WETTABILITY OF POLY(ESTER-ETHER)S FOR TISSUE ENGINEERING

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Introduction

Wettability or wetting is a process when a liquid spreads on a solid substrate or material. Wettability can be estimated by determining the contact angle or calculating the spreading coefficient. Wetting or spreading of a liquid on a solid surface or material depends on the solid surface properties as well as the liquid used. Therefore, by manipulating the properties of surfaces one can optimize the function or performance of a solid surface or material for the purpose of interest. Likewise, if modifying the solid surface properties is not an option, one can manipulate the properties of the liquid of interest to achieve the desired wetting conditions [1].

Polyesters and their modifications are widely used for biomedical applications such as drug delivery systems and resorbable implants. The degradation kinetic of these biopolymers can be tailored by the introduction of functional groups in their backbone, leading to a modification of their morphology and hydrophilicity [2].

The shortage of tissues and organs for transplantation has led to the rapid development of tissue engineering as an alternative. Tissue engineering aims at replacing or facilitating the regrowth of damaged or diseased tissues by applying a combination of biomaterials, cells and bioactive molecules. Certain tissues in the body contain cells capable for initiating regeneration or repair after injury. The regeneration potential varies among different cell types and depends on the nature of the injury or disease. Tissues undergoing constant renewing are capable for a complete regrowth, however this ability depends on a variety of factors such as injury size and cause and the person's age. Other tissue types such as heart muscle and central nerves lack regeneration ability in the adult. For these tissue types, stem cell biology offers the potential to grow tissue by following a developmental pathway [3].

The development of new materials for a biomedical field requires different polymer systems characterized by a combination of specific physico–chemical, mechanical, processing and biological properties. The interesting group of biodegradable and biocompatible polyesters are materials containing oligo(butylene succinate) segments and sequences of a dimmerized fatty acid (saturated dilinoleic acid - DLA) [4]. When appropriately modified with poly(ethylene glycol) (PEG), they can form terpolymers of the increased hydrophilicty and the controlled degradation time.

In presented work, we report on the comparison of different methods used for determining the wettability of multiblock poly(ester-ether)s containing PEG of 1000 g/mol.

Experimental part

The materials were prepared by a polycondesation reaction [4] in the presence of vitamin E (α-tocopherol, VE) as a thermal stabilizer [5] (TABLE 1).

TABLE 1. Composition of investigated materials.

Polymer composition	Content of poly(butylene succinate) PBS (wt.%)	Content of dimmerized fatty acid DLA (wt.%)	Content of poly(ethylene glycol) PEG (wt.%)
PBS/DLA	50	50	0
PBS/DLA/PEG	50	25	25
PBS/PEG	50	0	50

The wettability of the prepared polymer surfaces was characterized by contact angle (CA) measurements. The water/air contact angles were determined by a sessile drop in a static or a dynamic mode (needle in sessile drop) using the Contact Angle Measuring System OCA_20 (Dataphysics, Germany) and using a dynamic Wilhelmy plate method (Tensiometer K12, Kruss Germany).

The samples for the optical methods were prepared by the spin casting from 1 % wt. polymer solutions in chloroform on the glass slides in dust–free laminar-flow box at a constant temperature 25°C. The static contact angle was measured by a contact angle goniometer using an optical subsystem to capture the profile of a pure liquid on a solid substrate (a sessile drop method). The angle formed between the liquid/solid interface and the liquid/vapor interface is the contact angle.

The dynamic measurements were conducted using a computer-controlled motor-driven syringe to pump water steadily into and from the sessile drop leading to an increase or decrease in drop volume, and hence the three-phase contact radius. The water drop volume was increased and decreased by 10µl with dosage rate 0.5µl/s, thus at ~0.4mm/s velocity of three-phase contact line. A sequence of pictures of the growing and diminishing drop was recorded by computer-controlled camera. Each image was analyzed by ADSA-P ("automated axisymmetric drop shape analysis-profile") using an ellipse fitting calculation for the PBS/DLA and PBS/DLA/PEG samples and using a circle fitting calculation for the PBS/PEG samples. The measurements were repeated at least with three drops on different places of each substrate, and the minimum number of substrates of each type was three. The water/air contact angle was calculated as an average from all measurements and the standard deviation was determined (based on at least 9 independent measurements).

The test by Wilhelmy plate method was carried on the polymer foils (15x20 mm). This method is suitable for calculating an average advancing and receding contact angles on solids. Both sides of the solid must have the same properties. The wetting force on the solid is measured as the solid is immersed in or withdrawn from a liquid of known surface tension. When the sample is immersed, the buoyancy force increases with the volume of the immersed sample and the resulting force provides the advancing CA (θ_A). When the sample comes up from the liquid, the resulting force provides the receding CA (θ_R).

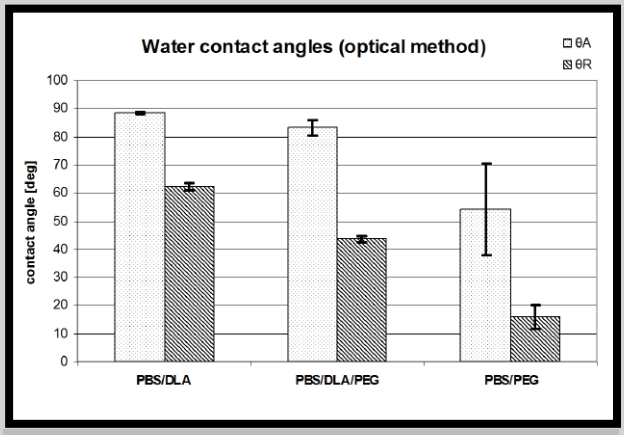


FIG. 1. Water/air contact angles measured by the optical method in dynamic conditions.

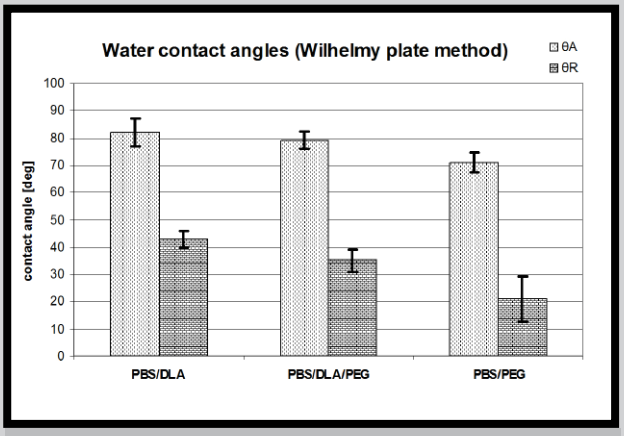


FIG. 2. Water/air contact angles measured by the dynamic Wilhelmy plate method.

Results

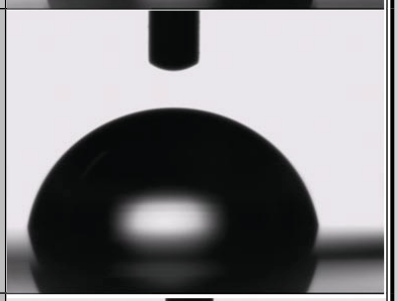
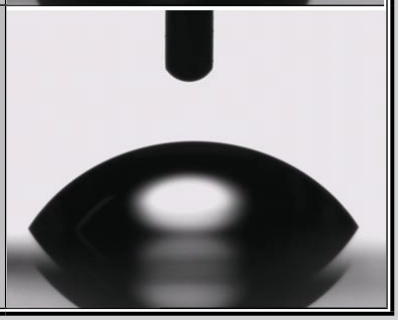
The contact angle measurement is an easy, an inexpensive and a fast method of the surface or the processes characterization. Since biomaterials are used in an aqueous environment, these methods are very suitable for the characterization of the biomaterial-water interface. The most widely used methods are: drop sessile methods (a contact angle goniometry (optical detection), a measurement of the drop diameters) and a tensiometric method - the Wilhelmy plate method.

Results of the wettability measurements obtained from dynamic CA measurements are presented in FIGURES 1 and 2. The PBS/DLA sample exhibits the most hydrophobic surface (the highest observed values of θ_A and θ_R) compared to other groups. The PBS/DLA/PEG sample with 25 % wt. of polyether shows similarity to PBS/DLA in terms of θ_A. However, θ_R is significantly lower than that of PBS/DLA what indicates the presence of the hydrophilic PEG component on this surface. In the case of the PBS/PEG surface with 50 % wt. of polyether, both advancing and receding contact angles were significantly lower compared to two previous polymers. This phenomenon indicates that this material contains a significant portion of the hydrophilic polyether component affecting the decrease in both contact angle values.

The results obtained from both dynamic methods are comparable, what makes possible to conclude, that the surfaces of model spin-cast films can be used in studies where pressed polymer foils cannot be applied (e.g. protein adsorption studies).

The static optical method demonstrated a similar trend in the decreasing of the overall surface wettability (the value θ) with the increasing content of the hydrophilic polyether component as observed by dynamic methods, too. The results together with the images of observed drops are presented in the TABLE 2. However, it is worth to point out, that in the case of the PBS/DLA/PEG surface, the obtained overall value of θ does not reflect the presence of the hydrophilic PEG domains on the surface, as it can be concluded from a decrease in θ_R determined by dynamic CA measurements.

TABLE 2. Static contact angles and representative drops.

Polymer	θ	Drop shape
PBS/DLA	90 ± 1	
PBS/DLA/ PEG	81 ± 1	
PBS/PEG	57 ± 1	

Additionally, the changes of the contact angle with time for the PBS/PEG surfaces with the highest content of the hydrophilic polyether are shown in FIGURES 3 and 4. The decrease in the observed θ with the prolonged droplet-sample contact time shows the strong interaction of water with the hydrophilic domains present on the surface.

Acknowledgements

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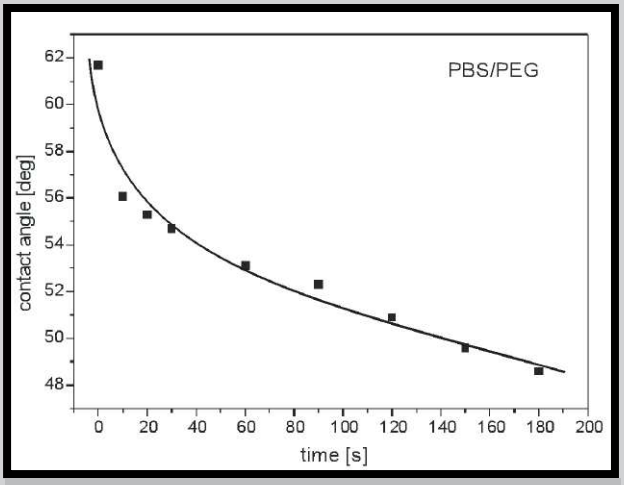

FIG. 3. The changes of the contact angle vs. time for the PBS/PEG surface.

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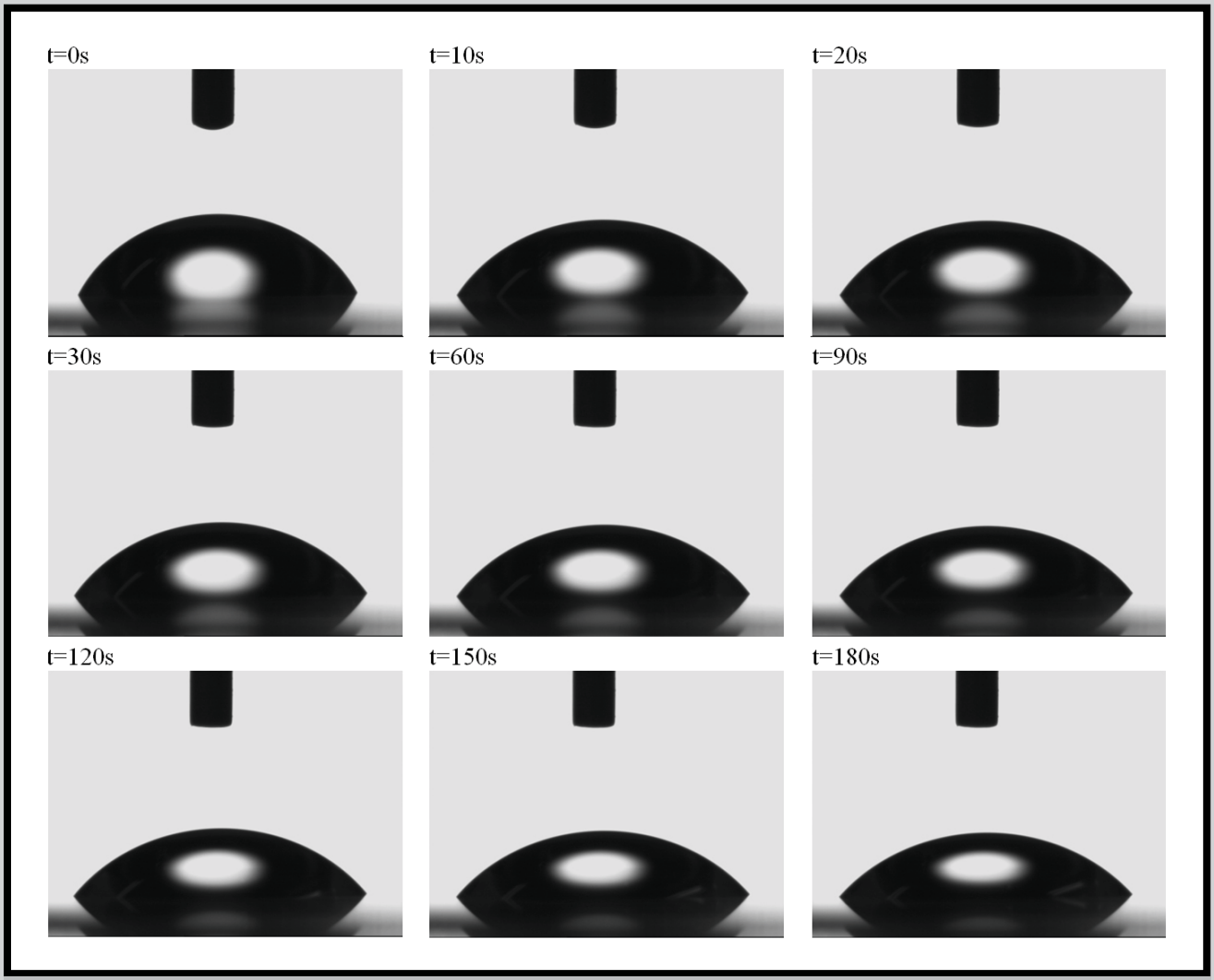

FIG. 4. The change of the drop shape vs. time on the PBS/PEG surface.