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Synthesis and characterization of chitosan-*g*-glycidyl methacrylate with methyl methacrylate

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Abstract

In this work, the properties of chitosan (CTS) and synthetic polymers are combined to produce a novel hybrid synthetic–natural material. Poly(methyl methacrylate) (PMMA) and glycidyl methacrylate (GMA) are reacted with CTS to produce a versatile material for dental filler applications. This process involves the synthesis of CTS-*g*-GMA that is further reacted with PMMA [(CTS-*g*-GMA)-*g*-PMMA]. The chemical structure and physical properties of the resulting materials is analyzed by FTIR, DSC, SEM, NMR and XRD. The results revealed the evidence of strong intermolecular interactions between CTS-*g*-GMA and PMMA by covalent bonding formation. Thermal stability of the final copolymer [(CTS-*g*-GMA)-*g*-PMMA] is higher than its precursor, CTS-*g*-GMA. Presented results show a simple route to produce natural–synthetic polymers for potentially useful applications.

Keywords: Biopolymers; Chitosan; Glycidyl methacrylate; Graft copolymers; Hybrid natural–synthetic; Poly(methyl methacrylate)

1. Introduction

Poly(methyl methacrylate) (PMMA) has been reacted or blended with many synthetic and natural polymers such as poly(butyl acrylate) [1], poly (methyl acrylate) [2], acrylic acid, poly(vilidene floride) [3], glycopolymers [4], cellulose diacetate [5], among others, with the purpose of increasing hydrophobicity, chemical and physical resistance of the new material [6–10].

Poly(methyl methacrylate) (PMMA) is a polymer with an amorphous structure. It has very low water absorption; PMMA has high mechanical strength

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and good dimensional stability. Other properties include a high Young's modulus and good hardness with low elongation at break. PMMA does not shatter on rupture which is one of the hardest thermoplastics and is also highly scratch-resistant [11].

Poly(methyl methacrylate) (PMMA) is one of the most commonly used plastics as dental-base materials due to its good compatibility and mechanical properties. This acrylic resin has been used in dentistry since 1937 [12] and is currently the most popular material for the construction of removable denture and as the basis of dental composite filling materials. It is superior to other materials in terms of aesthetics, easy manipulation and low cost. However it does not possess a sufficiently high mechanical strength and may fracture through uneven masticatory force or accidental damage [13]. The bond strength of PMMA composites have been studied by peel, tensile, and shear tests. It has been reported that the bond strength can be improved by modifying the surface topography of PMMA [14,15].

Although many studies have been carried out on fiber-reinforced plastics to improve the mechanical properties of acrylic resin, they have been hampered by difficulties in overcoming problems of aesthetics and manipulation [16,17]. Natural polymers such as chitosan can potentially be reacted with synthetic polymers to improve their mechanical properties [18–21].

Chitosan is a deacetylated derivative of chitin, a biopolymer second in abundance to cellulose; it is biodegradable, nontoxic, and biocompatible [22–25]. Chitosan has been subjected to chemical modifications to produce advanced functional materials [26–35]. In Dentistry it is used because it prevents the formation of plaque and tooth decay. Since chitosan can regenerate the connective tissue that covers the teeth near the gums, it offers possibilities for treating periodontal diseases such as gingivitis and periodontitis [36].

Blends of CTS with hydroxyapatite have been used as bone-filling paste for bone substitute and dental composite filling [37]. The inconvenience of these materials is that they are difficult to manipulate and they do not present good mechanical properties.

The objective of this work is to produce new polymeric materials that possess both good mechanical and biocompatibility properties. To accomplish this, CTS is initially reacted with GMA [21] (CTS-*g*-GMA). This molecule possesses reactive vinyl groups that ease further reaction via free radical polymerization. In the second step, MMA is added to promote polymerization with CTS-*g*-GMA to produce the final material (CTS-*g*-GMA)-*g*-PMMA.

The results reported in this study provide a useful and simple route for developing hybrid natural–synthetic polymers with highly functional performance.

2. Experimental

Glycidyl methacrylate (GMA), methyl methacrylate (MMA), acetic acid, and potassium hydroxide (KOH) were purchased from Sigma–Aldrich Chemical Co., USA.

Methyl methacrylate and glycidyl methacrylate were purified with 5% NaOH to remove the inhibitor then washed twice with a 10% (w/v) aqueous $NaHCO_3$ and dried over $MgSO_4$. Solutions were finally distilled. The initiator AIBN (2,2-azobisisobutironitrile) was obtained from Aldrich Chemical Co., USA and recrystallized from methanol prior to use. Solvents, tetrahydrofuran (THF) and toluene were refluxed and distilled prior to use.

For CTS, the degree of deacetylation is ca. 87% determined by a titration method and the average molecular weight (M_v) is 3×10^5 g/mol determined by viscosimetry in 0.1 M acetic acid and 0.2 M sodium chloride solution with constant temperature (25 °C).

CTS was purchased from Sigma–Aldrich Chemical Co., USA and was used as received.

Fig. 1 shows the schematic of the synthesis of the copolymer, which involved two processes: (1) functionalization of chitosan with glycidyl methacrylate (CTS-*g*-GMA) already described elsewhere [21], and (2) synthesis of the copolymer [(CTS-*g*-GMA)-*g*-PMMA].

The polymerizations were carried out in a sealed ampoule (previously flamed), equipped with a magnetic stirring bar connected to high-purity nitrogen gas continuous injection, using 0.4 M acetic acid-to-THF ratio of 7:3 as solvent medium. AIBN 1 wt% as initiator, (CTS-*g*-GMA) and MMA was added to mixture at a molar ratio of 1:1.

The mixture was stirred; air was evacuated by a flow of nitrogen, the polymerization reactions were run at constant temperature of 70 °C for about 3 h.

The copolymer was dissolved in a suitable solvent/no-solvent system (acetic acid/THF, 7:3), and

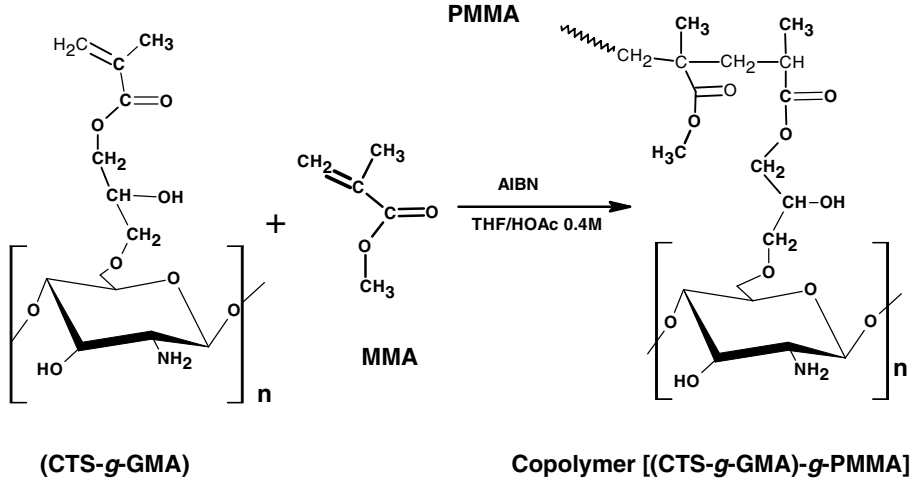

Fig. 1. Schematical description of (a) functionalization of chitosan with glycidyl methacrylate, and (b) synthesis of (CTS-*g*-GMA)-*g*-PMMA copolymer.

then was purified by several precipitation operations into acetonitrile.

3. Characterization techniques

Fourier-transform infrared (FTIR) spectra were obtained on a Nicolet Spectra 750 spectrometer in the 4000–400 cm^{-1} range at a resolution of 4 cm^{-1} in transmission mode. All samples were prepared in FTIR grade KBr (Sigma–Aldrich Chemical Co., USA) to form pellets of 12.8 mm of diameter.

Differential scanning calorimetry (DSC) was carried out in a thermal analyzer (DSC822 Mettler, USA). The samples were cut into small pieces and put into aluminum vessels. Sample vessels were initially heated from 0 °C to 180 °C at a heating rate of 1.0 °C/min under nitrogen atmosphere then cooled to 0 °C and heated to 500 °C at 10.0 °C/min. Second scans are reported.

Samples were sputter-coated with gold and were imaged using a scanning electron microscope Philips XL30.

X-ray diffraction (XDR) measurements were performed in a Rigaku D/max-2100 diffractometer (Cu Kα radiation) at 30kV and 16 mA, the angular resolution was of 0.02°.

Solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy was carried at 75.7 MHz at 18–19 °C on a Chemagnetics CMX-300 NMR spectrometer. Spectrometer was equipped with solid-state probes using 5 and 7.5 mm MAS zirconia rotors holding 150–200 and 600–700 mg of samples, respectively.

4. Results and discussion

FTIR spectra (KBr) of (CTS-*g*-GMA) and copolymer [(CTS-*g*-GMA)-*g*-PMMA] are shown in Fig. 2. The characteristic absorption at 1552 cm^{-1} corresponds to *st* C=C; the peak at 1650 cm^{-1} corresponds to a C=O vibration, and vs-OH at 3363 cm^{-1} all present in the CTS-*g*-GMA molecule. Other peaks in the functionalized materials are due to pure chitosan: C—H vibrations at 1400 cm^{-1} and to C—O—C at 1150 cm^{-1} and are in agreement to original chitosan [38,39].

In Fig. 2 a wide band in the 3100–3600 cm^{-1} region evidences hydroxyl groups present in the (CTS-*g*-GMA)-*g*-PMMA molecule. A band, due

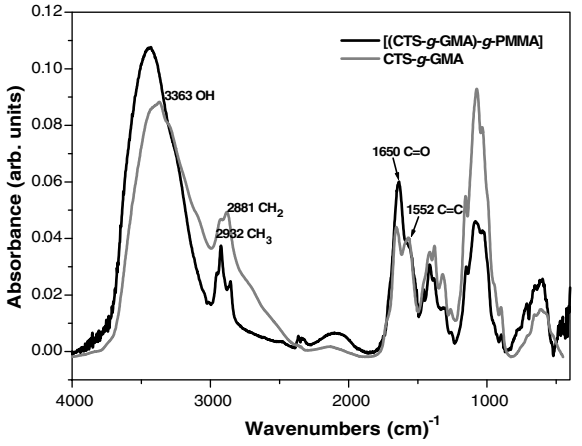

Fig. 2. FTIR spectra for (a) CTS-*g*-GMA, (b) (CTS-*g*-GMA)-*g*-PMMA copolymer.

to the bond C—H, appears in two distinctive peaks to 2932 cm^{-1} corresponding to the asymmetric stretching of the group CH_3 [40].

It can also be observed an absorption band at 1650 cm^{-1} that is assigned to *s* C=O of the ester group. Note that band 1552 cm^{-1} disappears in (CTS-*g*-GMA)-*g*-PMMA due to the insertion of the MMA group. A careful comparison of all spectra in Fig. 2 indicates significant differences in the position and magnitude of the IR bands for both CTS-*g*-GMA and (CTS-*g*-GMA)-*g*-PMMA.

Fig. 3 shows FTIR (KBr) spectra of the copolymer (CTS-*g*-GMA)-*g*-PMMA and pure PMMA. It is obvious to note the differences between the copolymer and PMMA; a broad absorption band of hydroxyl group in the region of 3100–3600 cm^{-1} (CTS-*g*-GMA) is absent in pure PMMA. In PMMA spectrum it was observed a strong absorption peak at 1735 cm^{-1} due to the carbonyl groups. In (CTS-*g*-GMA)-*g*-PMMA it is observed a peak associated with C=O group shifted at 1670 cm^{-1}, at 2950 cm^{-1} there appears the band corresponding to the asymmetric stretching of the C—H bonds. In summary, these results show a strong evidence on the chemical modification of chitosan to give CTS-*g*-GMA and (CTS-*g*-GMA)-*g*-PMMA, respectively.

Fig. 4 shows the spectrum of ^{13}C NMR for the copolymer (CTS-*g*-GMA)-*g*-PMMA. In the range of 40–70 ppm it is observed a chemical shift for structure of the polysaccharide (chitosan); the peaks at 44.96 ppm are attributed to the C-5 and C-3, for the anomeric carbon C-1 at 67.50 ppm and the sign at 49.28 ppm is attributed to C-4 [41].

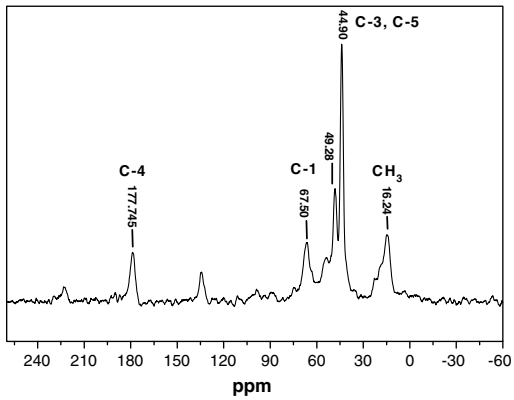

Fig. 4. NMR spectra (CTS-*g*-GMA)-*g*-PMMA copolymer. Note a sign at 177.74 ppm that is characteristic of the C-4 corresponding to CH_3 present in the acrylic material.

Analyzing the signs that correspond to the acrylic polymer (PMMA) it is observed at 16.24 ppm the characteristic band of the methyl group (CH_3) and at 177.745 ppm the sign that corresponds to C-4 of the acrylic material [42]. In summary, ^{13}C NMR and FTIR evidence chemical bonding formation of PMMA with CTS-*g*-GMA to obtain the copolymer (CTS-*g*-GMA)-*g*-PMMA.

DSC thermograms of both CTS-*g*-GMA and (CTS-*g*-GMA)-*g*-PMMA are shown in Fig. 5. CTS-*g*-GMA shows a melt point (T_m) at ca. 133 °C. The exothermic peaks at 284 °C and 410 °C may be associated with a partial and total decomposition (T_{PD}, and T_{TD}) of the CTS-*g*-GMA. A glass transition temperature is observed at ca. 91 °C.

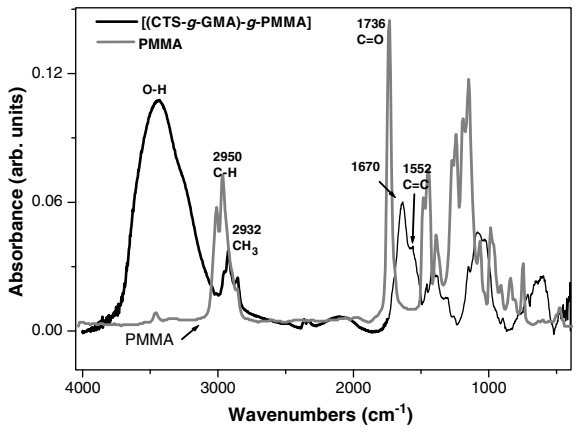

Fig. 3. FTIR spectra for (a) (CTS-*g*-GMA)-*g*-PMMA, (b) pure PMMA.

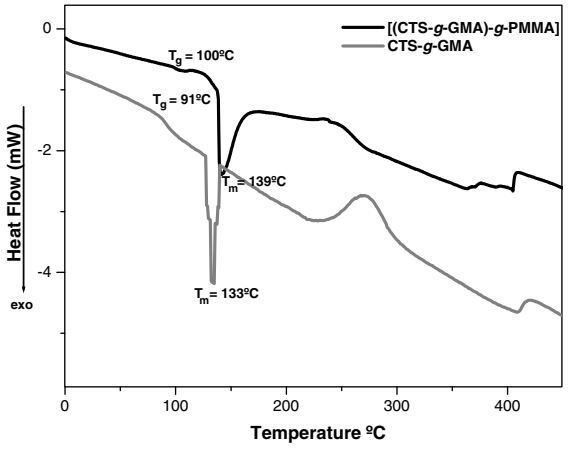

Fig. 5. Differential scanning calorimetry curves for CTS-*g*-GMA and (CTS-*g*-GMA)-*g*-PMMA.

Table 1
Differential scanning calorimetry analysis for chitosan, CTS-*g*-GMA, (CTS-*g*-GMA)-*g*-PMMA and PMMA

	T_g (°C)	T_m (°C)
Chitosan	–	151
CTS-*g*-GMA	91	133
(CTS-*g*-GMA)-g-PMMA	100	139
PMMA	110	–

Based upon DSC analysis, one may conclude that (CTS-*g*-GMA)-*g*-PMMA has higher thermal stability than CTS-*g*-GMA; the glass transition was observed at ca. 100 °C and melting point at ca. 139 °C. The occurrence of a single, broad glass transition in the (CTS-*g*-GMA)-*g*-PMMA is indicative of attractive molecular interactions and a high degree of compatibility of both materials. Based upon these observations, it is reasonable to assume the copolymer (CTS-*g*-GMA)-*g*-PMMA does not show phase separation.

Table 1 shows the summary of DSC results for pure CTS, PMMA, CTS-*g*-GMA, and (CTS-*g*-GMA)-*g*-PMMA. These results show the main thermal features of pure PMMA, which is due to high PMMA concentration in the copolymer matrix.

Fig. 6 shows scanning electron microscopy of: (a) pure chitosan, scale bar 20 μm; (b) CTS-*g*-GMA, scale bar 20 μm; (c) (CTS-*g*-GMA)-*g*-PMMA, scale bar 20 μm and (d) PMMA scale bar 10 μm. Pure chitosan exhibits a fibrous structure with not uniform microstructure. As observed in Fig. 6b CTS-*g*-GMA, the morphology of chitosan was affected by the presence of glycidyl methacrylate already described elsewhere [21].

Fig. 6c shows the surface morphology of (CTS-*g*-GMA)-*g*-PMMA; it is observed a homogeneous surface at the micrometer scale; the morphology is similar to that of the pure PMMA (Fig. 6d both are flat without the presence the aggregates. These results qualitatively support the chemical modification above described by means of spectroscopic studies.

Fig. 7 shows X-ray diffraction (XRD) patterns of (a) CTS-*g*-GMA, (b) (CTS-*g*-GMA)-*g*-PMMA, (c) pure PMMA, and (d) pure chitosan. Chitosan has two distinctive peaks at 11° and 20° (2θ), the areas of the two peaks are proportional to its crystallinity which is ca. 17% (Fig. 7d). In Fig. 7a XRD pattern of CTS-*g*-GMA shows similar peaks at pure chitosan; however both peaks at 11° and 20° (2θ) are reduced. This result is consistent with a lower crystallinity of ca. 6.14%. To calculate the crystallinity we used Sherrer formula $L = 0.9\lambda/(\beta \cos\theta)$, where λ is the wavelength of the Cu Kα radiation (1.5406 Å) and β the width at high degree of ordering. In Fig. 7b (CTS-*g*-GMA)-*g*-PMMA a similar trend is observed: crystallinity decreased to ca. 4.56%. Fig. 7c shows the amorphous nature of pure

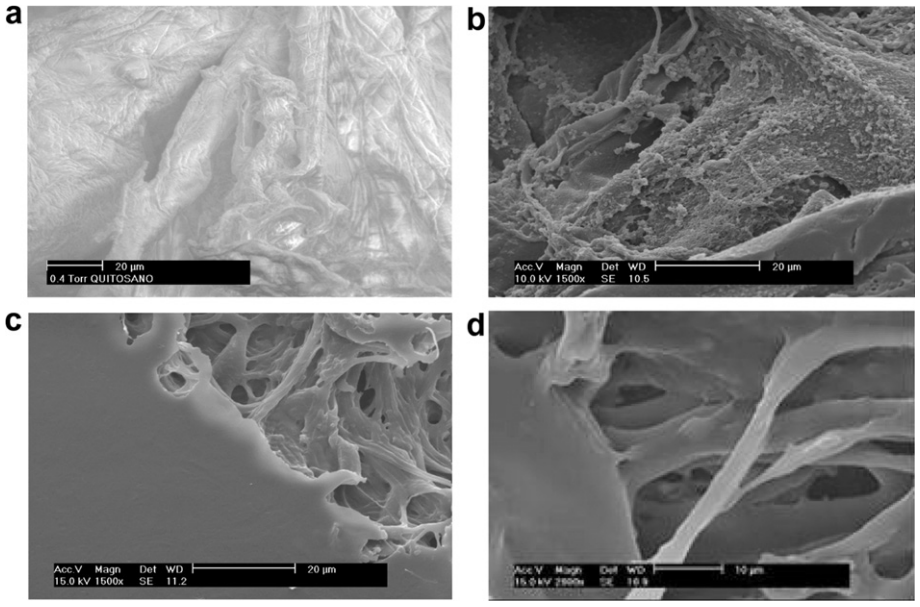

Fig. 6. Scaning electron microscopy micrographs of (a) Chitosan, scale bar 20 μm; (b) (CTS-GMA), scale bar 20 μm, (c) [(CTS-GMA)-*g*-PMMA], scale bar 20 μm and (d) pure PMMA, scale bar 10 μm.

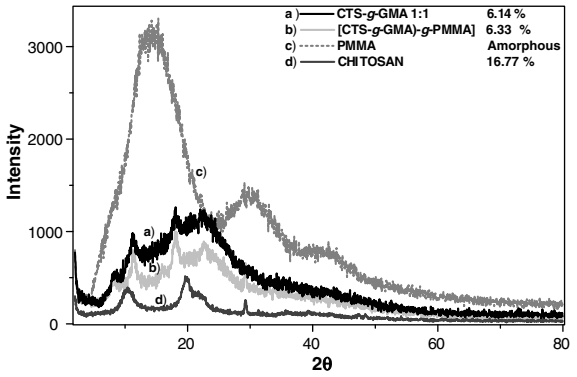

Fig. 7. X-ray diffraction spectra of: (a) CTS-*g*-GMA, (b) (CTS-*g*-GMA)-*g*-PMMA, (c) pure PMMA, and (d) pure chitosan.

PMMA. It is noteworthy that when PMMA reacts with chitosan, it induces thermal, morphological and structural changes that characterize the new materials.

5. Conclusion

The results reported in this study provide a useful and simple route for developing hybrid natural–synthetic polymers with highly functional performance. This study reports the successful synthesis of a copolymer (CTS-*g*-GMA)-*g*-PMMA through a two-step reaction process: CTS is initially reacted with GMA [21] (CTS-*g*-GMA), then MMA is added to promote polymerization with CTS-*g*-GMA to produce the final material (CTS-*g*-GMA)-*g*-PMMA.

All materials were characterized by FTIR, NMR, SEM, XRD, and DSC analyses. The copolymer (CTS-*g*-GMA)-*g*-PMMA shows superior thermal stability when compared to pure chitosan and MMA. FTIR and NMR spectroscopies were used to elucidate structural changes in the materials. These results showed strong interactions between CTS-*g*-GMA and PMMA. Morphological analysis by SEM revealed a transition from a 3-D fibrous structure to a flat structure with no aggregates. The copolymer obtained exhibits satisfactory properties when photopolymerized with PMMA that could be considered in dental filler applications. Work along this line is in progress.

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