $Ca(OH)_2$ were used, which were received *via* burning at 1323 K and subsequent hydration of chemically pure $CaCO_3$. As a source of phosphorus ions 5% solution of H_3PO_4 was used. HA synthesis was carried out in a reactor under constant stirring of $Ca(OH)_2$ and phosphoric acid. After 24 h of exposure the obtained hydroxyapatite was filtered and dried at 378 K for 48 h.

Linings of different nature, such as "organic glass", "silicate glass", "ceramics with glossy surface", "ceramics with untreated surface", "steel plate" and "bone" were used.

2.2. Preparation of Polymer Composition

Initial polymer compositions were prepared based on 2-hydroxyethylmethacrylate in the presence of peroxide benzoyl and polyvinylpyrrolidone with molecular weight of $28 \cdot 10^3$ g/mol and PVP content of 0.5, 1; 1.5 and 2 %. By the substitution method the low-molecular additives of different physical, chemical, structural and other properties, namely phosphoric acid, isopropyl alcohol, lecithin in concentrations of 0.3, 0.5 and 1 % were injected into compositions.

2.3. Analytical Methods

The contact angle was determined according to the method [12] using a microscope of MBS-9 type.

To determine the adhesive strength of the composition glue line we used the samples (fungi) with a diameter of 25 mm and a height of 20 mm, as well as 30x30 mm metal plates. Using a special device the sample was fixed in terminals of tensile machine and the force under which the sample was broken was fixed at a constant strain rate,. Measurements were performed on 050/RT-601U tensile machine ("Kimura machinery", Japan) at the break velocity of 25 mm/min.

The compositions were applied on the previous prepared metal plates and the sample (fungus) was kept at the temperature of 303 ± 2 K for 5 h. The resulting samples were tested for abruption according to the method [13]. The value of adhesion strength (*P*) was calculated using Eq. (1):

$$P = \frac{F}{S} \quad (1)$$

where *F* – breaking load, kgf; *S* – area of gluing, cm^2.

3. Results and Discussion

One of the most promising areas of biomedical composites formation is modification of a polymer matrix by inorganic filler. The injection of the filler into the HEMA:PVP composition enables to study the influence of mineral fillers on strength and adhesion properties of these compositions.

Polyvinylpirrolidone can be transformed under the influence of acids and the reaction nature; moreover the character of transformation significantly depends on the origin of the acid and its concentration.

The prepared compositions (see Subsection 2.2) were tested for adhesive ability *via* contact angle value, using the linings of different nature, namely: "organic glass", "glass silicate", "ceramics with glossy surface", "ceramics with untreated surface", "steel plate" and "bone".

Based on previous studies, the authors have determined [14] that the best properties have the HEMA:PVP compositions with the concentrations of low-molecular additive of 0.3 and 1 %. In the optimal composition the hydroxyapatite was injected at the concentrations of 1; 2.5; 5 wt % and the contact angle value (q) was determined on linings of different nature. Figs. 1-6 show the effect of HA and PVP concentrations effect on the contact angle of the HEMA:PVP compositions with isopropyl alcohol.

For the compositions with 0.5 % PVP the injection of isopropyl alcohol and HA in an amount of 0.3 and 2.5 %, respectively, leads to the decrease of contact angle values for linings based on both types of ceramics and "organic glass" (Fig. 1). At the same time for the rest of linings this value increases. Further increase of HA content increases q value, except the "bone" lining. The increase if isopropyl alcohol content to 1 % has the significant effect only for the "steel plate" lining. For instance, at HA content of 2.5% the q value decreases. Further increase in HA concentration increases the q value.

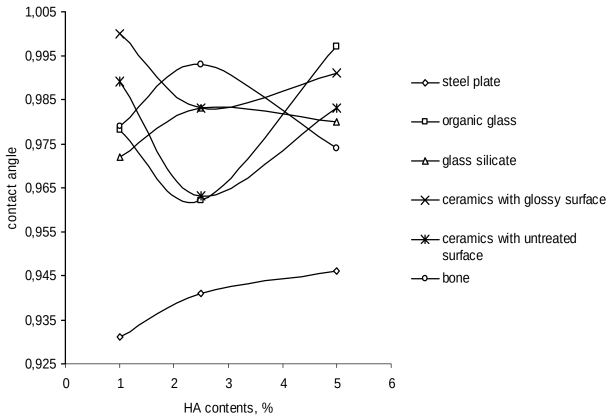

Fig. 1. HA content in the composition
0.5 % of PVP:HEMA : 0.3 % of $CH_3CH(OH)CH_3$

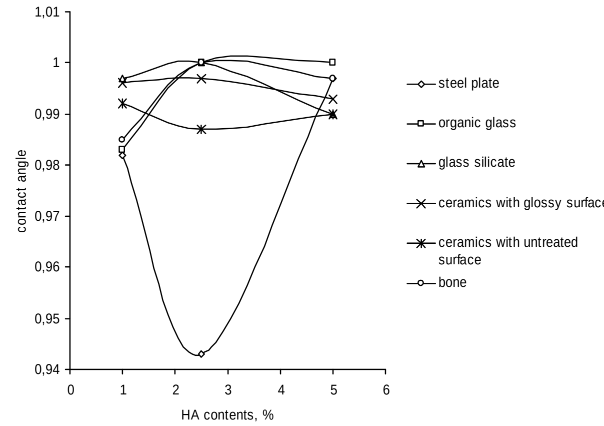

Fig. 2. HA content in the composition
0.5 % of PVP : HEMA : 1 % of $CH_3CH(OH)CH_3$

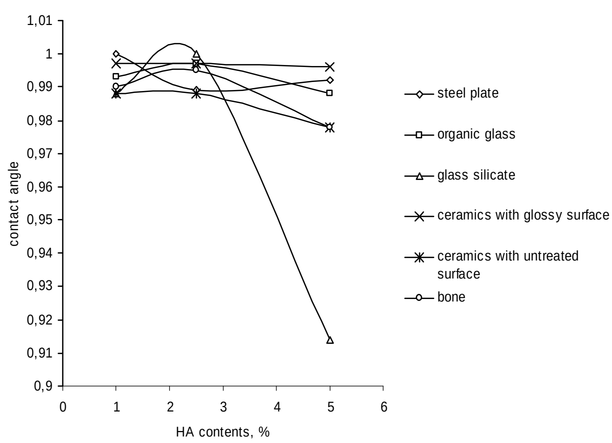

Fig. 3. HA content in the composition
1 % of PVP : HEMA : 0.3 % of $CH_3CH(OH)CH_3$

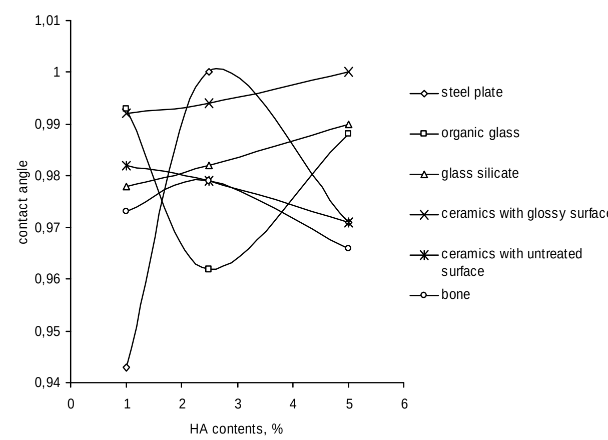

Fig. 4. HA content in the composition
1 % of PVP : HEMA : 1 % of $CH_3CH(OH)CH_3$

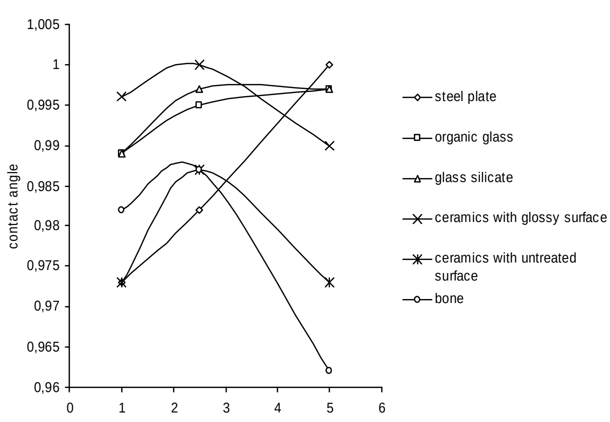

Fig. 5. HA content in the composition
2 % of PVP : HEMA : 0.3 % of $CH_3CH(OH)CH_3$

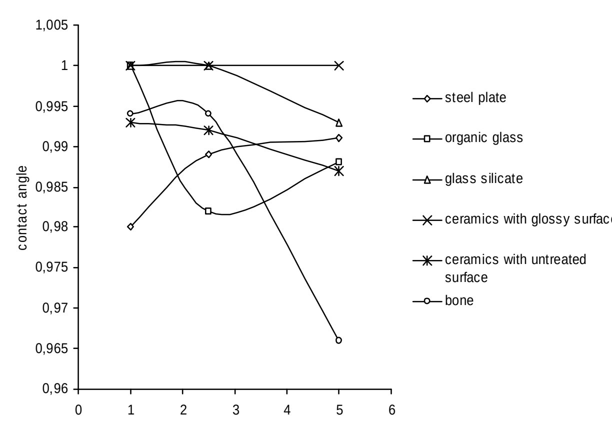

Fig. 6. HA content in the composition
2 % of PVP : HEMA : 1 % of $CH_3CH(OH)CH_3$

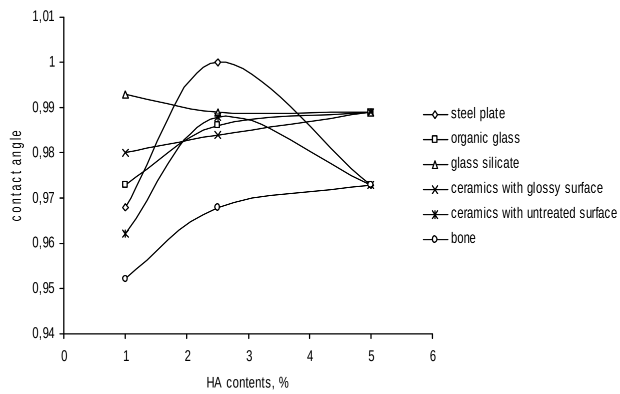

Fig. 7. HA content in the composition 0.5 % of PVP: HEMA : 0.3 % of H_3PO_4

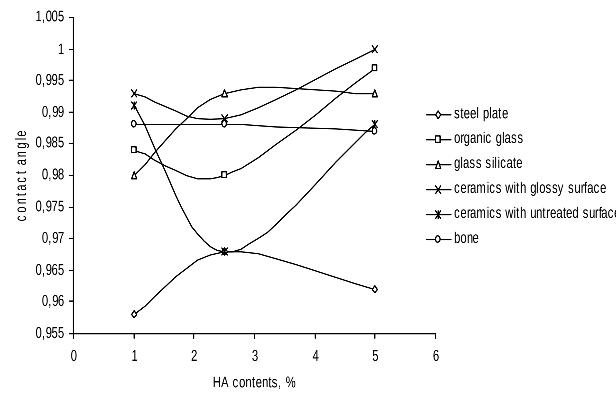

Fig. 8. HA content in the composition 0.5 % of PVP: HEMA : 1 % of H_3PO_4

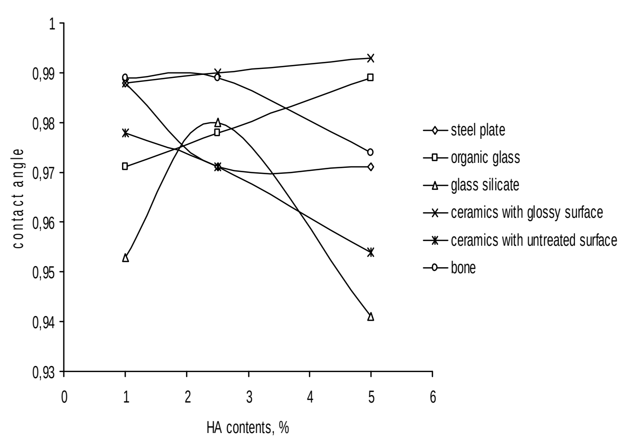

Fig. 9. HA content in the composition 1 % PVP: heme: 0.3 % H_3PO_4

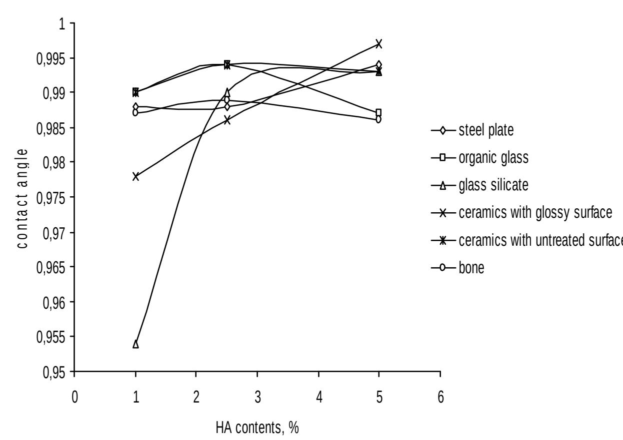

Fig. 10. HA content in the composition 1 % of PVP: HEMA : 1 % of H_3PO_4

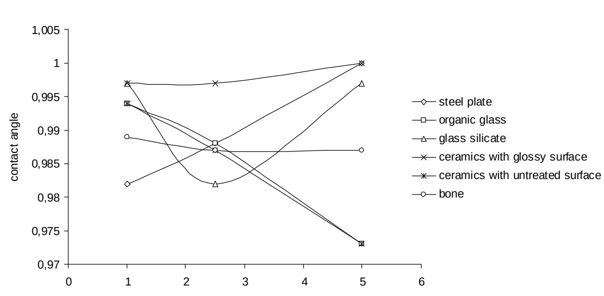

Fig. 11. HA content in the composition 2 % of PVP: HEMA : 0.3 % of H_3PO_4

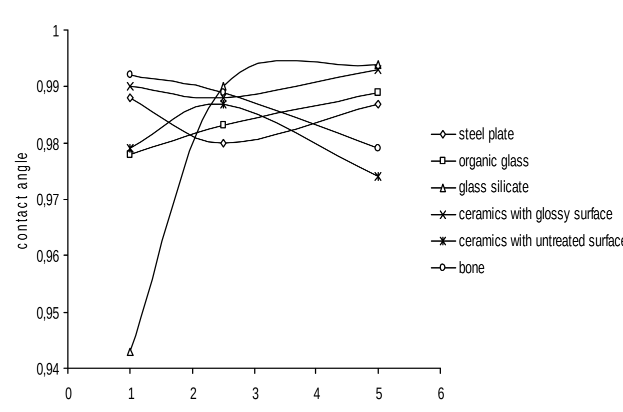

Fig. 12. HA content in the composition 2 % of PVP: HEMA : 1 % of H_3PO_4

With the increase of PVP concentration to 1 % and isopropyl alcohol content of 0.3 % (Fig. 3) the curves character is stable and the values of contact angle are sufficiently high.

For the compositions with 2 % of PVP and 0.3 % of isopropyl alcohol for all linings with HA content to 2.5 % the contact angle value slightly increases. With further increase of HA content the contact angle *q* reduces and it is especially noticeable for the "bone" lining. The exception is observed for the "steel plate" lining, where the contact angle value increases with the increase of inorganic filler content. Increasing the isopropyl alcohol concentration to 1 % and HA content we observe the decrease of *q* values, that is most noticeable for the "bone" lining. For the "steel plate" and "organic glass" linings a slight increase of the contact angle value is observed.

Similar studies were conducted for the compositions with phosphoric acid. Considering separately each lining for the compositions of phosphoric acid (Figs. 7-8) the character of the curve for the "steel plate" lining is invariable, but the *q* values decrease.

For the "organic glass" lining with increasing of acid concentration the *q* values slightly increase. For the "silicate glass" lining the increase of HA and phosphoric acid concentrations have not significant effect on the adhesion properties of the composition. For the "ceramics with glossy surface" lining the increase of phosphoric acid concentration and HA content leads to the *q* value increase. The same dependence is observed for the "bone" lining. For the "ceramics with untreated surface" lining we observe the contact angle value increase at HA content of 1 %. Further increase of H_3PO_4 and HA content of 2.5 % decreases the contact angle. At HA concentration of 5 % the *q* values increase.

Fig. 9 represents the results obtained at constant concentration of H_3PO_4 equal to 0.3 %. With the increase of PVP and HA content the contact angle value increases for the "ceramics with glossy surface" lining. For the "steel plate" lining the character of the curve is changed although the *q* values are not significantly affected. The *q* values for the "silicate glass" lining are changed inversely. For the rest of the linings the contact angle value reduces.

Similar studies concerning the adhesive ability were conducted for the compositions with H_3PO_4 concentration of 1 %. Here the increase in HA content increases the contact angle only for "organic glass" and "silicate glass" linings. In the case of "ceramics with glossy surface" lining the composition adhesive ability was not substantially changed. For other linings slightly smaller values of the contact angle were observed.

Similar studies concerning the influence of HA and PVP concentration on contact angle value for the HEMA: PVP compositions with lecithin were conducted.

The results indicate that the constant content of PVP and the increase in HA and lecithin contents has not significant effect on the adhesive ability of compositions for ceramic and "bone" linings. However, for the "organic glass" lining for HA concentration of 2.5 % the character of dependence was changed conversely. At PVP content of 1 % the increase of lecithin concentration for the "steel plate" lining slightly increases the contact angle, but further increase of lecithin and HA contents causes the decrease of contact angle values. For "organic glass", "silicate glass" and "bone" linings it is observed that with increasing of HA and lecithin concentrations the contact angle value reduces. For the "pottery with a glossy surface" lining the concentrations of HA and lecithin not significantly affect the adhesive ability value. For the "ceramics with untreated surface" lining the increase of HA content reduces the adhesion ability. For the studied compositions with 2 % of PVP the increase of HA and lecithin concentrations have slight effect on the adhesion ability.

Thus, the lecithin-containing compositions are characterized by good adhesion ability due to its nature, namely surface activity on the interface.

The effect of PVP and HA concentrations on the adhesive strength of glue line of 2-hydroxyethyl-methacrylate and polyvinylpyrrolidone compositions was studied according to the method [13]. The results are presented in Fig. 13.

As one can see (Fig. 13), the composition with isopropyl alcohol concentration of 0.3 % significantly improves the adhesive strength values, even with the increase of HA content and PVP concentrations. The increase of isopropyl alcohol concentration to 1 % increases the adhesive strength at PVP and HA maximum content of 2 and 5 %, respectively.

Fig. 14 shows the results of strength adhesive investigations for the compositions with phosphoric acid. Phosphoric acid concentration of 0.3 and 1 % and PVP content increase provide the improved adhesion properties. The highest values of the adhesive strength has HEMA:PVP composition with 1 % of HA and 1 % of H_3PO_4. The increase of HA does not lead to higher values of adhesion strength.

For the compositions with lecithin, at 2.5 % of HA and rise of PVP content (Fig. 15), the increase of lecithin content from 0.3 to 1 % improves adhesion properties. The increase of PVP content by more than 1 % improves adhesion ability for the following compositions: 1 % of HA and 0.3 % of lecithin; 5 % of HA and 1 % of lecithin.

Thus, the highest values of the adhesive strength have the compositions with isopropyl alcohol, and the lowest ones – the compositions with lecithin. So, the nature of additives has a significant effect on the adhesion properties of the compositions.

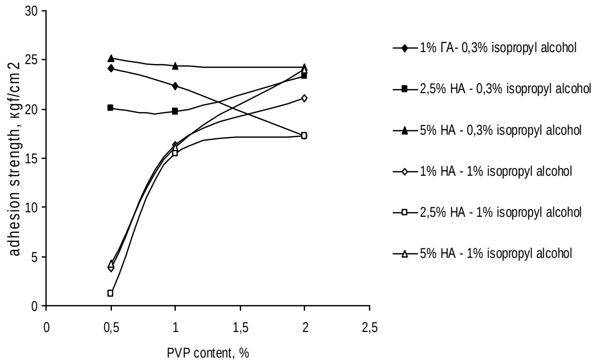

Fig. 13. Dependence of the adhesion strength on PVP and HA content for the compositions with isopropyl alcohol

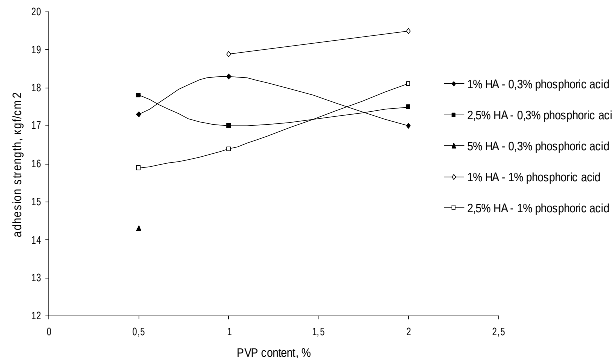

Fig. 14. Dependence of adhesion strength on PVP and HA content for the compositions with phosphoric acid

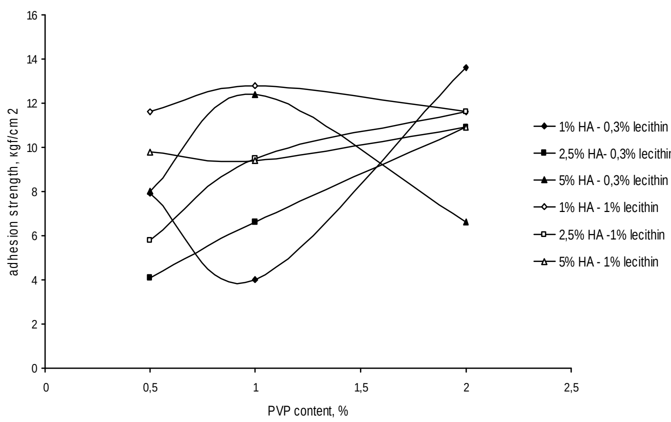

Fig. 15. Dependence of the adhesive strength on PVP and HA content for the compositions with lecithin

4. Conclusions

The influence of different structure additives on the adhesive strength of glue line for the compositions based on polyvinylpyrrolidone has been studied. The increase of PVP content in HEMA increases the adhesive strength for all additives.

The increase of phosphoric acid and HA concentrations in the compositions improved the adhesive ability for "steel plate", "ceramics with glossy surface" and "bone" linings. The maximum adhesive strength was found to be for HEMA:PVP composition (1 % of HA and 1 % of H_3PO_4).

The highest value of adhesive strength was found for the HEMA:PVP composition with isopropyl alcohol content of 0.3 % and HA of 5 %.

In the case of lecithin, the highest strength properties showed the composition with low-molecular additive and mineral filler of 1 %.

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ВПЛИВ ГІДРОКСИАПАТИТУ НА МІЦНІСТЬ КЛЕЙОВОГО ШВА КОМПОЗИЦІЙ З ПОЛІВІНІДПІРОЛІДОНОМ

Анотація. *Встановлено вплив природи та кількості мінерального наповнювача на адгезивну здатність композиційних матеріалів на основі 2-гідроксиетилметакрилату та полівінілпіролідону, модифікованих низькомолекулярними додатками. Досліджено вплив гідроксиапатиту на значення адгезійної міцності клейового шва композиційних матеріалів.*

Ключові слова: *полівінілпіролідон, гідроксиапатит, адгезійна міцність, клейовий шов, низькомолекулярні додатки.*