SUMMARY OF DOCTORAL DISERTATION

Modifications of dimethacrylate copolymers with compounds containing quaternary ammonium groups to obtain novel antibacterial dental composite adhesives

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The doctoral dissertation aimed to physically and chemically modify dimethacrylate copolymers, used as dental composite adhesives, to give them antibacterial activity without compromising their utility properties. These modifications were carried out using compounds containing quaternary ammonium groups.

The **physical modification** involved the dispersion of 0.5, 1, and 2 wt.% of bioactive quaternary ammonium polyethyleneimine nanoparticles (QA-PEI NP) in a 60 wt.% bisphenol A glycerolate dimethacrylate (Bis-GMA) and 40 wt.% triethylene glycol dimethacrylate (TEGDMA) monomer compositions and their subsequent polymerization. The study aimed to supplement the knowledge about the influence of QA-PEI NP on the physical and mechanical properties of dimethacrylate copolymers enriched with them. The obtained copolymers containing QA-PEI NP were tested for physicochemical and mechanical properties. They were characterized by a high degree of conversion (*DC*), low polymerization shrinkage (S_e), and high glass transition temperature (Tg_p). However, the introduction of QA-PEI NP into the copolymer caused an increase in water sorption (*WS*) and water solubility (*SL*) and the deterioration of most of the tested mechanical properties. Flexural strength and modulus decreased while hardness increased.

Taking into account the results of the physicomechanical testing of copolymers enriched with QA-PEI NP and the literature data on the antibacterial activity of dimethacrylate materials modified with the same amount of QA-PEI NP, it can be concluded that the system containing 1 wt.% QA-PEI NP revealed an optimal combination of physicomechanical and biological properties.

The **chemical modification** involved the copolymerization of a series of six newly obtained urethane-dimethacrylate monomers containing two quaternary ammonium groups (QAUDMA-m, where m corresponds the number of carbon atoms in the N-alkyl substituent) with dental dimethacrylates. The characterization of the physicochemical properties of the QAUDMA-m monomers carried showed that they are suitable for use as components of dental composite adhesives. Therefore, they were subjected to copolymerization with dental dimethacrylates. First, a 60 wt.% Bis-GMA and 40 wt.% TEGDMA copolymer was modified by a total replacement of Bis-GMA with QAUMDA-m. The obtained series of six QAm:TEG (where m corresponds the number of carbon atoms in the N-alkyl substituent in QAUDMA-m) copolymers had high antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* strains, high *DC*, low S_e, and high Tg_p. However, their *WS* and *SL* values were several times higher than those recommended for dental composite adhesives. On the other hand, their mechanical properties were insufficient. It suggested that QAm:TEGs had a chemical composition unsuitable for dental applications, but QAUDMA-m monomers may be used as highly active antibacterial components of dimethacrylates copolymers. For this reason, studies on copolymers with a reduced concentration of QAUDMA-m were carried out. The copolymer of 40 wt.% Bis-GMA, 40 wt.% urethane-dimethacrylate (UDMA), and 20 wt.% TEGDMA (BG:UD:TEG) was modified by the total replacement of UDMA with QAUDMA-m (BG:QAm:TEG, where m corresponds the number of carbon atoms in the N-alkyl substituent in QAUDMA-m). BG:QAm:TEGs had high antibacterial activity against *S. aureus* and *E. coli* strains, high antifungal activity against *Candida albicans*, high *DC*, low S_e, high Tg_p, low *WS* and *SL* (except for BG:QA8:TEG and BG:QA10:TEG), and appropriate mechanical properties. The studies also showed that the BG:QAm:TEGs had no cytotoxic effect on the L929 mouse fibroblast cells.

The analysis of all tested properties showed that the BG:QA12: TEG copolymer can be recognized as the most suitable potential dental composite adhesive. It was characterized by satisfying physical and mechanical properties, high microbiological activity, and no cytotoxic effect.

The research carried out within the framework of the doctoral dissertation has shown that compounds containing quaternary ammonium groups can be utilized as physical and chemical modifiers of dimethacrylate copolymers to provide them with high microbiological activity while maintaining appropriate functional properties.