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Antifouling Multifunctional Dental Material:” Zwitterionic”- A Scoping Review.

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ABSTRACT

Microorganisms often colonize dental biomaterials, which remains a major problem in restorative dentistry, orthodontics, prosthodontics, implant dentistry, and regenerative dental treatments. Traditional antibacterial methods mostly use agents that kill or inhibit bacteria, but these can have drawbacks such as short-lasting effects, toxicity, changes in material strength, and the risk of bacteria becoming resistant. Zwitterionic methacrylates are a new class of functional monomers and polymers that take a different approach, focusing on antifouling properties. These materials have both positive and negative charges in the same molecule and can hold a lot of water. This hydration layer helps prevent proteins from sticking and stops bacteria from attaching, which disrupts the early stages of biofilm formation. The most studied zwitterionic methacrylates include 2-methacryloyloxyethyl phosphorylcholine (MPC), sulfobetaine methacrylate (SBMA), and carboxybetaine methacrylate (CBMA). Researchers have tested these materials in resin composites, adhesives, orthodontic glues, denture bases, 3D printing resins, fluoride varnishes, and coatings for implants. Studies show they can repel proteins, reduce biofilm formation, and remain biocompatible while maintaining the necessary mechanical properties when formulated correctly. However, challenges remain, including increased water absorption, potential weakening of the material, effects of the curing process, and a lack of long-term clinical data. In the future, zwitterionic methacrylates may be used in materials that combine antifouling with antibacterial, remineralizing, regenerative, and tissue-integrating features. This review covers their chemistry, how they work, properties, dental uses, benefits, drawbacks, comparisons, and future directions, highlighting their potential in creating the next generation of dental materials that resist biofilm.

Keywords: Zwitterionics; 2-methacryloyloxyethyl phosphorylcholine (MPC), Sulfobetaine methacrylate (SBMA); Carboxybetaine methacrylate (CBMA); Antifouling materials.

Introduction

Microbial adhesion and biofilm formation on dental biomaterials are major biological challenges in dentistry. Materials such as restoratives, orthodontic adhesives, denture bases, implants, and provisional restorations are constantly exposed to saliva, proteins, microbes, food, and mechanical stress. Once placed in the mouth, these materials quickly become coated with salivary proteins and glycoproteins. This coating, called the acquired pellicle, gives microorganisms places to attach and helps complex biofilms form. When biofilm accumulates around dental materials, it can lead to complications such as secondary cavities, white spot lesions during orthodontic treatment, denture stomatitis, peri-implant mucositis, peri-implantitis, and failure of restorations or prosthetics.

Traditional methods for controlling dental biofilms typically involve antibacterial nanoparticles, antibiotics, chlorhexidine, and other antimicrobials. While these methods can work, they also raise concerns about toxicity, leaching, reduced material strength, shorter lifespan, and microbial resistance. A new idea has emerged: preventing microorganisms from attaching to biomaterial surfaces from the start. Zwitterionic polymers are especially promising for this. Unlike traditional antimicrobial materials that only work after bacteria make contact, zwitterionic materials are ionically water-loving surfaces that bond with water and form a hydration layer. This layer acts as a barrier, stopping proteins and microbes from sticking.

Among the zwitterionic materials studied for dental use, 2-methacryloyloxyethyl phosphorylcholine (MPC) has attracted considerable interest. Other key materials are Sulfobetaine methacrylate (SBMA) and Carboxybetaine methacrylate (CBMA). The development of these materials represents a conceptual transition from conventional "bacteria-killing" dental materials toward "biofilm-resistant" materials. Developing these materials marks a shift from traditional 'bacteria-killing' dental materials to 'biofilm-resistant' or 'bacteria-repellent' biomaterials.

Definition and Chemistry

Zwitterions used in dentistry are amphiphilic monomers. These include an ethacrylic or methacrylic polymerizable backbone and a side chain with equal numbers of positive (cationic) and negative (anionic) groups at physiological pH (pH 7.2–7.4).

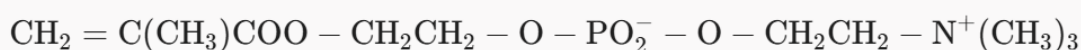
The three main types of zwitterions are Phosphobetaines (MPC), Sulfobetaines (SBMA), and Carboxybetaines (CBMA). They all have a similar polymerizable head, but their side-chain ionic chemistry is different.

Types of Monomer Composition

1. 2-Methacryloyloxyethyl Phosphorylcholine (MPC) — *Phosphobetaine Class*

MPC mimics the hydrophilic headgroup of **phosphatidylcholine**, the naturally occurring phospholipid that forms human cell membranes.

- **Chemical Formula:** $C_{11}H_{22}NO_6P$
- **Molecular Weight:** 295.27 g/mol
- **Chemical Structure:**



MPC has a methacryloyl-polymerizable group connected to a phosphorylcholine group via an ethylene spacer. The phosphorylcholine part includes:

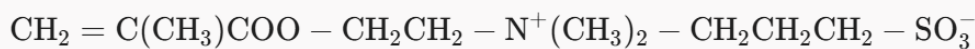
* a quaternary ammonium group with a positive charge; * a phosphate group with a negative charge; and * a very hydrophilic ionic environment.

After polymerization, MPC becomes poly(2-methacryloyloxyethyl phosphorylcholine), or PMPC. The phosphorylcholine structure is similar to the polar head group of phospholipids found in cell membranes, which helps it stay hydrated and biocompatible.

2. Sulfobetaine Methacrylate (SBMA) — *Sulfobetaine Class*

SBMA is a synthetic zwitterion featuring an inorganic sulfonate terminal group. It is widely used for titanium implant surface grafting due to its thermal and chemical stability.

- **Chemical Formula:** $C_{11}H_{21}NO_5S$ (specifically 2-(Methacryloyloxy)ethyl dimethyl-(3-sulfopropyl)ammonium hydroxide)
- **Molecular Weight:** 279.35 g/mol
- **Chemical Structure:**



SBMA includes:

* a methacrylate group that can be polymerized; * a quaternary ammonium group; and * a sulfonate group. When SBMA is polymerized, it forms poly(sulfobetaine methacrylate), also called SBMA. Materials made from SBMA remain well hydrated and strongly resist attachment by unwanted proteins and microbes.

3. Carboxybetaine Methacrylate (CBMA) — *Carboxybetaine Class*

CBMA incorporates an organic carboxylate terminal group that mimics amino acid betaines (e.g., glycine betaine).

- **Chemical Formula:** $C_{10}H_{17}NO_4$ (e.g., 2-(Methacryloyloxy)ethyl dimethyl-(carboxymethyl)ammonium inner salt)
- **Molecular Weight:** 215.25 g/mol
- **Chemical Structure:**



CBMA has both a quaternary ammonium group and a carboxylate group. Poly(carboxybetaine methacrylate) is highly hydrated, protein-resistant, and suitable for biological functionalization. Zwitterionic methacrylates also have a methacrylate group, so they can join in free-radical polymerization and become part of dental resin systems.

Mechanism of Antifouling Action

Mechanism of action:

The hydration shell concept explains how zwitterionic groups interact strongly with water. A dense layer of water molecules forms around the zwitterionic surface, creating a highly hydrated interface. As a result, several effects follow. A zwitterionic surface binds water strongly, forming a hydration layer. This layer makes it hard for proteins to approach or displace water, thereby reducing protein adsorption. With fewer places for bacteria to stick, less biofilm forms. This effect is known as antifouling or biofouling resistance. It is important to note that zwitterionic materials usually resist biofilm formation rather than directly killing bacteria.

This difference matters when designing dental materials. Recent reviews describe zwitterionic polymers such as PMPC and poly(CBMA) primarily as biofilm-resistant materials. They prevent microbes from sticking by using hydration-based antifouling. The main biological feature of zwitterionic methacrylates is their ability to form a highly hydrated surface. When these surfaces are in water, the charged groups attract water molecules, creating a tightly bound hydration layer.

This process can be summed up as follows:

A zwitterionic surface interacts strongly with water, forming a stable hydration layer. This leads to less protein sticking, less bacterial attachment, and less biofilm formation. This mechanism is very different from how traditional antibacterial materials work. Bactericidal materials aim to kill microorganisms after they reach the surface, while zwitterionic materials try to stop them from attaching in the first place. In summary, the conventional antibacterial approach involves bacteria attaching to a surface and then being killed.

In contrast, the zwitterionic approach uses a hydrated surface to reduce protein adsorption, which lowers bacterial adhesion and biofilm formation. This antifouling effect makes zwitterionic polymers especially useful in biomedical and dental fields.

Major Properties of Zwitterionic Methacrylates

1 High Hydrophilicity

Zwitterionic polymers can strongly bind water and typically exhibit very low water contact angles. This feature is key to how they prevent fouling.

2 Protein Repellency

The strong surface layer of water makes it hard for many proteins to push water molecules away. As a result, unwanted protein adsorption is greatly reduced.

3 Bacterial Anti-Adhesion

Bacteria often stick to surfaces by attaching to proteins or through direct contact. Lowering protein adsorption can also lower how much bacteria attach.

4 Biofilm Resistance

When fewer microbes initially stick, it becomes harder for complex biofilms to form.

5 Biocompatibility

Zwitterionic chemistry is often suitable for biological surfaces, but biocompatibility still depends on factors such as monomer concentration, polymer synthesis, and the presence of other ingredients.

6 Polymerizability

The methacrylate group allows these polymers to mix with standard dental monomers. This makes zwitterionic methacrylates especially useful in dental resin systems.

Applications in Dentistry

Restorative Dentistry

Zwitterionic methacrylates have strong potential for use in dental composites. Secondary caries often forms where the tooth meets the restoration, as plaque and bacteria can cause repeated demineralization. Resin composites with MPC have shown:

- * reduced protein adsorption;
- * reduced bacterial adhesion;
- * reduced biofilm formation; and
- * promising antibacterial and antibiofilm behavior.

MPC can also be mixed with standard antibacterial monomers. For example, combining MPC with dimethylaminododecyl methacrylate (DMAHDM) creates a complementary approach:

MPC → bacterial repulsion

DMAHDM → bacterial killing

This leads to the idea of dental materials that both repel and kill bacteria.

Endodontic Applications

In endodontics, possible uses include:

- * root canal sealers;
- * obturation materials;
- * intracanal coatings;
- * regenerative endodontic scaffolds; and
- * antibiofilm delivery systems.

The main expected benefit is less microbial attachment and biofilm growth. However, there is much less direct clinical evidence for these uses compared to restorative and orthodontic dentistry.

Zwitterionic Dental Adhesives

Dental adhesives are another key area for these materials. The adhesive layer is exposed to saliva and bacteria, which can lead to new caries. Researchers have studied adding MPC to adhesives to achieve:

- * protein-repellent interfaces;
- * reduced bacterial adhesion;
- * reduced biofilm formation;
- * antibacterial functionality; and
- * preservation of clinically relevant bonding performance.

But making the material more hydrophilic can cause it to absorb more water, which might hurt its long-term strength. So, it is important to find the right MPC amount and polymer structure.

Orthodontic Applications

Fixed orthodontic appliances have many areas where plaque can build up. Parts like brackets, archwires, ligatures, and adhesive edges make it easier for microbes to collect, which can lead to enamel demineralization. As a result, white spot lesions are a common problem during orthodontic treatment. Studies show that orthodontic adhesives with MPC can:

- * reduced protein adsorption;
- * reduced bacterial adhesion;
- * reduced biofilm formation;
- * reduced metabolic activity of biofilms; and
- * acceptable shear bond strength in experimental investigations.

Combining zwitterionic materials with fluoride-releasing or antibacterial ingredients may improve their ability to prevent cavities.

Fluoride Varnishes

Researchers have also studied zwitterionic methacrylates in light-curable fluoride varnishes. Adding MPC, SBMA, or CBMA can offer:

- * fluoride release;
- * reduced protein adsorption;
- * reduced microbial adhesion; and
- * improved biofilm resistance.

This opens the opportunity to develop preventive materials that both help remineralize teeth and resist the buildup of unwanted substances.

Prosthodontic Applications

Denture Base Materials

Polymethyl methacrylate (PMMA) is still one of the most common materials for denture bases. However, PMMA readily accumulates oral microbes, such as *Candida albicans*, which can lead to denture-related stomatitis. To address this, researchers have tested PMMA with MPC or SBMA to reduce microbe buildup. Studies using 3D-printed denture bases containing these zwitterionic materials have shown significantly reduced bacterial adhesion and biofilm formation.

CAD/CAM and Additive Manufacturing

Digital dentistry is creating new opportunities for the use of zwitterionic biomaterials. They could be used in:

- * CAD/CAM denture bases;
- * 3D-printed denture bases;
- * temporary crowns;
- * surgical guides;
- * printable restorative resins;
- * implant prosthetic components; and
- * customized biomedical devices.

Recent studies have examined dental resins produced via additive manufacturing using MPC and found that they perform well both biologically and mechanically. The idea of a:

"Biofilm-resistant 3D-printed dental prosthesis" may therefore become an important future research direction.

Maxillofacial Prosthodontics

Zwitterionic polymers may have potential applications in:

- * obturator materials;

- * intraoral maxillofacial prostheses;
- * implant-retained prostheses;
- * silicone interfaces; and
- * prosthetic surface coatings.

The main advantage would be less microbe buildup and biofilm on these surfaces.

However, more research is needed to determine whether these materials work well with elastomers, pigments, and adhesives, and whether they can withstand long-term use in prosthetics.

Implant Dentistry

Biofilm around implants is a key cause of peri-implant mucositis and peri-implantitis. Zwitterionic polymers can be added to titanium surfaces by:

- * covalent grafting;
- * surface polymerization;
- * hydrogel coatings;
- * polymer brushes; or
- * multifunctional surface layers.

Coatings made with SBMA and MPC have been shown in experiments to reduce protein buildup and bacteria sticking to surfaces. However, implant surfaces are challenging. The best implant would have both low bacterial adhesion and good interaction with bone cells for proper integration. So, it may not be best to make the whole implant surface completely resistant to all buildup. In the future, implants might use surfaces with different functions in specific areas.

Periodontal Applications

Potential periodontal applications include:

- * drug-delivery hydrogels;
- * periodontal wound dressings;
- * antibiofilm materials;
- * regenerative scaffolds; and
- * controlled-release systems.

CBMA-based hydrogels are promising because their strength and biological effects can be adjusted by varying the polymer concentration and the degree of cross-linking. However, there is still limited clinical evidence for using zwitterionic methacrylates in periodontal treatment.

Advantages

Zwitterionic methacrylates offer several key advantages:

1. They have excellent hydrophilicity.
2. They strongly repel proteins.
3. They reduce bacterial adhesion.
4. They help prevent biofilm formation.
5. They may also have excellent biocompatibility.
6. They can copolymerize with conventional methacrylates.
7. They can potentially be used for surface modification.
8. They are compatible with additive manufacturing.
9. They can potentially be combined with antibacterial agents.

10. They may also be combined with remineralizing agents.
11. They do not rely heavily on antibiotic mechanisms.
12. When covalently incorporated, they may provide long-term antifouling activity.

Disadvantages and Limitations

Although these materials show promise, there are several important limitations to keep in mind.

1. Increased Water Sorption- The same strong hydrophilicity that helps prevent fouling can also lead to higher water absorption.
- 2 Mechanical Property Alteration- Using high amounts of zwitterionic monomers may lower:
 - * flexural strength; * elastic modulus; * hardness; and * wear resistance.
- 3 Polymerization Effects - Zwitterionic monomers can change:
 - * polymerization kinetics; * degree of conversion; * network formation; and * residual monomer content.
- 4 Antifouling Does Not Always Mean Antibacterial- Most zwitterionic materials do not directly kill bacteria. As a result, it may be necessary to combine them with antibacterial or bactericidal agents to achieve the best clinical results.
- 5 Long-Term Stability- More research is needed to understand how well these materials keep their surface chemistry and resist breakdown when exposed to saliva over time.
- 6 Complexity of the Oral Environment- Lab studies usually use simpler bacterial models.

The human oral cavity contains: * hundreds of microbial species; * salivary proteins; * dietary components; * enzymes; * immune mediators; and * continuous mechanical abrasion.

So, results from lab antifouling tests do not always predict how these materials will perform in the long run in real patients.
- 7 Limited Clinical Evidence- Most research is still at the: in-vitro → laboratory biofilm → animal → early clinical stage. There is still a need for large-scale randomized clinical trials.

Comparative Evaluation

Parameter	Conventional methacrylate	Zwitterionic methacrylate	Zwitterionic + antibacterial
Hydrophilicity	Moderate	Very high	Very high
Protein adsorption	Relatively high	Very low	Very low
Bacterial adhesion	Relatively high	Reduced	Strongly reduced
Direct bacterial killing	No	Usually no	Yes
Biofilm resistance	Limited	High	Very high
Mechanical properties	Usually favorable	Concentration dependent	Formulation dependent
Water sorption	Moderate	Potentially increased	Variable
Clinical maturity	Established	Emerging	Emerging
Primary mechanism	Structural	Antifouling	Repel + kill

The comparison demonstrates that zwitterionic methacrylates should not necessarily be regarded as replacements for conventional methacrylates. Instead, they may function as **bioactive components within multifunctional resin systems**.

Clinical Indications

At present, most indications remain investigational. Potential applications include:

Restorative dentistry

- high-carries-risk patients;

- secondary-carries prevention;
- biofilm-resistant composites;
- dental adhesives.

Orthodontics

- fixed orthodontic appliances;
- prevention of white spot lesions;
- orthodontic adhesives and cements.

Prosthodontics

- denture bases;
- CAD/CAM PMMA;
- 3D-printed dentures;
- temporary prostheses.

Implantology

- antifouling implant coatings;
- peri-implantitis prevention.

Preventive dentistry

- fluoride varnishes;
- protective surface coatings.

Regenerative dentistry

- hydrogels;
- tissue-engineering scaffolds;
- drug-delivery systems.

Future Perspectives

Future zwitterionic dental materials will probably do more than just repel proteins.

1 Repel + Kill: Mixing zwitterionic polymers with antibacterial monomers or nanoparticles could create materials with two functions.

The zwitterionic part stops things from sticking. The antibacterial part kills germs.

2 Repel + Kill + Remineralize

A future restorative material might combine the following: MPC + antibacterial monomer + fluoride + calcium phosphate/bioactive glass. This would allow the material to offer all of these benefits at once:

* protein repellency; * antibacterial activity; * remineralization; and * structural restoration.

3 Smart Implant Surfaces

In the future, implant surfaces could be designed so that each area has its own biological role.

For example: Bone-facing surface → osteogenic

Transmucosal surface → antifouling

Plaque-prone region → antibacterial

This approach might be better for biology than using the same surface across the entire implant.

4 Biofilm-Resistant 3D Printing

Combining zwitterionic chemistry with digital dentistry could make it possible to produce:

intrinsically biofilm-resistant 3D-printed dental prostheses. Instead of adding a coating after the part is made, the antifouling chemistry could be built directly into the printable resin.

5 Self-Healing Zwitterionic Hydrogels

In the future, self-healing zwitterionic hydrogels could be used for:

* periodontal wound management; * tissue engineering; * drug delivery; * implant interfaces; and * regenerative dentistry.

6 AI-Guided Polymer Design

Artificial intelligence and computational chemistry could one day help optimize:

* monomer structure; * zwitterionic concentration; * polymer architecture; * crosslink density;

* degree of conversion; * water sorption; * mechanical strength; and * antibiofilm performance.

These methods could speed up the development of dental biomaterials tailored to each person or use case.

Conclusion

Zwitterionic methacrylates are a new type of dental biomaterial that tackle microbial colonization in a different way than traditional antibacterial materials. Their zwitterionic groups create a water-rich surface, which helps prevent proteins and microbes from sticking and disrupts the early stages of biofilm formation. Of the available options, 2-methacryloyloxyethyl phosphorylcholine (MPC) has attracted the most interest in dentistry. Studies show it works well in restorative composites, dental adhesives, orthodontic materials, denture bases, 3D-printed resins, fluoride varnishes, and implant coatings. SBMA and CBMA are other zwitterionic materials that also show promise for antifouling coatings and hydrogels.

However, because these materials are highly hydrophilic, they can absorb more water and may weaken when used in large amounts. Also, most research so far comes from lab studies, and there is still little long-term clinical data. So, the best path forward may not be using zwitterionic methacrylates by themselves. Instead, creating dental materials that can repel, kill, remineralize, and regenerate could be the next big step. By combining zwitterionic chemistry with antimicrobial agents, demineralizing fillers, bioactive glass, nanoparticles, regenerative molecules, and digital manufacturing, we could make dental biomaterials that do more than just restore teeth—they could also help manage their biological environment. In summary, zwitterionic methacrylates could help shift dental materials from traditional antibacterial types to smarter, biofilm-resistant, and more interactive options.

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