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GRAFT POLYMERIZATION OF PMMA FROM SILICA SURFACE AND APPLICATION OF THIS METHOD TO THE IMPROVEMENT OF MECHANICAL PROPERTIES OF PMMA BONE CEMENT

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INTRODUCTION: Synthesis of polymer "brushes" on a solid substrate is an effective way for the control of surface properties which may have important application in medicine and biomaterials production[1].

METHODS: Recently we have synthesized oligomers with a variations in polarity and functionality moieties which could be effectively used for the modification of various inorganic as well as organic (polymeric) surfaces via two-stage process[2].

At the 1st stage, the oligomers are easily adsorbed on the various substrate surfaces due to discrepancy in polarity and reactivity groups present in oligomer macromolecules. This allows to immobilize the functional groups on the modified surface which are able to initiate the "grafting from" polymerization. At the 2nd stage, the immobilized macromolecules of oligomer, containing the peroxide groups, could serve as an initiator of radical polymerization at the elevated temperatures. Using N,N-dimethyl-p-toluidine as a catalyst of peroxide initiation permits grafting of the polymer layer at the reduced and even room temperatures.

Two peroxide oligomers were investigated in order to synthesize polymer "brush" on the surface of silica. PMI-1 oligomer was derived from peroxide monomer and maleic anhydride while the second oligomer PMI-2 was synthesized from the first one via its interaction with (diethylamino)ethanol. Both oligomers have been firstly adsorbed on the silica surface and afterwards used for grafting of poly(methyl methacrylate) (PMMA) chains.

Samples of ultrafine silica modified with PMI were used as a filler for PMMA bone cement. Filled bone cements were examined in mechanical tests.

RESULTS: The thickness of the adsorbed peroxide oligomers as well as the grafted polymer "brushes" was distinquished by spectroscopic ellipsometry. An essential influence of the solvent nature on the adsorption of peroxide oligomer was found[3]. The amount of the oligomer adsorbed from the polar solvents was usually lower in comparison with an adsorption from the solvents with a lower polarity. At low adsorption density an island-like type of covering was formed. With an increase of the amount of adsorbed macromolecules the morphology turns into the like-wise type. Presumably, it occurs in the range from 0.8 mg/m^2 to 1.4 mg/m^2. Interesting, that higher grafting density of PMMA "brushes" was nevertheless in both cases obtained for PMI-2 modified surface. The morphology of the grafted polymer layers was investigated by atomic force microscopy and the expected mechanism of PMMA "brushes" grafting has been proposed.

CONCLUSIONS: Using of two various peroxide oligomers immobilized on the SiO_2 surface as an initiators of polymerization allows us to synthesize PMMA "brushes" with a various thickness and density. Using of SiO_2 as a filler leads to an increase of the compressive strength and Young's Modulus, but sufficiently reduces the bending strength of the PMMA bone cements. Modification of the silica filler with PMI oligomers increases the bending strength of the bone cements up to 15% in comparison to unmodified one.

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