The Development of Biomimetic Nano $CaCO_3$/ PPBio Composites as Bone Repair Materials-Optimal Thermal Properties Evaluation

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Abstract:

$CaCO_3$/PP biocomposite have been proposed previously as biomaterial for bone repair applications.The effect of filler size and type on thermal parameters and crystallization behaviour have not been tacked thoroughly..

Enumeration search method (ESM) checks all possible combinations of design or processing variables in a bottom-up approach until it finds the global optimum solution for the design or processing conditions. In this paper, the optimum processing conditions for calcium carbonate/PP Nano composites as bone analogue biomaterials is sought. Also the effect of Nano sized Al_2O_3 on thermal properties and crystallization was studied. Enumeration search method (ESM) by Matlab software, give an indication for optimum processing conditions whose results are commensurate with those of the classical experiments design. Different compositions, compounding pressure, and processing temperatures were used in this work. Composites with 5% Al_2O_3/20 $CaCO_3$/75PP give the optimum thermal properties and uniform distribution of fillers in polymeric matrix.

Key words: Nano filler, biomaterial, Bone repair, Crystallization, Differential Scanning Calorimetry (DSC)

الخلاصة

تم اقتراح المادة المركبة الحيوية $CaCO_3$/PP سابقا كمادة مرممة للعظم. ان تاثير نوع وحجم المادة المضافة على العوامل الحرارية وسلوك التبلور لم يتم دراستها بشكل تام. طريقة Enumeration search method (ESM) تعطي الاحتمالية لكل الحلول الممكنة والتي تجمع بين متغيرات التصميم والتصنيع والخواص المثلى. في هذا البحث تم تحديد افضل ظروف التصنيع للمادة المركبة المقترحة كمادة مرممة للعظم وكذلك تم دراسة تاثير اضافة الالومينا كمادة مضافة نانوية في الخواص الحرارية وسلوك التبلور. تم استخدام برنامج ماتلاب لاجراء عمليه المفاضلة لاختيار افضل الظروف والتي اعطت نتائج تتوافق مع الطرائق التقليدية في الحسابات. تم دراسة ظروف مختلفة للتصنيع وتراكيز مختلفة في هذا البحث . المادة المركبة الحاوية على 5% Al_2O_3/20 $CaCO_3$/75PP اعطت افضل خواص حرارية وتوزيع متجانس للمادة المضافة في الارضية البوليمرية.

الكلمات المفتاحية: المواد المالئة النانوية، المواد الحيوية، ترميم العظم، التبلور، معيارية المسح التفاضلي(DSC)

1.Introduction

Calcium Carbonate with similar composition to natural bone, has been extensively developed for biomedical applications in the past decades because it has good biocompatibility and bioactivity and can be bonded with host bone directly (Shokrollahi *et.al.*,2010; Li *et.al.*,2013)

However, $CaCO_3$ ceramics devices, such as filler and porous scaffold, exhibit manifest brittleness, which vastly impedes their clinical applications.(Lin *et.al.*,2011). In order to obtain biomaterial with good bioactivity and good mechanical properties, more and more attention focuses on the researches and medical applications of a composite combining $CaCO_3$ with a polymer because such composite possesses are of good bioactivity($CaCO_3$)and good ductility (polymer)(Raj *et.al.*,1989; Kiss *et. al.*,2007; Karamipour *et.al.*,2011) Those biocomposites are biocompatible and osteoconductive and hence can be bonded with host bone directly and thus form a uniquely strong biomaterial-bone interface .(Mareri *et.al.*,1998)

Polymer Nano composites have attracted increasing attentions in recent years because of their significant improvement in mechanical performance, thermal stability and/or electrical properties over the matrix polymers (Liang,2007). The effects of filler nanoparticles on these properties have been extensively investigated. It has been found that the addition of a few percent by weight of these nanoparticles can result in

significant improvement in physical and chemical properties (Shentu *et.al*.,2006). However, these advantages can only be exploited if filler nanoparticles are distributed homogenously and do not form aggregates in the polymer matrix. Particle aggregation, which is often detected in particulate filled polymers, can result in a number of problems, including deteriorated mechanical properties and poor aesthetics (Zhang *et.al*.,2012).

One of the most efficient ways to hinder aggregate formation is the surface coating of the filler with a surfactant. Surface treatment leads to decrease of both particle/particle and matrix/filler interaction. As a consequence, surface coated fillers are used practically always for the production of the particulate filled thermoplastic products (Han *et.al*.,2010).

Polypropylene (PP) is a very versatile and adaptable polymer whose properties can readily be enhanced with the inclusion of various types of fillers. The advantages gained in price/volume/performance relations have resulted in PP composites successfully penetrating fields traditionally occupied by other engineering materials (Chan *et.al*.,2002; Zebarjad *et.al*.,2004;Saghi *et.al*.,2009).

Generally, properties of particle-filled PP are strongly dependent on the characteristics of the filler particles. Alumina considered as a good choice in case of mechanical properties enhancement. So that it proposed as a second filler in $CaCO_3$ and PP, in order to gain the envisaged enhancement in mechanical properties .

Effect of different filler types on the rheological and thermal properties of polymer matrix had been investigated by several authors (Josepha *et.al*.,2002; Lim,2005; Salkhi khasraghi *et.al*.,2011), in this study we focus on the influence of Nano sized fillers on the melting and crystallization kinetics for PP as an approach to understanding the particulate filler -polymer matrix interaction because it is an important factor that affects thermal, mechanical, and biological properties for this composite system.

Optimal thermal properties has been evaluated using Enumeration data method using MATLAB software.

2.Materials and Methods

2.1 Materials

PP powder is provide by Right Fortune Industrial restricted (Shanghai, China), with average particle size of 10 nm and a nominal density of 0.911 g/cm3 is used in this work. Nano $CaCO_3$ powder with 99% purity, having an average particle size of 20nm and a particle density of 2.93 $g.cm^{-3}$, and α-alumina powder with average particle size of 40 nm and density of 3.97 $g.cm^{-3}$ are also used as ceramic fillers. The ceramic powders are provided by M.K. Nano (Toronto, Canada).

2.2 Preparation of Nano composites

As shown in Table 1, Ball mill dry mixing is used to mix powders in different weight%. The hot pressing technique is utilized to prepare the samples by using hot pressing system designed, especially for work in different compression pressure and compounding temperatures as it is summarized in Table 1..

Table 1: Sample Preparation Conditions

Composition (weight%)	Compression Pressure (MPa)	CompoundingTemperature (°C)
10%$CaCO_3$+90% PP	30,60,90	180, 190,200
20% CaCO3 +80PP	30,60,90	180, 190,200
5%Al_2O_3+20% CaCO3 +75%PP	30,60,90	180, 190,200

2.3 Differential Scanning Calorimetry DSC

The crystallization behaviour and melting characteristics of the composite are investigated by Differential Scanning Calorimetry (DSC) using a Perkin–Elmer DSC-

8000 thermal system purged with nitrogen of 50 ml/min at a heating rate of 10 °C /min.

The crystallinity (Xc) for the composite materials is determined by using the following formula (Mai *et.al*.,2012):

$$\mathrm{Xc\%} = \left(\frac{\Delta \mathrm{Hf}}{\Delta Hf^{\circ}}\right) x\ 100\% \qquad (1)$$

Where $\Delta \mathrm{Hf}$ and ΔHf° are the enthalpy of fusion of the system and the enthalpy of fusion of perfectly (100%) crystalline PP, respectively. For ΔH_f° (PP), a value of 209 J/g is used for 100% crystalline PP.

2.4. Enumerated Data Method Using MATLAB Software

Enumerated data is data that is restricted to a finite set of values. An enumerated data type is a MATLAB class that defines a set of enumerated values. Each enumerated value consists of an enumerated name and an underlying integer that the software uses internally and in generated code(Joko *et.al*.,2015).

Enumeration method tests all the possible solutions one by one, searching for an optimal solution. This method lists all possible solutions and then eliminates the non-optimal schedules from the list, leaving those, which are optimal. The optimal criteria are considers by the decision makers. It is clear that searching for an optimal solution among all possible solutions using complete enumeration is not suitable even for problems of small size(Kathiravan and Ganguli,2007).

MATLAB software used in this work to estimate optimum properties depending on processing conditions. Moreover, strength/weight ratio has been calculated because in scaffold application this ratio is important to produce a bone or scaffold with both of suitable weight and strength.

2.4 SEM structure evaluation

LEO-SEM 1530 scanning electron microscopy has been used to study the morphology of the samples was studied using, at an accelerating voltage of 5kV and at a working distance of 6 mm.

The samples were prepared using silicon carbide papers with grids of 1000, 2500, and 4000within surface grinding step. After that, the samples have been polished using diamond foam with suitable cloth disk. After the surface preparation process, the samples were secured onto specimen holders by the conductive carbon cement and coated with 5 nm layer of Pd-Pt(20:80) by CVD technique. The imaging process was controlled using Smart SEM.

3. Results and Discussion

3.1 Melting and Crystallization Behavior

Effect of different filler types on the rheological and thermal properties of polymer matrix had been investigated by several authors (Josepha *et.al*., 2002; Lim,2005; Salkhi *et.al*.,2011), in this study we focus on the influence of Nano sized fillers on the melting and crystallization kinetics for HDPE as an approach to the understanding of the particulate filler -polymer matrix interaction because it is an important factor that affects thermal, mechanical, and biological properties for this composite system.

The collected data from DSC test are listed in tables 1-4, Thermal stability parameters have been investigated based on onset of melting T_o, the peak of melting T_p, and heat of fusion obtained from single non-isothermal DSC scan.

The peak melting temperature and extrapolated onset melting temperature are calculated from the peak position and intersection of the extrapolated linear section of the falling peak edge with the baseline extrapolated from temperatures

below the peak, while heat of fusion (ΔH) is calculated by integrating the area under the DSC endothermic peak (Hernández *et.al*.,2012).

In general, typical $CaCO_3$/PP, and Al_2O_3/$CaCO_3$/PP samples showed a single melting endotherm. The peak melting temperature and extrapolated onset melting

temperature and heat of fusion were affected significaly by Nano filler type and volume fraction.

All DSC scans show a single endothermic peak for melting. In some researches like (Josepha *et.al*.,2002; Salkhi *et.al*.,2011) existence of the single peak in the endothermic and exothermic curves has been attributed to the occurrence of co-crystallization.

However as it is mentioned by some authors (Hernández *et.al*.,2012) , the existence of single peak is not the only a reliable reason to confirm the occurrence of co-crystallization. In such cases, the analysis of the melting and crystallization temperature is inadequate and the other sensitive parameter in such situations is the half-width of the endotherms. Larger half-width is expected if two or more components form separate crystals, although the melting or crystallization peaks may be located in close proximity.

Crystallization is increased by adding nano particles, because of the nano particles role as nucleation site for the crystalline phase, and because the crystallization is judged via the heat of fusion ΔH. As the heat of fusion increases, so does the crystallization and this finding agrees with the previous literature(Josepha *et.al*.,2002; Fouada *et.al*.,2011).

Table 1 Thermal Data for DSC Curves (100%PP)

Sample Composition	Processing Temperature °C	Compression Pressure Mpa	Tp °C≠	T onset °C*	Xc%	Heat of fusion for melting J/g
100%PP	180	30	111.800	115.00	47.00	95.00
	190	30	111.830	115.40	47.30	96.00
	200	30	111.832	115.60	47.42	96.50
	180	60	111.850	115.70	47.50	97.00
	190	60	111.880	115.74	47.70	97.20
	200	60	111.890	115.78	47.74	97.60
	180	90	111.920	116.00	47.78	98.00
	190	90	111.931	116.20	47.81	98.32
	200	90	111.944	117.00	48.00	98.40

Table 2 Thermal Data for DSC Curves (10%$CaCO_3$+90% PP)

Sample Composition	Processing Temperature °C	Compression Pressure Mpa	Tp °C ≠	T onset °C*	Xc%	Heat of fusion for melting J/g
10%$CaCO_3$+90 % PP	180	30	118.900	120.00	46.80	76.00
	190	30	118.910	121.00	46.81	76.20
	200	30	118.917	121.30	46.81	76.23
	180	60	118.920	121.80	46.84	76.30
	190	60	118.932	122.00	46.86	76.50
	200	60	118.945	122.40	46.87	76.63
	180	90	118.976	123.00	46.88	76.72
	190	90	117.000	123.22	46.89	77.00
	200	90	117.210	124.00	46.92	77.10

Table 3 Thermal Data for DSC Curves (20% $CaCO_3$ +80PP)

Sample Composition	Processing Temperature °C	Compression Pressure Mpa	Tp °C ≠	T onset °C*	Xc%	Heat of fusion for melting J/g
20% $CaCO_3$ +80PP	180	30	120.00	126.00	48.20	82.000
	190	30	120.33	126.40	48.22	82.1000
	200	30	120.54	126.45	48.23	82.140
	180	60	120.55	126.61	48.40	82.145
	190	60	120.65	126.77	48.45	82.230
	200	60	120.66	126.81	48.52	82.400
	180	90	120.95	126.84	48.63	82.420
	190	90	121.00	126.85	48.7	82.44
	200	90	121.40	127	48.72	82.47

Table 4 Thermal Data for DSC Curves (5%Al_2O_3+20% $CaCO_3$ +75%PP)

Sample Composition	Processing Temperature °C	Compression Pressure Mpa	Tp °C ≠	T onset °C*	Xc%	Heat of fusion for melting J/g
5%Al_2O_3+20% $CaCO_3$ +80PP	180	30	122.00	128.0	51.00	83.20
	190	30	122.30	128.2	51.40	83.24
	200	30	122.40	128.3	51.80	83.31
	180	60	122.50	128.7	52.00	83.40
	190	60	122.70	129.0	54.00	83.45
	200	60	123.00	129.3	54.20	83.52
	180	90	123.10	129.5	54.60	83.55
	190	90	123.50	129.7	55.00	83.56
	200	90	123.56	129.9	55.30	84.20

3.2 Optimization Results

Figure (1) shows the 3D plots for To,Tp, Xc%, and ΔHc respectively. The x-axis present the processing temperatures , while y-axis present the compression pressures.

Each level belongs to one of the proposed compositions from bottom to up with increasing the filler %.

Crystallization is increased by adding Nano $CaCO_3$ particles, because of their role as nucleation site for the crystalline phase, and because the crystallization is judged via the heat of fusion ΔH. As the heat of fusion increases, so does the crystallization and this finding agrees with the previous literature (Josepha *et.al*.,2002; Hernández- Montelongo *et.al*.,2012).

Figure (2) shows the mean values for all thermal properties. While figure (3) shows the MATLAB algorithm.

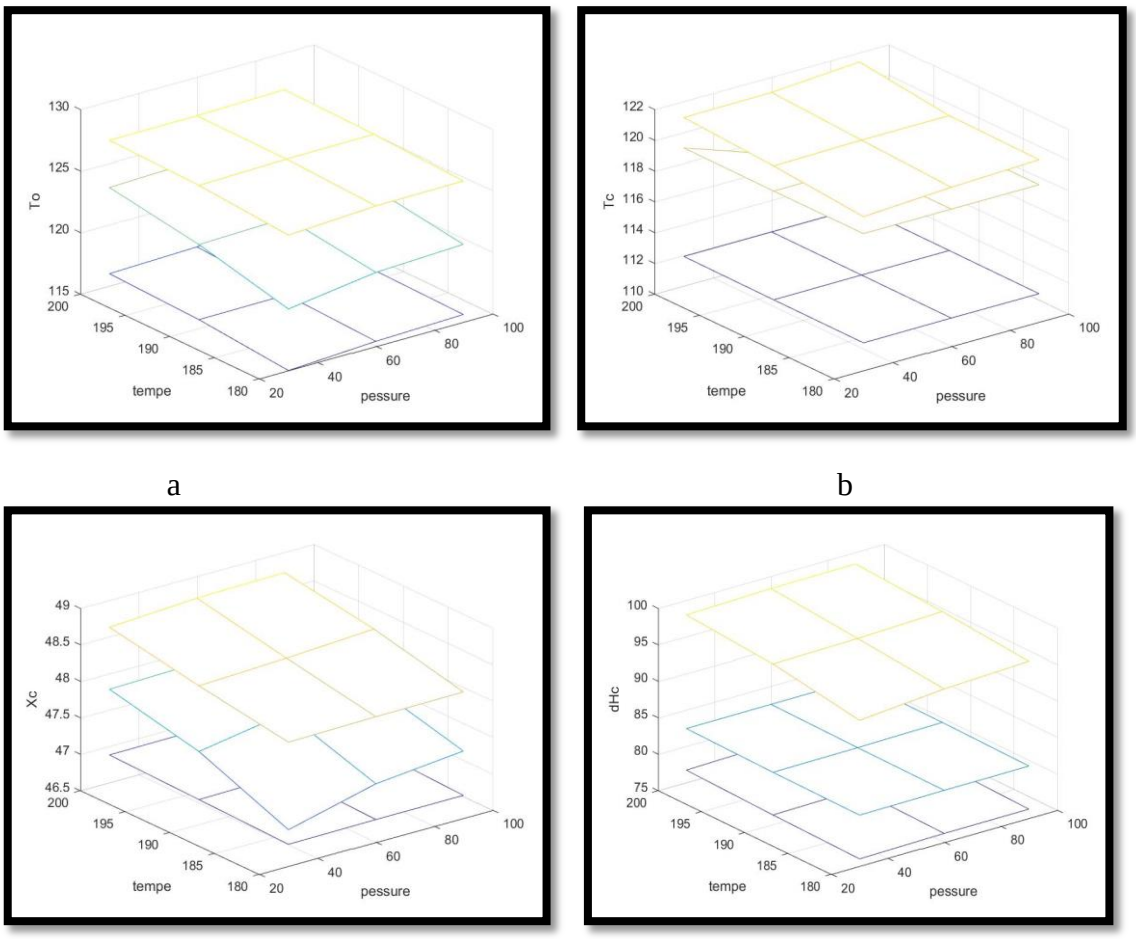


Figure 1: 3D Model for a) To-Temp.Pressure ,b) Tc(Tp)-Temp.Pressure ,c) Xc%-Temp.Pressure ,d) ΔHc-Temp.-Pressure (By MATLAB software).

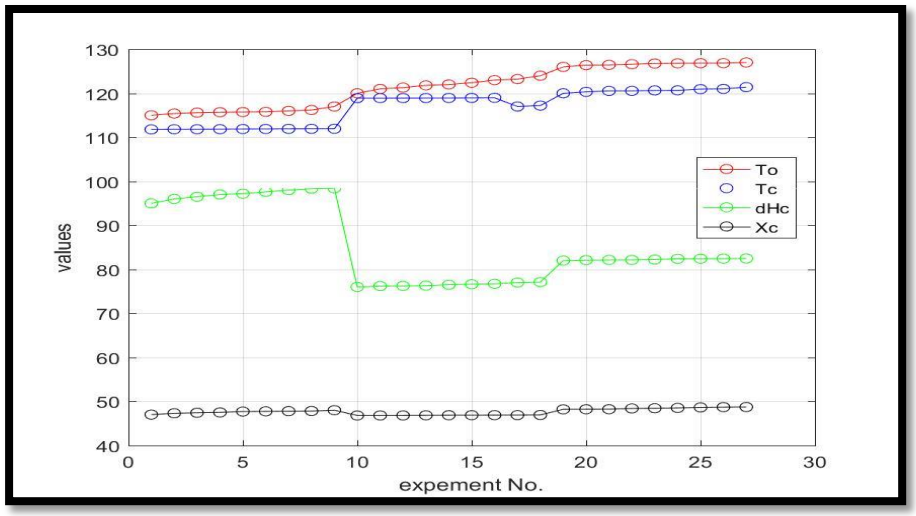


Figure 2: All Mean Values (By MATLB software)

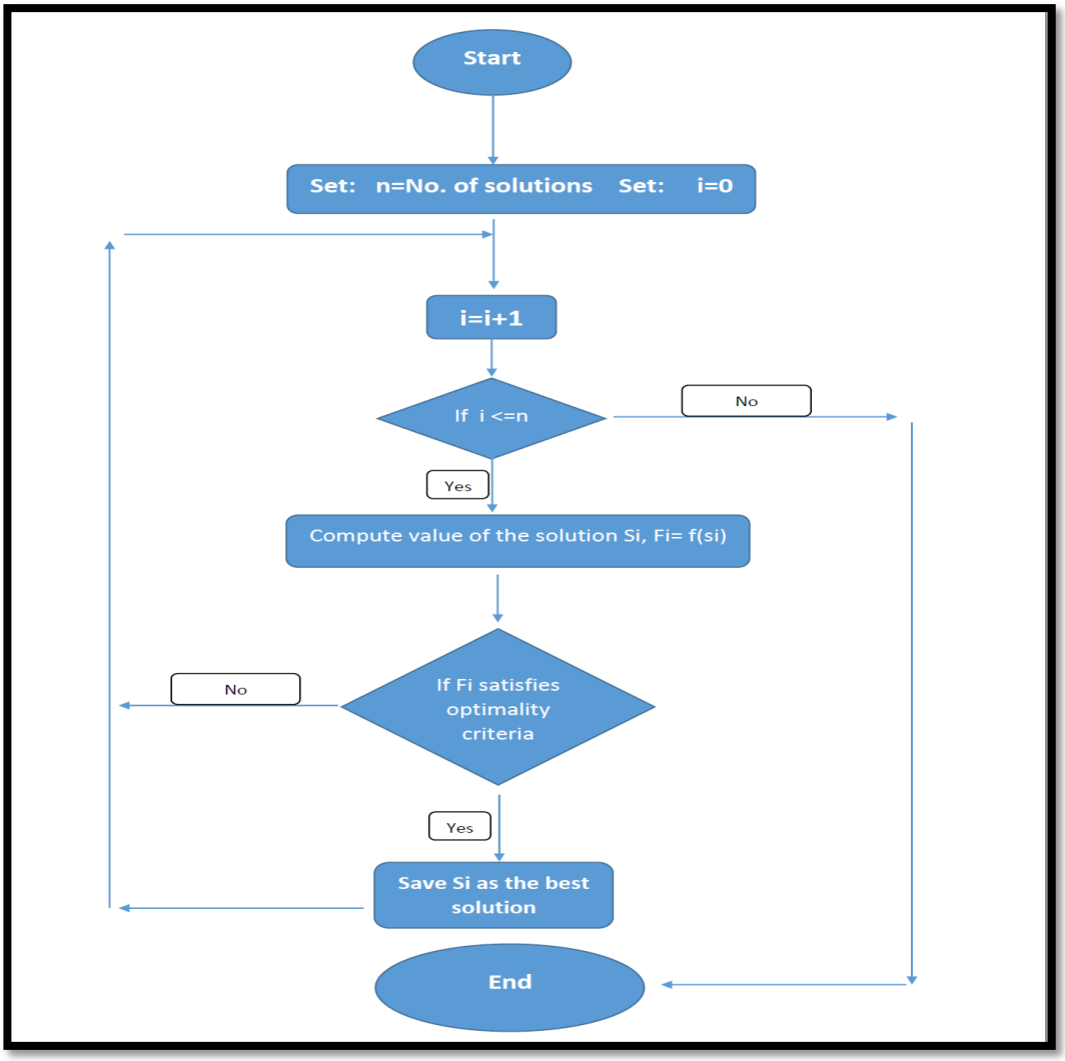
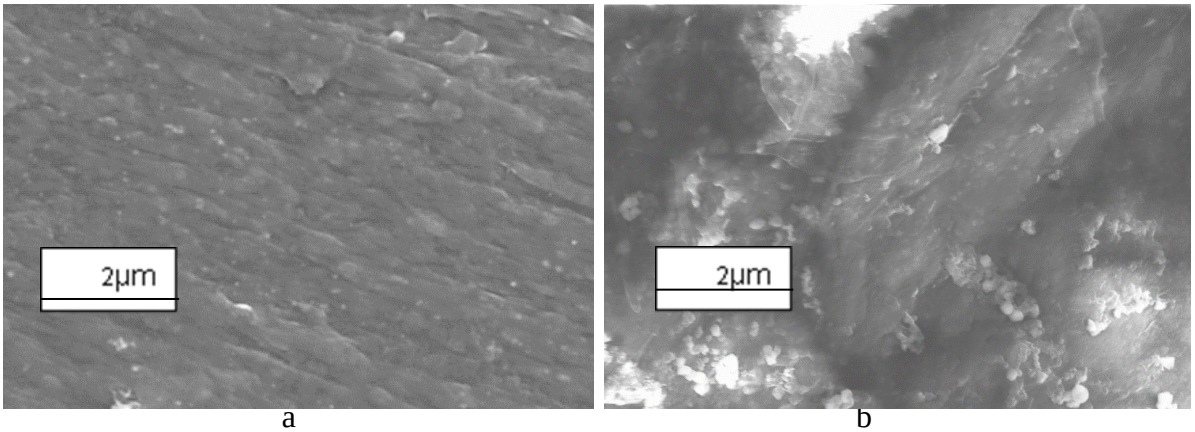


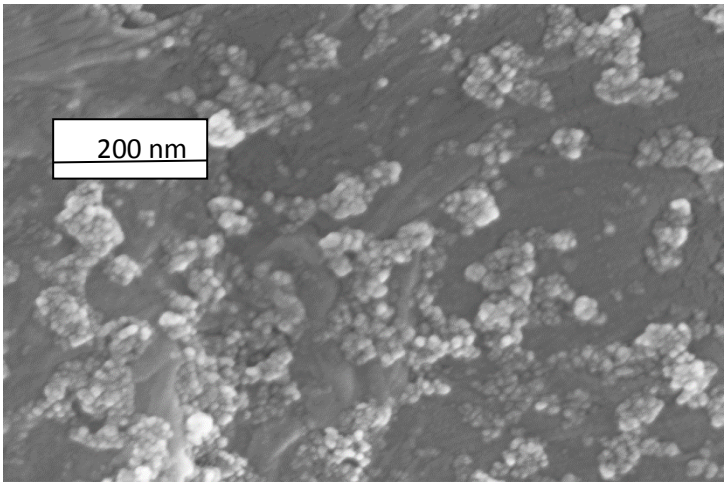
Figure 3: Algorithm Used by MATLAB Software to Optimization Method.

3.3 Morphology of Nano composites

Figure (4) shows a uniform distribution of Nano ceramic filler within polymeric matrix for the whole composition used in this work. Nano filler is distributed as a particles and a small agglomerates in PP matrix which have good impact on Thermal properties and crystalline behaviour for biocomposite materials are proposed in this work.



a b



c

Figure 4: SEM a) 10 $CaCO_3$/90PP Implant, b) 20 $CaCO_3$/80PP, c) 5Al_2O_3/20 $CaCO_3$/80PP all Photos Shows Uniform Distribution for Nano Filler in Polymer Matrix.

4. Conclusions

$CaCO_3$/PP Nano composite gives an interesting properties for the bone analogue and the substitute application. The addition of alumina enhances the thermal properties of the composite materials but within suitable range. Polymeric matrix biocomposite investigated in this work can be biomimetic for natural bone. Enumeration method using MATLAB software is considered an effective analysis tool when all the possible results must take place in optimization process.

Nano $CaCO_3$ filler has a remarkable effect on the thermal stability and crystallization behavior of PP polymeric matrix. This stability will be reflected on both of bonding between filler and matrix ,and the thermal stability during processing. Enhancement in crystallinity is considered a good factor for biocomposite materials during the process of implanting in a living tissue.

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