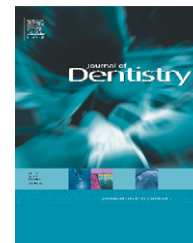


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The physical characterization of a thermoplastic polymer for endodontic obturation

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ARTICLE INFO

Article history:

Received 14 January 2006

Received in revised form

2 March 2006

Accepted 6 March 2006

Keywords:

Resilon™

Endodontic sealer

Root canal

Canal filling

Canal therapy

Thermoplastic polymer

Obturation

Polycaprolactone

Radiopaque fillers

ABSTRACT

Objective: To analyze a new endodontic sealer material commercially known as Resilon™ and to describe in detail the experimental techniques employed that lead to the identification of the composite material.

Methods: An extensive structural, thermal, and physical characterization was used to identify a new endodontic sealer material using the following techniques: Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) analysis, X-ray fluorescence spectrometry (XRF) technique, X-ray diffraction (XRD) measurement, thermo-gravimetric analysis (TGA) and a differential scanning calorimeter (DSC). The surface morphology was analyzed using a scanning electron microscope (SEM).

Results: The material was identified as a composite of polycaprolactone, which is a polymer of the polyester family and bioactive glass, which is radiopaque filler.

Conclusions: The Resilon™ sealer material is a thermoplastic synthetic degradable polymer (polycaprolactone), it contains bioactive glass. Its properties, such as strength, modulus, shape-memory effect and biodegradability depend on the crystalline fraction, which is affected in turn by conditions of crystallization. Investigation of the crystallization kinetics of PCL is of practical significance. It is especially necessary to study its the dynamic and non-isothermal crystallization process.

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1. Introduction

Dental root canal preparation aims to remove infected debris from the root canal system. The success of root canal therapy depends on related phases in root canal treatment: cleaning and shaping, sealing of the canal system and microbial control. Shaping the root canal allows for more efficient disinfections by creating a reservoir for irrigation and medication and it also provides a space for the root canal filling. Gutta-percha is generally used as a bonded root canal obturation system.

Gutta-percha has many advantages, such as being a non-toxic, biocompatible, thermoplastic and retractable material. Recently a new composite (Resilon™) has been made available for root canal sealing. Resilon™ can be used with all the common present forms of endodontic treatment. In the literature there is no work concerning the identification of this composite, which is important in order to ensure clinical accident prevention.

Composites comprising biodegradable polymeric matrixes and bioactive ceramic fillers are used extensively in the field of medical application. Several polymeric/ceramic combinations

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doi:10.1016/j.jdent.2006.03.002

can be used to confer to the composites different characteristics. They are also used for controlling properties such as biocompatibility, water-uptake, rate of degradability and mechanical properties, making these materials suitable for use on a wide range of biomedical applications. However, poor adhesion between the polymeric matrix and the ceramic particles often results in an early failure in the interface and in an accelerated degradation of the composite mechanical properties. This degradation phenomenon is even more significant if composites are placed in physiological environment.¹

Polycaprolactone (PCL) is a biodegradable polymer that has been intensively investigated as a biomedical material.^{2–5} It is biocompatible, has good water, oil, solvent and chlorine resistance, a low melting point and low viscosity, it is mechanically strong and is easy to process. It is used for drug delivery, a process where drug compounds are mixed in the polymer matrix and then they are gradually released as the polymer is dissolved in the tissue. In the emerging field of tissue engineering, biodegradable polymers are used for making polymer scaffolds to assist tissue and cell growth during the formation of artificial organs.^{6–8} In such applications, biodegradable polymers have allowed for successful cell attachment, proliferation, and functioning.

PCL has good mechanical and degradation properties. Yet, the complete breakdown of this polymer can take up to 2 years to fully occur, rendering the use of PCL unsuitable in short term applications. However, the chemical structure of PCL is unusual, enabling compatible blends with a wide variety of polymers whilst retaining many of its own advantageous properties. PCL can be degraded by microorganisms as well as by a hydrolytic mechanism under physiological conditions.¹ It is reported by Tay et al.⁹ that PCL is susceptible to both alkaline and enzymatic hydrolyses. They examined the susceptibility of Resilon™, a polycaprolactone-based root filling composite, to alkaline hydrolysis using field-emission scanning electron microscopy and energy dispersive X-ray analysis. The surface resinous component of Resilon™ was hydrolyzed after 20 min of sodium ethoxide immersion, exposing the spherulitic polymer structure of PCL and subsurface glass and bismuth oxychloride fillers. More severe erosion occurred after 60 min of sodium ethoxide treatment. Another study¹⁰ provided definitive evidence that Resilon™ is biodegradable under the attack of hydrolytic ester bond-cleaving enzymes (termed enzymatic surface erosion) that may exist as a component of the salivary enzymes¹¹ or as extracellular enzymes from endodontically relevant microbes. They hypothesized that biodegradation of this material may also occur because of enzymatic hydrolysis via a surface degradation mechanism, similar to that, which has been previously reported for polycaprolactone.^{12–14}

The PCL material has a significantly slower biodegradation rate than other biodegradable polymers (BDP) biomaterials, making it suitable for the design of long-term implantable systems such as Capronor, a US FDA approved contraceptive device.¹⁵ The toxicology of PCL has been studied as part of the evaluation of Capronor, it is currently regarded as non-toxic and tissue compatible.¹⁵ PCL is especially appealing for such applications as it also has the lowest unit price amongst all of the common off-the-shelf BDP products.

Bioglasses are also considered to be another important biomaterial within the tissue-engineering industry, and are suitable for end applications such as devices for guided tissue regeneration and the treatment of bone defects due to their osteoconductive nature.^{16–18}

The aim of the present work is to study a new endodontic sealer material, namely, Resilon™, which is being used to seal the dental root canal system. A structural, thermal, and physical characterization was used to identify the unknown composition of the Resilon™ composite.

2. Materials and methods

The material analyzed was a composite marketed under the brand name Resilon™ (Pentron Clinical Technologies, Wallingford, CT, USA). Resilon™ is a commercial composite material with conic shape like the available gutta-percha, which is being used to seal the root canal system.

To identify the Resilon™ chemical composition the following techniques was used: a Fourier transform infrared (FTIR) spectroscopy, a nuclear magnetic resonance (NMR) analysis, an X-ray fluorescence (XRF) technique, an X-ray diffraction (XRD) measurement, a thermo-gravimetric analysis (TGA) and a differential scanning calorimeter (DSC). The surface morphology was analyzed using a scanning electron microscopy (SEM).

The FTIR spectroscopy measurements in a 400–4000 cm⁻¹ range were performed on a 1720× Perkin-Elmer spectrometer using the multiple internal reflectance (MIR) technique with a KRS-5 crystal (45°) and a TGS detector. The spectra were obtained at a 2 cm⁻¹ resolution, 100 scans and processed by a Perkin-Elmer IR data manager (IRDM).

For the C¹³-NMR analysis, the sample was dissolved in deuterated chloroform and filtered through glass wool before transferring it to the NMR tubes. Then the sample was dissolved in CDCl₃ and sealed in an NMR tube. After being degassed, samples were analyzed using a Varian VXR 300 NMR spectrometer.

The qualitative elemental composition of the sample was determined with the XRF technique. The X-ray diffraction (XRD) spectrum was measured with a Rigaku diffractometer with a Cu K α radiation at a continuous 2 θ scanning of step 0.05°/s. A high voltage of 30 kV and a current of 15 mA were used.

(TGA) was performed on a Shimadzu TGA-50. Samples of about 10 mg were heated in air from 25 to 700 °C at a heating rate of 10 °C/min.

The melting temperature of the sample was determined on a Perkin-Elmer Model DSC-4 equipped with a Thermal Analysis Data Station (TADS) using standard aluminum pans. Measurements were made on 10 mg samples in the temperature range between 20 and 350 °C at a scanning rate of 10 °C/min. Nitrogen was used as a sweeping gas. The instrument was calibrated with indium.

A model JSM 5800LV JEOL scanning electron microscope (SEM) was used to analyze the morphology of the longitudinal surface and the transversal cross-section samples previously cut off from the point using scissors. The samples were sputter-coated with a thin gold film in a vacuum chamber before examination.

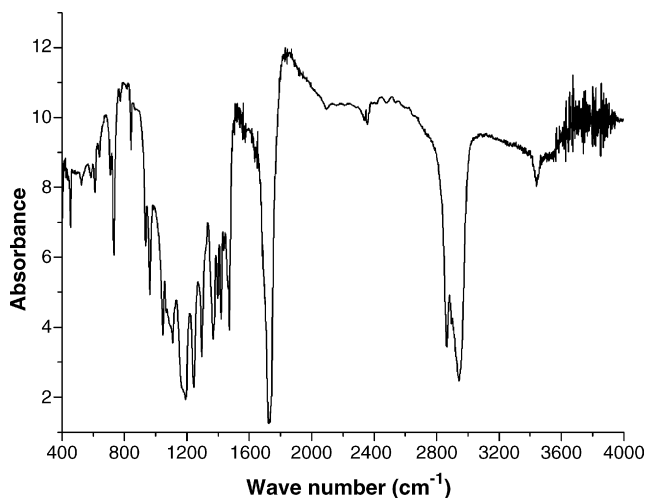


Fig. 1 – The FTIR spectrum where the absorption lines were identified as characteristic infrared bands of polycaprolactone (PCL).

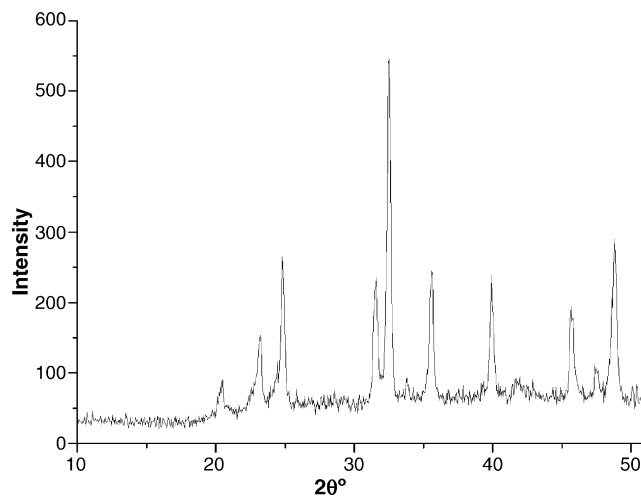


Fig. 3 – The X-ray diffraction (XRD) spectrum of the sample indicating a well crystalline peaks.

Table 1 – Characteristic infrared bands of PCL¹⁹

Position (cm ⁻¹)	Vibrator	Abbreviation
2949	Asymmetric CH ₂ stretching	$\nu_{as}(\text{CH}_2)$
2865	Symmetric CH ₂ stretching	$\nu_s(\text{CH}_2)$
1727	Carbonyl stretching	$\nu(\text{C}=\text{O})$
1293	C–O and C–C stretching in the crystalline phase	ν_{cr}
1240	Asymmetric COC stretching	$\nu_{as}(\text{COC})$
1190	OC–O stretching	$\nu(\text{OC}-\text{O})$
1170	Symmetric COC stretching	$\nu_s(\text{COC})$
1157	C–O and C–C stretching in the amorphous phase	ν_{am}

3. Results

Fig. 1 shows the FTIR spectrum result where the absorption lines were identified, using the database of the system, and this was found to fit with polycaprolactone. **Table 1** shows the characteristic infrared bands of PCL, as found by other research groups that fit perfectly with the spectrum.¹⁹

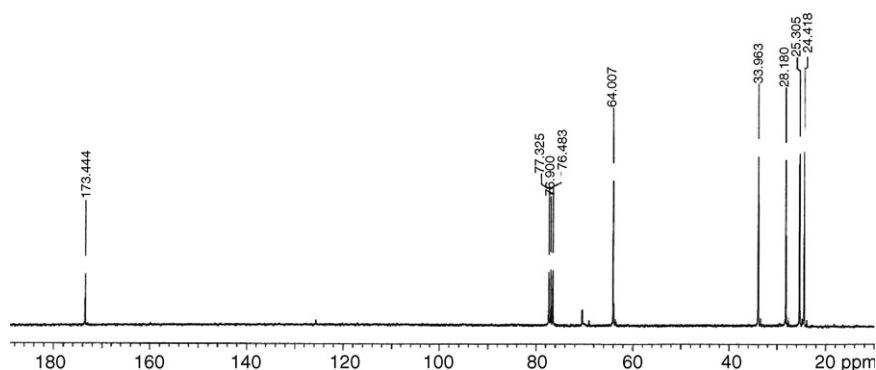


Fig. 2 – C¹³-NMR spectrum of Resilon™ sample dissolved in chloroform, as can be seen in the chemical formula of polycaprolactone is obtained when each shift is assigned to each carbon position.

The FTIR spectrum result was confirmed by the C¹³-NMR spectrum of a sample dissolved in chloroform, as can be seen in **Fig. 2**. The structural formula of polycaprolactone is obtained when each shift is assigned to each carbon position.

Fig. 3 shows the X-ray diffraction (XRD) spectrum of the sample indicating a well crystalline peaks.

The thermal and morphological properties of PCL and DSC thermographs proceeded to be studied. **Fig. 4** shows that the melting point of polycaprolactone is 59.5 °C.

Thermo-gravimetric analysis (TGA) was carried out to evaluate the degradation temperature of PCL. **Fig. 5** shows the weight loss till 150 °C, which is associated with water evaporation, the degradation (or decomposition) of the material starts at approximately 260 °C.

The point morphology cut with the scissors was observed by SEM. Micrographs of the cross-section of the point (**Fig. 6**) shows that the deformation suffered by the polymer is due to the high shear forces caused by the scissors.

A micrograph of the surface of the Resilon™ sealer (**Fig. 7**) shows that the adhesion between the polymer and the inorganic fillers (white particles) was not so good and the surface was not smooth.

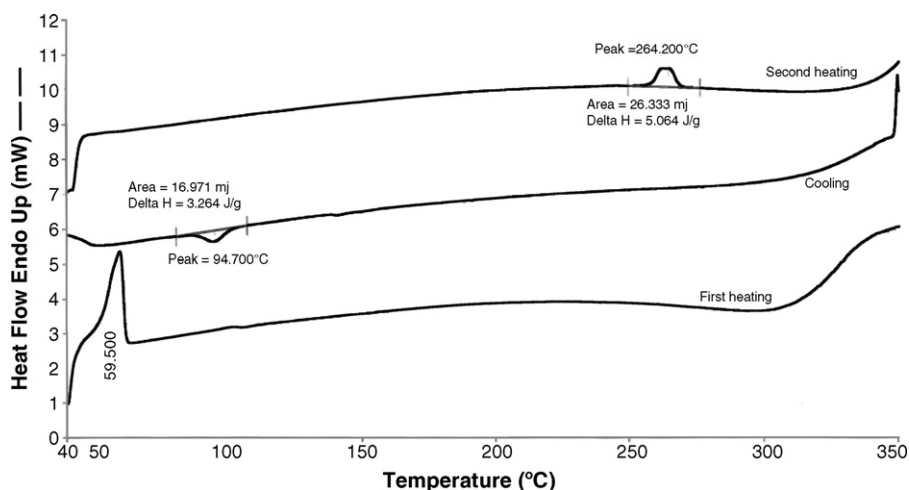


Fig. 4 – DSC heating curve showing the melting point of polycaprolactone to be 59.5 °C.

4. Discussion

As a first step in the direction of the identification of the root canal filling material, FTIR and NMR spectroscopy measurements were carried out. However, regarding these two techniques, two problems had to be overcome: in the case of NMR, the material needed to be dissolved and thus the adequate type of solvent needed to be selected. Various solvents were tried, such as acetone, methylene chloride, chloroform, methyl ethyl ketone, dichloro-methane, etc. The material was found to easily dissolve in chloroform and when the solvent evaporated, a thin film was formed on the walls of the test tube, together with an orange precipitation at the bottom. Thus the first conclusion was that: the cone (Resilon™) is a composite of polymeric matrix and inorganic filler materials.

On the other hand, for the FTIR case, the sample needed to be either in the form of a film, powder or a liquid. The sample is difficult to manipulate since it is soft and elastic and as such,

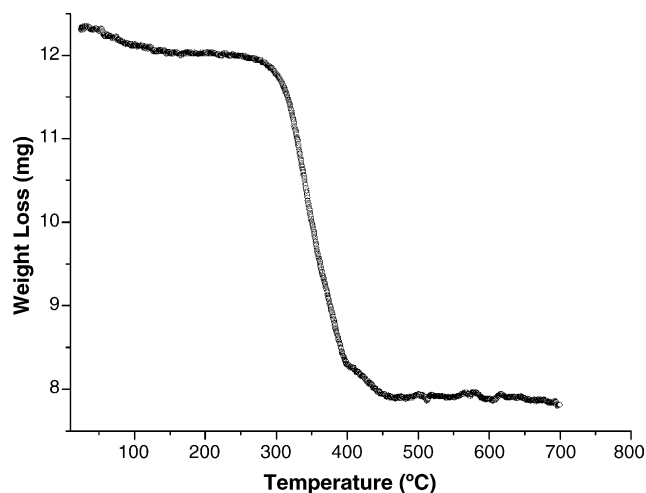


Fig. 5 – Thermo-gravimetric curve of polycaprolactone shows the weight loss till 150 °C, which is associated with water evaporation, the degradation (or decomposition) of the material starts at approximately 260 °C.

could not be ground. Therefore, a decision was taken to use the polymer film that had formed on the wall of the test tube when the material was dissolved in the chloroform. Thus, it was possible to identify the polymeric matrix.

Once it was possible to identify the polymer, the next stage consisted of identifying the inorganic composition of the material. This was carried out through a qualitative elemental analysis by the XRF spectroscopy. It was not possible to conduct an exact quantitative analysis. Nonetheless, this analysis indicated the presence of the following elements: C, Si, P, Cl, Ca, Fe, Zr, Ba, Ce and Bi. The elements C, Si, P, Ca and Fe were also found in the composition of the myler sheet, which is part of the equipment. Thus, it is difficult to state whether this was due to the material or not. The next step was to identify the filler compounds according to these elements.

The XRD spectrum (Fig. 3) shows crystalline peaks. Pure PCL is a semi-crystalline material, which shows two crystalline peaks at about 23.8 and 21.3°, indicating highly ordered chain folding characteristics. The less ordered amorphous regions in which the polymer chains are randomly arranged are thought to be the initial sites of hydrolysis. The low peak intensity of PCL may be assigned to the increased peak intensity of the inorganic crystalline fillers. This may indicate that, the filler percentage is higher than the polymer one. The fillers crystalline peaks were identified by the powder diffraction files (PDF) as calcium-rich hydroxyapatite, silica, bismuth oxychlorate, zirconium oxide, barium sulphate, barium oxide and cerium phosphate. Most of these materials are very insoluble crystals (generally known as bioglass materials) that are opaque to X-rays. Under stress, the polymer chains slide over each other and allow the material to flow. This allows it to adapt to the irregularities of root canals, the filler particles are there to make obturation point radiopaque.

Concern to the melting point of polycaprolactone, according to Oliveira and Glasser,²⁰ PCL is a semi-crystalline polymer which reveals three thermal transitions: a first order transition at ~60 °C corresponding to a melting endothermic; a second order glass transition at -60 °C; an exothermic crystallization peak around -25 °C, the last two temperatures are out of the range of the equipment.

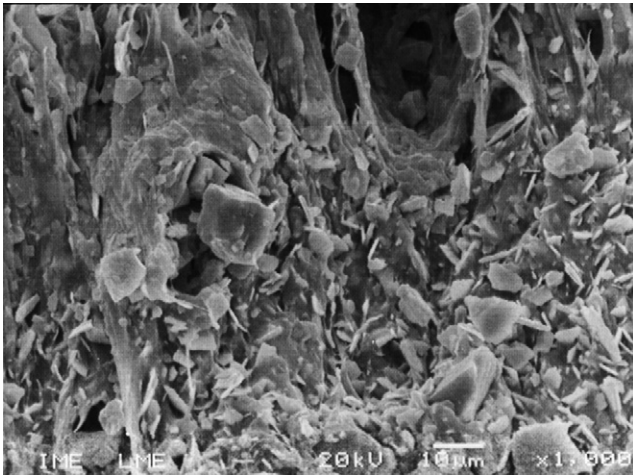


Fig. 6 – Scanning electron microscope (SEM) micrograph of the cross-section of point morphology cut with the scissors from Resilon™ shows that the deformation suffered by the polymer is due to the high shear forces caused by the scissors.

The peaks in the cooling and second heating curves may be associated with the degradation of the products of PCL and some inorganic fillers.

The degradation (or decomposition) of the material (Fig. 5) that starts at approximately 260 °C, probably is due to the degradation of polycaprolactone; this is confirmed from the DSC curve where in the second heating curve we observed that there is no melting point of PCL. This means that it had already degraded after heating up to 350 °C. Above 400 °C, commences the decomposition of the inorganic fillers commences.²¹

Fig. 7 shows that the adhesion between the polymer and the inorganic fillers was not so good and the surface was not smooth, some filler agglomerations could be observed which might be evidence that the filler particles were not homogeneously dispersed in the composite.

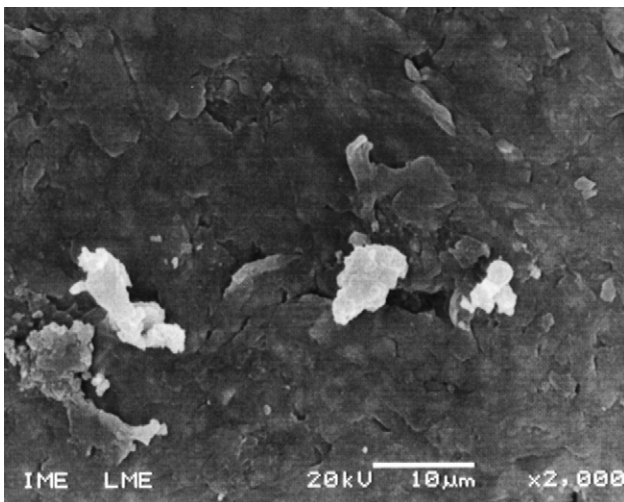


Fig. 7 – A micrograph of the surface of the Resilon™ sealer shows that the adhesion between the polymer and the inorganic fillers (white particles) was not so good and the surface was not smooth.

Gutta-percha, the traditional endodontic filling material, does not adhere to sealers or dentin, which can provide a relatively poor to non-existent barrier to prevent the coronal to apical migration of bacteria after obturation. It is not an ideal filling material, but it is metabolically inert, and it is thermoplastic. The new PCL (polycaprolactone) composites are thermoplastic and somewhat adhesive. Tay et al.²² study the ultrastructural quality of the apical seal in Resilon™ filled versus gutta-percha filled root canals that were created with the same compaction technique, using a silver tracer penetration protocol that has been employed in leakage evaluation of adhesive-bonded coronal dentin.²³ They were examined for gaps along canal walls using SEM, and for apical leakage using a transmission electron microscopy (TEM). They concluded that the quality of apical seal achieved with the new polycaprolactone-based root filling material and methacrylate-based (Resilon™/Epiphany) sealer is not superior to gutta-percha and a conventional epoxyresin sealer (gutta-percha/AH Plus).

More research is needed in order to determine whether the incorporation of more methacrylates into the polymer would improve its adhesiveness. However, PCL-based polymers and composites are not metabolically inert. Many different types of esterase enzymes can attack them.^{9,10}

5. Conclusions

The Resilon™ point material is basically a thermoplastic synthetic degradable polymer-based (polycaprolactone, PCL) root canal filling material. It contains bioactive glass and radiopaque fillers. It performs like gutta-percha, has the same handling properties, and for retreatment purposes may be softened with heat (T_m is very low), or dissolved with solvents like chloroform.

PCL is a semi-crystalline polymer, and its final properties, such as strength, modulus, shape-memory effect and biodegradability depend, to a great extent, on the crystalline fraction, which is affected in turn by conditions of crystallization. Therefore, investigation of the crystallization kinetics of PCL is of considerable practical significance. In order to obtain a material with better physical properties, it is especially necessary to study the dynamic, non-isothermal crystallization process.

Acknowledgments

The work described in this paper was supported by two grants from CNPq (Process 472449/2004-4, 400603/2004-7 e 500126/2003-6) and one from FAPERJ (Process E-26/151.970/2004).

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