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# Wetting properties of phospholipid-polypeptide monolayers deposited onto polyethylene terephthalate

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The paper presents changes in wettability of the unmodified and modified polyethylene terephthalate (PET) surfaces. A low temperature air plasma was used to activate the polymer surface and to change its hydrophilic–hydrophobic properties. Then, using the Langmuir–Blodgett technique, the Langmuir monolayers of 1,2–dipalmitoyl–sn–glycero–3–phosphocholine (DPPC) and cyclosporine A (CsA) with different molar fractions, i.e. $\chi$=0.25, 0.50, 0.75, were deposited onto the activated PET surface. Besides, a series of DPPC and CsA monolayers was also transferred onto the chitosan layer, previously produced on the plasma treated PET by the dip–coating method. The wetting properties of such modified PET surfaces were then investigated by the contact angle measurements using three test liquids with well–known surface tension components. The obtained results show that wettability depends on the composition of the deposited DPPC/CsA layer with or without chitosan. Presence of chitosan makes the DPPC/CsA film surface more polar due to specific organization of molecules that expose their polar heads outside.

## 1. INTRODUCTION

Polyethylene terephthalate (PET) belongs to linear polymers with the ester groups (Fig. 1).

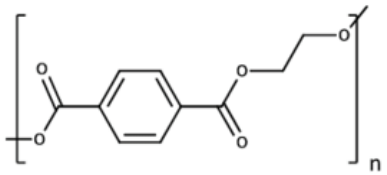

Fig. 1 PET structure.

PET is a plastic with a high proportion of the crystalline phase. The crystal structure and strong intermolecular interactions determine its physical and mechanical properties. PET has thermoplastic properties. It is also chemically resistant, not affected by acids (except oxidizing acids) and diluted alkali even at elevated temperatures. In addition, it is physiologically inert and easy to recycle [1]. Owing to these properties PET is widely used in food and pharmaceutical industry to produce packaging for food, medicines and waste as well as containers to protect sterilized devices and various medical items. Importantly PET is used in medicine for the production of prostheses of blood vessels and other artificial organs, such as temporary tendons. In the case of artificial heart PET is applied also to cover the chamber surface [2]. However, a disadvantage of the PET using is a hydrophobic character and chemical inertness of its surface. This results in poor compatibility with human tissues which in turn becomes the main reason for implant rejection [3, 4]. Moreover, in the biological environment PET exhibits poor stability. In contact with pumped blood PET can be degraded causing unfavourable biological reactions [3]. In order to avoid this negative effects which finally can lead to implant rejection, it is necessary to modify the material surface to increase its biocompatibility to human tissues.

Stents placed in a living body should have adequate porosity or rigidity as well as a negative electrokinetic charge to prevent platelet adhesion [5, 6]. On the one hand, chitosan (Ch) seems to be a suitable candidate for the PET surface modification. This compound can introduce the desired porosity, and additionally it is biodegradable, biocompatible, non–toxic, and bacterio– and fungistatic. Ch can

increase the implant's contact with the surrounding tissues, and can also significantly improve the stability of PET after entering the body [7]. On the other hand, a positively charged surface of chitosan in the pH of human blood, due to the presence of $-NH_3^+$ groups, can cause adhesion of blood components. This can result in forming a blood clot. For this reason, further modifications of the Ch surface are necessary [3, 8–11].

Moreover, it is reported that Ch can be used to close drugs while creating a controlled drug release system [12]. Through the Ch–drug interactions, the properties of the Ch surface can be changed to be more compatible with the surrounding tissues. At the same time drug obtains the right carrier to facilitate its location reaching the destinations. One of the drugs that is widely used in implantology is cyclosporine A (CsA) [13].

CsA is an aromatic, cyclic polypeptide which naturally is produced by Tolypocladium inflantunm [14]. It is a strong immunosuppressant used to treat dry eye disease and to prevent transplant rejection [14, 15]. However, long–term oral intake of CsA does not guarantee its complete absorption and causes nephrotoxicity and hepatotoxicity which makes damages in patients organisms. Then, it would be possible to avoid the problem of poor absorption of the drug in the digestive system or failure to locate it in the desired place [16].

In this study we have made efforts to design such complex systems which contained PET with deposited layers of the biologically active substances to increase their assimilation in the body. To ensure a stable binding of the PET surface with the biological molecules, the low–temperature plasma was used. The effectiveness of the modification depends on the plasma power, plasma time and its type. It is important that the above modification does not lead to changes in the properties of the bulk phase of the material. The activation only changes the physicochemical properties of the polymer outer layer leading to the surface hydrophobicity decrease. It is associated with the introduction of new functional groups on the polymer surface, among others –OH, –C–O, –C=O [3]. These groups can promote the binding of the biological substances used as a cover for the polymer surface. The proper selection of the biological compound being the link between the artificial material and living tissue may contribute to the increase of biocompatibility of the polymer surface. It seems that a phospholipid DPPC, the major

component of natural membranes, is promising substance, especially that it can facilitate the introduction of a drug with immunosuppressive properties to prevent the implant rejection. It is also suitable for creating a model biological membrane and studying the interactions between the membrane and the active substances.

Thus, the drug can be applied on the implant surface and released in a controlled way at the implantation site. That is why it is so important to design a biocompatible system that will allow to provide the drug in the right dose, in the right place, without undesirable side effects. Therefore the modified surfaces containing Ch/DPPC–CsA can exhibit a large application potential.

In this aspect wettability of materials used to create the implants is of major importance because it strongly determines the interactions with the biological environment (surrounding tissues). After the implant introduction into the human body, there is a competition in adsorption of water molecules, ions, proteins, bacteria and tissues, thus substances of different character, onto the material surface. It is necessary to design the surface of defined wettability to limit the adsorption of undesired molecules and to increase the implant biocompatibility.

In our studies, the wetting properties of biomaterial surfaces were investigated by contact angle measurements of different liquids. Hence, the changes in character of the PET surface due to modification with plasma and layer deposition, were determined.

## 2. EXPERIMENTAL

### *2.1. PET surface cleaning*

A commercially available polyethylene terephthalate slab (Bayer Ayer Axpet) was cut into smaller (20 × 30 × 4 $mm^3$) plates. In order to clean the surface of the polymeric plates, a blue protective foil was removed from them. Then the plates were placed in a glass beaker filled with methanol (99.8%, Avantor Performance Materials Poland S.A.) and sonicated (ultrasonic bath, UM4, Unima, Olsztyn) for 15 minutes. After that time, they were rinsed five times with fresh portions of the deionized water (Milli–Q, a specific resistivity of 18.2 MΩcm). After pouring with water, the plates were placed again in an ultrasonic bath for 15 minutes. The rinsing procedure described

above was repeated twice. The plates were then put on a Petri dish and dried in a vacuum oven for 24 hours at room temperature. The PET plates were stored in the desiccator before further testing.

### *2.2. Plasma modification*

The washed and dried PET plates were subjected to the air plasma treatment. For this purpose, the plates were placed vertically in the plasmatic chamber (Plasma type system, Diener Electronic, Germany). In this device, the polymer surface was activated with the low temperature and low pressure (0.35 mbar) air plasma for 1 minute. The air plasma power was 160W, and the process ran with a continuous air flow of 22 sccm. After the time of the plasma action, when the pressure in the plasma chamber was equal to the atmospheric pressure, the PET plates were removed from the device and directly used for further modifications.

### *2.3. Solutions preparation*

In order to prepare the solutions of substances used for the film formation on the activated PET, the appropriate amounts of 1,2–dipalmitoyl–sn–glycero–3–phosphocholine (DPPC, 99%, SIGMA) and cyclosporine A (CsA, 98.5%, Alfa Aesar) were weighed on the analytical balance (Sartorius, BP 211D). They were dissolved in a chloroform: methanol 4:1 (v:v) mixture (methanol 99.8%, chloroform 98.5%, both purchased from Avantor Performance Materials Poland S.A.) to obtain concentration of 1 mg/cm$^3$. From the pure DPPC and CsA solutions, the mixtures of different CsA molar fractions ($\chi$ = 0.25, 0.5 and 0.75) were prepared. In addition, chitosan (Ch, MW 100,000–300,000, deacetylation degree 82%, Acrōs Organics) due to lack of solubility in solvents such as chloroform and methanol, was dissolved in 0.1% acetic acid to the final concentration of 0.1 mg/ml. The diluted acetic acid was obtained from the concentrated one (99.5%–99.9%, Avantor Performance Materials Poland S.A.).

### *2.4. Chitosan film formation by dip–coating*

The chitosan films were formed during immersion of the plasma–modified polymeric plates into acidic chitosan solution (Fig. 2). The PET plates were placed vertically in the plastic screw–top cups with solution for 5 minutes. After that time, the plates were

rinsed three times with water and placed on the Petri dishes for drying or used as a support for the Langmuir monolayers of DPPC and/or CsA.

Fig. 2. The plasma activated PET plate immersed in the chitosan solution.

### *2.5. Langmuir–Blodgett monolayer formation*

The Langmuir monolayers of the DPPC, CsA or their mixtures were deposited onto the activated PET or PET/Ch surface using an automatically controlled Langmuir–Blodgett trough (KSV 2000, KSV, Finland) coupled with a thermostat (THERMOSTAT U1). Washing of the trough was done with methanol. This operation consisted of thoroughly wiping the trough and barriers with a dust–free handkerchief soaked in methanol. The trough was then rinsed with Milli–Q water which was sucked out using a vacuum pump (Suction Pump SP20, Air Liquide Medical System). After rinsing, the trough was re–filled with water and the surface tension was measured by means of the Wilhelmy plate method. Before each measurement the Wilhelmy plate was heated up to redness in the flame of the burner to remove possible impurities. The plate was then hung on the hook. The subphase surface was considered to be clean when the surface tension did not change more than 0.3 mN/m during compression by the barriers. Then the polymer support was fastened to the handle of the submerging mechanism and it was submerged to the subphase. After that, the chloroform–methanol solutions of DPPC, CsA or their mixtures were placed onto the subphase with a microsyringe (Hamilton–Bonaduz, Schweiz) by squeezing small droplets of the

solution. The volumes (30–80 $mm^3$) depended on the type of solution. Then the entire system was left for 10 minutes. That period of time allowed for evaporating the solvents. The next step was the monolayer compression. For this purpose, the barriers on the Langmuir–Blodgett trough were automatically moved toward its centre. The symmetrical compression was at a constant speed of 20 mm/min and lasted until the surface pressure set in the control program was reached. In the case of DPPC the pressure was 30 mN/m, in the case of cyclosporine A and DPPC/CsA mixtures, the pressure was 15 mN/m. At the same time, the π–A isotherm was registered on the computer screen. After reaching the given surface pressure, the barriers began to oscillate in order to maintain its constant value. When the surface pressure value stabilized (about 20 minutes), i.e. the pressure changes were negligibly small, the process of the Langmuir monolayer transfer onto the PET or PET/Ch surface was started. This stage was carried out by withdrawing the plate, previously immersed in the subphase, through the compressed monolayer. At that time, the coverage degree of the support surface by monomolecular film was monitored on the computer screen, and was numerically displayed as a transfer ratio. After the monolayer deposition the procedure was completed. Each plate was pulled from the holder, left on a Petri dish and placed in a vacuum oven for 24 hours to dry.

### *2.6. Contact angle measurements*

The plates with suitably prepared layers were transferred directly from the vacuum dryer to the chamber of the apparatus for measuring the contact angles (DGD ADR, GBX S.A.R.L). The chamber was equipped with a camera and an automatically tilting table controlled by Windrop++ software. With this device, the contact angles of three test liquids with well–known surface tension values, two polar (Milli–Q water and formamide, 99.5%, Aldrich) and one apolar (diiodomethane, 99%, Aldrich) were measured. The measurements were carried out on the PET plates after modification with plasma as well as with chitosan film and/or DPPC–CsA monolayers. The measurement consisted of placing the droplets of test liquid with a volume of 6μl using a micro–syringe, then so–called the advancing angle $\Theta_A$ was measured. Subsequently, 2$mm^3$ of liquid was drawn from each drop placed and the receding contact angle $\Theta_R$

was determined. The same procedure was repeated for the formamide and diiodomethane droplets. 4 to 6 drops were placed on each plate depending on the type of measuring liquid and from 8 to 12 contact angles on the right and left side of each drop were measured. The data presented in our paper are expressed as an arithmetic mean of the measured contact angles with standard deviation (SD) in the range of 0.2º – 3.9º (for $\theta^{W}$), 0.1 – 3.6º (for $\theta^{F}$) and 0.1 – 2.7º (for $\theta^{D}$). This indicates that the contact angles are reproducible.

## 3. RESULTS AND DISCUSSION

The aim of this paper was to investigate the properties of the biological substance films deposited onto the PET surfaces activated by plasma. The low temperature plasma of air was used to make the polymer surface hydrophilic. That facilitated adsorption of the Ch film and/or the DPPC–CsA monolayers. To determine the wetting properties the contact angles of water, formamide and diiodo-methane were measured.

### *3.1. Advancing and receding contact angle of water*

The unmodified PET surface has weakly hydrophobic character which is reflected in the values of water contact angle in the rage of $90^{o} > \theta > (56–65^{o})$ [17], i.e. $\theta_A^W = 75.6°$ and $\theta_R^W = 66.6°$ (Fig. 3). In this case one can say that the interactions between molecules of water are stronger than between water molecules and those of the PET surface. Plasma treatment caused significant changes in the polymer wettability. The values of advancing contact angles decreased from 75.6° ($PET_{unmod.}$) to 14.7° ($PET_p$) and those of receding contact angles from 66.6° to 9.0° proving that the type and/or strength of interactions were different in the case of unmodified and modified PET. It is worth mentioning that as a result of plasma action the new functional groups (such as –OH, C–O, O=CO–O, C=O, N–CO–N [3]) were formed onto the PET surface and they changed the surface character to be more polar. Presence of the Langmuir–Blodgett monolayers caused the lower values of water contact angles, both advancing and receding, compared to those measured on the unmodified PET ($\theta_A^W/\theta_R^W$=75.6°/66.6°) (Fig. 3). The

difference is within 15.7°–33.1° for $\theta_A^W$ and 22.1°–37.9° for $\theta_R^W$ taking into account all DPPC–CsA layers. But the contact angles on the Langmuir–Blodgett films are higher than those obtained on the plasma activated PET ($\theta_A^W/\theta_R^W$=14.7°/9.0°). In this case the difference is in range of 27.8°– 45.1° and 19.7°–35.5° for advancing and receding contact angles, respectively (Fig. 3).

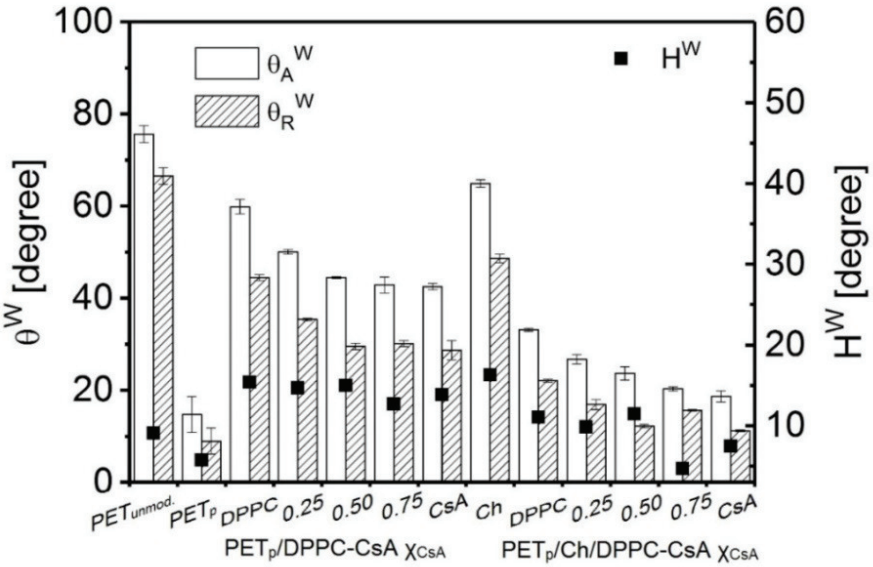


Fig. 3. Advancing $\boldsymbol{\theta_A^W}$ and receding $\boldsymbol{\theta_R^W}$ contact angle of water and its hysteresis $H^W$. Error bars denote the standard deviations of the mean contact angle values.

In the next step the wettability of the activated polymer after application of the Ch layer and monolayers containing DPPC–CsA was tested. The presence of Ch film caused the increase in the values of advancing and receding contact angle when compared to $PET_p$. Ch has the –OH and $–NH_2/NH_3^+$ functional groups as well as hydrocarbon backbone in its structure. The latter moiety mainly determines the character of the biopolymer surface.

Deposition of the DPPC–CsA monolayers increased the Ch surface hydrophilicity which was manifested through smaller contact angles of water. For instance, on $PET_p$/Ch/DPPC the contact angles $\theta_A^W/\theta_R^W$ equalled 33.2°/22.1°, and additionally they were lower than those measured on $PET_p$/DPPC without chitosan, i.e. $\theta_A^W/\theta_R^W$ = 59.9°/44.5°, respectively (Fig. 3).

The reason for that can be found in the specific organization of DPPC molecules on or within the Ch layer exposing the polar groups outside [3]. They were accessible for the water molecules during the contact angle measurements. Hence, the higher hydrophilicity of the $PET_p$/Ch/DPPC surface was observed than that of $PET_p$/Ch. The same conclusion can be applied to the mixed $PET_p$/Ch/DPPC–CsA systems. There was also visible relation between the wettability (values of contact angles) and amount of CsA in the monolayers. The higher molar fraction of CsA in the monolayers the lower values of water contact angles were measured.

To clearly demonstrate above dependence, the data were placed in Fig. 4 along with the fitted curve and the estimated regression equation.

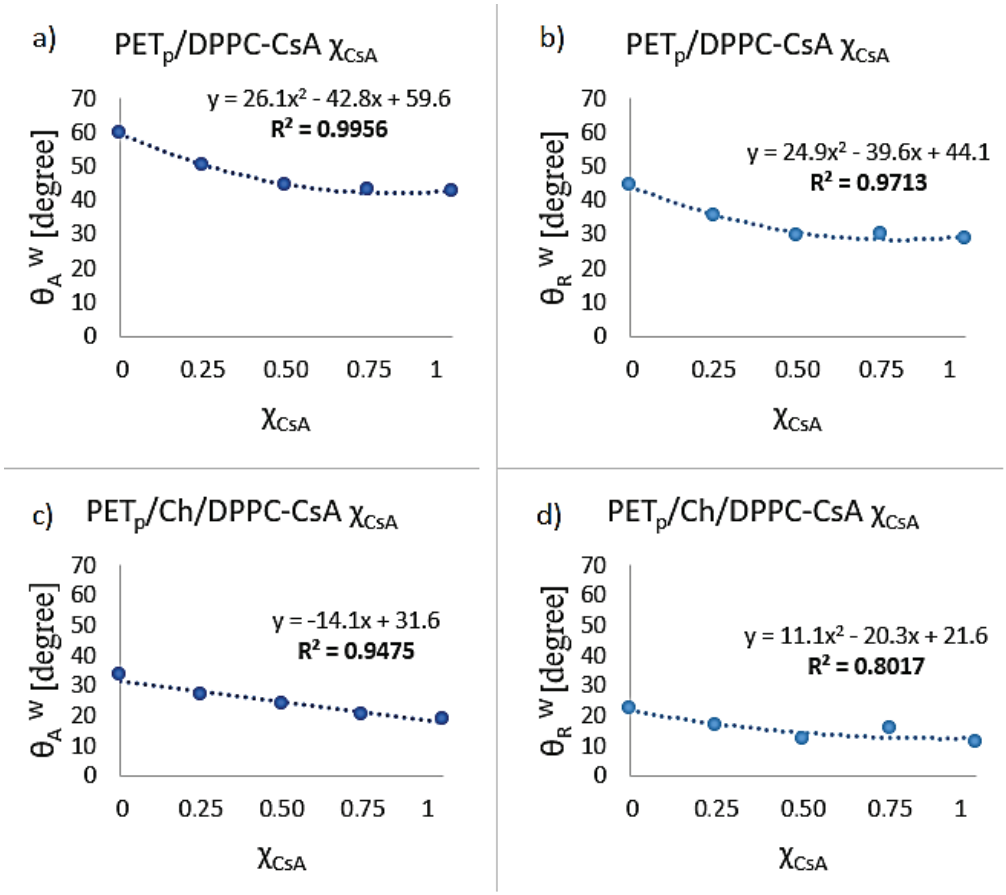


Fig. 4 a–d. Dependence of the advancing $\theta_A^W$ and receding $\theta_R^W$ contact angles of water on the DPPC–CsA monolayers composition ($\chi_{CsA}$) with or without the chitosan (Ch) film. The function equation fitted to the experimental data along with the correlation coefficient ($R^2$) is also presented.

As can be seen, in most cases the best fitting to the experimental data Is the quadratic function (second-order polynomial) with a correlation coefficient greater than 0.8, up to 0.9956 (Fig. 4a,b,d). Only for the case presented in Fig. 4c, a strong linear relationship between $\theta_A^W$ vs. composition ($PET_p$/Ch/DPPC–CsA), reflected by $R^2$ = 0.9475, was found.

As reported in our previous paper CsA made the DPPC monolayer less condensed [18]. Therefore, water can penetrate the monolayer deeply interacting with the polar groups of molecules that are inaccessible for liquids when the monolayer is more condensed.

### *3.2. Advancing and receding contact angle of formamide*

When formamide was used as a test liquid to measure the contact angles on the PET surfaces, the similar dependences to those determined for water were observed (Fig. 5). On the unmodified PET surface $\theta_A^F$ = 61.0° and $\theta_R^F$ = 50.4° were obtained. These values of formamide contact angle suggest that the unmodified PET has weakly polar character because the liquid forms droplets on the polymer surface.

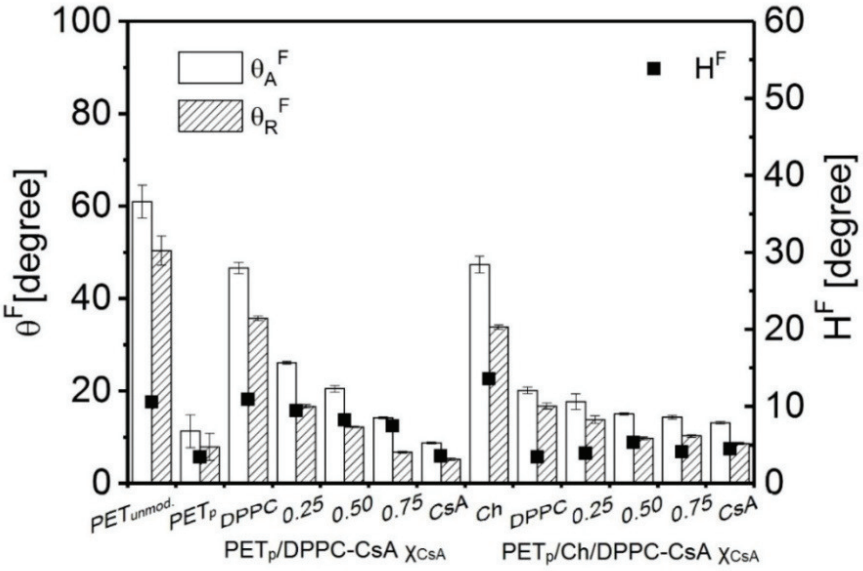


Fig. 5. Advancing $\boldsymbol{\theta_A^F}$ and receding $\boldsymbol{\theta_R^F}$ contact angle of formamide and its hysteresis $H^F$. Error bars denote the standard deviations of the mean contact angle values.

After plasma activation the advancing and receding contact angle on $PET_p$ was $\theta_A^F$=11.3° and $\theta_R^F$=7.9°, respectively. That modification caused the biggest changes in wetting properties because during plasma treatment new polar functional groups were added to the surface capable of interacting with formamide. Deposition of one or two–component monolayers on the activated PET also caused changes in its wettability.

The presence of Langmuir–Blodgett monolayers gave the better wettability in comparison to the unmodified PET surface (Fig. 5). It can be related to involvement of the polar groups being on PET and within the monolayer in the interactions with formamide. With the CsA molar fraction increase, the lower values of contact angles were measured, i.e. the better wettability was obtained. To be evidently seen the obtained dependences between contact angles of formamide and the DPPC–CsA monolayer composition are additionally shown in Fig. 6, separately for $\theta_A^F$ and $\theta_R^F$, with or without Ch.

Presence of the Ch layer with the deposited Langmuir–Blodgett monolayers on the activated PET caused the increased wettability. Only on $PET_p$/Ch/CsA and $PET_p$/Ch/DPPC–CsA with $\chi_{CsA}$ = 0.75 the higher values of formamide contact angles were measured. The advancing contact angle obtained on $PET_p$/Ch/CsA was $\theta_A^F$ = 13.1° while the receding one was $\theta_R^F$ = 8.6° and on $PET_p$/Ch/DPPC–CsA with $\chi_{CsA}$ = 0.75, $\theta_A^F$ = 14.4° and $\theta_R^F$ = 10.3°. The values of contact angles on $PET_p$/Ch/DPPC–CsA $\chi_{CsA}$ = 0.25, 0.50, 0.75 were lower by 5–9° ($\theta_A^F$) and 3° ($\theta_R^F$) than those for the systems without chitosan, i.e. $PET_p$/DPPC–CsA (Figs 5 and 6). In the case of $PET_p$/Ch/DPPC the difference was 26.4° ($\theta_A^F$) and 19.0° ($\theta_R^F$). This can be a result of specific molecular organization of DPPC–CsA, as well as strength of interactions of these molecules with Ch. Additionally, the relation between values of contact angles and molar fractions of CsA was also observed. Similarly to the surfaces without Ch film, when the deposited monolayers contained more CsA, the better wettability was gained (Figs 5 and 6).

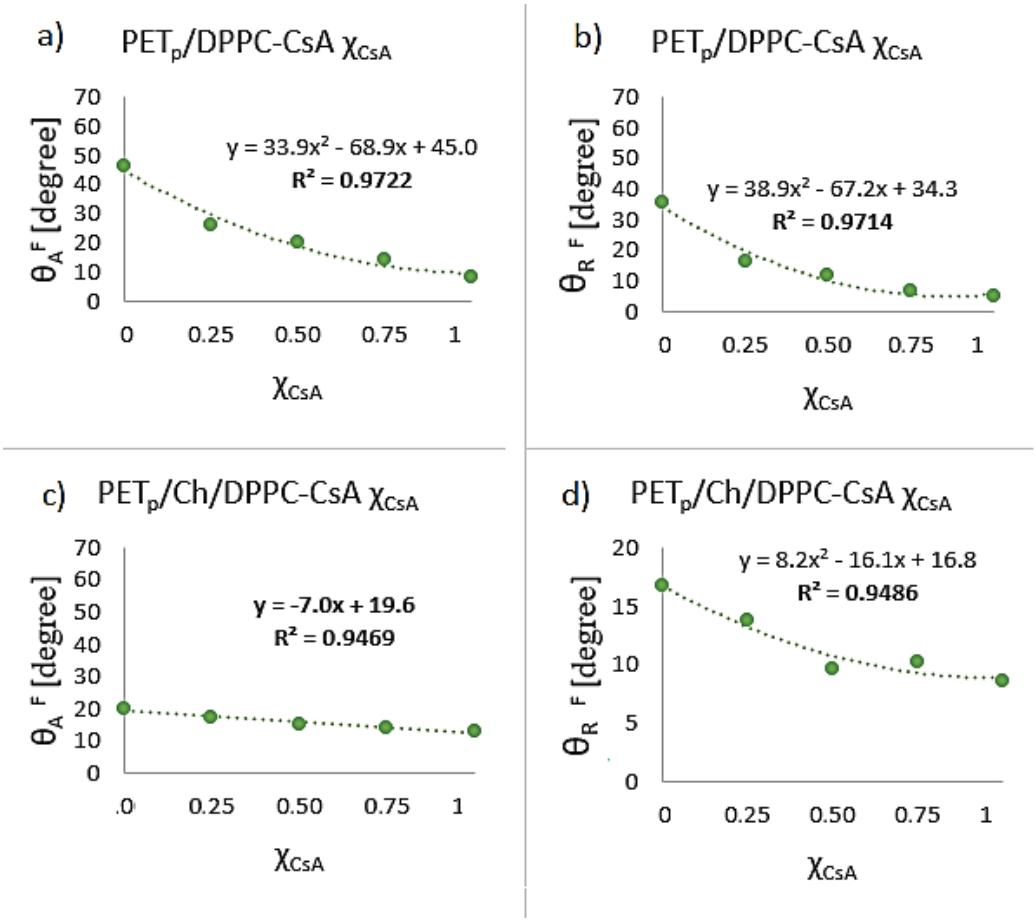


Fig. 6 a–d. Dependence of the advancing $\theta_A^F$ and receding $\theta_R^F$ contact angles of formamide on the DPPC–CsA monolayers composition ($\chi_{CsA}$) with or without the chitosan (Ch) film. The function equation fitted to the experimental data along with the correlation coefficient ($R^2$) is also presented.

These results coincide with the changes of water contact angle versus the CsA molar fractions. In a like manner, the best linear fit appeared for $\theta_A^F$ versus $PET_p$/Ch/DPPC–CsA composition ($R^2 = 0.9469$, Fig. 6c). The other relationships can be described by the second–order polynomial regression function with a *high* level of *fit* ($R^2$ higher than 0.9, Fig. 6 a,b,d). Besides, compared to the values of water contact angles, those of formamide are lower by about 10°–30° depending on the type of surface modification. This indicates better wettability of the studied surfaces by formamide than by water.

### *3.3. Advancing and receding contact angle of diiodomethane*

In contrast to previously discussed results the diiodomethane contact angles obtained for the unmodified PET surface were the lowest ones. The advancing contact angle was $\theta_A^D = 26.4°$ and the receding contact angle was $\theta_R^D = 20.0°$ (Fig. 7). These results provided information that the interactions between diiodomethane and PET were stronger than between the polar liquids and PET. This confirmed an apolar character of PET because diiodomethane can interact with different molecules only by dispersion forces.

Action of the low temperature air plasma on PET weakened the interactions of the polymer surface with diiodomethane which was seen in the increased values of contact angles, i.e. $\theta_A^D = 33.7°$ and $\theta_R^D = 28.3°$ (Fig. 7).

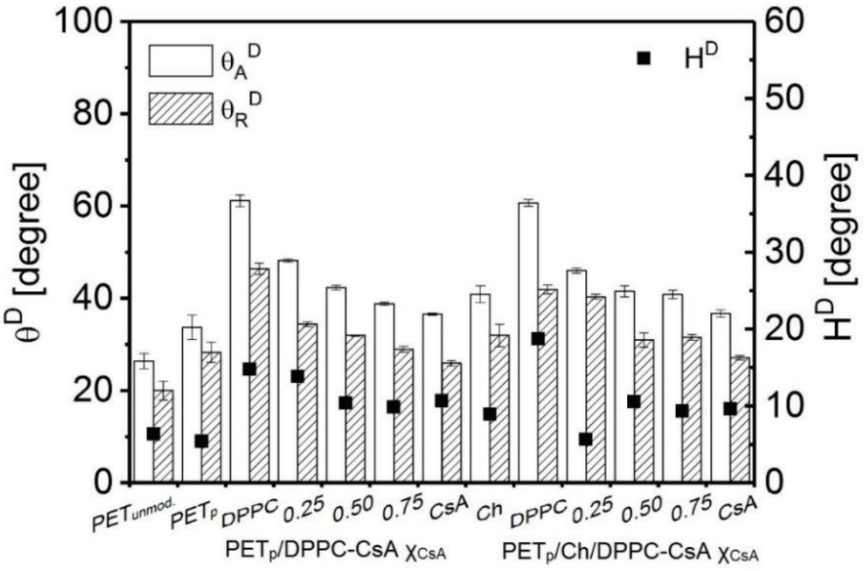


Fig. 7. Advancing $\boldsymbol{\theta_A^D}$ and receding $\boldsymbol{\theta_R^D}$ contact angle of diiodomethane and its hysteresis $H^D$. Error bars denote the standard deviations of the mean contact angle values.

These results also proved that plasma treatment introduced the polar groups (–OH, –C–O, O=C–O, C=O and N–CO–N [3]) onto the PET surface. They interacted weakly with diiodomethane of dispersive nature. Both, presence of the Langmuir–Blodgett monolayers and chitosan on $PET_p$ induced less wettability by diiodomethane, and caused the increase in the contact angles values as compared to those

on both unmodified and plasma modified PET. But in the case of Ch–containing layers it was slightly lower. For instance, on $PET_p$/DPPC $\theta_A^D = 61.2°$ and $\theta_R^D = 46.4°$ while on $PET_p$/Ch/DPPC $\theta_A^D = 60.7°$ and $\theta_R^D = 42.0°$.

When the CsA amount in the monolayer increased, the lower values of contact angles, thus better wettability, were achieved. This is presented in detail in Fig. 8.

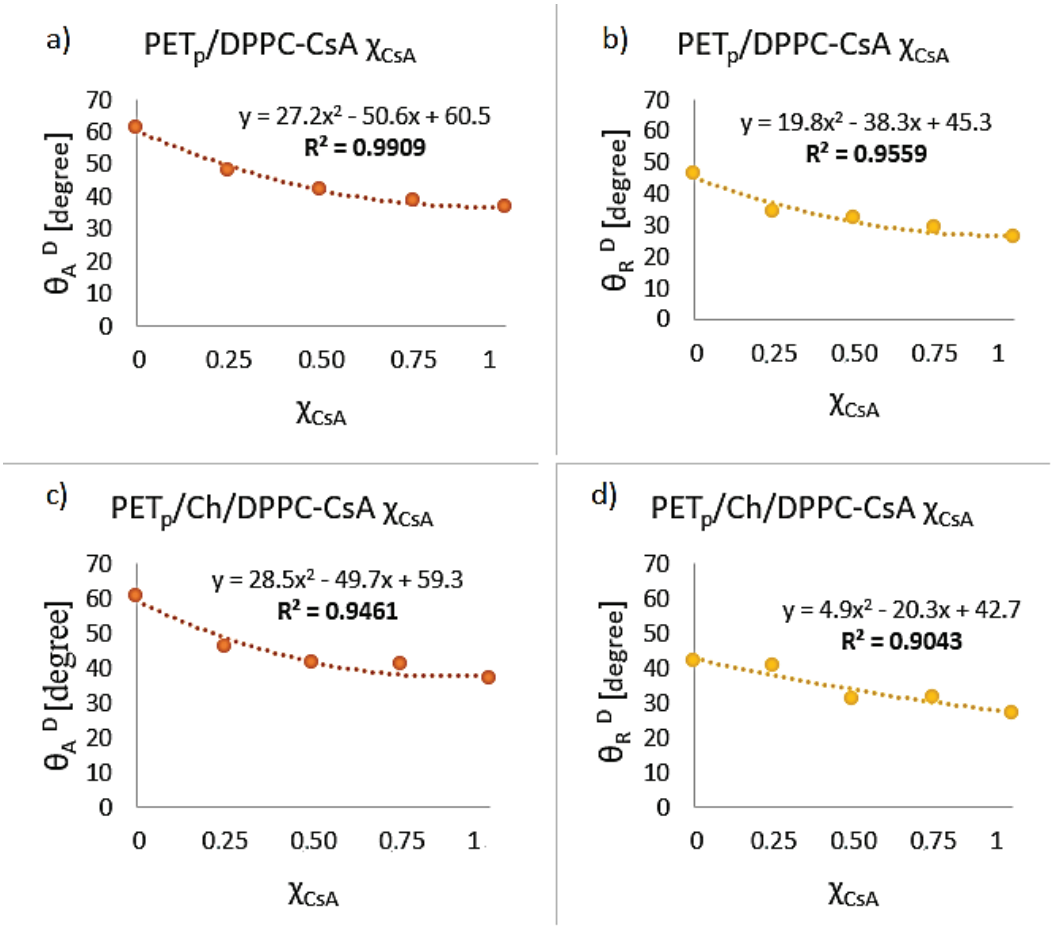


Fig. 8 a–d. Dependence of the advancing $\theta_A^D$ and receding $\theta_R^D$ contact angles of diiodomethane on the DPPC–CsA monolayers composition ($\chi_{CsA}$) with or without the chitosan (Ch) film. The function equation fitted to the experimental data along with the correlation coefficient ($R^2$) is also presented.

The trend of these data changes, can be very well featured by a quadratic function with the correlation coefficient $R^2$ higher than 0.9. The above observations proved that the dispersive interactions between molecules of diiodomethane and $PET_p$ with layers were

getting stronger as more CsA was present, i.e. they were stronger than between molecules of that test liquid.

### *3.4. Contact angle hysteresis*

To better characterize the surface wettability, the contact angle hysteresis (H) was calculated. H means the difference between advancing and receding contact angle of water (W), formamide (F) and diiodomethane (D). Figures 3, 5, 7 and Table 1 show the obtained results.

For unmodified PET, the H of polar liquids (water, formamide) was about 3–4° larger than that obtained for diiodomethane. After plasma treatment the H values of all test liquids decreased due to the higher surface free energy of the activated PET and better liquid spreading (lower contact angles and lower H were obtained).

Deposition of the DPPC–CsA monolayers onto the $PET_p$ caused the increase of $H^W$ by 6.9°–9.6° for the films without Ch and by 1.7°–5.7° for the films with Ch in respect to the $PET_p$ support. Only, for $PET_p$/Ch/DPPC–CsA $\chi = 0.75$ lower $H^W$ than that for $PET_p$ was obtained. In the case of formamide, for the systems without Ch layer the $H^F$ increase was by 0.1°–6.0° while for the Ch–containing systems by 0.5°–1.9°. Only for $PET_p$/DPPC the $H^F$ was not changed. The increase of H compared to that of $PET_p$ was also observed for diiodomethane contact angle, i.e. by 4.4°–9.4° and 0.3°–13.3°, for the films without or with Ch, respectively.

Differences in the H values for every test liquid (Table 1) can be associated with different type and strength of interactions. Water can interact in the same way by electron–donor and electron–acceptor interactions ($\gamma^- = \gamma^+ = 25.5$ mJ/m$^2$) while formamide shows stronger electron–donor ($\gamma^- = 39.6$ mJ/m$^2$) than electron–acceptor ($\gamma^+ = 2.28$ mJ/m$^2$) interactions. In turn, it is assumed that diiodo-methane interacts by Lifshitz–van der Waals (mainly dispersive) forces ($\gamma^{LW} = 50.8$ mJ/m$^2$) [19].

The reason of the increased hysteresis can be penetration of the liquids into the monolayer and/or reorientation of the DPPC–CsA molecules during the prolonged their contact with liquids when receding contact angles were measured. Generally, the H values of polar liquids determined for $PET_p$/Ch/DPPC–CsA systems were lower than those for layers $PET_p$/DPPC–CsA without Ch. It is likely that as a result of the interactions between Ch, DPPC and CsA the hybrid films were less permeated for the liquid molecules.

Table 1. Contact angle hysteresis (H) for all studied surfaces.

| Modification | Contact angle hysteresis [°] | | |
|---|---|---|---|
| | Water, $H^W$ | Formamide, $H^F$ | Diiodomethane, $H^D$ |
| PET unmod. | 9.1 | 10.6 | 6.4 |
| $PET_p$ | 5.8 | 3.4 | 5.4 |
| without chitosan | | | |
| $PET_p$/DPPC | 15.4 | 10.9 | 14.8 |
| $PET_p$/DPPC–CsA $\chi_{CsA}$=0.25 | 14.7 | 9.4 | 13.8 |
| $PET_p$/DPPC–CsA $\chi_{CsA}$=0.50 | 15.0 | 8.3 | 10.4 |
| $PET_p$/DPPC–CsA $\chi_{CsA}$=0.75 | 12.7 | 7.4 | 9.8 |
| $PET_p$/ CsA | 13.8 | 3.5 | 10.7 |
| with chitosan | | | |
| $PET_p$/ Ch | 16.3 | 13.6 | 8.9 |
| $PET_p$/Ch/DPPC | 11.1 | 3.4 | 18.8 |
| $PET_p$/Ch/DPPC–CsA $\chi_{CsA}$=0.25 | 9.9 | 3.9 | 5.7 |
| $PET_p$/Ch/DPPC–CsA $\chi_{CsA}$=0.50 | 11.4 | 5.3 | 10.6 |
| $PET_p$/Ch/DPPC–CsA $\chi_{CsA}$=0.75 | 4.7 | 4.1 | 9.3 |
| $PET_p$/Ch/CsA | 7.5 | 4.5 | 9.6 |

This conclusion seems to be reasonable in the light of the fact that the H of polar liquids for the $PET_p$/Ch surface without the deposited DPPC–CsA monolayers was the largest ($H^W$=16.3° and $H^F$=13.6°). The absence of DPPC–CsA monolayers facilitated penetration of liquids into the Ch film when their contact time increased during the receding contact angle measurements. It is worth highlighting that when the DPPC–CsA layers were considered the largest value of the $H^W$ was obtained for DPPC–CsA at $\chi_{CsA}$=0.50. At this composition, the strongest repulsive interactions between components were determined at the air–water interface [18]. Such partial miscibility can favour appearance of the increased hysteresis.

## 4. CONCLUSIONS

The interesting changes in contact angles and their hystereses of three test liquids: water, formamide and diiodomethane, depending on the biological film presence and/or components proportions in the monolayers are obtained. Generally, when the bigger molar fraction of cyclosporine A is in the monolayers, the wettability of surfaces is better in the case of polar water and formamide. Wetting by diiodomethane is also better but less noticeable than in case of water or formamide. The results confirm additionally the apolar character of the unmodified PET surface, and every type of applied modification changes this character to be more polar. The activated by the low temperature air plasma PET with deposited by *dip–coating* chitosan film ($PET_p$/Ch) is the most hydrophobic among the biological films. But, even the small addition of cyclosporine A to the DPPC monolayer causes significant change in the wettability of the newly obtained surfaces. Moreover, in the presence of chitosan specific organization of the DPPC–CsA molecules in the monolayers takes place. Deposition of the bacteriostatic Ch layer on the activated PET surface, phospholipid (DPPC) and/or immunosuppressive drug (CsA) deepens the application aspect of this type of research in the implantology.

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