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Coating of bioactive glass 13-93 fibres with biomedical polymers

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The aim of this study was to coat bioactive glass 13-93 fibres with biomedical polymers. Two methods were used to coat the fibres, namely, dipping and pulling through a viscous solution. With both methods the fibres were successfully coated. Dipping was preferred for thin fibres (20–50 μm) and with this method approximately 2–5 μm thin polymer coat was obtained on the fibre surface. Pulling through viscous solution was preferred for thicker fibres (150–250 μm) and with this method approximately 10–30 μm polymeric coat was obtained. Coating the fibres enables further processing of the bioactive glass fibres and improves the mechanical properties and processibility of fibres.

1. Introduction

Composite materials comprising a polymer reinforced with high-strength glass fibres have been employed extensively in non-medical applications. For medical purposes, there have been numerous studies published, in which biomedical polymers have been reinforced with bioactive ceramic particles, but only a limited number of publications in which bioactive glass fibres have been used to reinforce the polymer.

The properties of brittle glass fibres are highly sensitive to all types of contamination and for instance the abrasion in fibre surfaces reduces the mechanical properties of the fibres drastically. Therefore in bulk glass fibre industry the coating of the glass fibres plays an important role in composite production right after fibre formation process. Due to the toxicological nature of coating agents used in industry, they can not be used with medical composites.

Hench and colleagues discovered in 1969 that bone can bond chemically to certain glass compositions [1]. These glasses have become known as bioactive glasses. Most bioactive glasses do not have suitable properties for fibre spinning. Maria Brink has studied different glasses of system which contains boron, sodium, potassium, magnesium, calcium and phosphorus oxides and silica. She found that some of the glasses had a wide working range, which enables the production of fibres [2]. One of the most potential from the studied glasses was bioactive glass 13-93. Histological studies by Brink *et al.* with bioactive glass 13-93 rods have shown that this glass is bioactive (and slowly resorbable) in bone tissue [3] and resorbable in soft tissue [4].

The aim of this study was to investigate possible methods of coating the fibres of bioactive glass 13-93 with biomedical polymer and to characterise the coated fibres obtained.

2. Materials and methods

2.1. Materials

The bioactive glass 13-93 contains 6 weight-% Na_2O, 12 wt-% K_20, 5 wt-% MgO, 20 wt-% CaO, 4 wt-% P_2O_5 and 53 wt-% SiO_2. Various different biomedical polymers were used to coat fibers, namely poly(L-lactide-co-D, L-lactide), poly(L-lactide-co-trimethylene-carbonate), poly(L-lactide), poly(DTE Carbonate), Polyactive®, and poly(ε-caprolactone-co-L-lactide). In Table I suppliers of the materials and acronyms are shown. These acronyms are used later in Tables and Figures.

2.2. Coating of fibres

In order to melt spin the fibres, bioactive glass 13–93 block was melted in a platinum crucible, which had 7 orifices at the bottom [6]. Immediately after the fibre formation process, the fibres were coated by immersing them into a viscous solution, which contained biomedical polymer and appropriate solvent. Two coating methods, namely dipping and pulling through were applied. For the dipping

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TABLE I Suppliers and acronyms of the coating polymers

Polymer	Supplier	Cons./Solvent	Acronym
Poly(L-lactide-co-D,L-lactide) (70/30)	Boehringer Ingelheim, Germany	5 g/acetone	PLA 70/30
Poly(L-lactide-co-trimethylene-carbonate)	Boehringer Ingelheim, Germany	17.5 g/chloroform	LTMC
Poly(L-lactide)	Purac, Holland	3.2 g/chloroform	PLLA
Poly(DTE Carbonate)	Intrgra LifeSciences Corporation, USA	24.3 g/chloroform	DTEC
Polyactive®	H.C.Implants B.V., Holland	20 g/acetone	Polyactive
Poly(ε-caprolactone-co-L-lactide) (50/50)	Helsinki University of Technology, Finland [5]	12 g/acetone	CL/L 50/50
Poly(ε-caprolactone-co-L-lactide) (80/20)	Helsinki University of Technology, Finland [5]	14 g/acetone	CL/L 80/20

TABLE II Number of tested samples, averages and standard deviations for diameter and maximum apparent strain measurements

Fibre type	N	Average diameter of fibre (μm)	Stdev (μm)	Average coating thickness (μm)	Stdev (μm)	Average total strain (%)	Stdev (%)	Average strain for glass (%)	Stdev (%)
modif. glass	14	184.4	6.9					0.28	0.05
pure glass	20	189.5	10.5					1.81	0.50
LTMC	20	255.8	6.5	40.3	0.9	1.56	0.03	1.35	0.04
CL/L 50/50	20	276.8	2.3	31.8	0.9	3.61	0.21	3.24	0.18
DTEC	20	255.9	3.3	71.4	2.4	2.82	0.07	2.21	0.04
PLLA	20	263.9	10.2	11.4	0.1	2.17	0.01	2.08	0.00
CL/L 80/20	20	223.2	3.0	46.2	1.6	3.94	0.23	3.26	0.21
PLA 70/30	16	223.1	28.4	15.3	8.0	2.46	1.42	2.31	0.60
Polyactive	20	297.4	1.9	34.5	6.4	1.95	0.03	1.75	0.00

experiment 1.5 g of PLA 70/30 polymer was dissolved into acetone. In pulling through experiments either chloroform or acetone was used as a solvent. The concentrations (g per 100 ml) used are shown in Table II. The solvent evaporated and fibres with a polymer coat were wound up with a spinning roll. With both methods fibres were either pulled as a bunch or fibres were separated and coated as single fibres.

2.3. Maximum apparent strain measurement for fibres

To compare coated and non-coated bioactive glass fibres the ultimate strains sustainable in bending were measured using a loop bending test which was modified from a knot bending test [7]. The test consists simply of tying a semi-circular loop in the fibre, pulling it progressively tighter with using a sliding gauge, and directly measuring the diameter (D) at which the failure occurs. The maximum apparent strain ε for a fibre of diameter d is calculated from the loop diameter D using the expression:

$$\varepsilon = \frac{d}{D} \tag{1}$$

in which it is assumed that the fibre neutral axis coincides with the central axis of the fibre at all states of stress. This test was done for fibres which were coated by pulling though gel as single fibres and for non-coated fibres (fibre diameter approximately 200 μm).

In order to estimate the effect of the abrasion in fibre surfaces the bunch of fibres was slightly chafed between fingers for approximately 10 s to introduce scratches on fibre surfaces. The strain of these treated fibres was then measured as described above. With the control of "pure fibres" extra care was taken to handle fibres as little as possible in order not to introduce scratches to the fibre surfaces.

In order to avoid the effect of variation in coating thickness to the strain value, the strain was also calculated so that the diameter of underlying glass fibre was measured immediately after testing and used as a d in the Equation 1. Elastic modulus of glass is approximately 10 to 15 times higher than the elastic modulus of polymer so the effect of the polymer coat to the value of measured strain is negligible.

2.4. SEM images

For microscopy observations, fibres were first immersed in liquid nitrogen and then bent to breaking point. Scanned electron microscope images were acquired using a JEOL JSM T-100 scanning electron microscope.

2.5. In vitro analysis

In order to study the surface reactions of coated fibres *in vitro*, fibre samples were immersed in simulated body fluid (SBF) by Kokubo [8]. The fibre samples were kept in closed plastic containers which were stored in thermo closet at +37°C. The sample surface area to SBF volume (SA/V) ratio of 0.1 cm^{-1} was used for all test samples. The pH on the solution was monitored and SBF solution was changed once in every two weeks. Scanned electron microscope images were acquired from the test samples using JEOL JSM T-100 scanning electron microscope.

3. Results

The bioactive glass fibres were successfully coated with biomedical polymers using two techniques, namely dipping and pulling through.

3.1. Dipping

The dipping procedure was optimal with thin fibres (fibre diameter less than 50 μm) and when only a thin layer of polymer was required (1–2 μm). The dipping of single fibres was difficult as thin fibres broke easily. The dipping of bunches of fibres presented no difficulties. Fig. 1 shows a SEM figure of a bunch of fibres being dipped with PLA 70/30.

Uncoated thin fibres (diameter 20–50 μm) can not be unwound from the roll without breakage. The coating strengthens the fibre bunch so that it can be unwound easily and processed further as a fibre bunch.

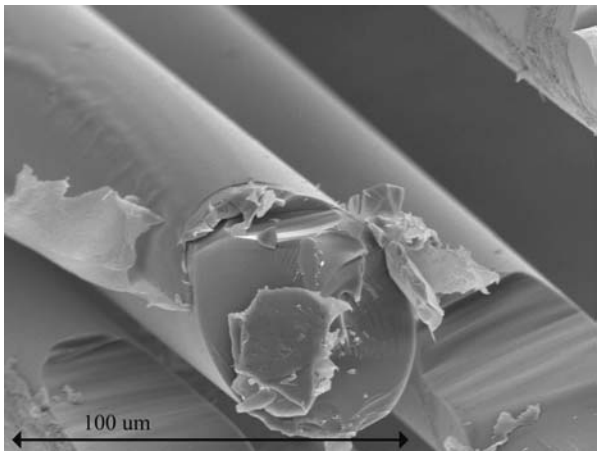

Figure 1 A bunch of fibres coated with poly(L-lactide-co-D,L-lactide) by dipping.

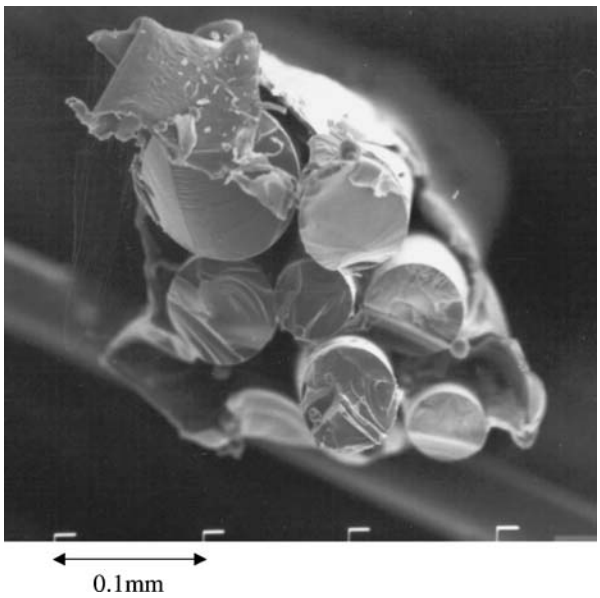

Figure 2 Fibres coated as a bunch by pulling through poly(L-lactide-co-D,L-lactide)/acetone solution.

3.2. Pulling through

Pulling through was optimal for thicker fibres (diameter 100–250 μm) and when a thicker polymer layer was required (10–30 μm). With this technique fibres could be coated as single fibres or as a fibre bunch. In Fig. 2, fibres have been coated with PLA 70/30 as a bunch of fibres.

As the fibre diameter and nozzle size was kept constant through coating experiments, the viscosity of solution had to be kept constant in order to obtain a homogeneous and smooth coat. The thickness of the polymer layer obtained consequently varied depending of the polymer used. Fig. 3 shows the diameter of the coated fibres with and without coating.

It is assumed that the thickness of the polymer layer can be varied under certain restrictions by modifying the polymer/solvent ratio and the nozzle size. Table II gives the number of tested samples, averages and standard deviations for diameter and maximum apparent strain.

3.3. Maximum apparent strain measurement for fibres

Fig. 4 shows the measured maximum apparent strains for coated and non-coated fibres. The slight modification of fibres to introduce scratches on fibre surfaces caused a huge decrease in the maximum apparent strain. The strain of pure fibres is 6.5 times larger than the strain

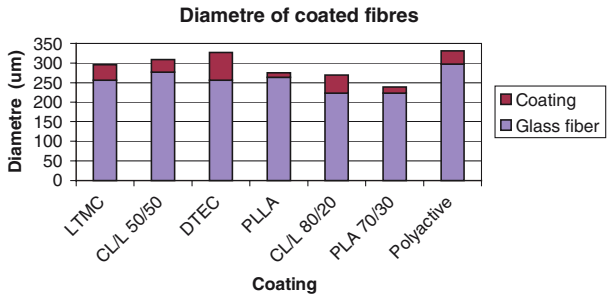

Figure 3 The diameters of the coated fibres.

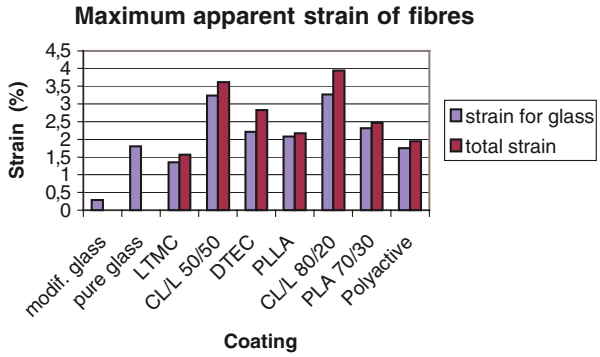

Figure 4 Maximum apparent strain of non-coated and coated fibres.

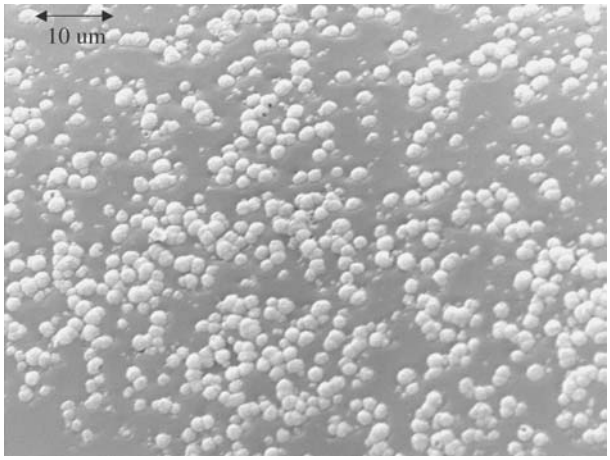

Figure 5 Calcium phosphate precipitation on Poly(DTE Carbonate) coating after two week immersion in SBF.

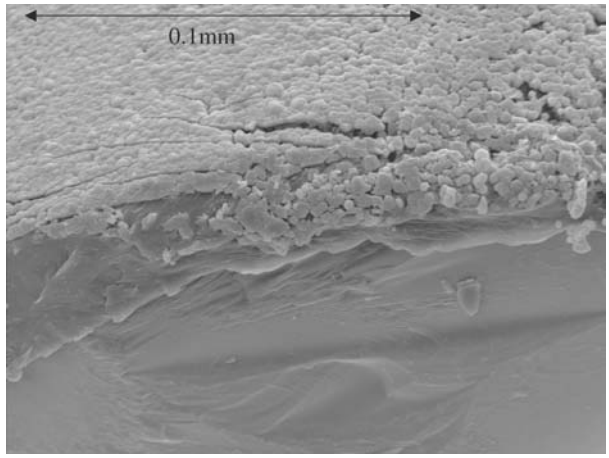

Figure 6 Thick calcium phosphate layer on top of Poly(ε-caprolactone-co-L-lactide) (80/20) coating after 7 week immersion time.

of modified fibres. With both poly(ε-caprolactone-co-L-lactide) polymer coats the maximum apparent strain is approximately twice as high as the strain of the "pure glass". The maximum apparent strain of the fibres with other polymer coats is approximately level with the "pure glass" control.

3.4. Surface reactions in vitro

Calcium phosphate like precipitation started to form onto the polymeric coating after 1–3 weeks immersion. With poly(L-lactide-co-trimethylene-carbonate), poly(DTE Carbonate), and Poly(ε-caprolactone-co-L-lactide) coating the calcium phosphate like precipitants formed an abundant layer after just 2–3 weeks and after 7 weeks, consistent calcium phosphate like precipitation encircled the whole fibre. Figs 5 and 6 show the calcium phosphate precipitation on top of poly(DTE Carbonate) and poly(ε-caprolactone-co-L-lactide) (80/20), after 2 and 7 weeks immersion in SBF. With the poly(L-lactide-co-D,L-lactide), poly(L-lactide) and Polyactive® polymer coatings some calcium phosphate like precipitates formed, but the precipitation was not significant.

A SEM analysis showed clear cracks between the polymeric coating and fibred surface with all different types of polymer coatings that were immersed in SBF. The poor adhesion between fibre and polymer coating is most probable due to water diffusion into the polymer coating.

Fig. 7 shows a poly(L-lactide) coated bioactive glass fibre after 3 weeks immersion. Degradation of bioactive glass fibre has initiated under the defects in polymeric coating. There are no signs of degradation of bioactive glass in areas where poly(L-lactide) coating is intact after 3 weeks immersion.

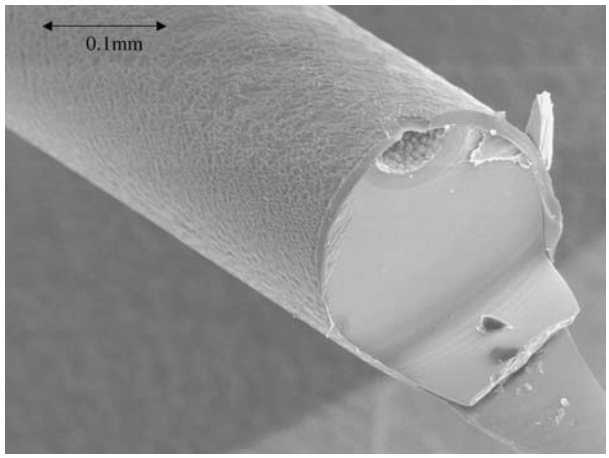

Figure 7 Poly(L-lactide) coated bioactive glass fibre coated after 3 weeks immersion in SBF. Degradation of bioactive glass fibre has initiated under the defect in polymeric coating. There are no signs of degradation in areas where poly(L-lactide) coating is intact.

4. Discussion

Even though fibre glass reinforced polymeric composites have been widely used in non-medical applications for a long time, bioactive glass fibre composites have reportedly not yet been applied for medical use. There is interest in the study and development of methods to enable the manufacture of composites for bioactive glass fibres and biomedical polymers. In this study experimental coating methods for bioactive glass fibres were developed. As bioactive glass fibres are highly sensitive to abrasion and the flaws drastically affect the strength properties, it is beneficial to use coating, sizing or coupling agents for bioactive glass fibres. This study showed that the effect of polymeric coating to the initial mechanical properties and handling of used bioactive glass fibres were significantly improved when polymeric coating was applied.

The use of bioactive glass fibres as a part of a polymeric composite enhances the properties of the composite in the following ways: (1) bioactive glass fibres reinforce the polymer and the mechanical properties of the resulting composite may reach the level of hard bone tissue and (2) bioactive glass brings osteoconductive nature to the composite. It is interesting to notice that even though

biomedical polymers themselves do not possess "bioactive nature", a thick calcium phosphate like layer does form on the polymer surfaces as a coating for bioactive glass. In this study the precipitates were not quantitatively analysed, though the precipitation on top of the polymeric coating is visually identical when compared to the calcium phosphate precipitations previously analysed by Kokubo [9] and Kellomäki [10]. The formation of calcium phosphate layer on organic materials has previously been reported also for instance by Abe *et al*. [11], and Marcolongo *et al*. [12], while Niiranen *et al*. [13] have also reported the "halo" effect, in which the polymeric phase of composite containing bioactive glass and biopolymer also has calcium phosphate precipitating into its surface when immersed in simulated body fluid.

Calcium phosphate layer formation in fibre surface is delayed when bioactive glass fibre is coated with biopolymers when compare to the non-coated fibre. The hydrophobic poly(L-lactide) coating does not allow water penetration to the glass and the degradation and dissolution of bioactive glass is delayed. Thus defects in coating allow water penetration into the glass enabling glass resorbtion in areas which are in contact with SBF.

The idea of using bioactive glass fibres to reinforce biopolymers has been studied by several research groups: the processing and mechanical properties of bioactive or resorbable glass fibre reinforced composite materials were reported already in 1985 by Dunn *et al*. [14], in 1986 by Lin [15] and in 1993 by Krebs *et al*. [16]. The performance of various fibre-matrix composite systems has been studied by Slivka *et al*. The composites studied were poly(L-lactid acid) (PLLA) matrix reinforced with continuous fibres of either non-absorbable AS4 carbon, absorbable calcium phosphate, poly(glycolic acid), or chitin [17]. Storey *et al*. studied polyester-fibre and matrix composites for totally absorbable biomaterials [18]. Marcolongo *et al*. have also published *in vitro* and *in vivo* studies about bioactive glass fibre reinforced polysulfones. They found that bone tissue exhibited direct contact with the glass fibres and adjacent polymer matrix, resulting in interfacial bond strengths significantly higher than with polymer controls [19]. Andriano *et al*. have performed experiments in which absorbable crystalline, calsium-sodium-metaphosphate microfibers were treated with trimethoxy-based silane coupling agents. Treated fibres were further used as a reinforcing part in a composite, with poly(L-lactic acid) and poly(ortho ester) used as a polymer phase. In both experiments the treatment increased the mechanical properties of the composite compared to the composites reinforced with untreated fibres [20, 21]. Early composite manufacturing experiments were also performed in our laboratory, where it was noted that strength and modulus values of polylactide rods significantly increased when bioactive glass fibres were used as a reinforcing phase to form a composite structure [22, 23].

Besides using bioactive glass fibres as reinforcement in a composite, interest exists to produce fabrics which are woven from bioactive glass fibres. In our experiments we found that even a slight abrasion of the surface of the fibres drastically reduces the maximum apparent strain. With a polymer coat the abrasion can be avoided. Without coating bioactive glass the fibres cannot be fabricated further as long fibres. Moreover, thin fibres cannot even be unwound from the coil without coating. Both of the coating methods produced a smooth polymeric layer on the surface of bioactive glass fibres. We assume that tailor-made coats can be produced for bioactive glass fibres in order to find the optimum properties required by different manufacturing applications. A fibre-polymer coating adhesion is not optimal with the samples manufactured in this study, though. When high strength composites are manufactured, the fibre-matrix interface plays significant role and in order to achieve high strength biomedical composites, the surface adhesion between fibre and coating should be studied and most likely improved.

5. Conclusion

Bioactive glass fibres are sensitive to surface abrasion and can not be fully utilised as long fibres without coating. With both the coating methods used, namely dipping and pulling through, a smooth polymeric layer was obtained to the fibre surface. A coating protects the fibre and improved mechanical properties were initially obtained. A coating on the surface of the fibres also enables the further processing of the fibres, thus enabling the bunch of fibres to be processed further for instance by braiding, weaving or knitting. For high strength composite applications fibre-polymer surface attachment would need further improvement, though.

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