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POLYMER-POLYMER COMPLEX AT THE INTERFACE OF POLYMETHYLMETACRYLATE WITH HYDROXYAPATITE

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Chemical modification of HA with PAA and PVP solutions prior to PMMA/HA composite synthesis gave rise to a significant improvement of the bending and impact strength as well as a hardness and emollescence temperature of the final product. Polymer-polymer complexes, formed as a result of chemical interaction of non-reacted (with HA calcium ions) carboxyl group of PAA with PVP at the interface of HA with PMMA, play a key role in this improvement. Using IR spectroscopy and X-ray photoelectron spectroscopy, it was shown that all components of PMMA/HA composite can be linked together either by ionic bonds or by hydrogen bonding. This significantly enhances the mechanical properties of such bioactive polymer systems, and their functionality as an implant material.

Keywords: Polymethylmetacrylate, polymer-polymer complex, hydroxyapatite, biocompatibility

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INTRODUCTION

Development of new polymers and mineral-polymer composites for bone repair and replacement as well as for guided bone tissue regeneration in orthopedics and maxillofacial surgery is one of the most rapidly growing fields of modern biomaterial science and technology. During the last decade, hydroxyapatite- and tricalcium phosphate based polymer composites have been considered as the most attractive and promising materials, both from the biomechanical and biomedical points of view [1, 2]. Hydroxyapatite (HA)-[Ca₁₀(PO₄)₆(OH)₂] is the main mineral content of the natural bone. In combination with the collagen fibers, it forms the porous framework providing strength, which allows bones to flex under stress. Moreover, as a source of calcium, HA takes part in the biochemical cycle of bone tissue regeneration. That is why introduction of HA into the structure of synthetic implant materials can be considered as a natural method to enhance its osteoinduction and osteointegration ability. A combination of modern biotechnologies and technologies of polymer synthesis enables us to create a biostable and biodegradable mineral-polymer porous matrix containing all necessary bone-forming cells (osteoclasts, osteoblasts, fibroblasts, etc.), morphogenetic proteins and enzymes that initiate and control both the processes of new bone tissue formation and polymer degradation or/and resorption. However, the problem of biocompatibility and bioactivity enhancement of these materials combined with the lack of mechanical strength required for load-bearing implants has not yet been solved.

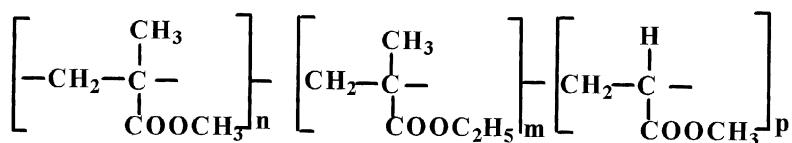
Acrylic polymers, and polymethylmethacrylate (PMMA) in particular, is one of the most widely used polymer matrices for biomedical applications in dentistry, maxillofacial surgery and orthopedics [3, 4]. The enhancement of their biocompatibility as well as biomechanical characteristics by HA reinforcement is a general trend in modern biomaterial research. However, introduction of significant amount of dispersed inorganic filler in thermoplastic polymers leads to a dramatic decrease of the composite impact and tensile strength and their ductility. Several approaches have been used in different research groups to solve this problem by chemical modification of HA particles targeted to adhesion increase of hydroxyapatite surface to the polymer matrix [5–7]. It was shown that co-ordination bonding followed by mechanical properties enhancement of such composites can be achieved by HA modification with acrylic acids [6].

In this paper, we present the results of our study of HA powder treatment with polyacrylic acid and polymer complex (polyacrylic acid/polyvinylpyrrolidone) prior to PMMA/HA matrix synthesis and

the effect of this treatment on the physical-mechanical properties of the final composite material.

MATERIALS AND METHODS

Polymer-monomer mixture ("powder-liquor of hot solidification") for PMMA synthesis was obtained from commercial sources. Copolymers of methylmethacrylate (MMA) (89%), ethylmethacrylate (EMA) (8%), and methylacrylate (MA) (2%)



plasticized with 1% dibutylphosphate were used as a "powder." Mixture of MMA and EMA inhibited by hydroquinone was a "liquor."

Synthetic hydroxyapatite powder ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) with a mean particle size $\sim 1 \mu\text{m}$ was obtained from "Polystom Ltd." (Moscow, Russia). Polyacrylic acid (PAA)- $[\text{-CH}_2\text{-CH}(\text{COOH})\text{-}]_n$ with molecular mass M_w ranged from 2000 to 450000 and polyvinylpyrrolidone (PVP) were obtained from Aldrich and used as modifiers.

There were two methods of PMMA/HA composite sample preparation: mold casting and compression molding. Gypsum molds were made up using standard cylindrical (7 mm in diameter, 6 mm high) and cubic-shaped ($20 \times 6 \times 2$ mm) wax samples. These molds were then filled with mixture consists of powder (copolymers), liquor (mixture of MMA and EMA monomers) and filler (HA powder). Modification of HA particles was performed either by mixing with PAA and PVP in dry and moisturised phases using "drunk barrel" type mixer or by mixing all components in a mortar with ethanol or chloroform. Polymerization was performed in water bath during one hour at 100°C . In compression molding, steel molds were loaded with initial mixture (see above) under pressure of 24 MPa followed by heating up to 180°C for 30 min. and left then to cool down to room temperature.

Mechanical testing of the samples was performed with modified "Dinstat" type pendular unit (bending and impact strength) and homemade systems for measurement of thermoelastic deformations under pressure. Infrared spectroscopy and X-ray photoelectron spectroscopy have been used to analyze the chemical modification of HA powder after treatment and its interface with the polymer matrix.

RESULTS AND DISCUSSION

The effect of HA treatment with PAA on impact and bending strength of PMMA/HA composites as well as their hardness and emollescence temperature is presented in Table 1.

Noticeable changes of all parameters mentioned above indicate positive influence of HA powder modification with polyacrylic acid and can be explained by possible transformation of the composite chemical structure. To verify this assumption and to understand the details of the process, thermomechanical properties of initial and modified compositions have been evaluated. The experimental results of this study are shown in Fig. 1.

The behaviour of thermomechanical curves demonstrates the formation of rather more thermostable complex with preserved thermoplastic properties as compared with the initial (non-modified) composite. It is interesting to note that PAA emollescence temperature (60–100°C) is lower than for PMMA/HA alone (as it comes from Fig. 1). However, incorporation of PAA into the composite structure leads to increasing but not by decreasing of its emollescence temperatures about 15–20°C.

IR spectra of pure HA and PAA, calcium salt of PAA (CSPAA) and HA samples treated by 2 wt.% of polyacrylic acid (HA + PAA) are presented in Fig. 2. For HA + PAA there is a peak in 1550 cm⁻¹ region, which corresponds to the calcium-carboxyl group bond (1560 cm⁻¹) in CSPAA and which is absent in IR spectra of pure PAA and HA. It means that treatment of HA by PAA in ethanol (or chloroform) solution leads to interaction of carboxyl groups of PAA with calcium ions at HA surface and formation of the salt-like bonding.

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TABLE 1 Physical-Mechanical Properties of PMMA/HA Composites with Pure and PAA Modified HA

No	Composition	Impact Strength A (kJ/m ²)	Bending strength σ (MPa)	Hardness H (MPa)	Emollescence Temperature (°C)
1.	PMMA/HA	2,7	51,0	14	180
2.	PMMA/(HA + PAA)	3,1	61,0	16	200

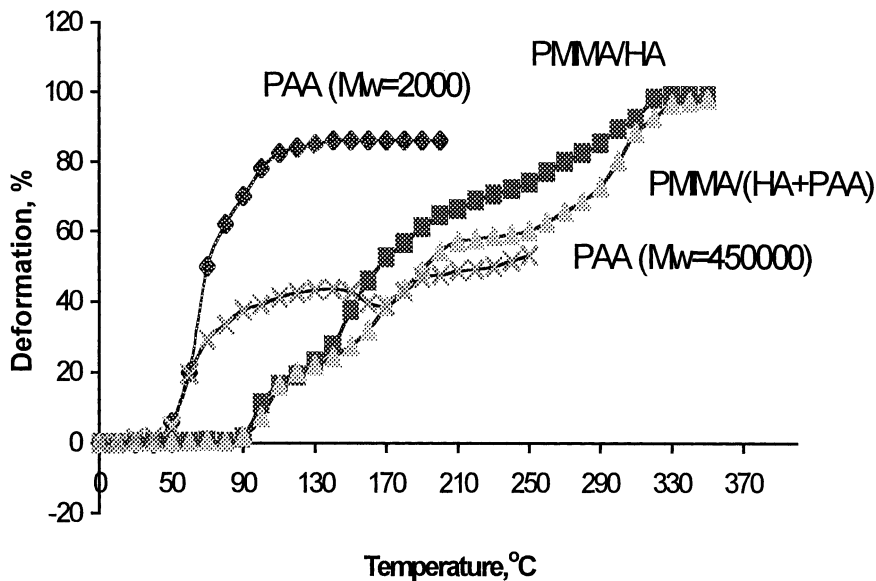


FIGURE 1 Thermomechanical curves of pure PAA ($M_w = 2000$ and 450000), PMMA/HA, and PMMA/(HA + PAA) (samples treated by 2 wt.% of polyacrylic acid).

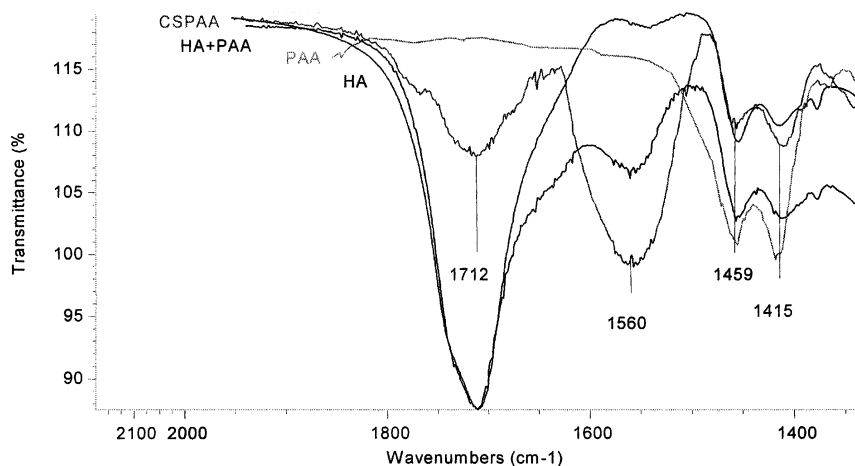


FIGURE 2 IR spectra of pure HA and PAA, calcium salt of PAA (CSPAA), and HA samples treated by 2 wt.% of polyacrylic acid (HA + PAA).

TABLE 2 Element Content on PMMA/HA and PMMA/(HA + PAA) Surface Before and After Boiling

Elements	PMMA/HA				PMMA/(HA + PAA)			
	Initial (%)		After boiling (%)		Initial (%)		After boiling (%)	
C _{1S}	65.1	63	72.5	74	74.2	78	69.8	62
CO		17		12		11		20
CO ₂		20		14		11		18
O	31.9		25.7		23.7		27.8	
Ca _{2P}	2.5		1.1		1.8		1.4	
P _{2P}	0.5		0.7		0.3		1.0	

To analyze the effect of this process on the structure transformation of the composite surface before and after boiling (sterilization), X-ray photoelectron spectroscopy has been used. The results of these measurements are presented in Table 2.

According to these data PMMA/HA samples possess quite high hydrolytic resistance. The amount of carbon oxidation products (CO, CO₂) on the composite surface after boiling did not increase but decreased from 37% (17%CO + 20%CO₂) to 26%, as well as, the amount of oxygen (from 31,9% to 25,7%). As for PMMA/(HA + PAA) samples, the amount of oxidized carbon on the surface after boiling decreased significantly (from 37% to 22%). It reflects lyophobic properties of the composite surface with modified HA due to interaction of carboxyl groups of PAA with calcium ions of HA and formation of less polar surface.

In X-ray photoelectron spectrum (Fig. 3) the peak in the region 290 eV, corresponding to CO groups, noticeably grows after boiling. However, PMMA/(HA + PAA) composite surface was hydrolytically unstable (see Table 2). At the same time, the amount of oxidized carbon (CO, CO₂) has increased remarkably (from 22% to 38%). It can be explained by the fact that PAA carboxylic groups (non-reacted with HA surfaces during the treatment) are capable, in principle, to modify PAA macromolecule configuration by hydrogen bonding in boiling water environment. Thus, only a part of PAA carboxyl groups was involved in salt-like bond formation with HA, and the rest were present at PAA/HA interface in non-bonded state.

There are stable polymer-polymer systems that can be formed by reaction of acrylic acids with polyvinylpyrrolidone (PVP) and other N-vinyl-amides in aqueous solution [8]. We applied this method to immobilize unreacted PAA carboxyl groups on HA surface. There were

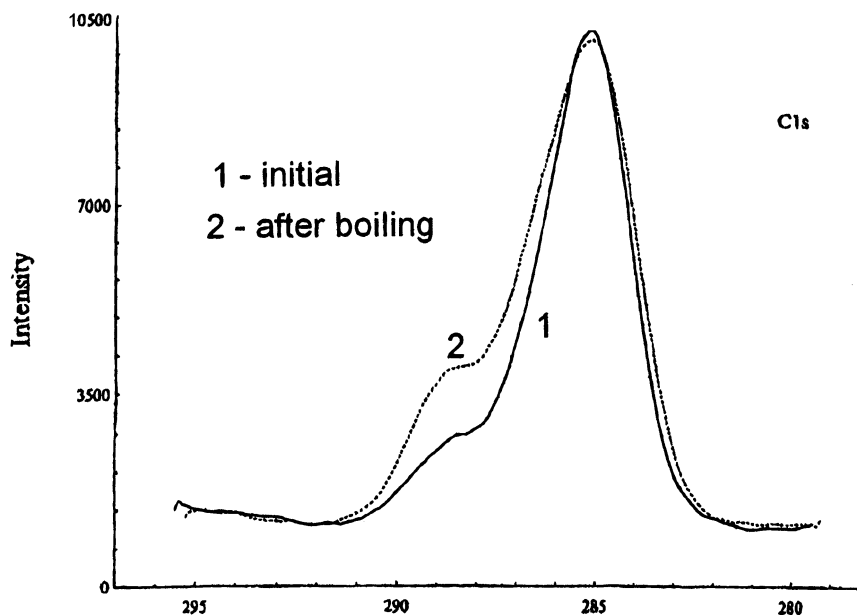


FIGURE 3 Chemical state of oxygen on the surface of modified PAK filled by PMMA (PMMA-70% + HAP-30%).

two ways of HA powder modification with PAA and PVP (molar ratio = 1:1) in aqueous solution: A one-step treatment (PAA and PVP solutions were mixed together with HA at the same time), and a two-step process (HA was mixed first with PAA solution and then PVP solution was added to the mixture). High molecular weight PAA ($M_w = 450000$) and PVP with $M_w = 12600$ and $M_w = 300600$ have been used. The results of these experiments are presented in Table 3.

TABLE 3 Element Content on PMMA/(HA + PAA + PVP) Surface in Dependence on PVP Molecular Weight and Experimental Procedure

Elements (%)	One step treatment		Two step process	
	PVP _{Mw=12600}	PVP _{Mw=300600}	PVP _{Mw=12600}	PVP _{Mw=300600}
C _{1s}	44.8	42.3	51.6	43.1
O _{1s}	31.3	35.8	29.8	34.4
Ca _{2p}	12.3	11.4	9.2	10.7
P _{2p}	10.8	9.8	8.2	9.7
N _{1s}	0.8	0.7	1.2	2.1

According to the data in Table 3 the percentage of nitrogen sorbed on HA surface relies more on the modification method rather than PVP molecular weight one step Treatment leads to the amount of sorbed nitrogen 1.5–2 times higher then after the two step process. Moreover, the amount of nitrogen is almost independent of M_w of PVP in the two step case. This can be explained by the fact that after the first step (mixing HA with aqueous solution of PAA) of the two step process, unreacted carboxyl group concentration at HA surface must be less (about 50%, according to spectroscopic data in Fig. 2) than in the initial mixture of HA with PAA and PVP solutions to one step treatment followed by polymer-polymer system formation.

The percentage of nitrogen sorbed on HA surface strongly depends on PVP molecular weight for one step treatment. It changed from 1,2% ($M_w = 12600$) to 2,1% ($M_w = 300600$) compared with the two step process—from 0,8% to 0,7% correspondingly. This is possibly because the polymer-polymer system formation in aqueous solution might be more effective for complementary polymers with high molecular masses rather than with the low ones [9].

In accordance with the experimental results, the two step process automatically optimizes the amount of PVP interacting with non-reacted carboxyl groups of PAA, regardless of PAA and PVP molar ratio (1:1 for our study) in the initial solution. The excess PVP can be simply removed from the surface during the boiling procedure.

Table 4 presents the results of mechanical testing of PMMA/HA(30 wt%) composites with HA modified by various methods.

TABLE 4 Physical-Mechanical Properties of PMMA Composites with Modified HA Fillers

No	Composite	Bending strength σ (MPa)	Bending strength (after boiling) σ (MPa)	Bending angle \angle (grad)	Impact strength A (kJ/M ²)
1	PMMA	90	88	29	10
		84	95	27	
2	PMMA/HA	48	45	19	2,9
		44	40	17	
3	PMMA/HA + PAA	57	48	22	3,5
		53	46	20	
4	PMMA/HA (PAA + PVP ₁₂₆₀₀ = 1:1)	58	51	22	
		56	47	20	
5	PMMA/HA (PAA + PVP ₁₂₆₀₀ = 1:0,5)	61	55	22	3,6
		64	52	22	

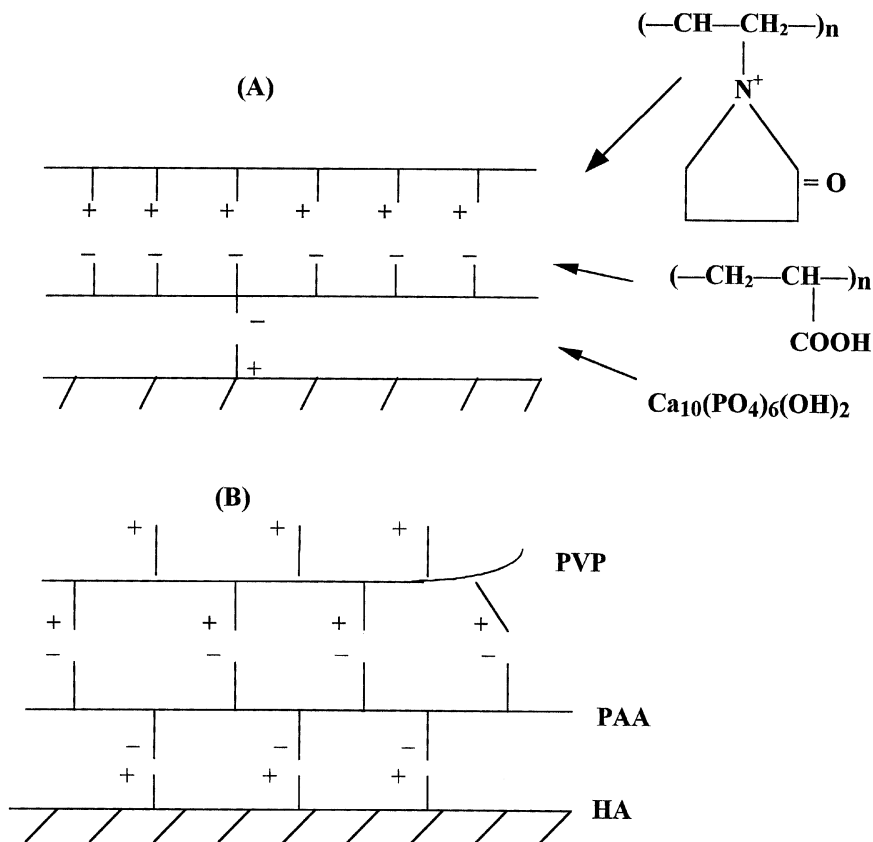


FIGURE 4 Schematic diagram of HA, PAA, and PVP interaction in (a) "at one stage" and (b) "two stage" processes.

It is clear from the data listed in Table IV that the use of HA modified by PAA and PVP leads to the enhancement of physical-mechanical properties of PMMA/HA composites compared with the use of non-modified HA. PAA-PVP polymer-polymer complex formed at the interface between PMMA matrix and HA surface has a crucial importance for this enhancement. At the first stage of modification HA by polyacrylic acid, only a part of functional carboxyl groups were sorbed on HA surface, forming a salt-like bonding with calcium ions. The rest of non-reacted carboxyl groups preserved their activity. At the second stage of modification these groups interacted with PVP, followed by polymer-polymer complex formation. Both ionic interaction [8] and hydrogen bonding [9] are responsible for the stability of the final polymer-mineral interface. (Fig. 4).

Besides interaction with PAA, PVP is capable of forming hydrogen bonding with PMMA matrix. Thus, all components of PMMA/HA composite can be chemically linked together.

CONCLUSIONS

Chemical modification of HA with PAA and PVP solutions prior to PMMA/HA composite synthesis gave rise to a significant improvement of the bending and impact strength as well as a hardness and emollescence temperature of the final product. Polymer-polymer complexes formed as a result of chemical interaction of non-reacted (with HA calcium ions) carboxyl group of PAA with PVP at the interface of HA with PMMA play a key role in this improvement. Using IR spectroscopy and X-ray photoelectron spectroscopy it was shown that all components of the PMMA/HA composite can be linked together either by ionic bonds or by hydrogen bonding. This significantly enhances the mechanical properties of such bioactive polymer systems and their functionality as an implant material.

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