

Synthesis and Characterization of Hybrid Polymers for Bone Regeneration based on Polymethacrylate

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Abstract

The study was mainly focused on the synthesis and identification of hybrid polymers based on the reversible additions of a series of methyl acrylate monomers, which are iso-Butyl methacrylate and Hydroxypropyl methacrylate using 3-(trimethoxysilyl)propyl methacrylate monomer to form an artificial silica. The produced silica is used in numerous applications that could be transformed into hybrid polymers to restore human bones. Three sections that the study addressed. The copolymers (IBMA-TMS) and (IBMA-HEMA) were synthesized using benzoylperoxide as an initiator through free radical polymerization. Then, the chemical structures of the polymers were identified using the X-ray analysis to find out the changes that occurred on the polymer's surface. The FT-IR spectrophotometry was utilized to ensure the skeletal structure of the polymers, which then confirmed that all the obtained bands corresponded to the chemical structure of the polymers. Additionally, difference Thermogravimetry (DTG) was conducted on the polymers to find out their thermal and oxidative stabilities. Likewise, thermogravimetric analysis (TGA) has been used to monitor the percentage of the lost polymers at various temperatures until reaching the max-temperature where the polymers are dissociated at. It was found that the best-synthesized polymer was conducted during the period of (3 hr.) at (70 °C). The dryness of the polymer was achieved at (40 °C) for (15 days), and then at (60 °C) for (10 days) to obtain the solid hybrid polymer.

Keywords: Polymer, sol-gel, methacrylate

1. Introduction

For the recent years, the free radical polymerization has been obtained a significant attention when it comes to the scientific research field. Suspension polymerizations and Emulsion have been relied on as foremost industrial methods for a quite time. Nitroxide mediated polymerization (NMP), and reversible addition fragmentation chain transfer (RAFT) polymerization, and atom transfer radical polymerization (ATRP) are techniques that have been significantly developed for the recent years that could be utilized to control the distribution of the polymer's molecular weight, as well as the chain architecture. Polar solvents and Lewis's acids could be considered to programing the stereocontrolled radical polymerization (1)

Bones are considered to be the essential tissue in physiology because they provide a structural support, protect the tissues and the core soft organs, produce white blood cells, and balance the ionic metals. It is believed that the mechanical bones's properties are derivative from a Nano molecule of collagen's fiber and (Hydroxy apatite HA) based on $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. The tensile hardness of collagen and the compressive strength of HA metal create a bonding in the mechanical properties where which could be achieved by the Macropore architecture (2) Justin J. Chung was proposed a synthesis to copolymers. The synthesis of copolymers 3-

(trimethoxysilyl)propyl methacrylate and of methyl methacrylate was carried out via reversible addition fragmentation chain-transfer (RAFT) and group transfer polymerisation (GTP) to produce well-known polymers. Additionally, a different polymer that possesses unique properties was synthesized which differ from the branched and linear types that previously proposed. Those polymers were utilized with the hybridized second category through sol-gel process. Compared to previous studies, the hybridized molecules have been shown better mechanical properties than glass and bioactive hybrids. Additionally, osteogenic cells were able to adhere and multiply on the hybrids. To increase the flexibility of the hybrids, a star polymer based on n-butyl methacrylate has been studied as an alternative to methyl methacrylate copolymers. The hybrid based on butyl methacrylate has been able to meet the mechanical properties of trabecular bone (3). In 2005, Angelika and Silvia on the other hand proposed a method to synthesize novel organic and inorganic hybridized molecules through the Free Radical polymerization of methylene. A methacrylate-substituted cluster of exotantalum $[\text{Ta}_4\text{O}_4(\text{OEt})_8(\text{OMC})_4]$ with methacrylate (MMA) and their properties was studied. The cluster was obtained by reacting the original alkoxide with methacrylic acid samples Hybrid materials with Ta-cluster were prepared in a ratio of 1:50 and 1:100 with methyl methacrylate. It is characterized by spectroscopic and thermal methods. Glass transition

temperature of hybrid materials Cross-linking of exotal polymer leads to higher temperatures than pure PMMA clusters. An increase in T_g is also noticed in dynamic mechanical analysis (DMA). A piece of evidence of the correlation between the T_a cluster and PMMA was acquired by infrared spectroscopy. X-ray photoelectron spectroscopy (XPS) provided insight into the surface's concentration which then stated that tantalum is bonded to oxygen. (4)

While in 2009, Rhee and Kyu-Hyeon were able to synthesize (PMMA / SiO₂ – CaO) nano compounds by utilizing tetraethoxysilane (TEOS) and dimethyldiethoxysilane (DMDES). After the sol-gel reaction, two and four siloxane bonds can be formed. Dimethyldiethoxysilane was used as a source of silica. It was found that there is a notable development in the fracture hardness even though that there was a slightly decrease in fracture toughness, the hardness, and the ability to produce forming ability in simulated body fluid (SBF).

The improved fracture toughness of sample D without losing its ability to form apatite is attributed to the reduction in the number of siloxane bonds and the addition of alkyl groups to the silica structure, as the siloxane bonds yield a tough and brittle fracture behavior in the nanocomposite. Alkyl groups, on the other hand, help produce silica as a linear structure. (5)

The general objective of the study is to synthesize solid and porosity hybridized scaffolds to renew bones as hybridized polymers using iso-butyl methacrylate (IBNA) monomer, 3-trimethoxysilyl propyl methacrylate (TMSPMA) monomer, hydroxypropyl methacrylate (HPMA) monomer through free radical polarization. Benzoyl peroxide (BPO) was the initiator used in the process using sol-gel method to produce porous solid polymer (ceramic) from tiny molecules in presence of methanol as a solvent to help in the formation of high-quality molecules with improving the structural properties of the silica particles.

2. Experimental

Methodology

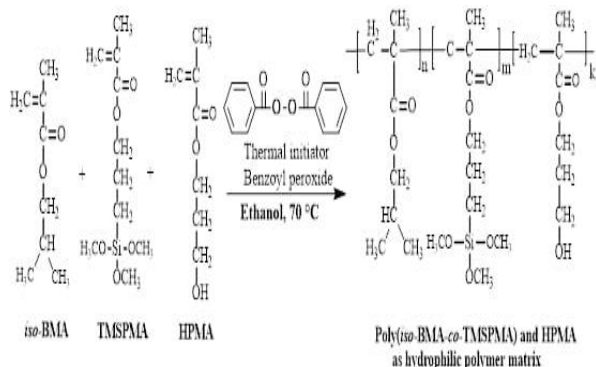


Figure (1) (iso-BMA-b-TMSPMA-b-HPMA)

The polymerization reactions carried out using a 250 ml Schlenk flask that is made of a high-quality and

thermal resistance borosilicate glass. The flask consists of a one neck round bottom flask that possesses a wide surface for heating compared to the flat flasks. This allows to the heat to be distributed equally when heating it up.

The random hybridized polymer was synthesized from an organic monomer which is butyl methacrylate (iso-BMA) (5 ml), the inorganic monomer 3-(Trimethoxysilyl) propyl methacrylate) (0.9 ml), and (5 ml) hydroxypropyl methacrylate that provides a hydrophilic polymer matrix in the hybridized. It also helps in the formation of silanol groups after degradation. The polymerization process was carried through the free radical polymerization using the thermal initiator (Benzoyl peroxide). The flask was sealed tightly, and then the initiator was injected with (0.5 ml) Benzoyl peroxide under nitrogen gas. Afterward, the flask was placed in an oven at (70 °C) for (3hr) to initiate the polymerization. While the flask mixture was in the oven, (10 ml) CaCl₂ was which added. A layer of apatite was formed when integrate the hybridized with the salt by dissolving the calcium ions with the biological active glass. In the presence of the silanol group (Si-OH) in the sol-gel formed on the surface, the (Ca+2) and (Si-OH) in a bi-system (CaO-SiO₂). The figure (1) shows the general equation of the reaction.

Figure (2) shows the dried hybridized packed sample for the solid hybridized polymer (iso-BMA-b-TMSPMA-b-HPMA). As it is shown in figure (II) that the solid hybridized polymer is formed when combining the hybrid with the CaCl₂. The combination of this monomer with 3-(Trimethoxysilyl)propyl methacrylate) monomer and calcium salt provides conventional bone cement based on methacrylate polymer with an ability to form apatite.



Figure (2) the dried hybridized packed sample for the solid hybridized polymer (iso-BMA-b-TMSPMA-b-HPMA).

3. Results and Discussion

The thermal analysis for the solid hybrid co-polymer iso-BMA-b-TMSPMA-b-HPMA that is made of an organic monomer, which is iso-butyl methacrylate

(iso-BMA) with the inorganic monomer (3-Trimethoxysilyl) propyl methacrylate (TMSPMA), as well as hydroxypropyl methacrylate HPMA as a hydrophilic monomer that was synthesized thermally analyzed using thermo-gravimetric analysis (TGA) and derivative thermo-gravimetric (DTG). The reason for the thermal analysis was to find out the qualitative and quantitative analysis for the TGA curve, which could have been impossible without obtaining the thermal gravimetric analysis derivative that, provides the highest peak DTG at any temperature particularly (T_i , T_f , and T_{max}) for the lost mass average. The analysis was carried out under (25 °C to 805 °C) and heating rate 20 °C/min. The sample's weight used in the degradation was (7.7375 mg). Figure (3) shows four steps for the analysis. The first step shows a slight decrease in the weight of the hybrid polymer in the beginning of the analysis at 125.33 °C, which has been recorded as 0.1075 mg (1.39%). While in the second step, there is a slight decrease as well of the sample's weight in about 0.2135 mg (2.76%) at 240.83 °C. The third step focuses on the core degradation of the hybrid polymer that accompanied with a weight lost (90.89%) (7.0326 mg) of the sample's weight at (483.50 °C). The final step of the degradation exhibits a weight loss of the polymer by 2.66 % of its weight at 805.50 °C. Therefore, the black residue of the co-polymer is (0.1781 mg) of the sample's weight [2,3] The figure (3) manifests a huge endothermic peak at 358.66 °C that corresponds with TGA that included a loss of the greatest mass, which resulted in the degradation of the hybrid polymer.

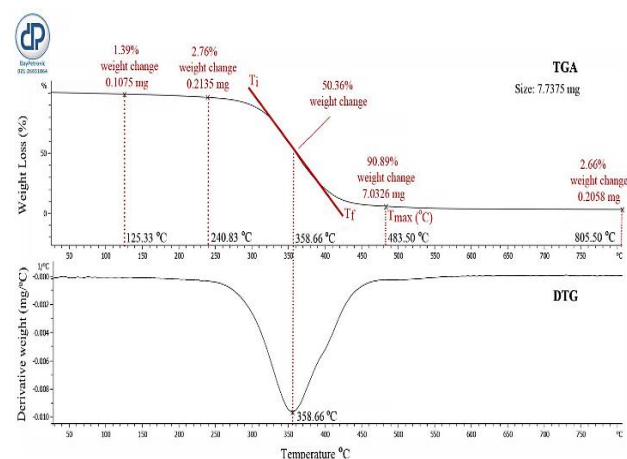


Figure (3) Thermal Degradation TGA/DTG of the hybrid polymer Poly (iso-BMA-b-TMSPMA-b-HPMA).

The synthesized polymer is sol-gel at first; however, it solidified after two weeks to form a biological active glass. Figure (4) shows the X-Ray Diffraction (XRD) for the polymer. The analysis was carried out without any cure to the synthesized polymer, nor any immersing in the simulated body fluid (SBF) or as it is called Kokubo (6). For investigating the changes that take place on the surface of biological active glassy ceramic, it was observed a wide peak at 17.60° (2θ at 17.60°) that indicates the presence of the binary system (CaO-SiO₂). Additionally, apatite phase was

determined using the peaks located between (2θ at 25°-30°) with a slight crystallization.

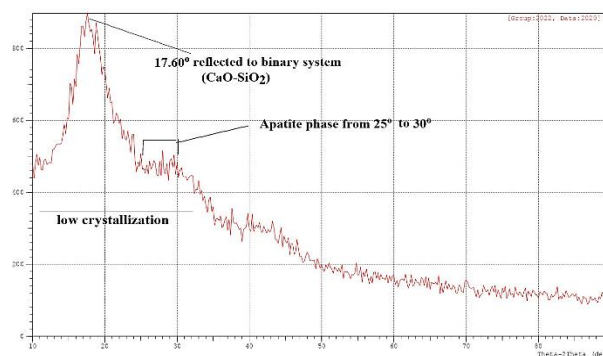


Figure (4): X-ray diffraction for the hybrid polymer (iso-BMA-b-TMSPMA-b-HPMA).

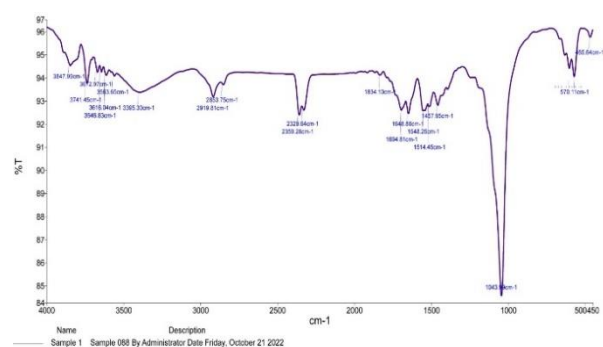


Figure (5) FT-IR spectrum for the biological active co-polymer (iso-BMA-b-TMSPMA-b-HPMA)

Figure (5) shows the FT-IR for (iso-BMA-b-TMSPMA-b-HPMA). Seven signals were observed for the biological active hybrid polymer, which are located at (3541, 3616, 3641, 3672, 3741, 3395, 3847 cm⁻¹). Table 00.5 shows the signals observed. The main signals at (3874 and 3741 cm⁻¹) are corresponded to the terminals and precipitated silanols groups. The other small peaks are attributed to the various (OH) groups. Those groups were observed due to the presence of the dilute alcohol group especially the one at (3672 cm⁻¹) might be attributed to hydrogen bounded to the (OH) (3,7). Si-OCH₃ has been shown a sharp signal at (1043 cm⁻¹).

Table (1): The vibrational transition for iso-BMA-b-TMSPMA-b-HP

| description | Wavenumber(cm ⁻¹) Pure | T% | |
|-------------------------|---------------------------------------|-----------|-----------|
| | | I | II |
| iso-BMA-b-TMSPMA-b-HPMA | v Si-OH precipitated | 3847 | 3741 |
| | v Si-OH terminal | 3742 | 3741 |
| | OH monomeric | 3200-3700 | 3646 3672 |
| | | 3610-3640 | 3616 3563 |
| | OH-stretching, weak, broad | 3200-3600 | 3395 3395 |
| | v CH ₂ (CH...OSi) | | 2853 2919 |
| | v Si-H | 2100-2360 | 2329 2359 |
| | v C=O as anhydride | 1818 | 1834 1834 |
| | v C=C monosubstituted | 1638 | 1648 1694 |
| | H ₂ O | 1365-1545 | 1514 1548 |
| | CH ₂ bend | 1400-1450 | 1457 1457 |
| | v Si-OCH ₃ | 1070 | 1043 1043 |
| | Si-C | 626 | 570 570 |
| | Si-O | 455 | 465 465 |

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