Influence different amount of cellulose on the mechanical strength of dental acrylic resin

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Abstract. The mechanical strength of PMMA is not sufficient when a patient applies high mastication force to the denture base plate. Many fillers to reinforce PMMA was used. However, cellulose incorporated into dental acrylic resin has never been reported. In this work, two types of modified cellulose were incorporated in the heat-cured acrylic resin, and the flexural strength was investigated. The conclusion is that the addition of properly modified cellulose could have good influence on the flexural strength of dental acrylic resin. The addition of cellulose modified by 3-Methacryloxypropylmethylmethoxysilane has increased average flexural strength and the standard deviation was satisfactory. However, Triethoxy(octyl)silane may not appropriate to achieve the intended purpose, or the modification of the cellulose by this silane itself must still be subjected to further testing. The ability to form new chemical chains between the cellulose and acrylic surfaces had a greater impact on the strength of acrylic than facilitated even distribution of cellulose.

1. Introduction
Poly(Methyl Methacrylate) (PMMA) is the most commonly used material for fabricating denture bases since 1937 [1]. Despite its advantages, such as biocompatibility, ease of processing, and low toxicity, the mechanical strength of PMMA is not sufficient when a patient applies high mastication force to the denture base plate [2]. Therefore, mechanical reinforcement is a long-term pursuit to prolong the service time of denture bases. Up to now, plenty of studies have been conducted to solve this problem, and the results exhibit that blending with proper fillers is the most efficient way. The fillers reported previously includes: metals [3], carbon fibers [4], glass fibers [5], SiC [6], SiNi [6], ZrO₂ [6], [8], TiO₂ [8], [6], SiO₂ [8], Al₂O₃ [8], [9], silver [6], graphene [10], hydroxyapatite [6], rubber [4] or polyethylene [4], [6]. However, all the methods have suffered from either limited values of enhancement or high dependence on the brand of acrylic resin.

Cellulose is known as a popular renewable and biodegradable material, exhibiting excellent mechanical properties due to its abundant hydrogen bonding and crystalline regions. It has been used to improve the mechanical properties of PMMA. Figure 1 shows how much reinforcement by properly modified cellulose can improve the tensile strength of PMMA. Figure 2 shows an increase in the Young Modulus. In both cases, modified cellulose was used 2,2,6,6-Tetramethyl-1-piperidinyloxy.
However, cellulose incorporated into dental acrylic resin has never been reported. Moreover, it is well known that the dispersion and adhesion of fillers have a great effect on the mechanical properties of composites. To achieve high compatibility between hydrophilic cellulose and hydrophobic matrix, cellulose should be modified before blending with acrylic resin.

In this work, two types of modified cellulose were incorporated in the specific heat-cured acrylic resin, and the flexural strength was investigated. That kind of acrylic resin was chosen, because this material is characterized by the highest strength of all dental acrylic resins [15] - [21]. Improvement of the strength of dental acrylic resin would reduce the thickness of the denture plate while maintaining the same strength of the material.
2. Materials and methods

2.1. Materials

Dental technicians in their laboratory use ready-made acrylic resin consist of powder and liquid. They are mixing these two products with a ratio based on manufacturer instructions. For this research, the powder stays in original form, and it was a heat-cured acrylic resin Vertex® Rapid Simplified (from Vertex Dental company). The liquid was recreated based on monomer Vertex® Rapid Simplified, and it consists of methyl methacrylate (99%) stab. (CAS number: 80-62-6, from Alfa Aesar) and ethylene glycol dimethacrylate (98%) (CAS number: 97-90-5, from Sigma-Aldrich). The second reagent was used as a cross-linking agent.

To reinforced acrylic resin was used Arbocel® UFC100 Ultrafine Cellulose for Paper and Board Coating (CAS number: 9004-34-6, from J. Rettenmaier USA LP company) after surface modification by two silanes:
- Triethoxy(octyl)silane (97%) (CAS number: 2943-75-1, from Sigma-Aldrich)
- 3-Methacryloxypropylmethyldimethoxysilane (92%) (CAS number: 14513-34-9, from ABCR company)

2.2. Methods

First, modification of cellulose was conducted to change the character of cellulose from hydrophilic to hydrophobic and to help the creation of chemical chains between methacrylic polymer and surface of cellulose. Then modified cellulose was added to the acrylic powder and mixing well. Both modified cellulose was added in three different amounts: 0,5 g, 1,0 g, and 1,5 g.

Final properly amount of acrylic liquid was added to the mixture. In the phase of hard rubber during pre-polymerization process - acrylic resin was put to the forms. Created specimens were finished with grinding machines to achieve dimensions shown in Figure 3 to the 3-point bending test. The speed test was 1 mm/min and was conducted with a universal testing machine (from Zwick/Roell).

![Figure 3. A diagram of force action in a 3-point bending test [source: own picture].](image)

Also, the observation was made using SEM. This test was carried out with JSM-6610LV Scanning Electron Microscope (from JEOL USA company). To observe results specimens were covered with a thin layer of gold.

3. Results and discussion

The results of the 3-point bending test are shown in Figure 4. Prepared specimens also differed of cellulose and amount of modified cellulose. Specimen marked as “C” was pure commercial acrylic resin. Moreover, the average strength was 88,8 MPa. It is similar to information given on manufacturer’s website [22], which is 85,2 MPa.
Next is “UC” and this result is a representation of addition unmodified cellulose to commercial acrylic resin. The amount of addition was 0.5 g. Results of bigger amount are not on diagram, because agglomeration of cellulose was too extensive, that sample preparation was impossible. In this case results were not the worst, but agglomeration was visible which significantly deteriorated the strength of these samples compared to commercial acrylic. Figure 5 shows that the agglomeration of cellulose was shown. During cutting process, part of the cellulose felt off, which led to the formation of holes. This completely rejects the material for use in the creation of dental prostheses because final machine processing would be impossible.
Figure 5. Image from SEM observation with a visible agglomeration of unmodified cellulose [source: own picture].

Last six results in Figure 4 are a representation of addition of cellulose modified by silanes. First set is cellulose modified by Triethoxy(octyl)silane and second- by 3-Methacryloxypropylmethyldimethoxysilane. Specimens with the addition of both modified cellulose in the amount of 0.5 g, 1.0 g, and 1.5 g were good at preparation. The addition of 2.0 g was too much, and there were difficult to mix the powder and liquid. The best results have been achieved after addition 0.5 g cellulose modified by 3-Methacryloxypropylmethyldimethoxysilane (marked on the diagram as 3_0,5). This silane was used to modify surface of cellulose to make possible to create connections between methacrylic polymer and surface of cellulose. So, addition just 0.5 g of this cellulose had positive impact on flexural strength (94.0 MPa). Both- average strength and standard deviation were satisfactory. The more this type of cellulose was added- the worse the strength and the spread of results were.

The situation is different with the addition of modified cellulose by Triethoxy(octyl)silane. This silane was used because it could change the nature of the cellulose surface from hydrophilic to hydrophobic. In this case- the addition of 1.0 g modified cellulose given the best results but still worse than in case of 3-Methacryloxypropylmethyldimethoxysilane.
SEM was observed not only to check the influence of modification on the agglomeration of cellulose but also fracture specimens. An example of fracture is shown in Figure 6. All fractures were the same, and it was a brittle type. So addition of cellulose does not have impact on type of fracture. However, during observations at higher magnification the differences were noticeable. Cellulose is visible on the picture B and C as more rough areas. The surface of pure acrylic resin is smooth. In case of cellulose modified by Triethoxy(octyl)silane cellulose fibers took up a larger area of fracture. This shows that modification with this kind of silane changed character of surface of cellulose from hydrophilic to hydrophobic and this enabled even distribution of the fibers in the PMMA core. Compare this with cellulose modified by 3-Methacryloxypropylmethyldimethoxysilane- this silane did not allow such even distribution, but the likely formation of bonds between the cellulose surface and PMMA resulted in increased acrylic strength.

4. Conclusion
Conclusion of this study is that the addition of properly modified cellulose could have good influence on the flexural strength of dental acrylic resin. Addition of cellulose modified by 3-Methacryloxypropylmethyldimethoxysilane has increased average flexural strength and standard deviation was satisfactory. However, Triethoxy(octyl)silane may not appropriate to achieve the intended purpose, or the modification of the cellulose by this silane itself must still be subjected to further testing. Improvement of modification process could have good impact on flexural strength in case of
3-Methacryloxypropylmethyldimethoxysilane. The ability to form new chemical chains between the cellulose and acrylic surfaces had a greater impact on the strength of acrylic than facilitated even distribution of cellulose. Further research can give even more visible results in this case.

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