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Investigating dynamic-mechanical properties of multi-layered materials for biomedical applications

Abstract: The development and advancement of polymeric implant materials is a frequent focus in current research. The combination of polymeric materials with diverging properties provides a wide range of new materials with innovative characteristics. One technology for combining materials is to apply a coated layer onto a base material.

In this work, a hyperelastic, synthetic base material was combined with a rigid biopolymer coating layer. A multi-layered material with combined characteristics of both was built. In the field of processed polymers, the analysis of coating adhesion is not feasible using established methods. Therefore, a dynamic-mechanical method was investigated, which supplements the uniaxial tensile test and provides knowledge regarding mechanical resistance of the multi-layered polymer structure. Furthermore, the method gets validated by SEM-imaging and evaluation of coating composition before and after testing under dynamic conditions.

Keywords: coating adhesion, multi-layered polymers, biomedical applications, dynamic mechanical testing

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1 Introduction

Polymers are widely used as biomedical implant materials. Although their characteristics are highly variable, the combination of two or more polymers can be beneficial for achieving certain properties. Several technologies are described for combining polymers, such as polymer blends or generating multi-layered structures with different technologies [1-5].

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Medical implant materials technologies that generate multi-layered structures with a thin top layer onto a base material, for example spray coating, dip coating or electrospinning, are frequently used in the field of polymeric material development. In particular, multi-layered structure could be beneficial, if material properties of the coating are complementary to those of the base material [6]. Some polycarbonateurethane-co-silicones (PCU-co-Si) generally show adequate material properties, but still lack in biocompatibility or mechanical rigidity, depending on their previous processing. Solution casted films in combination with a biopolymer coating layer made of chitosan (CS) could show improved mechanical properties as well as improved surface properties for implant-tissue interaction, such as high hydrophilicity. These multi-layered polymeric structures could be useful in various medical applications, such as wound pads, vascular scaffolds and covers for implants or implantable devices.

Established methods for the analysis of coating adhesion are not applicable to examine mechanical properties or durability for polymeric coating layers. Due to the high elastic characteristics and morphological structure, e.g. porosity, methods like cross-cut and pull-off tests are not expedient [7, 8]. Therefore, a method for dynamic-mechanical testing of multi-layered polymeric materials was investigated. Especially the examination of delamination, durability and applicability for medical applications, e.g. pulsating stress, or their specific implantation methods was intended.

2 Materials and methods

2.1 Sample preparation

As base material, a PCU-co-Si film (AdvanSource Biomaterials Corp., Wilmington, MA, USA) was chosen, which was subsequently dip-coated with CS (Chitosan highly viscous, Sigma-Aldrich GmbH, Steinheim, Germany).

The base material film was manufactured by casting a solution made of 1 g PCU-co-Si granules dissolved in 24 mL chloroform. After evaporation of the solvent, the film was washed in methanol and deionized water for 48 hours each. Subsequently, the samples were annealed at 40 °C for 7 days.

The dip-coated CS-layer was applied by dipping the film twice into 0.5% Chitosan dissolved in 0.1 M hydrochloric acid. The resulting CS-coating thickness is 10.1 ± 2.1 µm, measured at 20 points for each sample (n=3).

All tests were performed comparatively for reference samples without coating and coated samples.

2.2 Uniaxial tensile testing

Tensile tests were performed by using a universal testing machine Zwick/Roell Z2.5/TN. (Zwick GmbH & Co. KG, Ulm, Germany). All tests were performed at room temperature (20 °C) and a crosshead speed of 12 mm/min. According to DIN EN ISO 527 standards, all test samples for uniaxial tensile tests have a specimen geometry according to the standard test specimen 1BB [9].

2.3 Uniaxial dynamic-mechanical testing

For testing the dynamic-mechanical properties and the coating adhesion under tumescent load conditions, the test bench TA ElectroForce BioDynamic 5170 (TA Instruments Inc., New Castle, DE, USA) was used. Therefore, a test protocol with fixed displacement of 2 mm, which corresponds to 15% strain, was applied for 24 hours with a test frequency of 5 Hz. This results in a test with 432,000 load cycles. The tests were conducted in isotonic saline solution at 37 °C and under constant flow conditions. Due to the properties of highly elastic PCU-co-Si films and correspondingly low forces at low elastic deformations, the sample geometry, especially the length-to-width ratio, was adapted to a rectangular 7x20 mm² shape.

For further validation of the dynamic-mechanical test results, the morphological structure of the coating was investigated with scanning electron microscopy (SEM) using a Quanta FEG 250 (FEI/Thermo Fisher Scientific, USA).

3 Results and Discussion

3.1 Uniaxial tensile testing

Stress-strain curves from uniaxial tensile tests are shown in Figure 1 and Figure 2. The black graph illustrates the average-curve of reference film samples (n=3) and the red graph the average-curve of CS-coated films (n=3). Figure 1 shows the stress-strain curves up to ultimate tensile strength and material failure. The curve progressions seem to be consistent for uncoated reference samples and coated samples. Whereas Figure 2 shows the relevant strain range up to 100% strain, which reveals a slightly higher slope of the curve in the range below 100% strain for CS-coated samples compared to uncoated films. At higher strains, curve progression of coated samples and reference samples are congruent, see Figure 1.

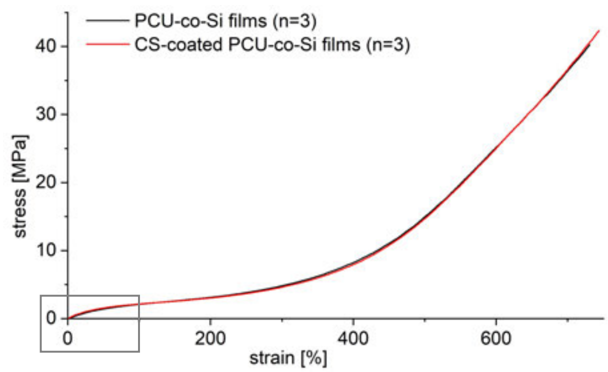

Figure 1: Stress-strain curves of reference PCU-co-Si films and CS-coated PCU-co-Si films, grey rectangle highlights enlarged section, see Figure 2

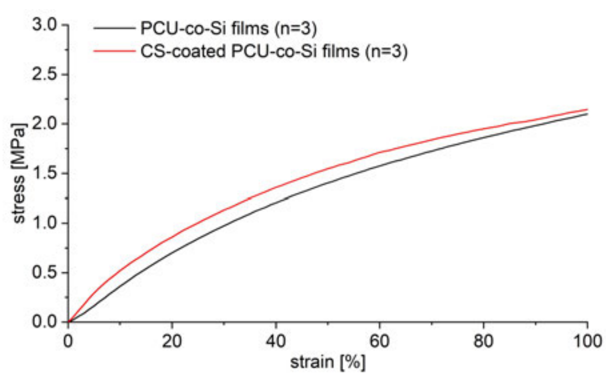

Figure 2: Stress-strain curves from uniaxial tensile tests of reference samples and CS-coated samples in relevant strain range for subsequent dynamic testing

The mechanical parameters derived from the results of the uniaxial tensile tests are summarized in Table 1. For quantitative comparison Young's modulus, ultimate tensile strength and elongation at break were determined and evaluated. The Young's modulus was calculated in the range of 0% to 2% elongation to ensure a reasonably accurate determination.

Table 1: Mechanical parameters of uncoated and coated PCU-co-Si films derived from uniaxial tensile tests

	Young's modulus [MPa]	Tensile strength [MPa]	Elongation at break [%]
PCU-co-Si (n=3)	2.9 ± 1.3	45.2 ± 4.3	767.4 ± 24.0
CS-coated PCU-co-Si (n=3)	5.8 ± 1.0	44.8 ± 3.0	760.2 ± 19.7

The CS-coating of PCU-co-Si films leads to a duplication regarding Young's modulus from 2.9 to 5.8 MPa. Tensile strength and elongation at break show less significant changes, a slight decrease is recognizable. An increase in tensile strength and a reduction in elongation at break could have been expected as a result of coating with CS, since coated samples show a higher Young's modulus.

3.2 Uniaxial dynamic-mechanical testing

The results of dynamic-mechanical tests for 24 hours (n=3) are illustrated in Figure 3. The curves show a typical progress for maximum sinusoidal tensile stress with a fixed displacement. The stress curves of reference films (black) and CS-coated samples (red) decrease with increasing load cycles due to relaxation effects. After 1,000 load cycles, the measured stress decreases slightly until 200,000 load cycles, for both reference and coated samples. From 200,000 load cycles onwards the curve progression remains almost constant. Further investigations of films under cyclic load conditions should provide supplemental information about relaxation effects.

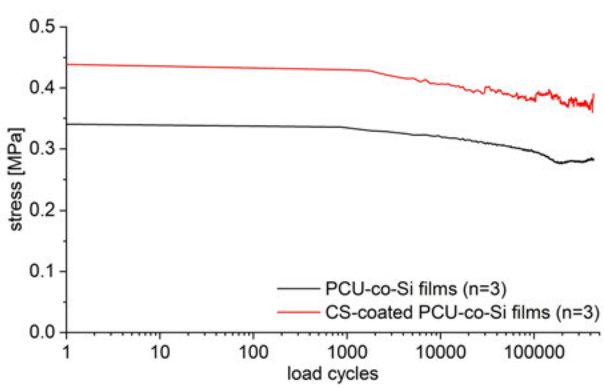

Figure 3: Dynamic-mechanical tests of reference PCU-co-Si films and CS-coated PCU-co-Si films

The curve progressions of reference and coated samples are very similar, except the stress-offset that can be observed in coated samples. Hence, the CS-coating on PCU-co-Si films results in a higher stress under dynamic stress conditions. These findings match the results of tensile tests, where a slight increase regarding Young's modulus and particularly higher tensile strength in lower strain ranges was determined with coated samples.

The morphological structure of the coating was investigated with SEM imaging. Figure 4 illustrates a coated sample before and after uniaxial cyclic stress conditions.

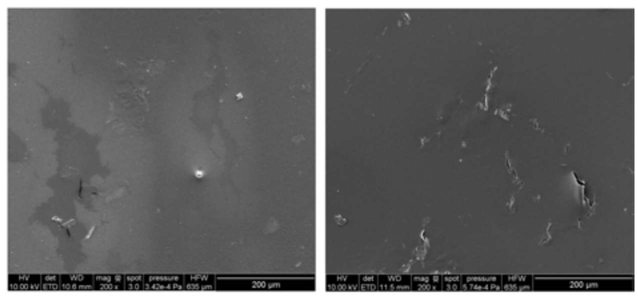

Figure 4: Morphological structure of coated PCU-co-Si films before (left) and after (right) dynamic-mechanical tests

The surface of untested samples shows some irregularities and minor cracks (Figure 4, left). Therefore, the layer integrity is not optimal before dynamic-mechanical testing. The right image in Figure 4 indicates the same surface damage following dynamic-mechanical stress that was determined even before mechanical testing. A material failure or delamination of the coating layer cannot be determined, since cracks appeared before and after dynamic-mechanical testing and are unlikely be due to the test itself. Consequently, by combining the results of dynamic-mechanical examinations and SEM-imaging, the mechanical resistance of CS-coatings on PCU-co-Si films to pulsating stress can only be partially assumed. The occurrence of stress cracks in the CS-coating itself should be prevented by adjusting the process parameters, e.g. dip-time, drying process and layer thickness or by adding plasticizers [10].

4 Conclusion

To summarize, a CS-coating was successfully applied to a PCU-co-Si film base material and a characterization regarding layer adhesion was performed. In addition to the tensile test, which characterizes mechanical properties under quasi-static conditions, a 24-hour dynamic-mechanical test was conducted to describe durability of the coating under cyclic load conditions. Furthermore, it should be taken into account that dynamic-mechanical tests were carried out in isotonic saline solution at 37 °C.

Coating of PCU-co-Si films with CS results in an increased Young's modulus and higher tensile strength in lower elongation ranges compared to uncoated reference samples. The general mechanical resistance of the generated multi-layered material was verified for 432,000 load cycles by validating the dynamic-mechanical tests with SEM-imaging. For the valuation of these findings the stress-induced crack formation that was observed before and after dynamic-mechanical testing, should be taken into account. These cracks could most likely be prevented by adding plasticizers or increasing the layer thickness of CS.

The dynamic-mechanical investigation in this study represents a first insight into fatigue testing of multi-layered polymer structures. The aim of this investigation was particularly the examination of coating adhesion. The integrity of the CS-coating itself should be optimized in following studies to prevent crack formation in the coating layer.

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