Dental Poly(methyl methacrylate)-Based Resin

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Poly(methyl methacrylate) (PMMA)-based resins have been conventionally used in dental prostheses owing to their good biocompatibility. However, PMMA-based resins have relatively poor mechanical properties. The filler was incorporated in the photocurable PMMA-based resin to improve the mechanical and physicochemical properties. The filler-loaded PMMA-based resin has the potential for use in dental restorative materials.

methacrylates   acrylic resins   silicate   composite resins   dental materials

1. Introduction

Polymethylmethacrylate (PMMA)-based resins are widely used in dental applications because of their excellent biocompatibility, stable physicochemical properties, easy manipulation, low cost, and appropriate aesthetics [1][2][3]. PMMA-based resins are commonly used for dental applications, such as denture bases, denture teeth, temporary crowns, provisional restorations, adhesives, and orthodontic retainers. However, clinical problems related to the use of PMMA-based resins include fracture and wear owing to their insufficient mechanical properties [4][5]. Improving the mechanical properties of PMMA-based resins is a critical issue for their long-term use in the oral environment without early failures.

To improve the mechanical properties, many studies have introduced fillers or fibers into a PMMA-based resin matrix [6][7]. A systematic review paper suggested that the addition of filler to the resin matrix can increase mechanical properties such as flexural strength, flexural (elastic) modulus, and fracture toughness [7]. For instance, the addition of microcrystalline cellulose at 5 wt % reinforced the PMMA-based resin in terms of increasing the flexural strength and modulus [8]. A double-modified organoclay was incorporated in the PMMA matrix at 0.5 wt %, resulting in increased flexural strength, flexural modulus, and fracture toughness [9]. Silanized alumina micro-particles with 0.1 wt % increased the flexural strength of PMMA-based resin [10]. ZrO_2 nanotubes were added to a PMMA-based resin, which increased its flexural strength [11]. Furthermore, the addition of silanized silica nanoparticles increased the flexural strength, flexural modulus, and fracture toughness of the PMMA-based resin [12]. Thus, the addition of fillers at an appropriate amount can reinforce the mechanical properties of PMMA-based resins.

However, the addition of large amounts of fillers often has adverse effects on the mechanical properties of PMMA-based resins. Excess filler (usually above approximately 5 wt %) degrades the mechanical properties of the PMMA-based resin, because the filler forms aggregates and voids in the resin matrix [7]. For instance, the flexural strength of heat-polymerized PMMA-based resin increased with increasing nano-filler (silica, alumina, and zirconia)

content up to 1 wt %, and decreased above 5 wt % [13]. The flexural strength of the PMMA-based resin containing 5 wt % silica nanoparticles was lower than that of the pure resin [14]. The flexural strength of a PMMA-based resin increased with the addition of fluoridated glass filler up to 5 wt %, and then decreased [15].

To overcome this issue, the present research focused on the development of porous fillers to improve the mechanical properties of PMMA-based resins. Porous filler containing continuous internal pores can form a mechanically interlocked structure at the interface between the infiltrated resin and filler surface [16]. Porous fillers have the potential to avoid degradation of the properties of the PMMA-based resin when a large amount of filler is added. In resin composites, some types of porous fillers have been introduced to improve the mechanical and physicochemical properties of resins [17][18][19][20][21]. For instance, a nanoporous silica filler prepared by thermal sintering increased the flexural strength, flexural modulus, and fracture toughness of copoly(bisphenol A-glycidyl methacrylate (Bis-GMA)/Triethylene glycol dimethacrylate (TEGDMA)) by adding 70 wt % of filler [19]. A wrinkled mesoporous silica improved the mechanical properties, including the flexural strength, flexural modulus, compressive strength, and Vickers microhardness of copoly(Bis-GMA/TEGDMA) [20]. A dendritic porous silica filler added at 36 wt % showed the best reinforcing effect on the flexural strength, compressive strength, and work of fracture of copoly(Bis-GMA/TEGDMA) [21]. Similarly, it is expected that porous fillers have the potential to improve the mechanical properties of PMMA-based resins.

2. Current Insights

The nanoporous silica filler was obtained via sintering, grinding, and silanization. During the sintering process, monolithic porous silica was produced by sintering the green body, containing the silica nanoparticles and PVA binder. During sintering, the PVA binder of the green body thermally decomposed, resulting in the formation of continuous pores in the body. Further details were reported in the researchers' previous research [22]. This previous research revealed that the porous structure can be controlled by the sintering temperature and time [22]; the pore volume and surface area decreased with increasing sintering temperature or time. Excessive sintering yielded a dense monolith with no pores, while insufficient sintering yielded a fragile monolith with poor consolidation of the nanoparticles. The sintering conditions were optimized to achieve a sufficiently porous and strong silica monolith. Then, the porous silica monolith was ground into a fine powder. Although the fabricated filler had microscale particles, it had a large surface area owing to the internal nanopores. This unique characteristic of the nanoporous filler significantly differs from that of conventional micro- or nano-fillers used in dental resin composites [23][24][25]. Furthermore, the present filler differs from the previously reported thermally sintered nanoporous silica filler in terms of its porous structure; the surface area of the present filler (61.3 m^2/g) is eight times higher than that of an existing filler (8.4 m^2/g) [19].

The resin matrix of the filler-loaded PMMA-based resin was prepared from appropriate amounts of pre-polymerized PMMA powder, MMA, EGDMA cross-linker, and BAPO photo-initiator. This system is similar to the powder–liquid mixtures used in many commercial self-cured acrylic resin systems [26][27]. In the researchers' system, the EGDMA cross-linker creates a three-dimensional polymer network with the MMA monomer via free-radical polymerization by light irradiation [28]. The pre-polymerized PMMA powder facilitated curing of the resin monomer. In the

researchers' preliminary experiments, the resin without EGDMA and PMMA powder did not cure under light irradiation. Hence, EGDMA and PMMA powders are essential components for the present PMMA-based resin. The BAPO photo-initiator is commonly used for free-radical photopolymerization in biomedical resin-based applications owing to its low cytotoxicity and high absorption coefficient under ultraviolet light [29]. A small amount of initiator achieved an efficient degree of conversion in the PMMA-based resins. The degree of conversion reached ≈90% in the PMMA-based resins, regardless of filler addition. This suggests that the infiltrated resin inside the filler particles can be polymerized under light irradiation. The degree of conversion for the PMMA-based resins is close to that of commercial heat-polymerized PMMA-based resin (≈92–97%) [30], whereas it is higher than that of commercial photo-polymerized resin composites for dental bulk-filled applications (≈30–80%) [31]. Hence, PMMA-based resins are considered acceptable as photocurable resins.

The PMMA-based resin contained 23 wt % filler. In this experiment, the researchers examined the upper concentration limit at which the filler was able to disperse into the resin matrix without forming agglomerates or voids. The researchers also prepared a filler-loaded PMMA-based resin using a non-silanized silica filler. In this case, the filler formed aggregates in the resin matrix at concentrations below 5 wt %. This means that silanization of the filler is essential and effective for homogeneous dispersion of the filler in the resin matrix. The present filler concentration (23 wt %) is higher than those of the previous filler-loaded PMMA-based resins listed in a review paper on filler-loaded PMMA-based resins [7]. The fillers often easily form aggregates in the resin matrix, and the upper limit of the filler load is approximately 5 wt % to avoid degradation of the mechanical properties, even when silanization of the filler is performed. In fact, the researchers tried to use the original fumed silica nanoparticles as the filler for the PMMA-based resin. However, homogeneous filler-loaded resin was not successfully fabricated because the fumed silica formed aggregates in the resin matrix, even at a concentration below 5 wt %, owing to their high surface area of 300 m^2/g. In contrast, the present micro-sized filler had a hierarchical structure containing nanopores. This unique microstructure of the filler allows the resin matrix to penetrate the continuous nanopores via capillary forces, leading to good wettability between the filler and resin matrix. This inhibits the aggregation of the fillers and void formation in the resin matrix.

The mechanical properties of the pure PMMA-based resin are comparable to those of commercial self-cured PMMA-based resins [32]. The addition of the filler significantly increased the mechanical properties of the PMMA-based resin. In particular, the flexural modulus and Vickers hardness of the filler-loaded PMMA-based resin were twice those of the pure PMMA-based resin. These improvements in the mechanical properties are notable in comparison with previous studies on filler-loaded PMMA-based resins. For instance, nanosized ZrO$_2$ filler added at 7 wt % increased the Vickers hardness only marginally, from 17.3 to 19.6 [33]. In another study, the addition of aluminum borate whiskers at 20 wt %, increased the Vickers hardness of the resin from 17.78 to 20.58 [34].

The physicochemical properties of the PMMA-based resin also improved with the addition of the filler. This suggests that the filler particles were well dispersed in the resin matrix and chemically bonded to each other. A previous study suggested that the water solubility and sorption of resin composites are affected by the material homogeneity [35], where highly homogeneous resin–filler composites have lower water solubility and sorption. In addition, the silane coupling agent on the filler surface can improve the bonding between the filler and resin matrix,

thereby enhancing the mechanical and physicochemical properties [36][37]. The mechanical and physicochemical properties of filler-loaded PMMA-based resin meet the criteria of ISO standard for polymer-based crown [38]. Overall, the filler-loaded PMMA-based resin is considered suitable for use in dental applications, such as temporary crowns, provisional restorations, and denture bases. However, there is scope for further assessment of the cytotoxicity of PMMA-based reins to confirm their biocompatibility using human gingival fibroblasts and gingival keratinocytes [39] and in vivo allergy tests [40]. Since TEGDMA has a risk of disruption of vital cell functions, the cytotoxicity due to the unpolymerized monomers will be examined further [41][42].

The present research demonstrated that the developed nanoporous silica filler can improve the mechanical and physicochemical properties of PMMA-based resins. In addition, the nanoporous silica filler has potential applications in other resins, such as multifunctional resins, urethane dimethacrylate, and bisphenol A-glycidyl methacrylate. Multifunctional resins have been widely used as resin composites for dental restorative materials owing to their excellent mechanical properties and biocompatibility. Commercial resin composites are generally loaded with nano- or micro-sized fillers to improve their mechanical properties [43]. The nanoporous silica fillers further improved the mechanical properties of the resin composites. The filler size and porous structure would be controlled to enable good dispersion in the resin matrix to achieve desirable properties. The potential applications of the newly developed filler will be examined in the future to expand the use of nanoporous fillers in clinical applications.

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