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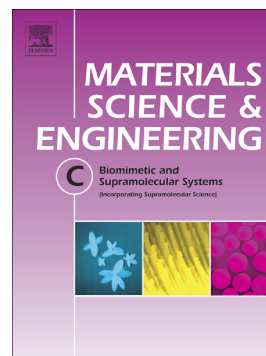
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**Modification of Ti6Al4V implant surfaces by biocompatible TiO<sub>2</sub>/PCL hybrid layers prepared via sol-gel dip coating: structural characterization, mechanical and corrosion behaviour.**

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**Abstract.**

Surface modification of metallic implants is a promising strategy to improve tissue tolerance, osseointegration and corrosion resistance of them. In the present work, bioactive and biocompatible organic-inorganic hybrid coatings were prepared using a sol-gel dip coating route. They consist of an inorganic  $\text{TiO}_2$  matrix in which different percentages of poly( $\epsilon$ -caprolactone) (PCL), a biodegradable and biocompatible polymer, were incorporated. The coatings were used to modify the surface of Ti6Al4V substrates in order to improve their wear and corrosion resistance. The chemical structure of the coatings was analyzed by attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy. Coating microstructure, mechanical properties and ability to inhibit the corrosion of the substrates were evaluated as a function of the PCL amount.

Scanning electron microscopy (SEM) showed that the polymer allows to obtain crack-free coatings, but when high percentages were added uncoated areas appear. Nano-indentation tests revealed that, as expected, surface hardness and elastic modulus decrease as the percentage of polymeric matrix increases, but scratch testing demonstrated that the coatings are effective in preventing scratching of the underlying metallic substrate, at least for PCL contents up to 20wt%.

The electrochemical tests (polarization curves acquired in order to evaluate the corrosion resistance) allowed to assess that the coatings have a significant effect in terms of corrosion potential ( $E_{\text{corr}}$ ) but they do not significantly affect the passivation process that titanium undergoes in contact with the test solution used (modified Dulbecco's phosphate-buffered saline or DPBS).

**Keywords:** Sol-gel process; organic-inorganic hybrid materials; dip coating technique; scratch test; corrosion behavior.

## Introduction

The combination of an excellent tensile and fatigue strength, osseointegrative properties and corrosion resistance make commercially pure titanium and titanium alloys materials of choice for many orthopedic and dental implant applications. The most commonly used is the Grade 5 Titanium, a titanium alloy referred to as Ti-6Al-4V because of its composition (6%Al and 4%V). Aluminium and Vanadium act as stabilizers of the two allotropic phases of titanium (hexagonal  $\alpha$ -phase and cubic  $\beta$ -phase), promoting the oxidation resistance and strength of the implant, respectively. However, the use of this material as implant present some main drawbacks. Its elastic modulus is higher than that of human bones: this can induces stress shielding and the failure of implant due to bone resorption. The low wear resistance can cause the release of debris and Al or V ions which can induce cytotoxicity or adverse tissue reactions. Moreover, as Ti6Al4V is a biologically inert material, it doesn't induce allergic reaction. However, the body recognize those implants as foreign and isolate them in a fibrotic capsule. Therefore, the osseointegration is hampered and the prostheses mobilization and failure is induced. To improve the lifetime of the titanium implants, their surface can be modified by applying a coating of bioactive and biocompatible glasses or glass-ceramics [1, 2]. This strategy allows to retain the favorable mechanical properties of titanium, favour its integration process improving the biological properties, inhibit wear, corrosion and ion release [3-9]. Sol-gel dip coating technique is an ideal technology to coat a wide range of substrates with bioactive and biocompatible glassy materials [2]. Sol-gel is the method used to synthesize ceramic and/or glass materials at a relatively low temperature [10] through the hydrolysis and condensation of metal alkoxide precursors. Sol-gel material are provided of intrinsic bioactivity [11, 12]. The hydrolysis reaction, indeed, generates –OH groups which are able to induce the hydroxyapatite nucleation in vitro and in vivo. The sol-gel method can be easily coupled with a range of coating techniques. When the dip coating method is used, a substrate is dipped into the starting colloidal solution (the 'sol') and withdrawn at a constant speed to enable the sol drainage and its instantaneous gelation. The thickness and the morphology

of the coatings is strongly influenced by the withdrawal speed and the viscosity of the sol, which must be carefully chosen [10, 13]. Many works reports the use of sol-gel coatings also as protective systems able to inhibit corrosion of metal substrates [6, 14].

The main limit of the inorganic sol-gel coatings is the brittleness. To overcome this drawback an organic component can be embedded into the inorganic sol-gel matrix to form an organic-inorganic hybrid sol-gel coating [6]. Organic-inorganic hybrid nanocomposite materials are homogeneous bicomponent systems in which the two components interact at the molecular level. Their properties derive from the synergic effect between the properties of each component. They can be easily obtained using the sol-gel technique by entrapping various organic polymers in a glassy matrix [15, 16]. The low processing temperature used during the sol-gel process, indeed, makes this technology compatible with thermolabile molecules.

In the present work, organic-inorganic hybrid coatings, consisting of a titania ( $\text{TiO}_2$ ) inorganic matrix and organic poly ( $\epsilon$ -caprolactone) (PCL), are prepared by means of the sol-gel dip coating technique and used to modify the surface of Ti6Al4V implants in order to improve their performances. The main idea in the development of such coatings was to combine the known anticorrosive properties of the titania with the mechanical properties of the polymer. It is known, indeed, that the high corrosive resistance of titanium and its alloys is due to the spontaneous formation of a dense and stable titanium dioxide surface layer which constitutes a barrier between the implant and the surrounding tissue [17]. However, local mechanical abrasion can lead its removal and, thus, a strongly decrease of the corrosion resistance [18]. Therefore, to avoid the early failure of the implants due to wear, the thickness of oxide layer can be increased using nitric acid passivation protocols [18, 19] or a protective layer can be applied. In the present work, the application of synthetic  $\text{TiO}_2$ -based sol-gel coatings is proposed for this purpose.

On the other hand, PCL is a biodegradable and biocompatible aliphatic polyester. Elsewhere [20], an improvement of mechanical properties of  $\text{TiO}_2$ -based sol-gel glasses was obtained by adding

PCL to the inorganic matrix. The addition of PCL also allowed to obtain crack-free organic-inorganic coatings [7].

Elsewhere [21] it was proved that TiO<sub>2</sub>/PCL coatings have high bioactivity and biocompatibility and that their application to titanium implants improves their biological performance. In the present work, the adhesion, the mechanical properties and corrosion behavior of TiO<sub>2</sub>/PCL coatings were investigated as a function of the PCL content, to evaluate the possibility of using them in biomedical field.

## Materials and methods

### *Sample preparation*

Inorganic TiO<sub>2</sub> and inorganic/organic TiO<sub>2</sub>/PCL hybrid nanocomposites containing 5, 10, 20 and 30 wt% of the organic component, were synthesized using the sol-gel route as reported elsewhere [21]. Therefore, Titanium(IV) butoxide (TBT, Sigma Aldrich) was used as metal alcoxide precursor of the inorganic matrix, 1-Butanol 99.8 % (BuOH, Sigma Aldrich) as solvent and glacial acetic acid (HAc, Carlo Erba) as chelating agent to control the hydrolytic activity of titanium alcoxide. To synthesize the hybrid systems, poly ( $\epsilon$ -caprolactone) (PCL Sigma Aldrich, M<sub>w</sub> = 65000) dissolved in chloroform (CH<sub>3</sub>Cl) was added to the inorganic sol in different amounts.

The materials in sol phase, before gelation, were used to coat Ti6Al4V (Titanium Consulting & Trading s.r.l. Milan, Italy) disks of 18 mm diameter and 1.5 mm thickness using a KSV LM dip coater. Before starting the coating process, the substrates were polished (with emery papers, until FEPA P#1000, and emery cloths imbued with a diamond suspension, 3  $\mu$ m grain size), ultrasonically cleaned with acetone and subjected to a passivation process with HNO<sub>3</sub> 65%, for 60 min. To dip coat the disks a withdrawal speed of the substrate equal to 10 mm/min was used. The coated substrates were heat-treated at 45°C for 24 hours to promote a partial densification of the film without any polymer degradation.

### 2.3. Coating Characterization

The chemical structure of the obtained coatings was investigated by Attenuated total reflectance - Fourier transform infrared (ATR-FTIR) spectroscopy. The spectra were recorded using a Prestige-21 FTIR spectrometer equipped with an AIM-8800 infrared microscope (Shimadzu, Japan), using the incorporated 3-mm diameter Ge ATR semicircular prism. The spectra were recorded using an incident angle of 30° with the sum of 64 scans at a resolution of 4 cm<sup>-1</sup> and in the 650-4000 cm<sup>-1</sup> region. The spectra were elaborated by Prestige software (IRsolution).

The microstructure and the morphology of the obtained coatings was investigated by a Scanning electron microscopy SEM FEI Quanta 200 equipped with EDX (energy dispersive X-ray spectroscopy).

### 2.4. Mechanical characterization techniques

Scratch tests (three scratches per sample) were carried out on a CSM Micro-Combi tester equipped with a diamond tip (Rockwell C diamond scratch indenter with tip radius of 200 μm), applying on the coated surface increasing load (from 0.1 to 20 N) at 4.98 N min<sup>-1</sup> rate, for an overall scratch length of 1 mm. The on board sensors (load cell for tangential force, acoustic emission transducer and optical microscope) allowed to determine the critical load (LC1), evaluated as the normal load at which the first damage occurred to the coating. Nanoindentation was performed using a Berkovitch indenter (Nanoindenter, CSM Instruments, Peseux, CH) operating at a maximum constant load of 25 and 50 mN (loading and unloading rate = 50 mN/min) applied for 15 s. The different loading conditions have been chosen in order to investigate possible effects related to the depth of indentation and to maintain the indentation depth below 1 μm. A second set of nanoindentations was performed in penetration depth control, imposing a maximum penetration depth of the indenter equal to 250nm. As a matter of fact, SEM observations on fracture surfaces (like the one in Figure 1) confirmed that the deposited coatings have a minimum thickness of 2.7 μm in the investigated zones, reaching a maximum value of 11.3 μm in case of the 30% PCL



samples. Nanoindentation results were analyzed according to the Oliver and Pharr procedure [22], allowing to evaluate the hardness and elastic module of the coatings. A tentative value of 0.27 was assumed as Poisson's ratio of the material, in agreement with literature data concerning titanium dioxide thin films [23], thus neglecting the contribution from the PCL phase, having a slightly higher Poisson's ratio of 0.3 [24]. The curves of penetration depth vs. applied normal load were also used to evaluate the amount of work required to cause the nanoindentation, and the percentage of this work performed in the elastic regime (integral of the unloading curve) or plastic regime (difference between the integral of the loading curve and the unloading curve). Ten nanoindentations were performed in different zones of each specimen, and the average values were calculated.

In order to assess the reproducibility of the measurements, under different conditions, four specimens belonging to the same  $\text{TiO}_2+10 \text{ wt\% PCL}$  series were preliminarily tested. Results demonstrated that the "within sample" variations resulted larger than the variations "between samples".

### 2.5. Corrosion tests

The corrosion resistance was evaluated by accelerated polarization tests, performed in an electrochemical cell (Flat Cell K0235 PAR), using the samples as working electrode (exposing a flat and circular area of area of  $1.6\text{cm}^2$ ), a platinum grid as counter electrode and an  $\text{Ag/AgCl/KCl}_{(\text{sat.})}$  electrode (SSCE) as reference electrode (all the potentials reported in this paper refer to this reference electrode). The electrolyte used for the corrosion tests was a Sigma Aldrich DPBS solution (Dulbecco's Phosphate-Buffered Saline solution, pH 7.4) with the addition of  $0.1 \text{ gL}^{-1}$  of  $\text{CaCl}_2$ ,  $0.1 \text{ gL}^{-1}$  of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $0.05 \text{ gL}^{-1}$  of BSA (bovine serum albumine) at  $37^\circ\text{C}$ . The electrochemical procedure is the same applied in our previous work [25]: each sample was immersed in the test solution for 1 hour before applying any polarization, in order to stabilize its rest potential ( $E_r$ ); then potentiodynamic polarization scans were carried out with a scan rate of  $0.5\text{mVs}^{-1}$  in the range from  $-0.8\text{V}$  (vs  $E_r$ ) to  $3.0\text{V}$  (vs  $E_r$ ) using a PAR VersaStat 3 potentiostat.

In addition to the five coated samples, i.e. TiO<sub>2</sub> + 5, 10, 20 and 30wt%, an uncoated titanium sample was tested to assess the corrosion behavior of the bare titanium; the uncoated sample was subjected to the same passivation process used as pretreatment for the coated samples (with HNO<sub>3</sub> 65% for 60 min).

## Results and discussion

### *Sample Characterization*

ATR-FTIR spectra of the inorganic TiO<sub>2</sub> coating (curve a) and pure PCL (curve f) compared to the spectra of TiO<sub>2</sub>/PCL hybrids with increasing amount of polymer (curves from b to e) are shown in Figure 2.

The spectrum of the TiO<sub>2</sub> coating (curve a) shows the main band of the acetic acid-containing titania sol-gel materials [26, 27]. The bands visible at wavenumber lower than 1000 cm<sup>-1</sup> are due to Ti-O and Ti-O-Ti vibrations in the lattice [26, 27]. The presence of the acetic acid in the inorganic matrix is proved by the shoulders at 1635 cm<sup>-1</sup> and 1336 cm<sup>-1</sup> and the doublet at 1527 cm<sup>-1</sup> and 1419 cm<sup>-1</sup>, due to the asymmetric and symmetric stretching vibrations of the acid carboxylic group coordinated to Ti as a bidentate ligand [26-28]. The literature, indeed, shows that if the separation between those signals is greater than 150 cm<sup>-1</sup> the acetate acts as bridging ligand between two titanium atoms, whereas if that is smaller than 150 cm<sup>-1</sup> (in the spectra reported in Figure 2  $\Delta\bar{\nu} = 108$  cm<sup>-1</sup>) it acts as bidentate ligand. The broad band centered at about 3100 cm<sup>-1</sup> is due to -OH vibrations.

All described peaks are visible also in the spectra of TiO<sub>2</sub>/PCL hybrid materials. When the 5wt% of polymer is added, a weak band at 2927 cm<sup>-1</sup> appears ascribable to CH<sub>2</sub> asymmetric stretching of the PCL. Moreover, when the 10wt% of polymer is added, other peaks appear whose intensities increase with the polymer amount (interpretation reported in table 1). In particular, the sharp peak at 1725 cm<sup>-1</sup> is typical of the stretching of C=O involved in H-bonds [29, 30]. Elsewhere [8], indeed, it was observed the shift to low wavenumbers of such peak in the spectra of TiO<sub>2</sub>/PCL

hybrid materials compared to that of the pure PCL, proving that the C=O groups of the polymer interact with the inorganic matrix by means of H-bonds.

The morphology of the coatings was observed by SEM microscopy. SEM micrographs of the top view of the PCL-free and hybrid coatings are shown in figure 3.

PCL-free coating (figure 3b) shows some cracks whereas the hybrid coatings (figure 3 c to f) appear crack-free. This effect of the polymer was predictable as the ability of PCL to improve the coating elasticity was known [7, 25]. However, uncoated areas were observed when an high PCL amount is present in the coatings. Their formation could be due to the removal of the polymer particles which occurred when the samples were subjected to SEM high vacuum. This hypothesis is in agreement with ATR-FTIR results which proved the formation of weak H-bonds between PCL chains and the TiO<sub>2</sub> matrix.

The comparison with the literature [21] also shows that the substrate roughness affects the coating structure

#### *Nanoindentation results*

Figure 4 shows the results in terms of the measured hardness, expressed in equivalent HV scale as converted from the Berkovich indentations and the calculated Young's modulus of the coatings as a function of the PCL content, for the two investigated loading conditions.

Average maximum nanoindentation depth resulted of 440 and 630 nm in case of applied loads of 25 and 50 mN, respectively. Hence a significant effect of the substrate is expected under these loading conditions. Nevertheless, it is evident, for the lowest loading conditions, the expected trend of surface hardness and elastic modulus decreasing as the percentage of polymeric matrix increases. Applying smaller loads, i.e imposing a maximum indentation depth of 250 nm, which experimentally corresponded on the average to 9.7 mN maximum load, the results shown in figure 5 are obtained.

Results are similar to the case of 25mN load indentation, with the expected decrease of surface hardness and elastic modulus as a function of PCL content in the coatings. Surface hardness of uncoated sample is in perfect agreement with literature data concerning annealed Ti6Al4V [31].

Instrumented indentation allowed to calculate the amount of energy required to deform the samples and to evaluate the amount of plastic or elastic work. Figure 6 shows the results for the three loading conditions tested.

The amount of deformation work increases as a function of applied load, as expected, but the ratio between elastic and plastic work remained almost constant for all the three series (77%). Elastic work, in each series, remained constant independently on the amount of PCL content, while it somehow affects the amount of plastic work. A possible explanation could be the presence of the titanium substrate, whose elastic recovery is predominant over the PCL one. This is particularly evident in case of the maximum applied load, where almost no effect on the PCL content is detectable: as a matter of fact, under these loading conditions, the substrate is surely involved in the deformation mechanisms due to the small thickness of the coatings.

#### *Scratch test results*

Scratch testing allowed to identify the occurrence of the first damage to the coating (Critical load LC1), by direct microscope observation, as well as to measure the residual depth (Rd) - i.e. the depth of the track after the pass of the indenter, deprived of the elastic deformation. Figure 7 shows the results of scratch testing, indicating that the coating results effective in preventing scratch of the underlying metallic substrate, at least for PCL contents up to 20wt%. In case of the 30wt% containing sample, the measured values indicate a much higher residual depth (i.e deeper scratch), but accompanied by a higher critical load value (i.e. higher tendency to protect the substrate).

This anomalous deviation could be ascribed to possible differences in the coating morphology and microstructure, as observed by SEM (Figure 3).

### *Corrosion resistance*

The potentiodynamic polarization curves of bare and coated titanium are shown in Figure 8. Uncoated titanium exhibits a corrosion potential of approximately -0.3 V (SSCE), a passivation potential of 0.7 V (SSCE) and a very low passive current density (ranging between 1 and 3  $\mu\text{Acm}^{-2}$ ), in agreement with the data reported in literature for corrosion test in this media [32, 33].

The polarization curves of sample coated with pure  $\text{TiO}_2$  and samples coated with  $\text{TiO}_2/\text{PCL}$  are very similar in shape and values. This behavior can be explained considering that: i) the pure  $\text{TiO}_2$  coating has defects (microcracks, previously seen) which permit the electrolyte to overcome the coating in some areas; ii) the samples with PCL suffer a partial dissolution of this compound (as reported in our previous work [25]) during the preliminary immersion of the samples in the test solution (1 hour); the partial dissolution of the PCL is confirmed by the trend of ocp (open circuit potential) vs time during the preliminary immersion of the samples in the test solution (1 hour), showing a very unstable trend (as already seen for similar samples in our previous study [25]). However, in both cases, the polarization curves show a very fast passivation process, reaching a shape (and a passivation current value) almost identical to that of pure titanium (solid curve in the figure).

The most important difference that arises from comparing the curves of the coated samples with that of the bare sample is the shift of the corrosion potential ( $E_{\text{corr}}$ ): the potential of the sample coated with  $\text{TiO}_2$  is shifted of about 300mV respect to that of the bare Ti6Al4V alloy, while those of the PCL-based coatings all fall at lower values (about 400mV lower respect to bare Ti6Al4V alloy). This phenomenon shows that the interface between the sample and the electrolyte is different at the start of the corrosion test (coating influence), although subsequently, moving toward potentials higher than  $E_{\text{corr}}$ , all coated samples reach the trend of the bare titanium curve (passivation). Probably the corrosion potential of the  $\text{TiO}_2$  applied as coating (with and without PCL) is different from the potential of the passivating products (mainly titanium oxides) obtained during the pre-treatment in nitric acid of the bare Ti6Al4V alloy. Despite this difference in terms of

$E_{\text{corr}}$  is quite interesting, it have a very little influence on the corrosion behavior of the different samples, as all them show a passive attitude and have a potentiodynamic curve comparable to that of the bare titanium from 0 V onwards.

Those results allow to assume that the  $\text{TiO}_2$  coating affect the corrosion behaviour of the titanium only in term of corrosion potential ( $E_{\text{corr}}$ ) but they does not modify the corrosion mechanism which takes place on the titanium at higher applied potential (anodic curve); this is justifiable considering that the defects in the  $\text{TiO}_2$  coating and the partial solubility of the coatings modified with PCL allow the electrolyte to reach the underlying titanium, therefore the electrochemical measurements show the well-known ability to passivate of the metal.

## Conclusions

Bioactive and biocompatible organic-inorganic hybrid coatings, consisting of PCL and  $\text{TiO}_2$  as organic and inorganic phases respectively, were obtained by means of a sol-gel dip coating route and used to modify the surface of Ti6Al4V substrates. PCL inhibits crack formation in the coatings. However, when 30wt%PCL was added in the inorganic matrix, uncoated areas appear.

Nano-indentation testing proved to be a useful tool to investigate the coating mechanical properties. As expected, and despite some effects of the substrate on the higher load measurements, surface hardness and elastic modulus decrease as the percentage of polymeric matrix increases.

Concerning adhesion, scratch testing with increasing loads demonstrated that the coatings are effective in preventing scratching of the underlying metallic substrate, at least for PCL contents up to 20wt%. Higher contents of PCL result less effective, due to the previously mentioned discontinuities in the coatings.

The results obtained in corrosion tests (polarization curves) allow to asses that the coatings have a significant effect in term of corrosion potential ( $E_{\text{corr}}$ ) but they do not significantly affect the passivation process that titanium undergoes in contact with the test solution used; this because the coatings differ (in terms of  $E_{\text{corr}}$ ) from the oxide formed on Ti6Al4V alloy after nitric passivation,

but the defects of the coatings (and their partial solubility in the electrolyte) allow the test solution to come to contact with the alloy, bringing it quickly to passivate in anodic conditions.

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**Caption to figures**

*Figure 1* SEM Micrograph of the fracture surface (cross section) of the TiO<sub>2</sub> + PCL 20 wt% coated sample

*Figure 2* ATR-FTIR spectra of (A) TiO<sub>2</sub>, (B, C, D, E) TiO<sub>2</sub> + PCL 5, 10, 20, 30 wt% coatings; (F) Pure PCL. (□) PCL peaks

*Figure 3* SEM micrographs of (A) Ti6Al4V uncoated disk (B) TiO<sub>2</sub> (C) TiO<sub>2</sub> + PCL 5 wt% , (D) TiO<sub>2</sub> + PCL 10 wt%, (E) TiO<sub>2</sub> + PCL 20 wt% and (F) TiO<sub>2</sub> + PCL 30 wt% coatings. In the ring an example of uncoated area. Instrumental parameters used to collect the images: HV = 20.0 kV; Mag = 1600x; Det = ETD (Everhart Thornley detector which detects secondary electrons); VacMode = High Vacuum.

*Figure 4* Equivalent Vickers hardness (HV) and Young module (E) for nanoindentations performed at: a) 25 mN; b) 50 mN

*Figure 5* Equivalent Vickers hardness (HV) and Young module (E) for nanoindentations performed at maximum depth of 250 nm

*Figure 6* Deformation energy for nanoindentations achieved: a) in depth control (250 nm); b) in load control (25 mN) and c) in load control (50 mN).

*Figure 7* Scratch test results (average residual depth, Rd and average critical load, Lc1) as a function of PCL content and reference optical micrographs showing the starting of damage of the substrate

*Figure 8* Potentiodynamic polarization curves for bare titanium and coated samples after 1 h of immersion in DPBS stock solution with the addition of 0.1 gL<sup>-1</sup> of CaCl<sub>2</sub>, 0.1 gL<sup>-1</sup> of MgCl<sub>2</sub>·6H<sub>2</sub>O and 0.05 gL<sup>-1</sup> of BSA. Scan rate 0.5 mVs<sup>-1</sup>

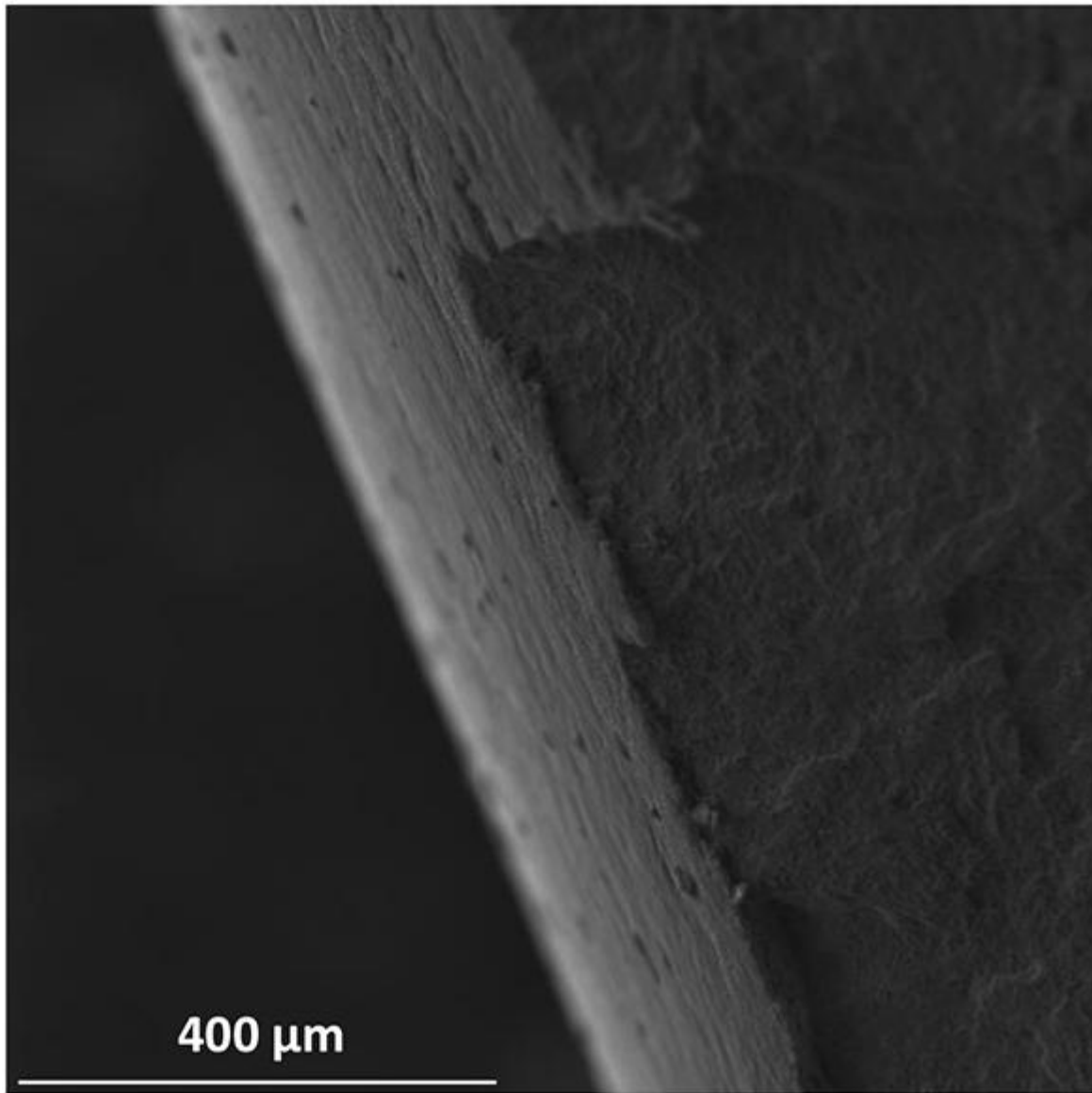


Figure 1

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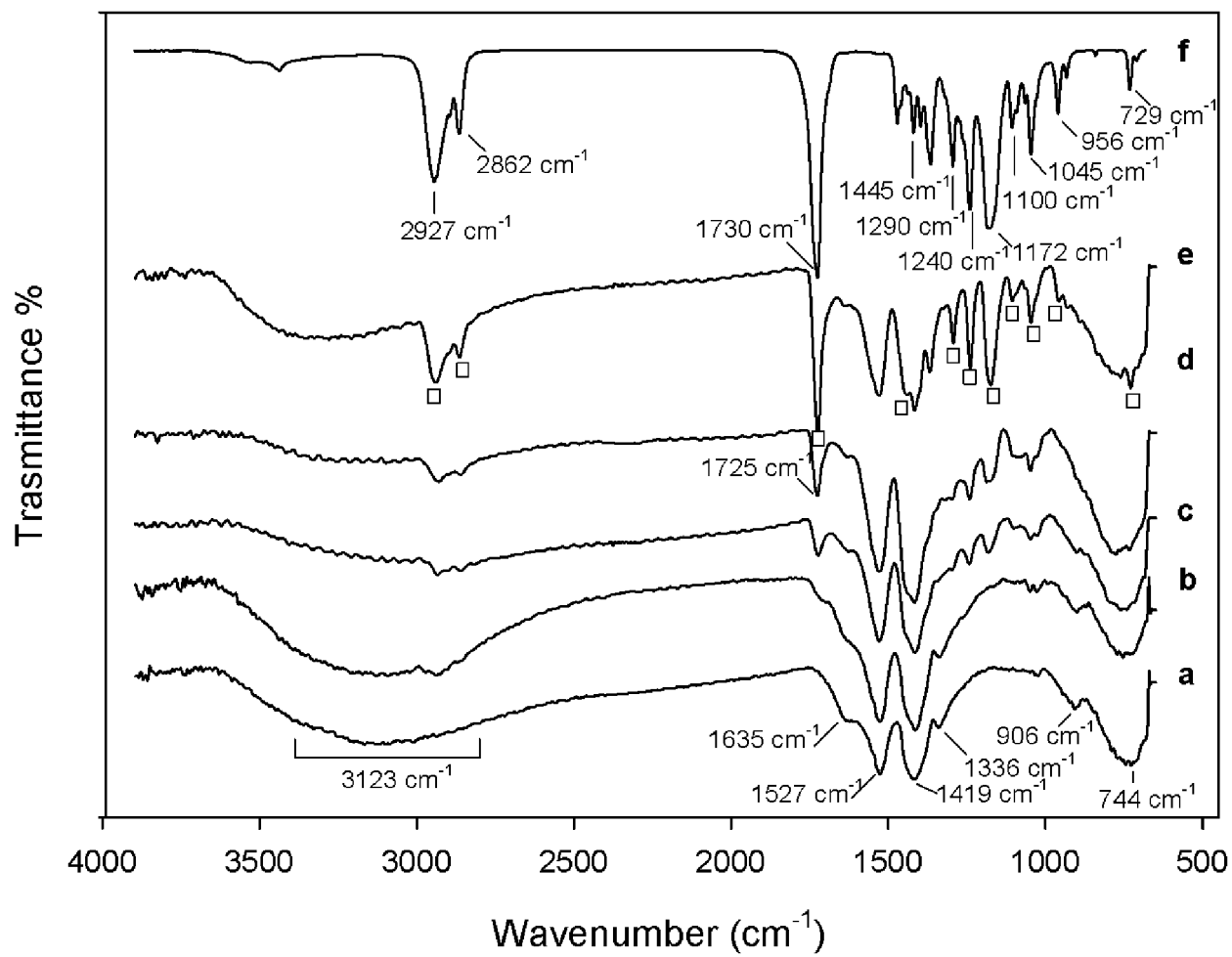


Figure 2

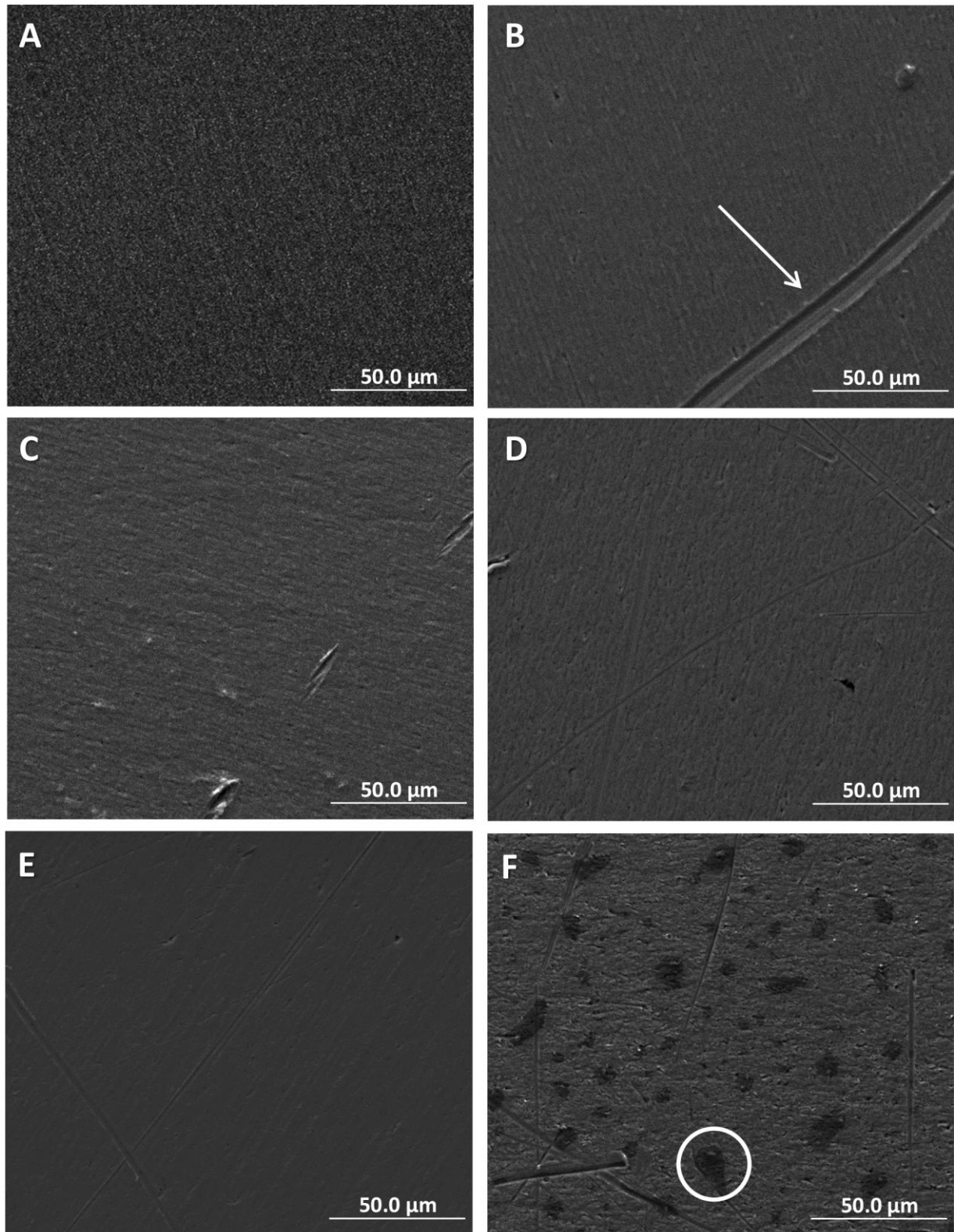


Figure 3

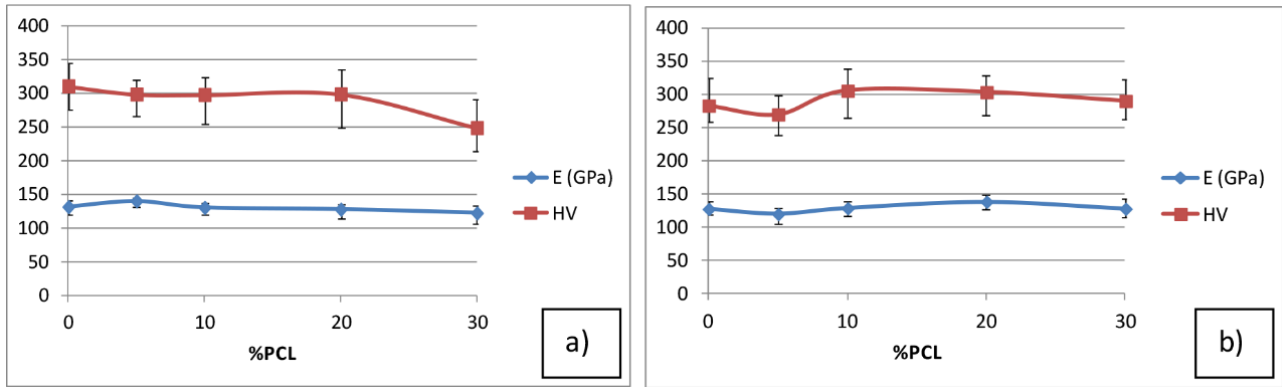


Figure 4

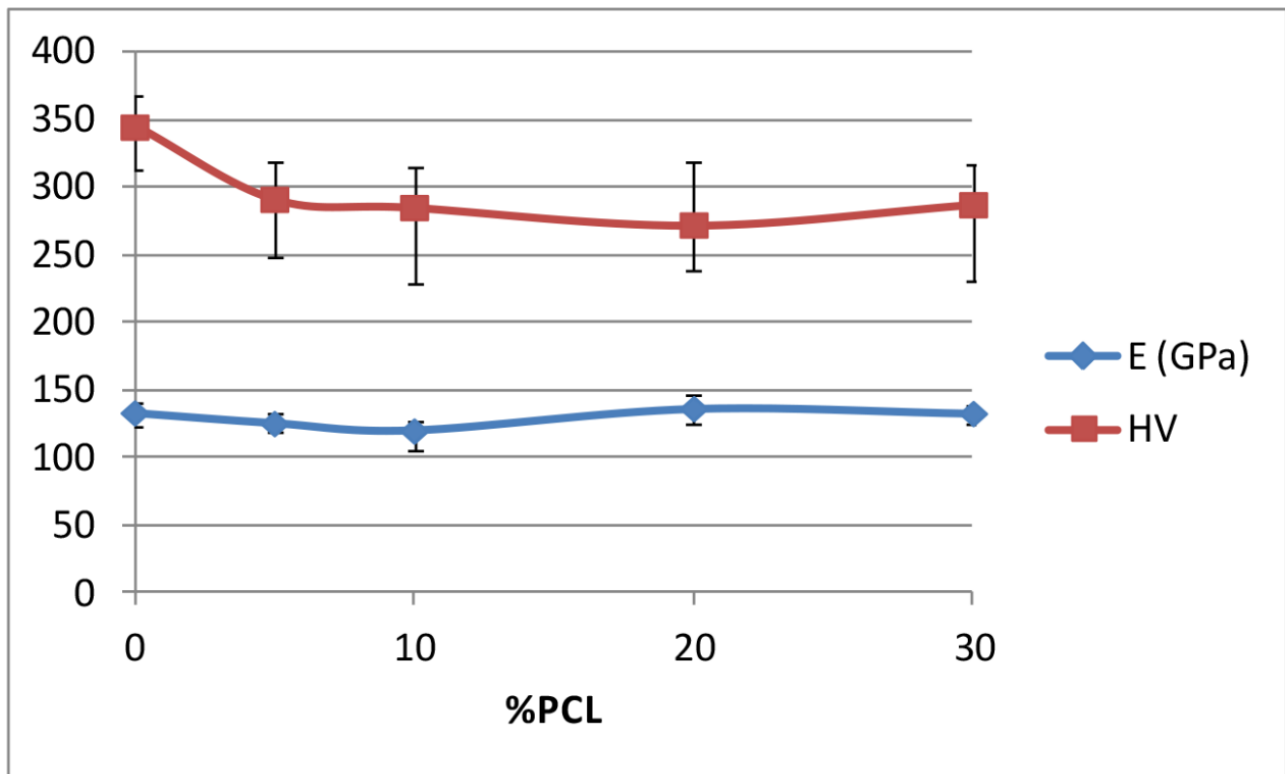


Figure 5



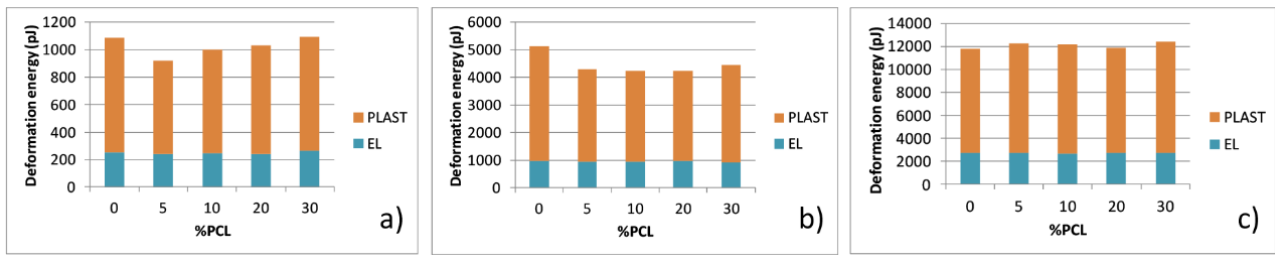


Figure 6

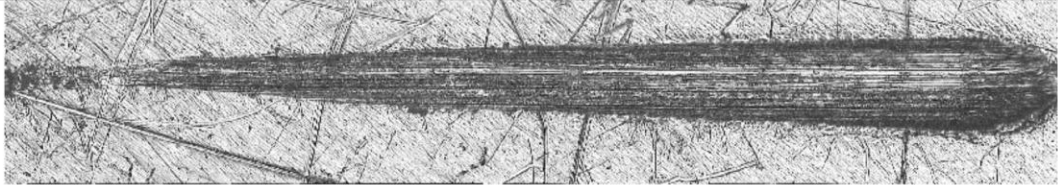
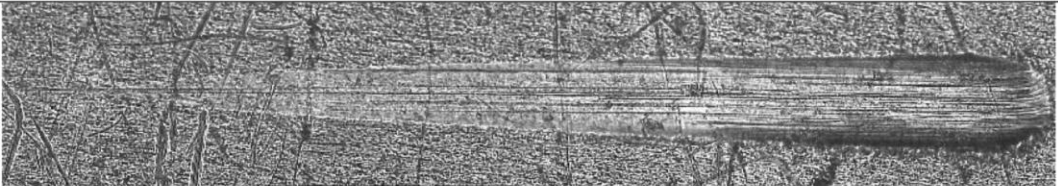
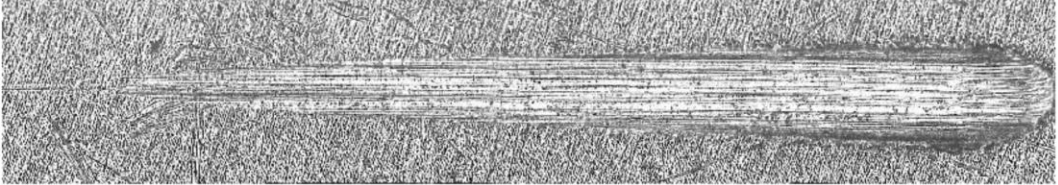
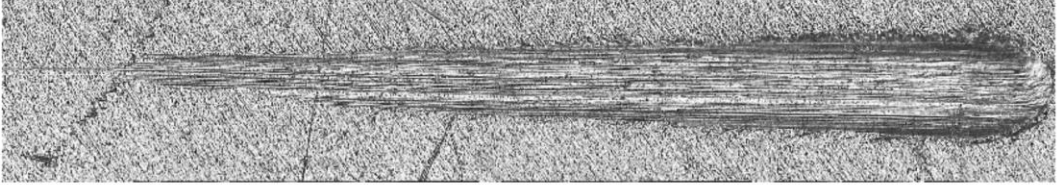
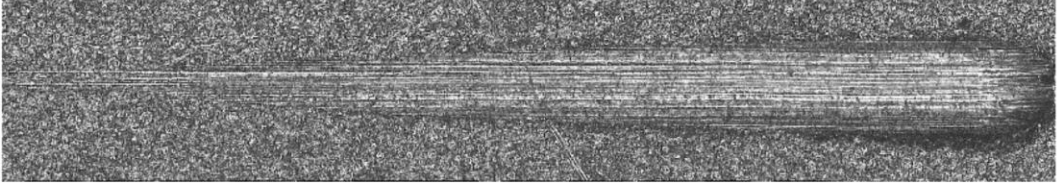
PCL (wt%)	Micrograph of the track - 1 mm length
Rd ( $\mu\text{m}$ )	
Lc1 (N)	
0	
2.3	
0.62	
5	
2.3	
0.78	
10	
2.2	
0.77	
20	
2.1	
1.12	
30	
4.3	
1.35	

Figure 7

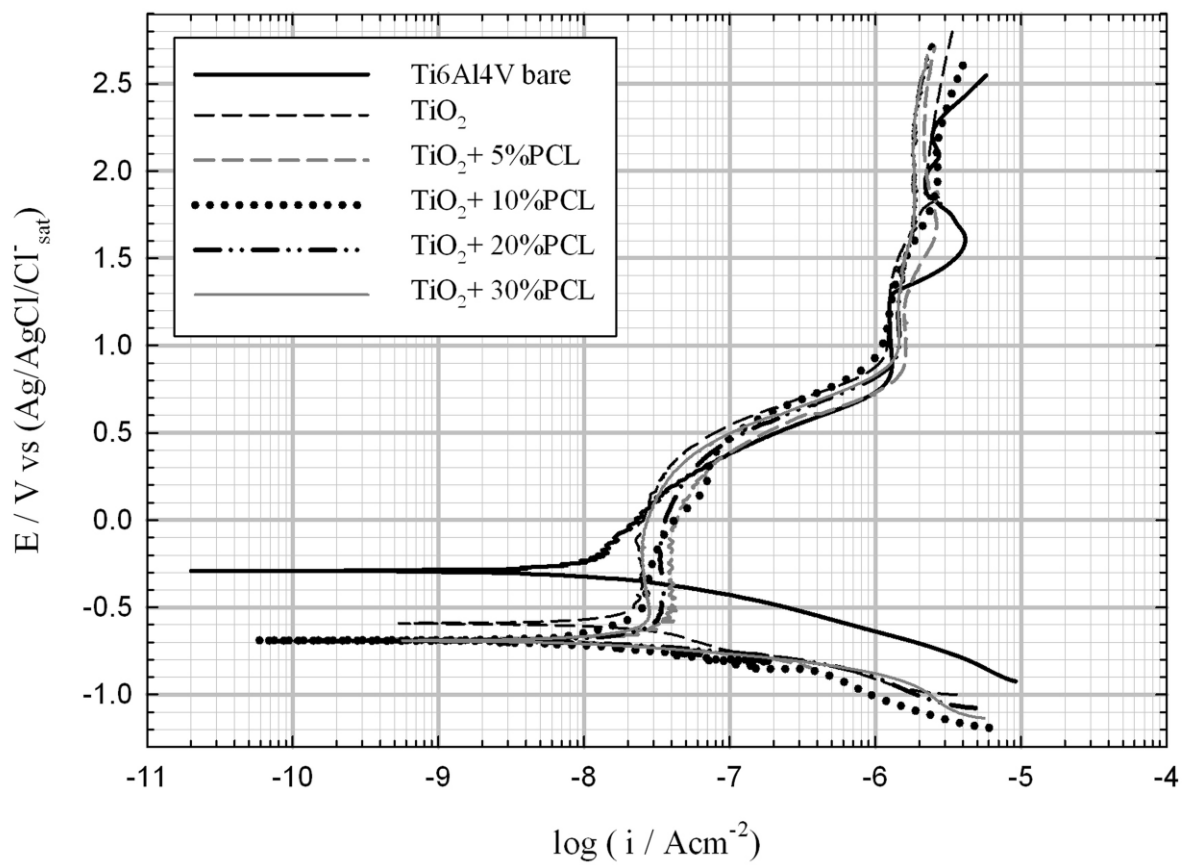
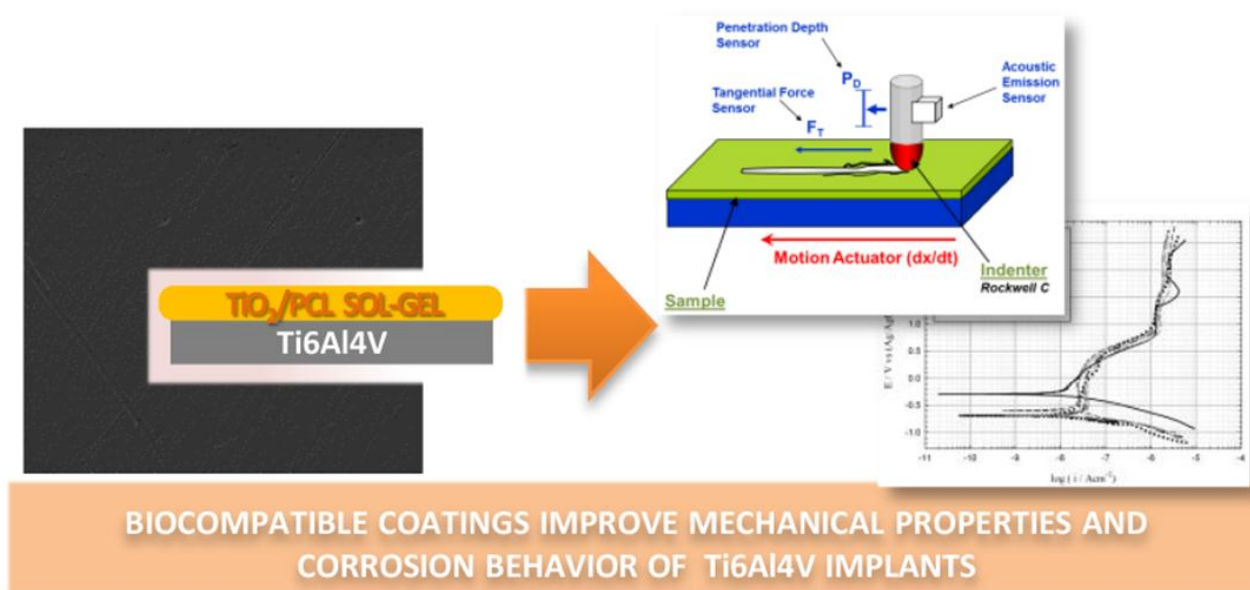


Figure 8

**Table 1.** Characteristic FTIR bands of PCL and their interpretation [30, 34]

<b>Absorption Bands of PCL</b>	<b>Interpretation</b>
2927 and 2862 cm <sup>-1</sup>	asymmetric and symmetric stretching of CH <sub>2</sub>
1725 cm <sup>-1</sup>	C=O stretching
1445 cm <sup>-1</sup>	methylene C-H bending
1290 cm <sup>-1</sup> and 956 cm <sup>-1</sup>	C-C stretching in the crystalline phase
1240 cm <sup>-1</sup> and 1172 cm <sup>-1</sup>	C-O-C asymmetric and symmetric stretching of PCL in amorphous phase
1100 and 1045cm <sup>-1</sup>	O-C vibrations
729 cm <sup>-1</sup>	CH <sub>2</sub> bending vibrations

## Graphical Abstract



## Highlights

- Bioactive TiO<sub>2</sub>/PCL hybrid coatings on Ti6Al4V were prepared via sol-gel dip coating
- Hybrid coatings are crack-free but when 50wt% PCL was added, uncoated areas appear
- Coating hardness and elastic modulus decrease as the PCL percentage increases
- The coatings prevent scratching of the Ti6Al4V substrates
- The coatings have a significant effect in term of corrosion potential

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