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ORIGINAL ARTICLE

Cellulose nanocrystals into Poly(ethyl methacrylate) used for dental application

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Abstract

Cellulose nanocrystals (CNCs) can improve the mechanical properties of dental resins. However, there is a deficiency of information about the behavior of physical properties of resins after this addition. The purpose was to evaluate the characterization and physical properties of hard chairside reline material modified with CNCs (0.25%, 0.5%, 0.75% or, 1.0%). Addition of CNCs at 0.5%, 0.75% and 1% increased Vickers hardness; 0.75% decrease surface free energy; 0.75% and 1% showed similar to control on the surface roughness. The simple and straightforward approach of adding CNCs, a renewable material, provides good potential for its future practical application as it has shown promise with increasing hardness. It means that the incorporation of CNCs into this denture reline resin could improve the abrasion resistance of this material, which is desirable in the long term.

Keywords: *reline, acrylic resin, physical properties, nanocrystal cellulose.*

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1. Introduction

Hard chairside reline for relining dental prostheses is commonly used in dentistry directly in the mouth to regain the adaptation of the denture base to the residual ridges as a consequence of constant bone resorption that provides to an improper fit and a deficiency of support for the denture base[1]. Chairside or direct relining presents as advantages, simpler, faster, less expensive, and more practical than indirect use of a laboratory setting[2].

In addition, the relined denture must exhibit satisfactory strength to prevent fracture during function[3]. However, there is always the presence of residual monomer in the polymeric material due the conversion of monomer into polymer is not complete during the polymerization reaction[4]. This has a potential impact and this residual monomer is extensively identified as a plasticizer that affects the mechanical properties[5]. A possible alternative to solve this problem could be to incorporated reinforcing material[6]. In this respect, with the natural resources in evidence and the advent of nanotechnology, the organic fillers such as nanocelluloses (nano-structured cellulosic materials) have emerged due to its inherent characteristics and appear to have quickly drawn the attention of both academia and industry[7,8].

Cellulose nanocrystals (CNCs) or cellulose whiskers obtained from cellulose are arranged in crystallized structures obtained through acid hydrolysis into nano-sized needle-like crystallites that supplies potential for reinforcing mechanical properties of polymer materials due to their great mechanical strength and elastic modulus, besides renewability, sustainability, abundance, low cost, lower density and biocompatibility[9].

CNCs have been used in the matrixes for collagen scaffolds, silk fibroin membranes and grafted onto the matrix of Poly(methyl methacrylate) PMMA for applications of packaging, flexible screens and optically transparent films[10-12]. The improvement of mechanical properties of composites of PMMA filled with cellulose has been reported, achieving promising results[13-15].

For dental application, the incorporation of CNCs in dental composites and glass ionomer cements has shown an improvement in the properties of these materials[16-18]. Previous studies have been demonstrated the strengthen of conventional PMMA denture base resins after the incorporation of cellulose fibers[19] microfibers[20], nanofibers[21] and microcrystalline cellulose[22], which may be promising materials to be used as active fillers. A recent study demonstrated that pure cellulose nanofiber could be used as a good substitute as a "petroleum-free" for the conventional PMMA denture base resin[23]. In contrast, Chen et al.[10] observed that the incorporation of CNCs modified by silver nanoparticles (AgNPs) did not improve the flexural strength of a 3D-printable PMMA denture base resin. Thus, little information is found

in the literature concerning the incorporation of cellulose nanocrystals into denture base resins, especially that used for denture relines.

In this study, based on the literature reports where it was assumed the CNCs could be used as an active filler of PMMA to be used for dentures, CNCs was incorporated to a hard chairside reline resin essentially composed by Poly(ethyl methacrylate) presuming to improve their properties. The objectives of this investigation were to characterize one hard chairside reline material to denture base containing CNCs and to evaluate the physical properties. The null hypothesis of this research was that the incorporation of CNCs would not modify these properties of the hard chairside reline resin.

2. Materials and Methods

The hard chairside reline resin tested was Soft Confort Dura (Poly(ethyl methacrylate), phtalate ester, ethyl alcohol; Dencril, Pirassununga, Brazil), a powder/ liquid resin. A control group (0% CNCs, unmodified acrylic resin) and four experimental groups of acrylic resins with CNCs in different ratios were prepared: 0.25%, 0.5%, 0.75%, and 1%. These concentrations were chosen in accordance with a previous study[24], considering that higher levels of CNCs beyond 1% did not allow to obtain the proper consistency of the mixture of powder and liquid.

2.1 Synthesis of CNCs

The isolation of the CNCs from bleached Kraft Eucalyptus wood pulp (Suzano Papel e Celulose S.A, São Paulo, SP, Brazil) in the form of sheets was obtained through acid hydrolysis, as previously described[15,25]. The sheets was triturated with the aid of a blender until the resulting material appeared to resemble cotton, centrifuged twice for 10 minutes at 10,000 rpm using a refrigerated centrifuge (Centrifuge 580 R; Eppendorf, Hamburg, Germany) at 10°C to remove any excess acid and the concentrated phase was then dialyzed against distilled water to neutral pH for removal of the excess sulfuric acid, salts and soluble sugars[25]. Then the material was treated with a probe ultrasound (UP100HP; Hielscher, Teltow, Germany) for 15 min (pulse used: 7s on and 2s off) and the resulting suspension was reserved under refrigeration at 4°C[25].

2.2 Solvent changes

A solvent change was performed, in decreasing order of polarity, of the CNCs that were initially in water for ethanol, acetone and finally the liquid used in the polymerization of the resin according to the manufacturer. Solvent changes were carried out at 7000 rpm at 10°C for 10 minutes twice with each solvent using a centrifuge (Centrifuge 580 R; Eppendorf, Hamburg, Germany). After the last liquid centrifugation, the CNCs were dispersed using a probe ultrasound (UP100H; Hielscher, Teltow, Germany) for 5 minutes (pulse used: 7s on and 2s off).

2.3 Chemical characterization

For the chemical characterization [Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM)], two glass slides (26 × 76 × 1mm) were invested in high-viscosity silicone (Zetalabor; Zhermack S.p.A., Badia Polesine, Italy), further flasks supported by dental stone (Herodent; Vigodent S.A. Ind. Com., Rio de Janeiro, RJ, Brazil)[26]. After the dental stone had set, the glass slides were removed from the flasks, replaced by mixtures of acrylic resin and CNCs and packed under 0.5kgf pressure, for 30 min until complete polymerization[26]. After polymerisation, excess was removed by polishing. The specimens were used 30 minutes after its making, simulating the minimum time for realization an immediate reline the clinic[26].

Infrared spectroscopy analyses were performed by the KBr pellet method[27]. FTIR spectra of samples (n=1) were obtained in a spectrometer (IR prestige-21; Shimadzu, Kyoto, Japan). Differential scanning calorimetry thermograms of the samples (n=1) were recorded between room temperature (~25°C) and 250°C with a DSC Q20 instrument (TA Instruments, New Castle, USA), operating at a scanning rate of 10°C min-1 in a nitrogen atmosphere with N2 flow of 50 mL.min.-1 For the experiments, approximately 5mg of the samples were encapsulated in aluminum sample pans.

A scanning electron microscope (Vega 3 SBH; Tescan, Kohoutovice, Czech Republic) was used to analyze the morphology of the fractured samples in liquid nitrogen (n=1), at an accelerating voltage of 20 kV[27,28]. After drying, the samples were sputtered with gold coating of 3 nm thickness in an argon atmosphere at 20 mA for 2 min.

For the physical evaluation [Surface free energy (SFE), surface roughness (SR), Vickers hardness (VH)], discs (15 mm diameter × 3 mm thickness) were produced using stainless steel mold placed on an acetate sheet and a glass slab technique[29]. After polymerization, excess flash of each disc was removed with a bur (Max-Cut; Densply Malleifer, Tulsa, OK, USA).

2.4 Physical evaluation

SFE was obtained through a goniometer (200; Ramé-hart Instrument Co., Succasunna, NJ, USA) and two wet agents: water and diiodomethane[30]. The test was performed twice for each agent on ten discs of each group. The Young–Laplace equation was used for right and left contact angles measured for each wet agent[31]. For the SFE calculation, a software (DROPimage Standard; Ramé-hart Instrument Co., Succasunna, NJ, USA) was used[31]. A profilometer (SJ 400; Mytutoyo Corp, Kanagawa, Japan) with 0,01µm resolution, interval (cutoff length) of 0.8 mm, transverse length 2.4 mm, stylus speed 0.5 mm/second, and the radius of the active tip of 5µm was used for measured SR, mean value Ra (µm), of each specimen (n = 10)[22]. A microhardness tester (Micromet 2100; Buehler, Lake Bluff, Illinois, USA) with a Vickers diamond was utilized to measure the VH of the specimens from each group (n = 10)[32]. Two measurements were made for each sample for 10 seconds with a force of 50 g.

2.5 Statistical analysis

Statistical analysis was performed using ANOVA/ Welch and the Games-Howell test for post-hoc comparisons for normal and heteroscedastic data of VH. Normal and homoscedastic data of SFE, and SR were evaluated by one-way ANOVA and the Bonferroni post-hoc test. All analyses

were performed at α=0.05, using the with the PAWS Statics software (v. 19, SPSS Inc). For the FTIR, DSC and SEM descriptive analyses were performed.

3. Results and Discussions

According to the results of this study, SC had the highest mean hardness values in 0.5, 0.75% and 1% (Figure 1). The favorable results of the present investigation may have been attributed to the formation of a highly crystalline CNCs structure or to the reduction voids and distances between CNCs within the hard liners, compared to the macroscale structures[33,34]. In this study, we used CNCs that are rigid and dense nanoparticles with nanometric dimensions and acicular shape, where lengths are around 200 nanometers and thicknesses around 5 nanometers. Due to the rigid and dense structure of these CNCs, we obtained a stronger material in the hardness tests than when using commercial fibers, because these fibers are flexible and hollow, and would result in loss of stiffness in the material with its insertion in the polymeric matrix.

Hardness is a physical property that has been utilized to predict the wear resistance and to the resistance to plastic deformation of dental materials, that is, it higher hardness increases the longevity of the denture because it reduces the risk of fracture and also reduces abrasion, preserving aesthetics and biofilm formation difficult[35,36]. In addition, it is used as an indirect method of evaluating polymerization depth and self-curing, that is, to evaluate the degree of conversion of monomer to polymer during polymerization[35,37,38]. As the molecular weight of straight-chain alkyl groups increases, the hardness continues to decrease. Thus, poly (methyl methacrylate) is the hardest resin of polymethacrylate esters, then the isobutyl, and finally the n-butyl[39]. That is, denture base resins have a greater hardness when compared to hard chairside resins. For this reason, the increase in hardness provided by the addition of the CNCs proved to be favorable.

Nanofillers are recognized to be promising fillers for resins owing to their high specific surface area and high surface free energy, that improve the bending strength and fracture toughness of the resin effectively[10]. Studies have evaluated the effect of adding nanoparticles on the mechanical properties of acrylic resins[10,40] since denture fractures are one of the deficiencies of current denture base materials[40]. It has been observed that 56% of dentures fractures were accidental[40]. These fractures usually occur due to the flexural stress generated by chewing, so high resistance to flexural strength is required[41]. Data shows monomer residues ratios are higher auto-polymerized resins and they may adversely affect the mechanical properties and they are associated low wear resistance by a plasticizing effect, which decreases interchain forces so that deformation happens more swimmingly under load throughout flexural strength tests[42-44]. Moreover, adverse effects of certain foods and beverages can affect the mechanical properties consequently the longevity of the dentures relined with certain hard liners[45]. Previous reports showed improvement of mechanical properties by adding modified CNCs by silver nanoparticles in dental resin[10].

FTIR analyses demonstrated that there was no change in the structure of the hard chairside resin after the addition of CNCs, probably due to the small amount of this component (Figure 2). In contrast, Silvério et al. (2021)[24] observed typical peaks and bands related to the structure of the cellulose in the FTIR spectra obtained from a denture resin after the incorporation of CNCs using the same concentrations (0.25%, 0.5%, 0.75%, 1%). The FTIR technique uses a very small amount of sample, with the fraction used containing 1% or less of CNC. This makes the detection of CNC difficult, as it is a technique in which the peaks are proportional to the concentration of the constituents of the analyzed sample.

A little variation was observed in the DSC thermograms of hard chairside resin increasing the Tg values when the CNCs was added suggesting that nanocrystals are affecting the molecular organization of the polymer, which consequently interfered in the Tg of the materials (Figure 3). These results are in accordance with previous studies, in which the CNC presence in the polymer enhanced the Tg values. Voronova et al. and Qin et al. explained that it might be due to the macromolecular nanoconfinement provided by the CNC surfaces[46,47].

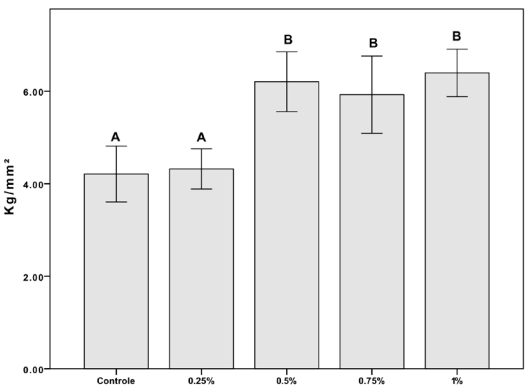

Figure 1. Effect of CNC incorporation into SC specimens on Vickers hardness, according to the group. Different capital letters indicate significant differences among groups. (ANOVA/Welch and Games-Howell test for post-hoc comparisons, p=.000 and p=.000, respectively).

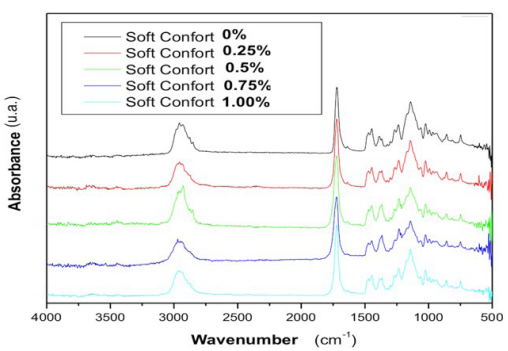

Figure 2. Infrared spectrum of CNC incorporation into SC specimens.

The SEM image showed a change in the structure of the resin; however, it was not possible to observe the distribution of the CNCs in the polymer matrix (Figure 4). It can be seen that in the images presented using nanocrystals, it is difficult to identify their presence because they are in a nanometric scale. Thus, it could be hypothesized that CNCs are perfectly compatible and dispersed in the polymeric matrix. In contrast, if commercial fibers were used, their presence in the matrix would be displayed, and the presence of two phases, the fiber phase and the matrix phase, would be very evident.

SR and SFE values of the SC resin were shown in Table 1. The results showed that the incorporation of CNC did not affect the roughness for groups 0.5 and 0.75% of SC, however for other groups there was an increase. This property is directly related to microorganism accumulation once microorganisms adhere to the surface of hard liners, colonize these abiotic structures and can lead to the development of oral pathologies[48]. Thus, to facilitate the hygiene of dentures, the smoother the prosthetic surface the better[48].

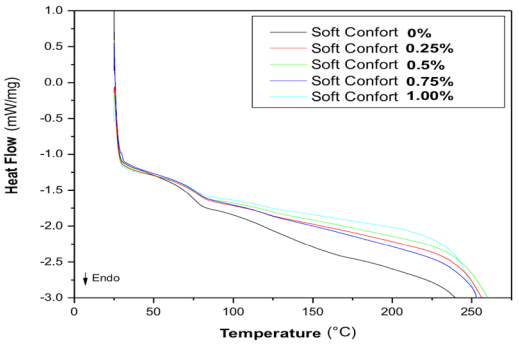

Figure 3. DSC thermograms of CNC incorporation into SC specimens.

The SFE determines the interaction between cohesion and adhesion forces and the wetting capacity of a solid[49]. The clinical significance of this physical property is related to its surface wetting capability, where high SFE is desired when adhesion is required, but undesirable if plaque resistance is required[50]. In the present study, the addition of CNCs to SC (0.75%) was also favorable for the variable SFE where a decrease was noted. Studies have been conducted to verify the association between SFE and *Candida* spp. adhesion and it was observed that the surface of polymeric materials with high SFE may induce greater adhesion and proliferation of *Candida albicans*[48]. The attraction forces for liquid (or microorganism) with the same chemical composition could be explain for a high SFE, that is understood as a high number of active ions on surfaces[51].

Nanometric materials, such as CNCs, diamond, carbon and metal oxide, have been incorporated into acrylic resins for reinforcement purposes[10,52]. The use of CNCs stands out because it is a material from renewable and easily found sources. Complementary studies with microbiological and cytotoxic tests should be carried out before applying this material in clinical research.

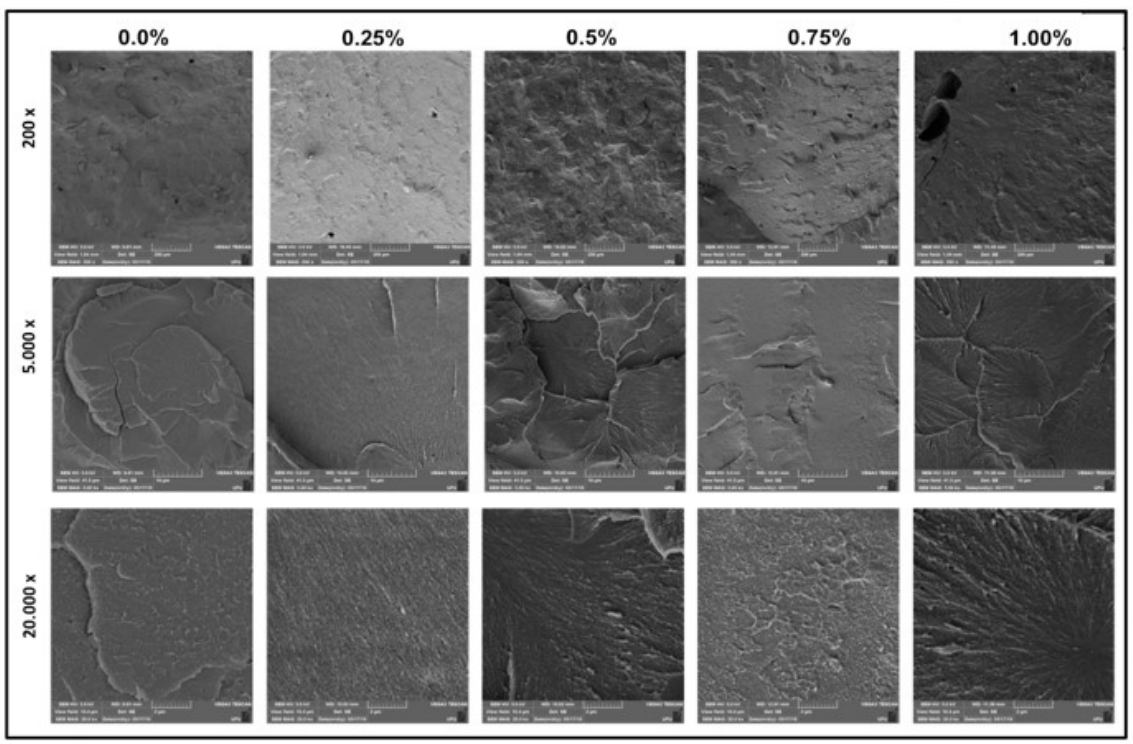

Figure 4. Surface morphologies of the samples obtained from SEM of CNC incorporation into SC specimens.; original magnification ×200, ×5000, and ×2000.

Table 1. Mean results and standard deviation for the flexural strength, surface roughness and surface free energy assessment according to different CNC concentrations for SC.

Title	Surface Roughness (μm)	*P*	Surface Free Energy (erg cm^{-2})	*P*
Control	2.23 (1.05) A	.019	40.76 (3.01) A	.019
0.25%	3.56 (0.47) B		43.89 (2.41) AB	
0.5%	3.18 (1.19) AB		44.48 (4.34) AB	
0.75%	3.14 (0.80) AB		40.38 (2.94) B	
1%	3.65 (1.17) B		41.85 (3.01) AB	
Control	2.23 (1.05) A		40.76 (3.01) A	

Means (SD) followed by the same uppercase in columns are significantly similar (P>.05).

Promising results were obtained when the CNCs was associated with a commercial resin with increased surface hardness and decreased SFE of the material, which was not harmful to the other physical properties evaluated here. CNCs within the hard liners can be used to customize temporary or long-term use of dentures with better physical properties when compared to conventional hard chairside resins. It means that the incorporation of CNCs into this denture base resin could improve the abrasion resistance of this material, which is desirable in the long term since the denture base is constantly subjected to brushing[53].

Further studies are required to assess other proprieties of CNCs within hard liners and characterize conditions of maintenance in long-term use, for a better clinical application in dentistry. In addition, the evaluation of the antimicrobial activity and biocompatibility are recommended before these findings can be applied in a clinical environment.

The present study has the potential to present as an alternative the improvement of hard chairside reline resins produced from residual vegetable biomass and should be considered promising in future studies, which may provide technological, economic and environmental benefits since they can promote the increase of the useful life of the complete dentures through the use of a renewable material.

4. Conclusions

The simple and straightforward approach of adding CNCs, a renewable material, provides good potential for its future practical application as it has shown promise with increasing Vickers hardness. It means that the incorporation of CNCs into this denture reline resin could improve the abrasion resistance of this material, which is desirable in the long term.

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