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A novel nano-calcium carbonate-polyurethane-based root canal obturation material: synthesis and evaluation of some physical properties

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A NOVEL NANO-CALCIUM CARBONATE-POLYURETHANE-BASED ROOT CANAL OBTURATION MATERIAL: SYNTHESIS AND EVALUATION OF SOME PHYSICAL PROPERTIES

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Abstract

The aim of this study was to prepare a new root canal obturation material named "nano-calcium carbonate-polyurethane" and to evaluate three of its physical properties which are solubility, water sorption and radiopacity.

Polycarbonate 1, 6-hexamethylene diisocyanate, NCO 49.79%, and 1, 4-butanediol were mixed together to form polycarbonate-based thermoplastic polyurethane (TPU). Additive materials like nano-calcium carbonate powder, zinc oxide, calcium hydroxide and barium sulfate with different ratios were blend together with the polycarbonate-based thermoplastic polyurethane to form the final obturation material.

The nano-calcium carbonate-polyurethane was found to be a promising root canal filling material; the percentages of solubility, water sorption and radiopacity were consistent with ISO standards.

Keywords: Polyurethane - nano-calcium carbonate - root canal obturation - water sorption – solubility – radiopacity.

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UN NOUVEAU MATÉRIAU D'OBTURATION CANALAIRE À BASE DE POLYURÉTHANE DE CARBONATE DE NANO-CALCIUM : SYNTHÈSE ET ÉVALUATION DE QUELQUES PROPRIÉTÉS PHYSIQUES

Résumé

Le but de cette étude était de préparer un nouveau matériau d'obturation canalaire et d'évaluer trois de ses propriétés physiques qui sont la solubilité, l'absorption d'eau et la radio-opacité. Le polycarbonate 1, 6-hexaméthylène diisocyanate, NCO 49,79%, et le 1, 4-butanediol ont été mélangés pour former le polyuréthane thermoplastique à base de polycarbonate (TPU). Des matières additives comme le nano poudre de carbonate de calcium, l'oxyde de zinc, l'hydroxyde de calcium et le sulfate de baryum ont été mélangés à des proportions différentes au polyuréthane thermoplastique à base de polycarbonate pour former le matériau d'obturation définitive. Le produit obtenu est un matériau de remplissage canalaire prometteur, les pourcentages de solubilité, d'absorption d'eau et de radio-opacité étant conformes aux normes ISO.

Mots-clés: polyuréthane - nano poudre de carbonate de calcium - obturation canalaire - absorption d'eau - radio-opacité – solubilité.

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Introduction

The success of endodontic therapy depends not only on adequate access and thorough biomechanical preparation but also on proper obturation. Several techniques and materials have been used for root canal obturation. The most popular and tested materials of choice are gutta percha and Resilon™. Despite its several advantages, gutta percha has some disadvantages such as the lack of bonding to root dentin leading to microleakage, the increased shrinkage when used as thermoplasticized material and the non-reinforcement of the root structure. Resilon™ has been introduced as a superior alternative to gutta percha. This synthetic polymer provides a better seal and reinforces the tooth structure through a combination of primer, dual cure sealer and resin obturating material [1].

The polyester chemistry containing bioactive and radiopaque fillers have been developed and tested. It performs and looks like gutta-percha. In addition, when used in conjunction with a resin-based sealant or bonding agent, it forms a monoblock that bonds to the dentinal walls. However, Resilon™ presents some disadvantages such as low push-out bond strength [1], low cohesive strength and stiffness [2] and inability to achieve a complete hermetic apical seal [3]. These results indicate that a more appropriate material for root canal obturation still needs to be developed. Lee et al. [4] in 2008 developed a new polyurethane-based composite to serve as a root canal obturation material and a visible-light curable urethane-acrylate/tripropylene glycol diacrylate (UA/TPGDA) oligomer to serve as a root canal sealer. This material has excellent properties; its major disadvantage was its chemical composition containing polybutylene adipate polyol (PBA) which decomposes with time [4]. So, in the long run, this material may lose some of its physical and mechanical properties.

Polycarbonate is a stable polyol and lasts for long time without biological disintegration. Calcium carbonate nanopowder exhibited good properties when mixed with polyurethane.

The major aim of this study was to prepare a root canal filling material by using polycarbonate polyol in combination with calcium carbonate nanopowder and other additives to enhance the physical properties of the previously prepared thermoplastic polyurethane obturating material [5].

The absorption of water by polymers is a phenomenon of considerable importance since it is accompanied by dimensional changes; it reduces the tensile strength of the material. Regarding the solubility, it represents the mass of soluble materials of the polymers that may affect the periapical tissue [6]. Moreover, the root canal filling material should present enough radiopacity to allow its distinction from the adjacent anatomical structures (bone, tooth structure).

Materials and Methods

Preparation of Nano CaCO3/TPU composite as a root canal–filling material

Polycarbonate (Poly-CD® CD220, carbonic acid, dimethyl ester, polymer with 1,6-hexanediol. MW 2000. Arch Chemicals, Inc, USA), 1,6-hexamethylene diisocyanate, NCO 49.79%, (HDI, Bayer Material Sciences, USA), and 1,4-butanediol (1,4-BD, Alfa Aesar, USA) were mixed in 1:1.12:0.1 molar ratios, dissolved in acetone (Acetone 99.5%, Sigma-Aldrich, USA) and reacted to form polycarbonate based TPU. All chemicals used in this study are listed in tables 1 and 2.

Polycarbonate polyol and chain extender were checked for H2O content using Karl –Fischer device. Water content was in the range of 0.01-0.05. Isocyanate was used as received from the supplier and isocyanate content was determined by the di-n-Butylamine method. The NCO content was 49%. All other additives ingredients were used as received. The polymerization reaction was carried out in 600 ml reaction cattle which were equipped with a mechanical stirrer, thermocouple, heater, nitrogen inlet and reflux condenser.

Polycarbonate polyol was weighted and added to reaction cattle, then 1,4-BD was added, followed by the catalyst. Then acetone was added to the mixture and mixed with a stirrer. The reaction mixture was heated up to 50°C and the HDI was added via funnel. After addition of HDI, the funnel was rinsed with a small amount of acetone and the reaction was continued for 2 hours at 50°C.

During the synthesis, additional amount of acetone was added due to the high viscosity of polymer solution. After 2 hours of synthesis, clear viscous polymer solution was obtained. When polymerization was achieved, a sample for NCO% determination was taken.

Additives mixing ratio

Filler materials shown in table 3 were added to the solution of polyurethane in the following ratios: 50 (%) weight of polyurethane solution and 50% fillers to form CaCo3/TPU composite .

Water sorption and solubility

Specimen preparation

A total of 10 discs of the new materials were prepared using a metal mold. Each specimen disc was 20 mm in diameter and 1.5 ± 0.1 mm thickness. A plastic spatula was used to condense the mixed material. A piece of polyester transparent film was placed below and over the mold.

Test procedure

The specimens were transferred to the desiccators containing silica gel, freshly dried for 5 hours at 130°C. They were maintained in the desiccators at 37 ± 1°C. After 24 hours, the specimens were removed and stored in a second desiccator which contained silica gel (freshly dried for 5 hours at 130°C) and stored at the lower temperature (room) of 23 ± 1°C for 1 hour. The specimens were weighed using an analytical

	Designation	Composition	Supplier
Polyols	Poly-CD® CD220 (PCA)	Carbonic acid, dimethyl ester, polymer with 1,6- hexandiol. MW 2000, OH-number 55.6	Arch Chemicals, Inc.USA
Chain extender	1,4 BD	1,4 –butanediol equivalent weight 45 (MW 90)	Alfa Aesar, USA
	Isocyanate : Desmodur H (HDI)	Hexamethylene-1,6-Diisocyanate, NCO %49.79.	Bayer Material Sciences, USA
Catalyst	Dabco® T-12 (0.1%)	Dibutyltin dilaurate	Air Products, USA
Solvent	Acetone	Aceton C3H6O 99.5%	Sigma –Aldrich,USA

Table 1: Raw materials used in the study.

Designation	Composition	Supplier
Zinc Oxid (ZnO)	ACS reagent ≥99.0%	Sigma- Aldrich
Barium Sulfate (BaSo4)	Reagent plus 99%	Sigma-Aldrich
Calcium hydroxide (Ca(OH)2)	ACS reagent ≥95.0%	Sigma –Aldrich
Calcium carbonte nanoparticles (CaCo3)	15-40 nm surface modified for adhesives	Sky Spring Nanomaterials, Inc.

Table 2: Additives raw materials.

% weight of additives	Calcium Carbonate	Zinc Oxide	Calcium hydroxide	Barium sulfate
50%	12	25	10	3

Table 3: Weight percentage of the fillers.

balance (Mettler Analytical Balance, Gallenkamp Mettler, E. Mettler, Zurich, Switzerland) to an accuracy of ± 0.1mg. This cycle was repeated until a constant mass (m1) was obtained, i.e. until the mass loss of each specimen was not more than 0.2 mg in any 24-hour period. The specimens were immersed in distilled water, and maintained at 37°C for seven days. After that, the specimens were removed, washed with water, surface water blotted away until free from visible moisture, and waved in the air for 15 seconds, then finally weighed 1 minute after being removed from the water. Their mass (m2) was recorded. The specimens were placed in the desiccator using the same cycle as described above to obtain m1. This cycle was repeated until constant mass (m3) was obtained.

Finally, the thickness of the specimens was measured by taking three readings in the center of each specimen. The mean value of thickness of each specimen was used to calculate the volume (V) in cubic millimeters [6].

Calculations and expression of results

The values of water sorption (WSP) were calculated in micrograms per cubic millimeter for each specimen by applying the following equation:

$WSP = (m_2 - m_3)/ V$

where:

- m_2 is the mass of the conditioned specimen in micrograms, after immersion in water for seven days.
- m_3 is the reconditioned mass of the specimen in micrograms.
-V is the volume of the specimen in cubic millimeters.

The values of water solubility were calculated in micrograms per cubic millimeter for each specimen by applying the following equation:

$WSL = (m_1 - m_3)/ V$

where:

-m_1 is the conditioned mass in micrograms.
-m_3 is the reconditioned mass of the specimen in micrograms.

Fig. 1: Densitometer, some specimens and aluminum step wedge used for radiopacity test.

	N	Minimum	Maximum	Mean
m1	10	.576	1.079	.869±.147
m2	10	.577	1.088	.875±.149
m3	10	.563	1.059	.851±.145
Volume of cylinder = r2*height *3.14	10	3.45	6.500	5.105±.880
Water sorption	10	.004	.007	.0047.0.001
Water solubility	10	.003	.004	.0035±.0001

Table 4: Percent of solubility and water sorption of nano-calcium carbonate polyurethane material in micrograms per cubic millimeter.

-V is the volume of the specimen in cubic millimeters [6].

Radiopacity

A washer of 10mm internal diameter and 1mm height was filled with the mixed material and radiographed together with an aluminum step wedge having an incremental thickness of 1 to 9mm. The radiopacity of ten specimens was compared with that of the step wedge by means of a densitometer (Heiland electronic, Wetzler, Germany (Fig. 1).

The minimum requirement is 6 mm Al-equivalents, which may be on the low side considering that conventional gutta-percha points are about 6mm Al-equivalents. Most materials are in the range of 4–9 mm (ANSI/A.D.A Specification No.78) [7].

Results

Solubility and water sorption

The solubility of nano-calcium carbonate polyurethane material in micrograms per cubic millimeter was 0.0035 ±.0003, while the water sorption was 0.0047±.001. The allowable ratio for solubility for our material according to ISO specification is 0.026 g which represents 3% of the total weight (0.869 g) as shown in table 4 and figure 2.

Radiopacity

Tables 4 and 5 show the mean gray value and equivalent aluminum thickness (mm) of nano-calcium carbonate polyurethane. Radiopacity was expressed in millimeters of aluminum and higher value represented greater radiopacity. Nano-calcium carbonate polyurethane possessed a radiopacity equal to 0.92 mm which is closest to the 0.93, the score of aluminum with 6 mm, complying with the ISO requirements (Fig. 3).

Discussion

The ideal root canal filling material that fulfills all the requirements for a successful endodontic treatment doesn't exist.

Preparation of new root canal material that can overcome the drawbacks observed with previous material is a realistic demand [8]. The polyol used for the thermoplastized polyurethane preparation by Lee et al. [4] in 2008 had a short life span and it was liable for biological disintegration.

The aim of this study was to prepare a canal filling material using polycarbonate polyol that has a very good stability in time in combination with calcium carbonate nanopowder and other additives to enhance the mechanical and physical properties of previous materials [9].

ISO and ANSI/ADA have standardized some technological tests to investigate the physical properties of endodontic filling materials. Assessment of radiopacity, solubility and water sorption properties were realized as recommended by ISO standard (4049:1988). It appears from the results of water sorption and solubility that nano-calcium polyurethane material behaved satisfactorily with this standard.

Solubility of a root canal filling is undesirable since it can cause the release of components biologically incompatible; moreover, the formation of gaps can negatively affect the hermetic seal of the root canal filling. According to ISO standards, the solubility of a root canal filling should not exceed 3% mass fraction. The value of solubility of nano-calcium carbonate polyurethane was within this limit (0.4%) [6].

Gravimetric analysis and SEM showed exposure of glass-filler particles of Resilon™ following surface dissolution of the polymer matrix, creating a rough surface topography after incubation in lipase PS (from Burkholderia cepacia; Amano Enzyme Inc., Nagoya, Japan) or cholesterol esterase (from Pseudomonas species; Amano Enzyme Inc.) for 96 hours.

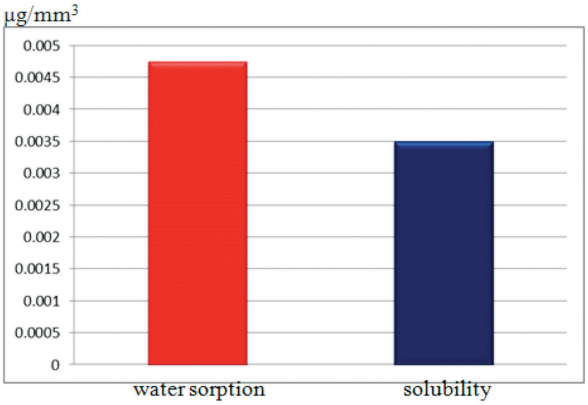
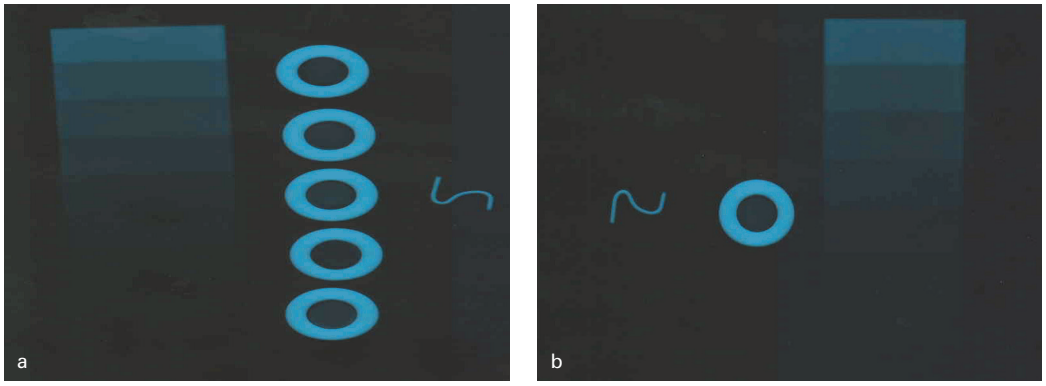


Fig. 2: The result of solubility and water sorption of nanocalcium carbonate polyurethane material in micrograms per cubic millimeter.

Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10	Mean	Standard deviation
0.92	0.89	0.84	1.07	0.89	0.89	1.07	0.84	0.89	0.92	0.92	±0.02

Table 5: The mean and standard deviation of radiopacity of nano-calcium carbonate polyurethane.



Figs. 3a and 3b: The mean gray value and equivalent aluminum thickness (mm) of nano-calcium carbonate polyurethane.

Similarly, the presence of spherical polymer droplets that appeared deformed, pitted or much reduced in dimensions was seen with Resilon™ after enzymatic hydrolysis. Rates of hydrolysis of Resilon™ by lipase PS and cholesterol esterase were much faster than those of polycaprolactone at 1 × or even 4 × enzyme concentrations. Field-emission SEM and energy dispersive spectrometric analyses showed that the resinous surface component of Resilon™ was hydrolyzed after 20 minutes of sodium ethoxide immersion, exposing the spherulitic polymer structure, the subsurface glass and the bismuth oxychloride fillers. More severe erosion occurred after 60 minutes of sodium ethoxide treatment, while gutta-percha remained unaffected [9].

Furthermore, gutta-percha exhibited minimal surface changes after 4 months of incubation in wet dental sludge, while polycaprolactone and Resilon™ exhibited severe surface pitting and erosion. In the latter, disappearance of the polymer matrix was accompanied by exposure of mineral and bioactive glass fillers. Bacteria and hyphae-like structures were present on the Resilon™ surfaces [9].

Radiopacity is widely acknowledged as a desirable property of all intraoral materials, including the endodontic root canal material. The root canal filling material must be radiopaque in order to detect the extension and the quality of the filling. Beyer-Olsen &

Orstavik [10] established a standardized system to evaluate the radiopacity. They used an aluminum step-wedge with 2mm increments as a reference to determine the equivalent aluminum thickness of the studied materials. In literature usually, conventional radiographic films and optical densitometers were used to evaluate the radiopacity of filling materials. However, in some studies, converting the radiographs to digital images was also used as an alternative to optical densitometer [8].

Rasimick et al. [11] stated that the imaging technique could affect the measured radiopacity values of the materials. Barium containing materials could have different radiopacities on film and phosphor store plates. Also differences could be found in the aluminum alloy of the step-wedge, exposure time, focal film distance, kVp, and mAs affects the radiopacity measurements of materials in situ [12].

The radiopacity of root canal filling should be at least 6 mm Al, but excessive radiopacity of the material is not mentioned by ISO standardization. The thermoplastic polyurethane base (TPU) is a radiolucent material, corresponding to 1 mm of the aluminum step wedge.

Conclusion

The radiopacity rates of nano-calcium carbonate polyurethane used in the present study was consistent with ISO standards. The inorganic fillers like nano-calcium carbonate, zinc oxide, calcium hydroxide in addition to barium sulfate are considered radiopaque fillers, so they confer the radiopacity for the TPU.

As a conclusion, the nano-calcium carbonate polyurethane is a promising root canal filling material with good physical properties that comply with ISO standardization.

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