Improvement of thermal stability and mechanical properties of medical polyester composites by plasma surface modification of the bioactive glass particles

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Abstract

Poly(L-lactide)(PLLA), poly(ε-caprolactone)(PCL) and poly(L-lactide/ε-caprolactone)(PLCL) are medical (co)polyesters that are conventionally manufactured by thermoplastic processing techniques, such as injection molding or extrusion. However, the addition of bioglass particles causes a degradation reaction of the matrix at high temperatures and could limit the fabrication of composite systems by the above mentioned processes. In this work, a surface modification of bioactive glass particles by plasma polymerization of acrlylic acid is proposed as a strategy for the improvement of thermal stability of bioglass filled composite systems. The developed poly(acrylic acid) layer on the surface of bioglass particles, hinders the degradation reaction between the $Si\text{-}O^-$ groups present in the surface of the particles and the C=O groups of the polymer´s backbone. As an illustration, the onset degradation temperature (T_{onset}) of PLLA, PCL and PLCL increased respectively from 185.0, 240.1 and 192.2 for bioglass (BG) filled composites to 240.4, 299.5 and 245.7 ºC for their modified bioglass (mBG) filled counterparts. Finally, neat PLLA and composites having 15 vol.% of BG and mBG were melt-compounded and subsequently hot pressed to obtain tensile test samples. Non-modified bioglass filled PLLA film was too brittle and difficult to handle due to the sharp reduction of molecular weight during thermoplastic processing. On the contrary, modified bioglass filled PLLA presented a slight increase in Young´s modulus with respect to unfilled PLLA but a decrease in both tensile strength and elongation at break.

Keywords: polylactides, polylactones, bioactive glass, surface modification, plasma polymerization.

1. Introduction

The combination of medical biodegradable polymers with inorganic bioactive particles has emerged as a promising strategy to lead materials with applications ranging from structural implants to tissue engineering scaffolds, particularly in the field of bone tissue engineering [1]. Among the available inorganic bioactive particles, bioactive glasses (e.g. Bioglass45S5) present a rapid bone bonding and thus, are considered as Class A bioactive materials [2]. Bioglass is an osteoproductive and osteoconductive material and, in contrast to Class B bioactive materials, it also bonds to soft tissues providing an improved long-term survivability of the implant. The dissolution products of bioglass have a direct effect on the deposition of an hydroxyl carbonate apatite layer on the surface of the material [3] and on the gene-expression profile of surrounding cells [4], inducing the osteoblast proliferation and differentiation. Recent studies have also reported the pro-angiogenic properties of bioglass filled polymeric scaffolds, leading to a higher vascularization and percentage of blood vessels of the constructs [5]. To complement the properties of bioglass for specific medical application requiring load bearing, composite systems made of bioglass particles or fibers and biodegradable polymer matrix are being proposed. The commonly employed biodegradable matrices are lactide and caprolactone based polymers or copolymers, such as poly(L-lactide) (PLLA) [6], poly(ε-caprolactone) (PCL) [7] or poly(L-lactide/ε-caprolactone) (PLCL) copolymers [8], thanks to their biodegradability, biocompatibility and tunable mechanical properties.

The above mentioned polymers and copolymers are prone to be conventionally manufactured by thermoplastic processing techniques such as injection molding, blow molding, thermoforming or extrusion [9]. However, a previous work of our group [10]

revealed that these polyesters suffer a sharp decrease in their thermal stability in the presence of bioglass particles, which led to a high reduction in both molecular weight and mass of the polymer when maintaining at high temperatures. In this sense, PLLA, PCL and PLCL filled with 15 vol.% of bioglass lost respectively, ~60, 30 and 10% of their initial weight when they were subjected to an isothermal treatment at 210ºC during 20 minutes. On the contrary, their unfilled counterparts did not undergo significant weight losses (<1%) when they suffered the same isothermal treatment. Degradation during processing at high temperatures produced deterioration of the mechanical properties of the final product [11] and, moreover, any thermal degradation byproducts formed during processing may result to be toxic to the human body [12]. This fact would limit considerably the manufacturing and mechanical properties of these polyesters by the conventional processing techniques and would restrict their potential use as biomedical materials.

Surface modification of bioglass particles could offer a promising solution to the previously discussed problem. The attachment of organic molecules to the surface of bioglass particles has been previously proposed to improve the interphase adhesion between inorganic particles and polymer matrix [13] but has never been applied to avoid the degradation reaction between the $Si\text{-}O^-$ groups present in the surface of bioglass particles and the C=O groups present in the polymer´s backbone. Several methods have been reported in the current literature for the surface modification of inorganic bioactive particles [6, 13, 14]. However, all these surface modification methods require multiple steps of long duration and high quantities of organic solvents that can be harmful for health, limiting the application of these products in the biomedical field.

Plasma polymerization, which refers to the formation of polymeric materials under the influence of a partially ionized gas (plasma) [15], provides an alternative option to the above mentioned conventional coating processes. This method has been earlier successfully employed for the surface modification of hydroxyapatite particles using acrylic acid as monomer [16-17]. In these two investigations a successful surface modification of the particles was achieved reducing the tendency of the particles to form agglomerates and thus, improving the mechanical behavior of the composites. Plasma polymerization does not use organic solvents, reduces the quantity of reagents (monomer) and the time of the overall process, being a promising choice in regard to the traditional wet processes.

In this study, acrylic acid was plasma polymerized on the surface of bioglass particles and then, the surface of modified bioglass (mBG) particles was characterized by means of thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). Composites of PLLA, PCL and PLCL filled with modified (mBG) and non-modified bioglass (BG) particles were prepared by solvent casting/sonication procedure and their thermal degradation behavior was studied using dynamic and isothermal thermogravimetric analyses (TGA) and gas permeation chromatography (GPC) measurements. Finally, in order to investigate the performance of one of these systems in a real thermoplastic processing technique, PLLA/mBG and PLLA/BG composites were melt compounded and subsequently hot pressed. The mechanical properties of the final product were measured by tensile tests.

2. Materials and methods

2.1. Materials

PLLA of a weight-average molecular weight (M_w) of 500,000 g $mol^{-1}$and polydispersity index (PDI) of 1.56, PCL of a M_w of 120,000 g mol^{-1} and PDI of 1.61 and PLCL of LA/CL molar ratio approximately 70/30, a M_w of 190,000 g mol^{-1} and PDI of 1.67, were kindly supplied by Purac Biochem (The Netherlands). A PLLA with a M_w of 160,000 g mol^{-1} and PDI of 1.7, supplied by Biomer (Germany), was the polymer employed in the thermoplastic processing.

The 45S5 Bioglass® particles were supplied by Novabone® (US) having a composition (in wt.%) of 45.0% SiO_2, 24.4% Na_2O, 24.5% CaO and 6.0% P_2O_5. To measure their size distribution, a dispersion of these particles in ethanol was prepared and, after sonicating for 15 minutes, some drops were placed on a microscope glass slide. Finally, the sample was examined in a microscope and the size distribution was determined using the ImageJ software. The particles were of particle size <60 µm, a mean particle size of 9 µm and density of 2.75 g cm^{-3}.

2.2. Surface modification of bioglass particles

As mentioned in the introduction, surface modification of bioglass particles was carried out via plasma polymerization, which was performed in a PICO LF (low frequency-40 kHz) Plasma Polymerization System (Diener electronic GmbH + Co. KG, Germany). This system consists of a horizontal chamber of 32 cm length and 15 cm diameter, where the bioglass particles were placed between 20 µm meshes. The plasma treatment started with a cleaning process in which the chamber was evacuated until 0.2 mbar to remove possible humidity and followed by 10 minutes oxygen supply at a flow rate of 25 sccm and 700W. Secondly, the monomer inlet was opened and monomer (acrylic acid, anhydrous, 99%, Sigma-Aldrich) vapor was allowed to flow through the reactor for 2 minutes being the pressure within the chamber ~0.15 mbar. Then, power was

adjusted to 80W and the particles were exposed to glow discharge for 45 minutes. Finally, the power generator was turned off and a deactivation step was conducted, where the monomer was allowed to flow inside the chamber for five minutes. The optimization of all these conditions to obtain an appropriate surface modification and to prevent the fragmentation of the monomer structure during the plasma process has been thoroughly adjusted in a previous work of us [18].

2.3. Surface characterization of bioglass particles

10-15 mg of bioglass (BG) and modified bioglass (mBG) particles were placed in platinum pans and heated within a thermogravimetric analyzer (TGA Q50-0545) from room temperature to 600ºC at a heating rate (β) of 5ºC min^{-1} and a nitrogen flux of 60 mL min^{-1} for sample. During this process, heat flow, sample temperature, sample weight and its time derivative were recorded continuously. Thus, the mass of the poly(acrylic acid) deposited on the surface of bioglass particles was determined. This measurement was done in triplicate to check whether the plasma treatment was repetitive.

The infrared spectra of the BG and mBG particles were recorded on a Nicolet AVATAR 370 Fourier Transform Infrared spectrophotometer (FTIR). The samples were prepared as follows: a small quantity of bioglass particles was mixed with KBr and the mixture was manually milled until a fine powder was obtained. Finally, the resulting powder was pressed into a disc. Spectra of these samples were taken with a resolution of 2 cm^{-1} and were averaged over 64 scans.

X-ray Photoelectron Spectroscopy (XPS) of BG and mBG particles was performed with a SPECS (Germany) instrument equipped with Phoibos 150 1D-DLD analyzer and monochromatized Al Kα (1486.6 eV) radiation source. Wide scans (1100 to 0 eV

Binding energy, BE; step energy 1 eV; dwell time 0.1 s; pass energy 40 eV) and high-resolution spectra (C1s; step energy 0.1 eV; dwell time 0.1 s; pass energy 20 eV) were acquired with an electron take-off angle of 90º. The hydrocarbon peak component in the C1s spectra was set at 285.0 eV to correct sample charging. The spectrometer was previously calibrated with the peak of Ag 3d 5/2 (368.28 eV).

2.4. Preparation of samples

Neat polymers (PLLA, PCL and PLCL) and composite films of these polymers filled with 15 vol.% of non-modified (BG) and modified bioglass (mBG), were prepared by solvent casting using chloroform (Panreac, Spain) as solvent. Briefly, a dissolution of polymer was prepared at a polymer weight to solvent volume ratio of 5% (w/v). BG or mBG particles were added to the polymer solution, which was then sonicated for 15 min. This process was employed to obtain an homogeneous distribution of bioglass particles in the solution and to avoid the formation of agglomerates. Finally, the mixtures were transferred to Petri dishes and dried for 24 h at room temperature and another 24 h at vacuum.

2.5. Thermal degradation behavior of samples

Thermal degradation behavior of samples was studied by means of TGA. Samples of 10-15 mg were heated from room temperature to 500 ºC at a β=5ºC min^{-1}, recording continuously the heat flow, sample temperature, sample weight and its time derivative. In this temperature range, the polymer is degraded completely while the bioactive particles did not suffer significant weight losses [19].

Apart from dynamic experiments, isothermal degradation experiments were also performed within the TGA. Samples (10-15 mg) of neat polymer and composites filled

with 15 vol.% of BG and mBG particles were heated at 10 ºC min^{-1} up to the desired temperature (210 ºC) and maintained at this same temperature for 2, 10 and 20 min.

The progress of the molecular weight of the samples was determined by GPC using a Waters 1515 GPC apparatus equipped with two Styragel columns (10^2 - 10^4 Å). Chloroform was used as an eluent at a flow rate of 1 mL min^{-1} and polystyrene standards (Shodex Standards, SM-105) were used to obtain a primary calibration curve.

2.6. Thermoplastic processing and tensile tests of the derived samples

Neat PLLA and composites filled with 15 vol.% of BG and mBG were processed by a conventional thermoplastic processing technique. PLLA pellets and bioglass particles were dry-mixed and subsequently melt compounded in a corotating twin-screw microextruder (15ml microcompounder, DSM Xplore). The operating conditions of the microextruder were arranged as screw speed of 60 rpm, barrel temperature of 200 ºC and a mixing period of 3 minutes. The obtained melt was cooled at room temperature, treated by hot pressing at 200ºC during 4 minutes and water quenched in order to obtain 175-225 µm films. The molecular weight of the samples was measured before and after melt compounding and once the films were eventually conformed.

Finally tensile tests of these films were performed with an Instron 5565testing machine at a crosshead displacement rate of 10 mm min^{-1}. This test was carried out at 21±2ºC and 50±5% relative humidity following ISO 527-3/1995 (ISO 527-3/2/10).

3. Results and discussion

3.1. Surface modification of bioglass particles

After plasma treatment, the surface of the modified bioglass particles was analyzed by means of thermogravimetric analysis, infrared spectroscopy and X-ray photoelectron spectroscopy. In Figure 1 thermogravimetry (TG) profile of BG and mBG particles is represented. In this temperature range, BG particles did not suffer significant weight losses, whereas mBG particles lost 1.95±0.1% of their initial weight. The peak degradation temperature, determined as the temperature at which a maximum in the differential thermogravimetry (DTG) curve was achieved, was 440ºC. This temperature is similar to the peak degradation temperature reported in the literature [20] for poly(acrylic acid), indicating that the deposited compound on the surface of bioglass particles may have similar structure to poly(acrylic acid).

Figure 2 shows FTIR spectra of BG particles, mBG particles and poly(acrylic acid). The main characteristics of the spectrum of the unreacted bioglass are attributed to the amorphous silica glass. The two bands at 1050 and 950 cm^{-1} are assigned to Si-O-Si stretching vibration and the band at 450 cm^{-1} is assigned to Si-O-Si bending vibration [21]. The spectrum of poly(acrylic acid) shows the characteristic carbonyl group at 1710 cm^{-1}. Other bands, associated with scissors and bending vibrations of $–CH_2–$ and CH–CO groups appeared at 1456 and 1415 cm^{-1}, respectively. In the spectra of mBG particles, apart from those mentioned above for unreacted bioglass, another band appeared at 1710 cm^{-1}, which is ascribed to the C=O stretching. This new band in the spectra of mBG particles may indicate the presence of poly(acrylic acid) on the surface of bioglass particles since this band is the most prominent in the spectra of pure poly(acrylic acid) as seen in Figure 2 (below).

Figure 3 shows high-resolution XPS spectra of C1s for BG and mBG particles. The spectrum of BG particles was fitted with a single peak centered at 285.0 eV which corresponds to C-C/C-H bond. On the contrary, spectrum of mBG particles was best

fitted with 3 peaks: 285.0 eV (C-C/C-H), 288.5 eV (O-C=O) and 287.9 eV (C=O). This fact indicates the presence of additional molecular species on the surface of the mBG particles. The well defined peak at 288.5 eV denoted a high retention of carboxylic acid group, which is characteristic of the poly(acrylic acid) structure.

3.2. Thermal degradation behavior of samples

Figure 4 shows thermogravimetry and differential thermogravimetry profiles for unfilled PLLA(A) and PLLA filled with 15 vol.% of mBG (B) and BG (C) particles, named respectively PLLA+mBG and PLLA+BG. From this figure, peak (T_{peak}), onset (T_{onset}) and end (T_{end}) degradation temperatures can be determined, which are summarized in Table 1. The corresponding T_{peak} and T_{onset} were 312.5 and 261.6 ºC for PLLA, 275.4 and 240.4 ºC for PLLA+mBG and 241.3 and 185.0 ºC for PLLA+BG. As previously reported [10], the incorporation of non-modified bioglass caused a dramatic decrease in both T_{peak} and T_{onset} temperatures because of a degradation reaction between the $Si\text{-}O^-$ groups present in the surface of the particles and the C=O groups of the polymer´s backbone. However, the surface modification of the bioglass particles hindered this reaction and thus, the thermal stability of PLLA+mBG was considerably improved with respect to PLLA+BG. The activation energies, which were calculated by the Friedman approach [10], confirmed the improvement in thermal stability as a result of the surface modification of bioglass particles. In this sense, the activation energy dropped from 163.8 kJ mol^{-1} for unfilled PLLA to 85.0 kJ $mol^{-1}$for PLLA+BG, while it reached a value of 137.4 kJ mol^{-1} for PLLA+mBG. This same trend was observed for the other two studied polyesters (PCL and PLCL), which showed higher resistance to thermal degradation than PLLA thanks to the presence of more resistant caprolactone units. As an illustration, T_{onset} of PCL suffered a reduction of almost 100 ºC (from 339.8 to 240.1 ºC) when adding BG particles, whereas this reduction was 40.3 ºC when the

mBG particles were added. On the other hand, T_{onset} of unfilled PLCL decreased from 274.5 ºC to 192.2 and 245.7 ºC for PLCL+BG and PLCL+mBG, respectively.

For isothermal degradation experiments, a temperature of 210 ºC was selected because some of the polymers used in this work are usually processed around this temperature in conventional processing techniques like injection molding or extrusion. Figure 5 and Table 2 show the evolution of the weight-averaged molecular weight (M_w) and polydispersity index (M_w/M_n) of PLLA, PLLA+BG and PLLA+mBG during this isothermal treatment. The unfilled PLLA did not undergo important changes neither in its molecular weight (<5%) nor in its polydispersity index during the isothermal treatment. In the case of PLLA+BG, the M_w was reduced ~75% after 10 minutes at 210 ºC and the M_w/M_n increased from 1.6 to 2.0, indicating the random chain scission of the polymer chains. After 20 minutes at 210 ºC, the M_w was only 8.7% of its initial value and M_w/M_n reached a value of 2.2. PLLA+mBG did not suffer changes during the first 10 minutes at 210 ºC. After 20 minutes, M_w was 68.7% of its initial value and the M_w/M_n reached a value of 2.0. Table 2 also shows the progress in the mass of PLLA, PLLA+BG and PLLA+mBG during the isothermal treatment. After 20 minutes at 210 ºC, the mass of PLLA remained constant whereas PLLA+BG and PLLA+mBG lost respectively ~50% and ~10% of their initial mass. In view of these results, it can be seen that the modification of bioglass particles difficults the degradation reaction between the bioglass particles and PLLA and consequently, the PLLA+mBG maintained its initial molecular weight and mass longer than PLLA+BG during an isothermal treatment at 210 ºC.

This same trend was also observed for both PCL and PLCL. However, the improvement in thermal stability caused by the surface modification of bioglass particles was more clearly visible in the case of PLLA with respect to PCL and PLCL. As reported in our

previous work [10], PLLA is the most affected polyester to the above mentioned degradation reaction. This reaction involves the SiO^- groups of the bioglass particles and the ester groups of the polyesters. Since in PLLA the density of ester groups within the polymer structure is higher than in PCL and PLCL, the reaction may occur in a greater extent. Although unfilled PCL suffered minor M_w changes during the isothermal treatment, the addition of 15 vol.% of BG caused a reduction of ~35% after 20 minutes at 210 ºC. Surface modification of bioglass particles slightly improved the thermal stability and thus, the M_w loss was 24% during the isothermal treatment for PCL+mBG. Regarding the weight loss results, both PCL and PCL+mBG lost <1% of their initial weight, whereas PCL+BG lost ~9%. PLCL shows an intermediate performance between PCL and PLLA. In this sense, the M_w dropped to ~25% of its initial value when adding 15 vol.% of BG particles after 20 minutes at 210 ºC. On the contrary, PLCL+mBG maintained 80% of its initial molecular weight after the same isothermal treatment. Therefore, PLCL and PLCL+mBG did not undergo severe weight losses during the isothermal treatment while PLCL+BG lost 18% of its initial mass.

3.3. Thermoplastic processing and tensile properties of PLLA, PLLA+BG and PLLA+mBG

The polymers and copolymers presented in this work could fulfill the mechanical requirements for the regeneration of trabecular bone in load bearing applications. Trabecular bone can be found in the interior of long bones, such as femur, surrounded by a dense cortical bone shell. Flat bones, such as calvaria, presents a sandwich structure with dense cortical layers on the outer surface and a thin trabecular structure within [22]. The elastic modulus of trabecular bone is between 10-1570 MPa, whereas the strength range is between 1.5-38 MPa [23]. The deterioration of the mechanical properties of bioglass filled biodegradable polymers reported by some authors [11]

could limit the clinical applications of these systems. Figure 6 and Table 3 summarize the progress in number-averaged molecular weights (M_n) during thermoplastic processing of PLLA and PLLA filled with 15 vol.% of BG and mBG particles. Unfilled PLLA only lost ~15% of its initial M_w and M_n and its polydispersity index was maintained almost constant. It has to be pointed out that the M_w loss was more pronounced during this thermoplastic processing with regard to the isothermal treatment mentioned in the previous section. In this sense, the shear stresses produced in the twin-screws of the microcompounder could contribute to the degradation of polymer chains. PLLA+BG lost ~66% and ~72% of its initial M_w and M_n respectively after melt compounding. Moreover, polydispersity index increased from 1.7 to 2.1 indicating the random chain scission of polymer chains. Then, after hot pressing, PLLA+BG lost only 3.6% and 11.9% of M_w and M_n with respect to the material obtained from the melt compounder. This fact may indicate that melt compounding is much more aggressive than hot pressing because of the considerably higher shear stresses. PLLA+mBG showed better resistance to thermal degradation than PLLA+BG and maintained ~50% of its initial M_w and M_n after all the process.

After hot pressing, films of PLLA, PLLA+BG and PLLA+mBG were obtained and their mechanical properties are summarized in Table 4. PLLA showed a Young´s modulus of 1309 MPa, a tensile strength of 46.9 MPa and an elongation at break of 8.4%. PLLA+BG film obtained from the hot pressing was too brittle and difficult to handle. The sharp reduction of its molecular weight during thermoplastic processing may have caused a deterioration of its mechanical properties and thus, samples for tensile test were not possible to obtain. Finally, PLLA+mBG presented a slight increase in Young´s modulus with respect to unfilled PLLA due to the incorporation of stiff particles to the polymer matrix. However, probably because of the reduction in molecular weight and

the weak interphase adhesion between inorganic particles and polymer matrix at higher strains, the tensile strength and ultimate strain decreased from 46.9 to 36.1 MPa and from 8.4 to 5.3%, respectively.

4. Conclusions

In this work plasma polymerization was proposed as a method to modify the surface of bioactive glass particles. This surface modification hindered the degradation reaction between the $Si\text{-}O^-$ groups present in the surface of bioglass particles and the C=O groups present in the polymer´s backbone and thus, improved the thermal stability of the studied composites. As a result, PLLA filled with modified bioglass particles was prone to be manufactured by a conventional thermoplastic procedure, whereas its non-modified bioglass filled counterpart underwent sharp decrease in molecular weight and the resulted product was fragile and difficult to handle.

Plasma polymerization offers a rapid and clean alternative to traditional wet processes for surface modification of particles. However, the homogeneity of this treatment has to be still optimized in order to assure the modification of the whole surface of all particles. Plasma reactors with fuidized beds or circulating streams are being proposed to achieve this objective. The optimization of this process may result in the production of completely surface modified particles and would permit the manufacturing of bioglass particles filled polyester composites by the conventional thermoplastic techniques, avoiding the risk of thermal degradation during processing.

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Fig. 6 Progress in M_n of unfilled PLLA and PLLA filled with 15 vol.% of mBG or BG particles processed by a conventional thermoplastic processing technique

Table 1

	T_{onset} [a] (ºC)	T_{end} [b] (ºC)	T_{peak} [c] (ºC)	E_a (kJ mol^{-1})
PLLA	261.6	312.5	303.7	163.8
PLLA+BG	185.0	241.3	235.2	85.0
PLLA+mBG	240.4	275.4	266.6	137.4
PCL	339.8	401.4	377.7	228.9
PCL+BG	240.1	275.5	271.4	125.3
PCL+mBG	299.5	342.1	338.5	159.9
PLCL	274.5	362.7	326.8	136.3
PLCL+BG	192.2	299.2	282.5	92.0
PLCL+mBG	245.7	311.8	272.0	120.0

[a] Determined as the temperature at which 5% of polymer mass has been lost
[b] Determined as the temperature at which 95% of polymer mass has been lost
[c] Determined as the temperature at which a maximum in the DTG curve has been achieved

Table 2

	time (min)	*PLLA*	*PLLA +BG*	*PLLA +mBG*	*PCL*	*PCL +BG*	*PCL +mBG*	*PLCL*	*PLCL +BG*	*PLCL +mBG*
M_w (%)	0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	2	100.0	95.7	96.1	100.0	97.4	99.4	97.1	100.0	98.5
	10	100.0	24.9	99.7	98.6	80.3	88.4	98.6	38.3	96.0
	20	95.5	8.7	68.7	96.0	64.9	75.7	96.4	24.7	81.1
M_w/M_n (PI)	0	1.7	1.7	1.7	1.4	1.4	1.4	1.6	1.5	1.5
	2	1.6	1.6	1.6	1.4	1.6	1.5	1.7	1.6	1.6
	10	1.6	2.0	1.6	1.4	1.7	1.6	1.7	2.3	1.6
	20	1.6	2.2	2.0	1.4	1.7	1.7	1.7	6.2	1.6
Weight (%)	0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	2	99.9	94.9	99.7	100.0	99.4	99.9	100.0	97.2	99.8
	10	99.7	73.8	97.2	99.9	96.2	99.6	99.7	88.9	98.2
	20	99.4	49.9	89.6	99.9	90.5	99.4	99.3	82.1	95.3

Table 3

		As received	*Melt compounded*	*Hot pressed*
PLLA	M_w	159.8 (100%)	145.3 (90.1%)	136.2 (85.2%)
	M_n	92.1 (100%)	82.6 (89.7%)	77.0 (83.4%)
	PI	1.7	1.8	1.8
PLLA+BG	M_w	159.8 (100%)	53.9 (33.8%)	48.3 (30.2%)
	M_n	92.1 (100%)	25.3 (27.5%)	14.4 (15.6%)
	PI	1.7	2.1	3.4
PLLA+mBG	M_w	159.8 (100%)	95.0 (59.4%)	78.8 (49.3%)
	M_n	92.1 (100%)	53.8 (58.4%)	44.0 (47.8%)
	PI	1.7	1.8	1.8

Table 4

	Young´s Modulus (MPa)	*Ultimate tensile strength (MPa)*	*Ultimate strain (%)*
PLLA	*1309.0 ± 70.4*	*46.9 ± 1.3*	*8.4 ± 0.4*
PLLA+BG	-	-	-
PLLA+mBG	*1393.9 ± 84.3*	*36.1 ± 1.3*	*5.3 ± 0.5*

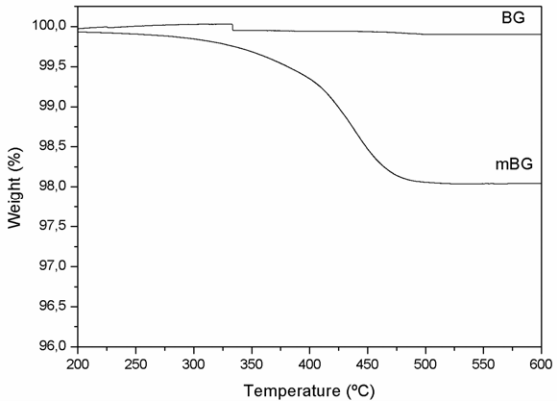

Figure 1

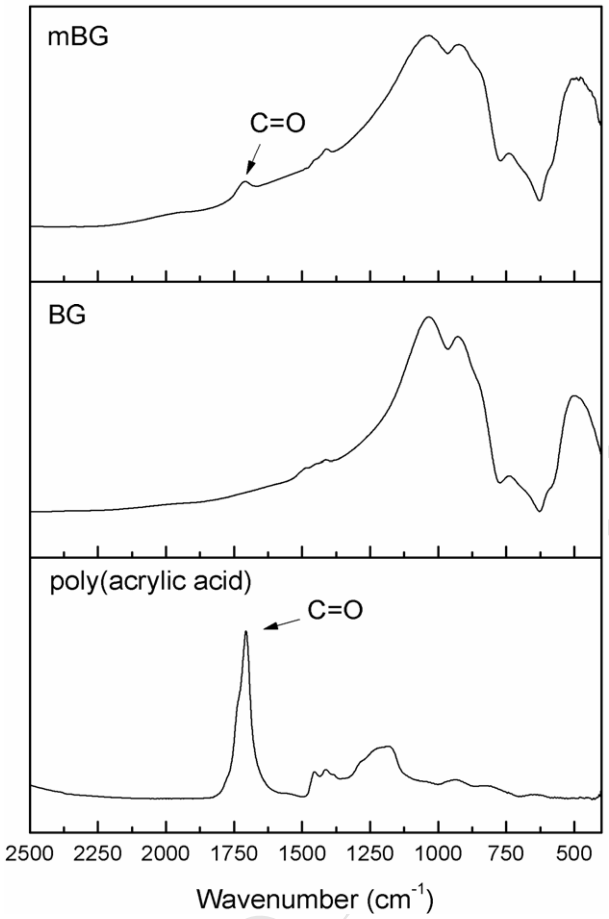

Figure 2

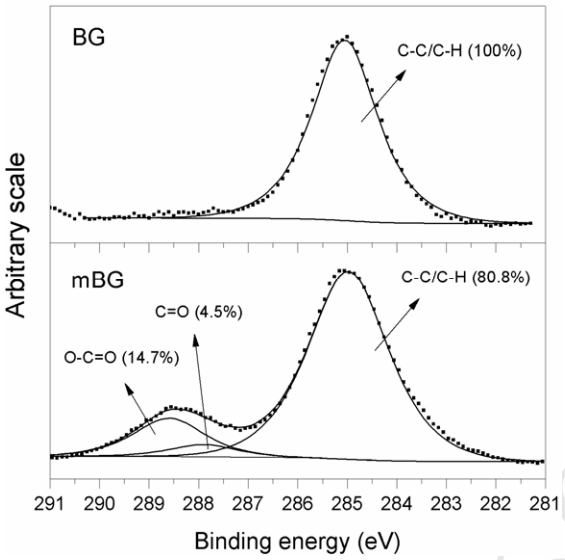

Figure 3

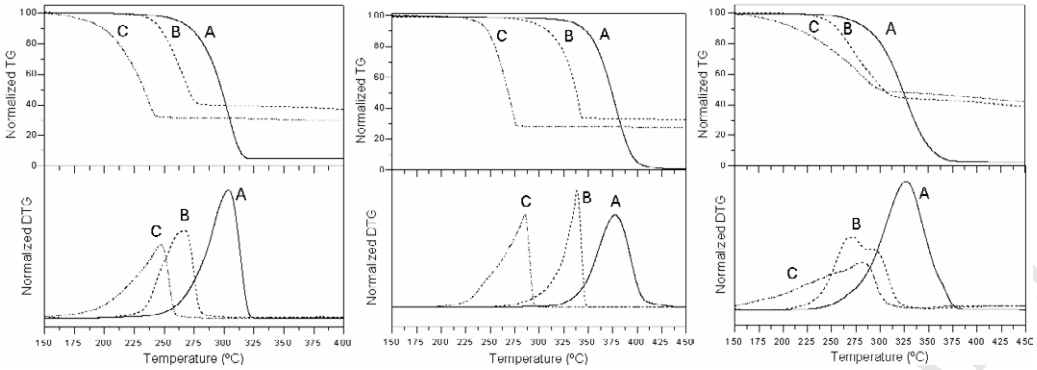

Figure 4

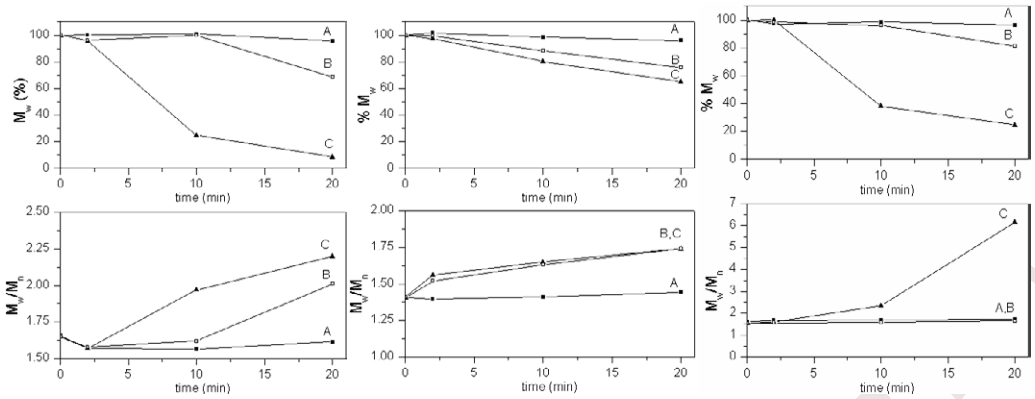

Figure 5

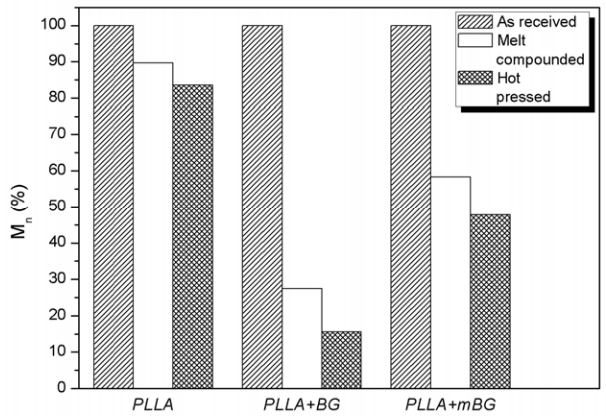

Figure 6