



## Wetting of bioactive glass surfaces by poly( $\alpha$ -hydroxyacid) melts: interaction between Bioglass<sup>®</sup> and biodegradable polymers

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**Abstract:** The interfacial characteristics between bioactive glass (45S5 Bioglass<sup>®</sup>) surfaces and poly( $\alpha$ -hydroxyacid) melts have been assessed by direct wetting measurements. In particular, the wettability of Bioglass<sup>®</sup> powder by poly(D,L-lactide) (PDLLA) and poly(D,L-lactide-co-glycolide) (PLGA) was assessed by imbibition measurements. Additionally, the equilibrium contact angles of PDLLA and PLGA melts on a sintered Bioglass<sup>®</sup> surface were measured. The surface energy of the bioactive glass and the polymers was determined from contact angles measured using various test liquids on PDLLA, PLGA and Bioglass<sup>®</sup> solid substrates. There are sufficient adhesive interactions between the polymers and Bioglass<sup>®</sup>. A simple heat treatment of the bioactive glass in an inert gas atmosphere leads to an improved wetting behaviour, indicating increased adhesive interactions. Scanning electron micrographs of the polymer + Bioglass<sup>®</sup> composites formed by polymer penetration into the powder bed show the formation of a 'good quality' interface.

### 1. Introduction

Tissue engineering presents an alternative approach to the repair and regeneration of damaged human tissue, avoiding the need for a permanent implant. The underlying principle involved is the regeneration of living tissue, where a loss or damage has occurred as a result of injury or disease [1-3]. The scientific challenge encompasses understanding the cells themselves, their mass transport requirements and biological environment as well as the development of suitable scaffold materials,

which are usually porous, and act as templates for cell adhesion, growth and proliferation [4,5].

Synthetic biodegradable polymer matrix composites are increasingly considered for use as tissue engineering scaffolds due to their improved physical, biological and mechanical properties, as well as having the capacity for tailoring their degradation rate to the specific need at the implant site [6-8]. The ideal scaffold for tissue engineering should be both biocompatible and biodegradable, with a highly porous, 3-dimensional nature, possessing an interconnected pore network to facilitate migration of cells and fluid flow, thereby allowing the supply of nutrients, removal of metabolic waste and permit vascular invasion [4]. Moreover, suitable surface chemistry must be presented for cell attachment, proliferation and differentiation.

It is considered that the next generation of synthetic biomaterials for tissue engineering should combine bioactive and resorbable properties to activate *in vivo* mechanisms of tissue regeneration, stimulating the body to heal itself and eventually becoming replaced by the regenerating tissue [2]. Moreover, addition of bioactive ceramic or glass phases, as fillers, to biodegradable polymers gives scope for controlling the *in vitro* and *in vivo* degradation behaviour by providing a pH buffering effect at the polymer surface, thereby preventing autocatalytic degradation of poly( $\alpha$ -hydroxyesters) [8].

A great variety of composites based on degradable synthetic polymer matrices and bioactive inorganic fillers, mainly hydroxyapatite or bioactive glass, have been developed in the last few years, as recently reviewed [9]. From the point of view of the mechanical properties, in most previous studies it has been assumed that the addition of stiff filler particles leads to improvement of elastic properties, fracture strength and structural stability of the porous scaffolds *in vitro* and *in vivo*. However, there have been very few specific studies focused on understanding the matrix/filler interfacial behaviour in these composites, which largely determines the composite mechanical properties [10].

In general, the characteristic of the interface between inorganic fillers and polymeric matrices, which is related to the wetting behaviour of fillers by polymers, is a key parameter affecting the overall performance of composites. In the area of reinforced polymers the nature of the extent of adhesion between filler and polymer melt (or pre-polymer solution) plays a fundamental role since external loads must be transferred from the matrix through the interface into the reinforcement. The wettability of the filler by polymer melts extensively determines the adhesion of the interface. Poor wetting of the filler by the molten matrix will lead to the formation of voids in the filler/solidified polymer interface, which will impair the final performance of the composite. The basic requirement for good adhesion is the close contact between the phases, as well as the formation of a cohesively strong solid of the matrix material [11]. Adhesion should improve if there is good wettability of the filler + polymer interface guaranteeing intimate contact between the phases [12,13]. A 'good' wetting behaviour would be indicated by a low contact angle between the two components. Moreover, the degree to which a polymer spreads over fillers determines how easily the viscous polymer can penetrate powder beds and this is most important for the processing of bioactive composite materials. In order to establish intimate contact between the filler and the liquid molten matrix, the liquid should not be too viscous, and there should be a thermodynamic driving force for obtaining good wetting [14]. The driving force is the thermodynamic work of adhesion,  $W_a$ , which is the work required to reversibly separate two bulk phases from their equilibrium separation

distance.  $W_a$  is defined as the sum of all interaction energies between the two phases:

$$W_a = \gamma_s + \gamma_l - \gamma_{sl} \quad (1)$$

For the adhesion of liquids that do not completely wet on solid substrates, the Young-Dupré equation holds:

$$W_a = \gamma_l \cdot (1 + \cos \theta) \quad (2)$$

where  $\theta$  represents the equilibrium or Young contact angle.

We have studied the wetting of bioactive glass (type 45S5 Bioglass<sup>®</sup>) surfaces by the melts of two synthetic biodegradable poly( $\alpha$ -hydroxyacid)s, namely poly(D,L-lactide) (PDLLA) and poly(D,L-lactide-co-glycolide) (PLGA), by imbibition measurements. Moreover, we shall present a simple way to improve the interaction between the polymer and Bioglass<sup>®</sup>. The imbibition of the polymers into bioactive glass porous powder compacts has been studied for as-received and cleaned Bioglass<sup>®</sup> pellets. For comparison the equilibrium contact angles of polymer melt droplets on a sintered bioactive glass substrate have been measured. Furthermore, the solid surface energy of the polymeric adhesive/matrix as well as the Bioglass<sup>®</sup> reinforcement has been determined by contact angle measurements using standard test liquids with known surface tension and components. The results are discussed in reference to the intended application of the composites as tissue engineering scaffolds.

## 2. Solid surface energy

Solid surface energies can be approximated using surface tension models from measurable contact angles of testing liquids on a solid. All surface tension models focus on two main aspects: to estimate the solid surface tension via physically acceptable combining rules to express the interfacial tension  $\gamma_{sl}$ :

$$\gamma_{sl} = \gamma_s + \gamma_l - W_a \quad (3)$$

This subject is everything but trivial, so many different approaches have been suggested and are controversially discussed in the literature. The scientific discourse is mainly dominated by two antagonistic concepts – the theory of surface tension components originally initiated by the works of Fowkes and the equation-of-state (EoS) approach formulated by Neumann [16].

The acid/base approach is a further development of the original dispersive/polar approach and was introduced by van Oss et al. [17,18]. This approach separates physical from chemical interactions. The physical interaction component  $\gamma^{LW}$  includes London, Keesom and Debye interactions (LW – Lifshitz/van der Waals). On the other hand, the chemical interaction or acid/base component  $\gamma^{AB}$  covers Lewis-acid/base (including proton donor/acceptor) interactions as well as hydrogen bonding:

$$\gamma^t = \gamma^{LW} + \gamma^{AB} \quad (4)$$

The acid/base approach combines all symmetrical and non-specific forces in the LW component and separates specifically and complementarily acting forces in the AB component.

$$\gamma_s^{LW} = \frac{\gamma_l \cdot (1 + \cos \theta)^2}{4} \quad (5)$$

$$\gamma_s^{AB} = 2\sqrt{\gamma_s^+ \cdot \gamma_s^-} \quad (5a)$$

Since acid/base interactions are intrinsically specific and depend on the complementary availability of corresponding sites at the interface, the AB term has to be subdivided resulting in an acid or electron acceptor parameter  $\gamma^+$  and a base or electron donor  $\gamma^-$  parameter of the surface tension. The LW component of the solid surface energy can be determined by measuring the contact angle of completely non-polar (or dispersive) liquids, such as diiodomethane (DIM), on a solid by using Eq. (5). The total surface energy can be determined by measuring the contact angles of at least two more liquids with known surface tension components and parameters (see Tab. 1) using Eq. (6):

$$(1 + \cos \theta) \cdot \gamma_l = 2(\sqrt{\gamma_s^{LW} \cdot \gamma_l^{LW}} + \sqrt{\gamma_s^+ \cdot \gamma_l^-} + \sqrt{\gamma_s^- \cdot \gamma_l^+}) \quad (6)$$

The basic idea of the EoS approach is to assume that the relationship between  $\cos \theta$  and  $\gamma_{lv}$  is universal, i.e., the contact angle  $\theta$  is solely determined by the solid surface tension  $\gamma_s$  and the liquid surface tension  $\gamma_l$ . Thus, a three-phase-two-component system with the same surface tensions of the solid and the liquid should always give equal contact angles, independent of type and strength of the molecular interaction. The surface energy of a solid  $\gamma_s$  can be calculated by measuring the contact angle of a liquid with known surface tension (Tab. 1) on a solid by combining the Young-Dupré equation with Neumann's (semi-empirical) equation of state for the work of adhesion

$$W_a = 2 \cdot \sqrt{\gamma_l \gamma_s} \cdot e^{-\beta \cdot (\gamma_l - \gamma_s)^2} \quad (7)$$

where  $\beta$  is Neumann's constant,  $\beta = 0.000115 \text{ (m}^2/\text{mJ)}^2$ .

**Tab. 1.** Liquid surface tension, its components and parameters ( $\gamma^{LW}$  = Lifshitz-van der Waals component,  $\gamma^{AB}$  = acid-base component,  $\gamma^+$  = electron acceptor or proton donator (acid) parameter, and  $\gamma^-$  = electron donor or proton acceptor (base) parameter of the liquid surface tension  $\gamma_l$ ; all quantities in mN/m) for different test liquids at 20°C according to van Oss, Chaudhury, and Good

Test liquid	$\gamma_l$	$\gamma_l^{LW}$	$\gamma_l^{AB}$	$\gamma_l^+$	$\gamma_l^-$
water	72.8	21.8	51.0	25.5	25.5
glycerol (G)	64.0	34.0	30.0	3.92	57.4
diiodomethane (DIM)	50.8	50.8	$\approx 0$	—	—
formamide (FA)	58.0	39.0	19.0	2.28	39.6

The critics of the surface tension component approaches stress that there is no thermodynamic basis to the separation approach. This approach is indeed violating the Gibbs phase rule. On the contrary, the advocates of the separation approaches see the model in good agreement with the scientific ideas of intrinsically anisotropic and directed interaction mechanisms across interfaces. For instance, following the generally accepted theories of Brønstedt and Lewis, the development of acid-base interactions has to rely on the availability of a complete and complementary pair consistent of at least one acid and one base.

### 3. Experimental part

#### Materials

PURASORB<sup>®</sup> poly(D,L-lactide) (PDLLA) with an inherent viscosity of 1.6 dl/g was purchased from PURAC Biochem (Gorinchem, The Netherlands). Poly(lactide-co-glycolide) (PLGA) copolymers of the medisorb polymer range with a 75:25 LA:GA mole ratio and low molecular weight with an inherent viscosity of 0.61 dl/g was provided by Alkermes (Cincinnati, Ohio, USA). Both polymers are amorphous materials with glass transition temperatures,  $T_g$ , of about 58 and 53°C, respectively. The polymers were used without further purification. The bioactive material used was a melt-derived bioactive glass powder (Bioglass<sup>®</sup> grade 45S5, US Biomaterials Co., Alachua, FL, USA). The powder had a mean particle size < 5 µm. The composition of the glass used was (in wt.-%): 45% SiO<sub>2</sub>, 24.5% Na<sub>2</sub>O, 24.5% CaO and 6% P<sub>2</sub>O<sub>5</sub>, which is the original composition of the first bioactive glass developed by Hench and co-workers in 1971 [15]. For measurement of the interfacial properties, Bioglass<sup>®</sup> powder was used either as-received or 'cleaned' by heat treatment at 450°C in a stream of dry nitrogen (class V) for a period of 6 h.

#### Methods

##### Sample preparation

PDLLA strands with a diameter of 3 mm were prepared utilizing a high-temperature dosing system (Krüss GmbH, Hamburg, Germany) operated at 170°C. Polymer pellets with similar weight (c. 3 mg) were cut out of the solid extruded samples. As-received PLGA pellets (c. 1 mg) were used without any modification. A glass powder bed with an approximate thickness of 10 mm was prepared by manual compaction of the powder in a standard quartz glass UV cuvette (1 x 1 cm<sup>2</sup>). Even and repeatable compaction was produced by using a flat plate attached to a spring to compact the powder. A polymer pellet was placed onto the Bioglass<sup>®</sup> powder bed surface and heated in a dry nitrogen stream to avoid polymer degradation until a drop with a regular shape formed. Prior to any measurement it was ensured that the UV cuvette was aligned exactly perpendicular to the optical path. A bioactive glass substrate was also prepared by sintering Bioglass<sup>®</sup> powder to produce a dense glass plate, which was abraded and subsequently polished using diamond paste with a particle size of 1 µm. PDLLA and PLGA films were prepared by casting a polymer solution onto glass microscope slides, using chloroform as a solvent, with a polymer/solvent ratio of 4 wt.-%.

##### Characterisation of the surface energy of poly(α-hydroxy acid)s and Bioglass<sup>®</sup>

In order to estimate the solid surface energy of the separate phases, i.e., PDLLA, PLGA and Bioglass<sup>®</sup>, static advancing and dynamic contact angles of several test liquids with known surface tensions as well as surface tension components and parameters were measured using a drop shape analysis system (DSA 10 MK2, Krüss GmbH, Hamburg, Germany). Measurements were taken at room temperature (20°C). The following test liquids were used: deionised water (Millipore), diiodomethane (DIM) (99+% purity, Acros Organics, Belgium), glycerol (G) (Reag. Ph Eur, Merck, Germany), formamide (FA) (99.5% purity, Acros Organics, Belgium) and ethylene glycol (EG) (puriss. p.a. Ph Eur 99.5%, Fluka). Detailed surface tension components

and parameters for these liquids are summarised in Tab. 1a and b. Drops initially of 2  $\mu\text{l}$  were placed on the substrates and the volume continuously increased to 10  $\mu\text{l}$  and withdrawn from the drops at a rate of 6.32  $\mu\text{l}/\text{min}$  using a motorised microsyringe. The solid surface energies of the polymers and Bioglass<sup>®</sup> were calculated using Neumann's EoS approach [16] (using Eq. (7)) but also using the acid/base approach introduced by van Oss et al. [17,18] (using Eqs. (5) and (6)).

#### Characterisation of the wetting behaviour of Bioglass<sup>®</sup> by poly( $\alpha$ -hydroxy acid) melts: Imbibition rates and apparent contact angles

The imbibition of polymer melt droplets into the compacted Bioglass<sup>®</sup> powder bed was followed using a high-temperature environmental chamber and the Drop Shape Analyser (DSA 10 Mk2, Krüss GmbH, Hamburg, Germany). The imbibing of the droplets into the Bioglass<sup>®</sup> powder bed took place at 170 and 155°C, for PDLLA and PLGA, respectively. The drop profiles were recorded in intervals of 30 s until most of the drop vanished into the powder bed and the accuracy of the measurements impaired. Prior to each measurement the magnification factor, i.e., the number of pixels per millimetre, was determined. The Krüss drop shape analysis software allows the determination of the apparent contact angle, the baseline diameter and the drop volume. Images of the imbibing droplets were taken at different time intervals to illustrate the polymer penetration into the Bioglass<sup>®</sup> powder bed. Measurements were carried out at least three times on a fresh powder bed for each experimental setting to confirm reproducibility.

In an additional experiment, polymer pellets were placed on a dense Bioglass<sup>®</sup> sintered plate and molten. Finally, the quasi-static contact angle between the resulting polymer droplet and the glass surface was determined.

#### Scanning electron microscopy (SEM) of composite plugs formed by penetration of polymer melts into the Bioglass<sup>®</sup> powder compact

SEM was conducted using a JEOL 5610LV (Jeol-USA, Inc.) with an accelerating voltage of 20 kV. Composite plugs, formed due to the polymer melts penetrating the powder compact, were sectioned in the penetration direction using a razor blade to permit examination of the interfacial adhesion throughout the composite formed.

### 4. Surface energy determination

Wettability is defined as the tendency for one fluid to wet/spread on or adhere to a solid surface thereby replacing a gas (or the saturated liquid vapour atmosphere) or another liquid the solid was initially in contact with [19]. Therefore, wetting measurements can be used to determine the interaction that will affect the adhesion behaviour between two phases. However, the direct determination of contact angles between a polymer melt and any substrate is rather difficult, because of the high temperatures involved, the limited stability (degradation might occur) of the melt and its high viscosity. Therefore, the work of adhesion,  $W_a$ , of an imaginary filler/polymer combination is commonly used to estimate a trend of adhesion. In the present study, the most recent approaches to estimate  $W_a$  are used, i.e., Kwok's model [20] and the acid and base approach [21]. In order to determine the surface energy of PDLLA and Bioglass<sup>®</sup>, 'static' advancing and dynamic contact angles were measured for various test liquid droplets resting on the solid surfaces (Tab. 2).



**Tab. 2.** Static advancing ( $\theta$ ) and dynamic advancing ( $\theta_a$ ) and receding ( $\theta_r$ ) contact angles on Bioglass<sup>®</sup> (sintered disk), PDLLA and PLGA films

Material	$\theta_a$ (H <sub>2</sub> O)	$\theta_r$ (H <sub>2</sub> O)	$\theta_a$ (DIM)	$\theta_r$ (DIM)	$\theta_a$ (EG)	$\theta_r$ (EG)	$\theta$ (G)	$\theta$ (FA)
Bioglass <sup>®</sup> disk	31 ± 6°	a)	43 ± 4°	a)	-	-	29 ± 10°	54 ± 9°
PDLLA film	82.7 ± 3.4°	60.3 ± 2.7°	38.4 ± 2.3°	22.3 ± 1.5°	-	-	71.7 ± 1.7°	b)
PLGA film	77.3 ± 1.6°	49.6 ± 1.5°	42.0 ± 1.9°	28.6 ± 1.4°	53.6 ± 0.5°	34.2 ± 1.7°	-	-

a)  $\theta_r$  could not be determined, it was close to zero. b) FA dissolves PDLLA.

All measured contact angle values, either static advancing or advancing, were used to determine the solid surface energy using Neumann's EoS and acid/base approach (AB-a) (as shown in Tab. 3).

**Tab. 3.** Solid surface energies of Bioglass<sup>®</sup> (sintered disk), PDLLA and PLGA films determined using Neumann's EoS and the acid/base approach

	Bioglass <sup>®</sup>	PDLLA	PLGA
$\gamma^{(EoS)} / (\text{mN/m})$	50 ± 12	36.9 ± 4.2	36.4 ± 3.7
$\gamma^{(AB-a)} / (\text{mN/m})$	46.1 ± 9.5	40.8 ± 2.2	39.2 ± 1.5
$\gamma^{LW} / (\text{mN/m})$	35.6 ± 2.0	40.4 ± 1.1	38.6 ± 1.0
$\gamma^{AB} / (\text{mN/m})$	10.5 ± 7.4	0.4 ± 1.1	0.6 ± 0.5
$\gamma^+ / (\text{mN/m})$	0.5 ± 0.7	0.01 ± 0.04	0.01 ± 0.02
$\gamma^- / (\text{mN/m})$	51.1 ± 9.5	4.63 ± 2.57	8.68 ± 1.46
$\gamma^{AB}/\gamma^{(AB-a)}$	0.23	0.01	0.02
$\gamma^+/\gamma^-$	0.011	0.002	0.001

Glasses are usually 'high-energy' surfaces, however, the determined solid surface energy is quite low as can be seen from the results (Tab. 3). The surface energies for a Bioglass<sup>®</sup> and PDLLA are very similar considering the large error range. However, the absolute value of the estimated solid surface energy of Bioglass<sup>®</sup> stored in a normal laboratory atmosphere is larger as compared to PDLLA. Our results are in good agreement with surface energy values for Bioglass<sup>®</sup> ( $\gamma = 54.7 \text{ mN/m}$  [22]) and PDLLA ( $\gamma = 43.2 \text{ mN/m}$  [23]) reported in the literature. Irrespectively what approach was used in order to calculate the surface energy (EoS or acid/base) the actual values are in the same range. Irrespectively how the work of adhesion  $W_a$  was calculated, using the Kwok and acid/base approach, for the imaginary Bioglass<sup>®</sup>/PDLLA composite (83.2 and 80.2 mN/m, respectively) and Bioglass<sup>®</sup>/PLGA composite (82.5 and 79.7 mN/m, respectively) the values for the two systems are very similar, indicating that good adhesion between the bioactive glass and the two polymers could be expected.

## 5. Wetting of Bioglass<sup>®</sup> powder by polymer melts: imbibition rates and apparent contact angles

Images of the imbibing polymer melt droplets taken at different intervals, thereby illustrating penetration of the polymer into the Bioglass<sup>®</sup> powder bed, are shown in Fig. 1. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were used to verify that the polymers investigated are stable under the heating regimes applied in this study for at least 3600 s.

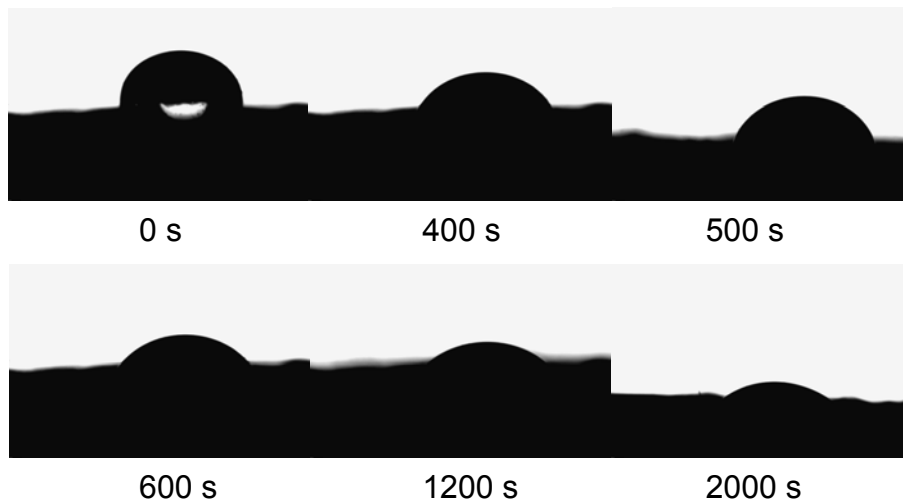


Fig. 1. PDLLA melt droplets at 170°C imbibing into a Bioglass<sup>®</sup> powder compact with respect to time

The change in normalised polymer melt droplet volume was observed as a function of time for PDLLA and PLGA. Both polymers can be seen imbibe at different rates into the powder compact (as shown in Fig. 2). Error bars are shown at significant points in the measurements to clarify the trend observed.

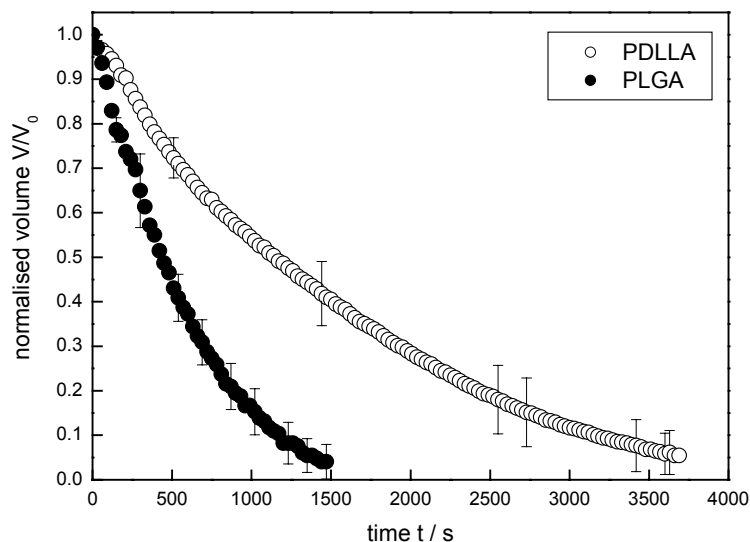


Fig. 2. Normalised volume as function of penetration time for PDLLA and PLGA into as-received Bioglass<sup>®</sup> powder compacts



It should be noted that the results of PDLLA and PLGA melt imbibition are not directly comparable because of the differences in their inherent melt viscosities (1.6 dl/g to 0.61 dl/g). However, the melt viscosity should not affect the equilibrium contact angle of the melt droplet resting on a sintered Bioglass<sup>®</sup> surface. Results of the measurements are summarised in Tab. 4. As can be seen the quasi-static equilibrium contact angle for PLGA is much lower as compared to the PDLLA melt contact angle. Assuming that the polymer melt surface tensions are similar, we could expect that interactions between PLGA and the bioactive glass are more favourable as compared to those between Bioglass<sup>®</sup> and PDLLA.

**Tab. 4.** Equilibrium quasi-static contact angles of PDLLA and PLGA melt droplets on sintered Bioglass<sup>®</sup> plates and initial apparent contact angles of PDLLA and PLGA melt droplets imbibing into as-received and heat-treated bioactive glass powder compacts

Polymer melt/Bioglass <sup>®</sup> system	Contact angle
PDLLA on disk	$38.9 \pm 1.4^{\circ}$ <sup>a)</sup>
PLGA on disk	$21.9 \pm 3.9^{\circ}$ <sup>a)</sup>
PDLLA on as-received powder	$115 \pm 2^{\circ}$ <sup>b)</sup>
PLGA on as-received powder	$114 \pm 6^{\circ}$ <sup>b)</sup>
PDLLA melt on clean powder	$107 \pm 10^{\circ}$ <sup>b)</sup>
PLGA melt on clean powder	$88 \pm 4^{\circ}$ <sup>b)</sup>

<sup>a)</sup> Equilibrium contact angles. <sup>b)</sup> Initial apparent contact angle of a polymer droplet resting on the powder compact.

The initial increase of the baseline diameter (Fig. 3) is due to the fact that spreading of the polymer melt on the powder bed is faster than imbibition. In case of PLGA the drop baseline diameter decreases with decreasing drop volume, which indicates that the contact line is moving over the powder compact surface. For PDLLA the baseline diameter stays almost constant, showing that the contact line is pinned to a fixed position during the penetration process.

A simple process that is expected to improve the adhesive interaction between the bioactive glass and the polymers is to remove all adsorbed impurities from the glass surface. This can easily be achieved by heating the glass under inert atmosphere to high temperatures. Even though the initial apparent contact angle between the polymer melt and the Bioglass<sup>®</sup> compact seems not to be affected (Tab. 4), the imbibition rates of the melts into the heat-treated Bioglass<sup>®</sup> for the two polymers greatly increased (Fig. 4). The slight jumps in Fig. 4 are due to averaging errors (based over at least three repeated runs).

The time needed until the melt droplets nearly completely penetrated into the powder compact dropped by 33% for PDLLA and by 66% for PLGA, indicating improved wetting and, therefore, better adhesive interactions between the melt and the glass. Our results evidence the successful and effective removal of adsorbed impurities and water from the glass surface by heat-treatment at 450°C in a dry nitrogen atmosphere.

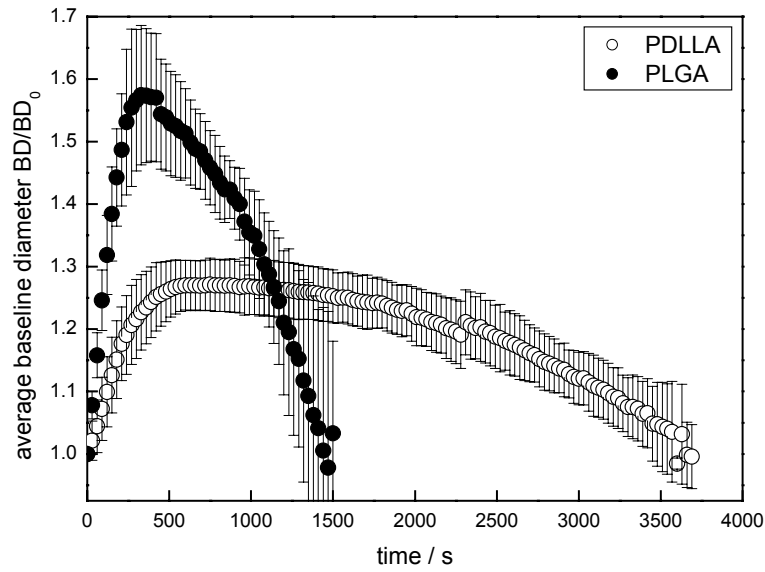


Fig. 3. Variation of the baseline diameter of the PDLLA and PLGA melt droplets during imbibition into an as-received Bioglass® compact

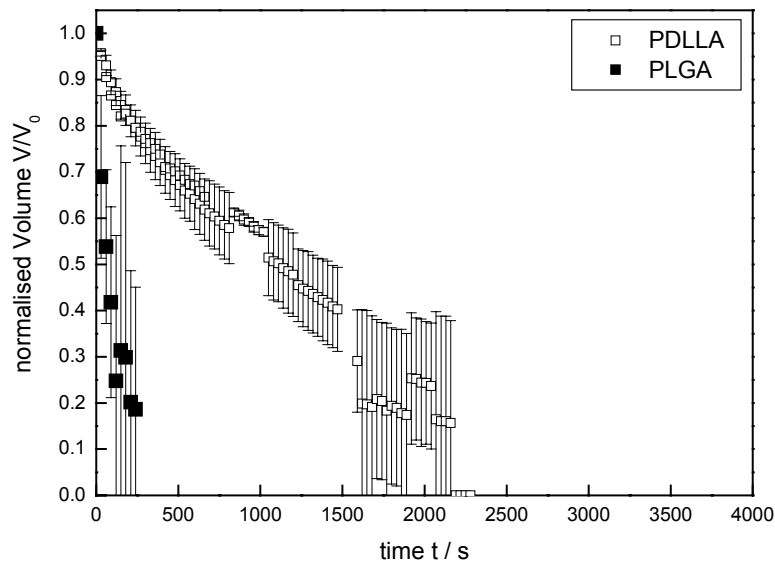
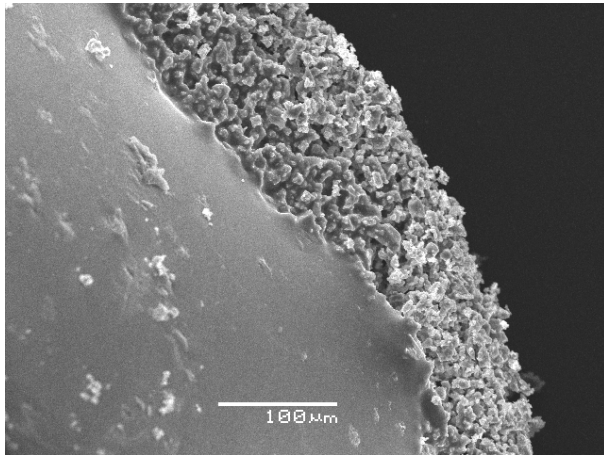
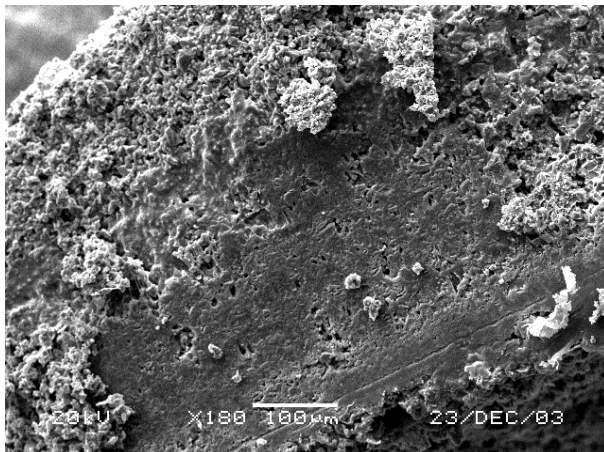


Fig. 4. Normalised volume as function of penetration time for PDLLA and PLGA into a heat-treated Bioglass® powder compact

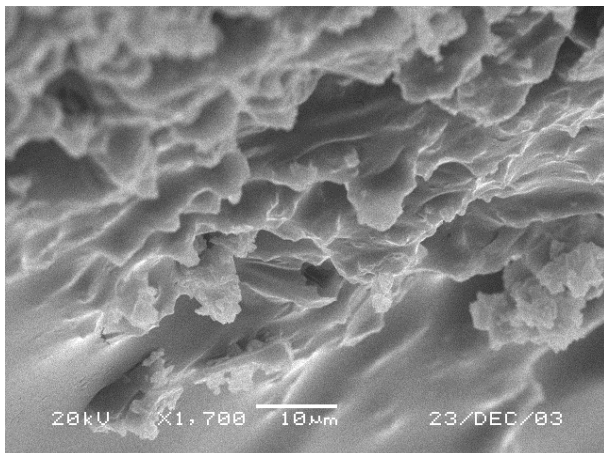
The action of melt penetration downwards as well as radial is further evidenced by SEM images of PDLLA into cleaned Bioglass® compacts, as shown in Fig. 5a-d. These micrographs demonstrate the penetration shape of the polymer and the interface of the composite formed. The polymer melt penetration occurs in a conical shape (Fig. 5b), with some radial spreading of the polymer, particularly towards the surface of the powder compact. There was no discernable difference between either the clean or the as-received Bioglass® or the polymer type used, in terms of SEM observation. In all cases visually 'good quality' interfaces were detected, which indicates, at least qualitatively, a good adhesion between the polymers and the particular bioactive glass used.



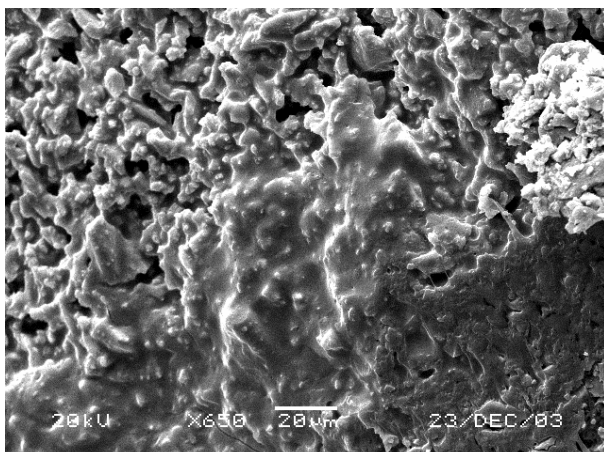
**Fig. 5a.** SEM micrograph showing the PDLLA polymer/heat-treated Bioglass® composite plug formed by polymer penetration at low magnification



**Fig. 5b.** SEM micrograph showing a section through a PDLLA polymer/clean Bioglass® composite plug at low magnification, demonstrating the predominantly conical penetration shape of the melt



**Fig. 5c.** SEM micrograph showing the edge of the PDLLA/clean Bioglass® compact, at the surface, demonstrating radial spreading of the melt into the powder



**Fig. 5d.** SEM micrograph showing a section through a PDLLA polymer/clean Bioglass® composite plug, towards the bottom of the penetration at high magnification

## 6. General discussion

Our results are relevant for the development of biodegradable composites for tissue engineering, as the interfacial properties have a significant impact on both the mechanical properties of the composites and their *in vitro* and *in vivo* biodegradation kinetics. The formation of a relatively good (defect-free) interface between the Bioglass<sup>®</sup> and the poly( $\alpha$ -hydroxyacid)s, as found here, is vital, as this parameter largely determines the mechanical and degradation properties of the composites. A weak interface will result in increased water absorption in the composite, especially at the bioactive glass/polymer interface due to the higher hydrophilic character of the glass component, thus affecting the degradation rate of the composite. The presence of Bioglass<sup>®</sup> as filler in highly porous PDLLA and PLGA scaffolds has been shown to increase the water absorption at the early stages of degradation and to prevent the autocatalytic acceleration of the degradation of the polymeric phase [24]. This is explained by a pH buffering effect as result of the release of basic ions from the glass [9,24]. The present results provide thus first evidence of the quality of the interfaces between 45S5 Bioglass<sup>®</sup>, a standard filler being extensively used in composites for tissue engineering scaffolds [9], and PDLLA and PLGA degradable polymers. For equal conditions of the glass particle surfaces, better adhesive interactions between PLGA and the Bioglass<sup>®</sup> were found. This result is relevant for analysing possible different degradation kinetics of composites made using the two different matrices with equal concentration of Bioglass<sup>®</sup> particles. Further quantitative characterisation of interfacial properties under different *in vitro* conditions, for example after different durations of immersion in simulated body fluid, must be carried out to gain a complete understanding of the *in vitro* degradation of the composites and the different behaviour of PDLLA/Bioglass<sup>®</sup> and PLGA/Bioglass<sup>®</sup> composites.

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