EFFECT OF CHITOSAN AND LIPID LAYERS DEPOSITED ONTO POLYETHYLENE TEREPHTHALATE (PET) ON ITS WETTING PROPERTIES

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Abstract

The wetting properties of chitosan (Ch) and single 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC), cholesterol (Chol) and binary DPPC-Chol $\chi_{Chol}=0.25$ layers deposited onto polyethylene terephthalate activated by low-temperature air plasma (PET_{air}) were examined. PET is widely used in tissue engineering, but its low hydrophilicity limits its integration with the surrounding tissues. Ch is a biocompatible polysaccharide, distinguished by its antimicrobial properties, widely distributed in medicine. DPPC and Chol are the major building components of cell membrane, so they can perfectly mimic membrane behaviour during contact with the Ch layer. Monolayers of lipids were deposited onto PET_{air} with or without the Ch layer using the Langmuir-Blodgett technique. The total surface free energy (SFE) and its components changes were calculated from theoretical approaches. Wettability strongly depended on the monolayer composition as well as the Ch layer. The Ch film decreased the contact angle and increased SFE of the PET surface with the lipid monolayers due to specific organisation of molecules within the chitosan scaffold. The most promising combination of surface modification for tissue engineering applications seems to be the $PET_{air}/Ch/DPPC-Chol$ system.

1. Introduction

Chitosan (Ch) is a homopolymer of β-(1,4)-2-amino-2-deoxy-D-glucopyranose and β-(1,4)-2-acetamido-2-deoxy-D-glucopyranose. It is one of the main members of polysaccharides. Ch is obtained as a product of chitin enzymatic or chemical deacetylation. The deacetylation degree as well as its molecular weight impact on the Ch physicochemical properties [1, 2]. The structure of Ch monomer is shown in Figure 1.

Ch is distinguished by biocompatibility, biodegradability, non-toxicity [3] and antimicrobial activity [4, 5]. Its activity against fungi and gram-negative and gram-positive bacteria is correlated with the presence of $-NH_3^+$ groups. These positively charged groups can interact with negatively charged cell membrane of microbes [2, 6-8]. Furthermore, Ch can amplify contact between tissue and implant, which is extremely important to prevent implant rejection [9]. Moreover, Ch is employed as a drug excipient (e.g. polypeptides) as well as in controlled drug release [10] and gene delivery [7] systems. Besides, Ch is used in microspheres and microcapsule production [11-13]. This biopolymer is also applied as tissue engineering scaffolds [7, 12, 13] and is widely used in wound healing [14]; this action is correlated with its haemostatic properties [2, 6]. Such properties come from the presence of positively charged $-NH_3^+$ groups that can react with negatively charged blood cells and erythrocytes [12, 13]. Therefore, due to haemostatic properties, Ch coatings can be potentially employed to improve the biocompatibility of vascular prostheses made of polymeric materials. One of them is the linear polyethylene terephthalate (PET) polymer. It has great mechanical and thermoplastic properties [15] that allow for use in medicine as material for prostheses, blood vessels and artificial organs [16, 17]. On the other hand, its low hydrophilicity, low surface free energy (SFE), inertness and poor adhesion could lead to implant rejection because of an unsuitable integration process [18]. To improve its compatibility with living tissue, there is a need to modify its surface but without changing bulk properties [15, 18]. Low pressure and low temperature plasma action is conducive to the addition of new functional groups on the polymer surface [15, 18, 19] and can sterilise it. This type of surface modification improves biocompatibility and enables immobilising biological substances onto solid support, such as Ch.
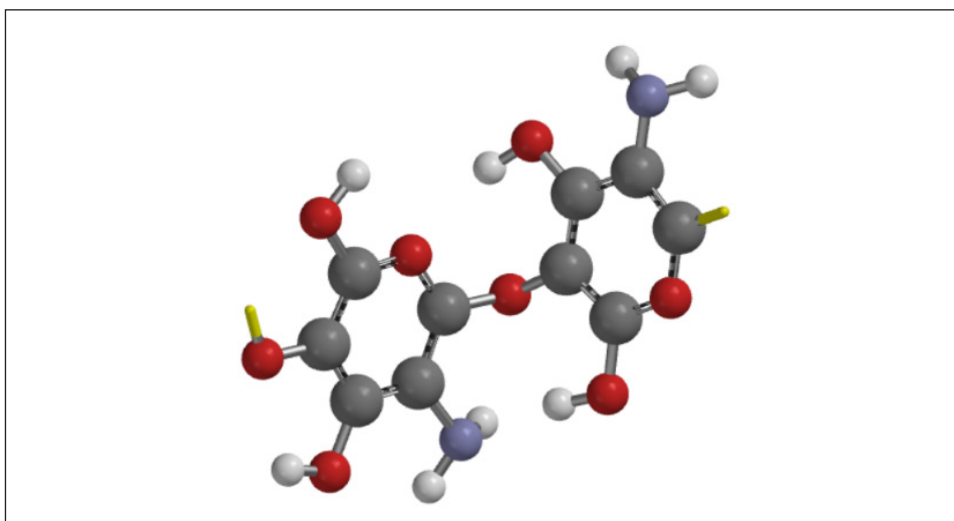
Figure 1. Chitosan monomer structure

The positively charged Ch coating can initiate clot formation [12, 13, 20]. This phenomenon leads to blood vessel occlusion and/or implant rejection. Therefore, further modification of the Ch surface is required as well as testing its effects on the cell membrane. Modification with lipids – for example, phospholipids and/or cholesterol – seems to be appropriate, taking into account the fact that they are the main components of biological membranes in the human body and that they can mimic interactions between the membrane and polymer/Ch system.

The wettability of thin films deposited onto a solid support is crucial. It provides information about possible interactions between the implant and surrounded tissues and allows obtaining high-quality layers. Wetting properties can be examined by contact angle (CA) measurements and calculated based on the changes in total SFE and its components. CA can be measured using two polar test liquids (water, formamide) and one apolar test liquid (diiodomethane), while surface free energy (SFE) can be calculated from the contact angle hysteresis (CAH) approach (Eq. (1) [21-23]) or the Lifshitz-van der Waals acid-base (LWAB) model (Eqs. (2)-(4) [24, 25]). In the CAH model, the advancing and receding CA are applied to calculate apparent total SFE:

$$\gamma_s = \frac{\gamma_l (1+\cos\theta_A)^2}{2+\cos\theta_R+\cos\theta_A},$$
(1)

where γ_s is the total SFE of a solid, γ_l is the surface tension of probe liquid, θ_A is the average advancing contact angle and θ_R is the average receding contact angle.

In the LWAB approach, the authors defined the SFE as the sum of the apolar Lifshitz-van der Waals and the polar Lewis acid-base interactions. The equations are:

$$\gamma_s^{tot} = \gamma_s^{LW} + \gamma_s^{AB},$$
(2)

$$\gamma_s^{AB} = 2\sqrt{\gamma_s^- \gamma_s^+},$$
(3)

$$W_A^a = \gamma_l(1 + \cos\theta_A) = 2\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + 2\sqrt{\gamma_s^+\gamma_l^-} + 2\sqrt{\gamma_s^-\gamma_l^+},$$
(4)

where γ_s^{tot} is the total SFE, γ_s^{LW} is the Lifshitz-van der Waals component, γ_s^{AB} is the Lewis acid-base component, $\gamma_{s/l}^-$ is the electron-donor parameter, $\gamma_{s/l}^+$ is the electron-acceptor parameter, W_A^a is the work of adhesion of a liquid to the solid surface and θ_A is the average advancing contact angle. The subscript 's' means solid and the superscript 'l' means liquid.

This paper describes the wettability and SFE changes of PET surfaces depending on the composition of the covering films. To obtain a stable binding between the deposited layers and the PET surface, low temperature and low pressure air plasma was used. After plasma action, the Ch layer was deposited by the dip-coating method following by the transfer of lipid (1,2-dipalmitoyl-sn-glycero-3-phosphocholine [DPPC], cholesterol [Chol] or mixed DPPC-Chol) monolayers by means of the Langmuir-Blodgett technique. Then the CA of three test liquids were measured on the PET surfaces with or without the coatings. The presence of Ch significantly affected the wettability of PET with deposited single DPPC, Chol or binary DPPC-Chol layers. Smaller CA were obtained on the PET$_{air}$/Ch/DPPC and/or Chol surface than in the absence of the Ch layer. Hence, Ch improved the hydrophilicity of PET modified with the DPPC and Chol film, while the best wetting properties were obtained for the PET$_{air}$ with the Ch layer and the binary DPPC-Chol monolayer (PET$_{air}$/Ch/DPPC-Chol).

2. Materials and methods

2.1. Materials

DPPC (99%; Sigma) and Chol (99%; Sigma) were dissolved in chloroform:methanol (4:1, v:v) to obtain basic solutions with a concentration of 1 mg/ml (chloroform 98.5% and methanol 99.8% were both from Avantor Performance Materials Poland S.A.). Then, by mixing proper volumes of the basic solutions, a two-component DPPC-Chol (χ_{chol} = 0.25) mixture was obtained. Moreover, 0.1 mg/ml Ch (MW 100,000-300,000, deacetylation degree 82%; Acrōs Organics - Fisher Scientiic) solution was prepared by dissolving an appropriate weight in 0.1% acetic acid (99.5%–99.9%, Avantor Performance Materials Poland S.A.).

2.2. Methods

PET plates were cleaned as described previously for use as a solid substrate for biological coatings [26]. For covering purposes, cleaned and dried PET (Bayer Axpet) plates with dimensions of $20 \times 30 \times 4$ mm³ were activated by a low-temperature and low-pressure (0.35 mbar) air plasma (Plasma type system, Diener Electronic, Germany) for 1 min. Immediately after modification, the PET plates were immersed in the liquid (subphase) filling the Langmuir-Blodgett trough (KSV 2000). The trough was cleaned earlier with methanol and rinsed three times by Milli-Q water with a specific resistivity of 18.2 MΩcm (purified by a Milli-Q Plus system). The surface tension was measured by the Wilhelmy plate method with accuracy of 0.1 mN/m. Subsequently, the proper volume of DPPC, Chol or DPPC-Chol solution was spread onto water subphase using a microsyringe (Hamilton-Bonaduz, Switzerland). After 15 min, to allow the solvent to evaporate, symmetrical compression with constant speed of 20 mm/min was performed to achieve the surface pressure of 30 mN/m. After reaching the target pressure, the system was left for 20 min to equilibrate; subsequently, the Langmuir monolayer was transferred onto the PET plate during its withdrawal towards the air. The same procedure was repeated for the activated PET plates, which were first immersed for 5 min in the Ch solution. Then, the samples were dried in a vacuum desiccator overnight. Afterwards, the advancing and receding CA of three test liquids (Milli-Q water, formamide 99.5% [Aldrich] and diiodomethane 99% [Aldrich]) were measured on their surfaces by means of DGD ADR, GBX S.A.R.L apparatus. Based on the measured CA, the SFE was estimated for all studied surfaces.

3. Results and Discussion

3.1. Contact Angle

As reported in previous papers, an unmodified PET surface has a weakly hydrophobic character [26-28], which was confirmed by the values of water CA of Q_A^W/Q_R^W 75.6°/66.6°. The obtained CA on unmodified and air-plasma-treated PET are shown in Figure 2. The presence of monomolecular layer of lipids (DPPC, Chol or DPPC-Chol mixture) strongly affected the PET wettability. The CA increased for all three test liquids compared with PET_{air}, while the CA decreased with respect to commercially available PET. On the DPPC monolayers Q_A^W increased by 45.2° (from 14.7° to 59.9°) while Q_R^W increased by 35.5° (from 9° to 44.5°) compared with PET_{air}. For formamide, the CA were also higher – Q_A^F by 35.3° (from 11.3° to 46.6°) and Q_R^F by 27.8° (from 7.9° to 35.7°) – than those on the modified PET_{air}. Furthermore, diiodomethane showed a similar change: Q_A^D increased by 27.5° (from 33.7° to 61.2°) and Q_R^D by 18.1° (from 28.3° to 46.4°). The increased CA are indicative of lower hydrophilicity of the surface. Interactions between liquid molecules are stronger than between these molecules and the solid support compared with PET_{air}. The increased CA measured on PET_{air} with the deposited DPPC layer is related to the presence of the hydrocarbon chains of phospholipid. These chains are directed towards the air while

polar groups are bound to the polymer surface. The Chol monolayer on PET$_{air}$ showed much lower hydrophobicity than DPPC: Q_A^W was lower by 23° while Q_R^W was lower by 18.5°. Formamide also showed decreased CA: Q_A^F by 27° and Q_R^F by 22.5°. The same dependence was noticed for diiodomethane, with Q_A^D changing from 61.2° to 49.6° and Q_A^D changing from 46.4° to 32.6°. In that case, the strongest interactions between the liquid molecules and layers could exist for formamide. Chol is not able to form as orientated and organised a layer as DPPC forms. Lower CA could be associated with the fact that the PET$_{air}$ surface is only partly coated by the Chol layer. Consequently, liquids have access to the polymer surface. As expected, addition of Chol to the DPPC monolayer also decreased its surface hydrophobicity. The average advancing CA of water changed from 59.9° (PET$_{air}$/DPPC) to 54.3° (PET$_{air}$/DPPC-Chol). This indicates that similarly to that of DPPC, the binary DPPC-Chol monolayer is condensed enough to be weakly permeable to liquids. For this reason, the difference between CA measured on PET$_{air}$/DPPC and PET$_{air}$/DPPC-Chol was only 5.6°. Surprisingly, the presence of Chol in the DPPC monolayer did not affect the measured CA of formamide and diiodomethane. The Chol monolayer was the most wettable by the probe liquids because it had the smallest CA. After transferring, Chol does not form the lamellar structure but aggregates. Hence, the liquids have access to the bare solid surface inducing better wettability than that of DPPC or DPPC-Chol, a similar outcome to what we have reported previously [29, 30]. The above results suggest that wettability of the PET surface covered with the monolayer is determined by its composition as well as by molecular packing. This suggestion could be very valuable as it implies indirectly that the choice of the composition of the layers could be a good tool to modify the PET wettability depending on the specific application or destination in the body.

Deposition of the Ch layer onto PET$_{air}$ entails introducing new functional groups such as -NH$_2$/NH$_3^+$, -OH and apolar hydrocarbon moieties. After immersion of PET$_{air}$ in Ch solution and drying the surface, the CA were higher for all test liquids than those on PET$_{air}$. Specifically, Q_A^W changed from 14.7° to 64.9°, Q_A^F from 11.3° to 47.4° and Q_A^D from 33.7° to 40.9° (Figure 2B). These changes are indicative of the decreased surface polarity. The apolar fragments of Ch are probably pointed outwards, while polar groups are located inside the layer, so they cannot interact with liquids directly. However, deposition of the DPPC
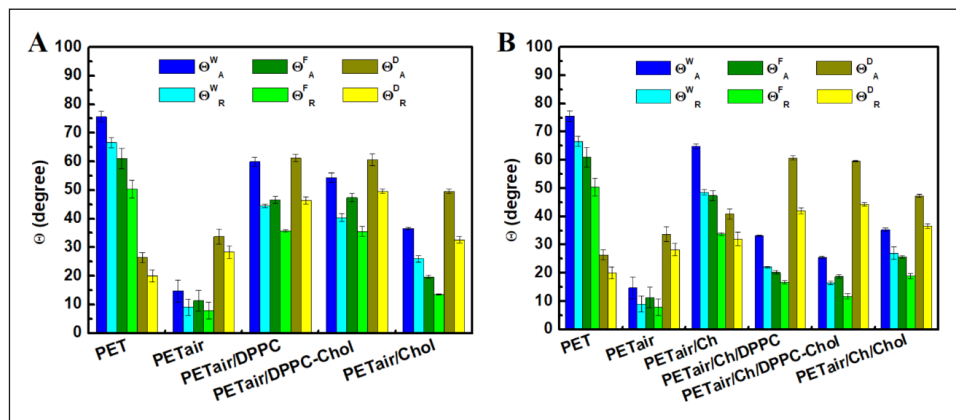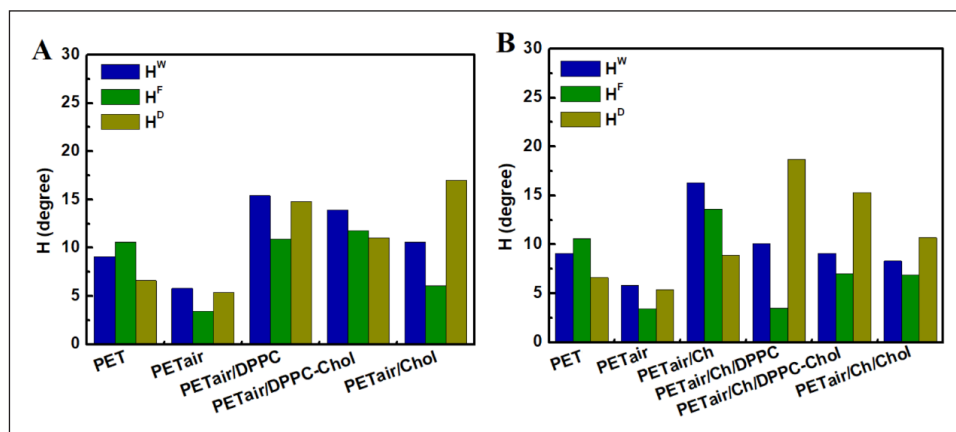

Figure 2. Contact angles of water (θ^W), formamide (θ^F) and diiodomethane (θ^D) measured on the unmodified commercial and modified polyethylene terephthalate (PET) surfaces **(A)** without and **(B)** with a chitosan (Ch) layer

and/or Chol layers increases the Ch film hydrophilicity, denoted by smaller CA. For example, compared with PET_{air}/Ch, on PET_{air}/Ch/DPPC the average CA were lower by 31.7°/26.5°, respectively, for Q_A^W/Q_R^W). Comparing PET_{air}/Ch/Chol with PET_{air}/Chol, the higher formamide and diiodomethane CA were measured on the latter one. The Q_A/Q_R changed from 19.6°/13.5° to 25.7°/18.9° and from 49.6°/32.6° to 47.3°/36.6° for formamide and diiodomethane, respectively. In the case of water CA, there were slight changes (Q_A/Q_R = 36.6°/26° on PET_{air}/Chol and Q_A/Q_R 35.3°/27° on PET_{air}/Ch/Chol). Additionally, CA depended on the layer composition. This could be related to the specific molecular organisation of the DPPC and/or Chol film as well as strength of lipid interactions with the Ch molecules. Owing to these interactions, some reorientation of DPPC and/or Chol molecules onto or inside the Ch layer can appear during the deposition of their Langmuir monolayers, in such a way that the polar heads of lipids are directed outwards, resulting in decreased CA [19]. As mentioned above, the smallest CA changes were observed for diiodomethane, and the CA were lower compared with the systems without the Ch layer.

3.2. Contact Angle Hysteresis

The contact angle hysteresis (H) was also calculated to analyse in more detail the hydrophobic-hydrophilic properties of the studied surfaces and the coating stability in contact with liquids (Table 1 and Figure 3). H indicates the difference between advancing and receding CA. As mentioned in our previous paper [26], the hysteresis of an apolar test liquid is lower than that calculated for polar ones. Additionally, plasma modification decreased the H values of all three liquids as an effect of additional functional groups presence, whereby interactions between the liquid molecules and the solid support were stronger. Deposition of the Langmuir-Blodgett monolayers of DPPC and/or Chol increased the H value in every examined systems with respect to PET_{air}. The contact angle hysteresis of water (H^W) changed by 4.8-9.6° for the systems without a Ch layer and by 2.5-4.3° for the systems with a Ch layer. The contact angle hysteresis of formamide (H^F) changed by 2.7-8.4° and by 0.1-3.6° for the films with and without a Ch layer, respectively. The contact angle hysteresis of diiodomethane (H^D) for the layers without Ch changed by 5.6-11.6° and with Ch

Figure 3. Contact angle hysteresis of water (H^W) formamide (H^F) and diiodomethane (H^D) calculated for the unmodified commercial and modified polyethylene terephthalate (PET) surfaces (A) without and (B) with a chitosan (Ch) layer

Table 1. Contact angle hysteresis values calculated for all layers

Modification	Hysteresis, *H* (°)		
	H^W	H^F	H^D
PET	9.1	10.6	6.4
PET$_{air}$	5.8	3.4	5.4
Without a chitosan layer			
PET$_{air}$/DPPC	15.4	10.9	14.8
PET$_{air}$/DPPC-Chol	13.9	11.8	11.0
PET$_{air}$/Chol	10.6	6.1	17.0
With a chitosan layer			
PET$_{air}$/Ch	16.3	13.6	8.9
PET$_{air}$/Ch/DPPC	10.1	3.5	18.7
PET$_{air}$/Ch/DPPC-Chol	9.1	7.0	15.3
PET$_{air}$/Ch/Chol	8.3	6.9	10.7

by 5.3-13.3°. The smallest changes were for H^F, particularly for the Ch-containing layer. On the contrary, the H^D showed the biggest changes compared with both polar test liquids. In principle, the presence of lipid monolayers causes the hysteresis decrease compared with PET$_{air}$/Ch. It is worth emphasising that diiodomethane in the PET$_{air}$/Chol system produced the highest *H* values, probably through the increased surface heterogeneity.

In general, greater *H* values of polar liquids were obtained for PET$_{air}$ with the deposited lipid monolayers than for the Ch-containing films (Table 1). This presumably results from reorganisation of the molecular lipid structure during the prolonged layer contact with a given liquid. Its molecules interact with the polar groups of DPPC and/or Chol determining the liquid penetration deep into the layer, particularly when the receding CA is measured. On the other hand, if the coating contains Ch the values of advancing and receding CA were smaller and the difference between them was also smaller. In this case the hysteresis was determined by the high density of the polar groups directed outwards (surface polarity). Hence, a main conclusion can be drawn that the hybrid Ch/lipid coatings are more stable when contacted with polar liquids that can simulate the layers behaviour in body fluids, providing hope for their potential application.

3.3. Surface Free Energy
3.3.1. Contact Angle Hysteresis approach

γ_s was evaluated from the CAH approach based on the Eq. (1) using the advancing and receding contact angles of water (γ_s^W), formamide (γ_s^F) or diiodomethane (γ_s^D) (Figure 4A and B). The total surface free energy (γ_s^{tot}) is an averaged value calculated according to Eq. (5):

$$\gamma_s^{tot} = \frac{\gamma_s^W + \gamma_s^F + \gamma_s^D}{3}. \tag{5}$$

The averaged total SFE determined for the commercial PET was 43.8 mJ/m²; after plasma activation it increased to 58.1 mJ/m². This confirms that the plasma action adds

new functional groups and changes the type of interactions between the surface and liquid molecules. The γ_s^W and γ_s^F values calculated for the commercial PET were quite similar but lower than γ_s^D. This suggests that both water and formamide molecules interact with the PET surface by dispersive interactions, but weaker by 4.7-6.6 mJ/m² than diiodomethane. After plasma action, γ_s increased for the two polar liquids, while the biggest increase for water (from 42.9 to 71.2 mJ/m²). This increase is induced by polar interactions, mainly by hydrogen bonds. Deposition of DPPC, DPPC-Chol and Chol monolayers decreased the averaged γ_s^{tot} to 44.5, 45.7 and 53.1 mJ/m², respectively, compared with PET$_{air}$. γ_s^W and γ_s^F were higher than γ_s^D. The Ch layer decreased the averaged γ_s^{tot} values from 58.1 to 45.9 mJ/m² compared with PET$_{air}$. After deposition of the lipid monolayers onto PET$_{air}$/Ch, γ_s^W and γ_s^F increased. The increase was the highest for γ_s^W for PET$_{air}$/Ch/DPPC-Chol, from 47.8 to 68.2mJ/m². Simultaneously, γ_s^D decreased. This phenomenon is related to reorganisation of molecules where polar groups are located outwards, while hydrocarbon chains are located inwards, whereby they are more accessible to liquid molecules. The above observations suggest that polar interactions are stronger than dispersive ones and contribute more to the total SFE. The highest γ_s^W value indicates that the above system is particularly capable of interacting with polar environment by hydrogen bonding. This fact may decide about its potential application in vascular engineering. Such a specific molecular organisation can increase the probability of the prosthesis assimilation, and at the next stage, multiplication of cells of a specific tissue depending on the implant site.

The apparent total SFE calculated based on the CAH approach were similar to those calculated from the LWAB approach (Figure 4; see sub-chapter 3.3.2). For the comparison purposes, the total SFE from the LWAB model is also shown in Figure 4.

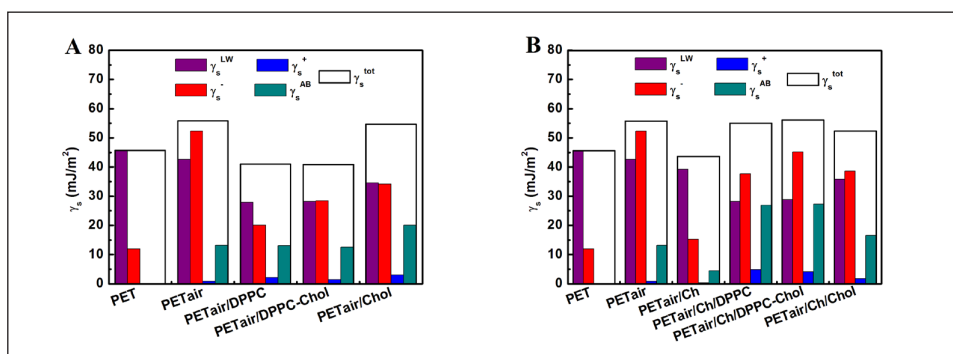### 3.3.2 Lifshitz-van der Waals - Acid-Base (LWAB) approach

Figure 5A and B show the total SFE and its components which were calculated from the LWAB approach. The calculation of these quantities can give much better insight into the physicochemical properties of PET surfaces than the CA contribute alone. For the unmodified PET surface, γ_s^{tot} was 45.6 mJ/m² while for PET$_{air}$ it was 55.8 mJ/m². For the unmodified PET, γ_s^{tot} was equal to the Lifshitz-van der Waals component (γ_s^{LW}) because there are no acid-base interactions (γ_s^{AB}). This means that interactions between the polymer surface and the test liquids have a principally dispersive character. In the case of PET$_{air}$, γ_s^{tot} increased because of acid-base interactions: γ_s^{AB} = 13.2 mJ/m² (γ_s^{LW} = 42.6 mJ/m²). For commercial PET, the electron-donor interaction (γ_s^-) was 11.9 mJ/m², while the low temperature plasma action increased this measure to 52.3 mJ/m². Moreover, after plasma action elector-acceptor (γ_s^+ = 0.83 mJ/m²) and acid-base interactions (γ_s^{AB}=13.2 mJ/m²) occurred. That phenomenon is correlated with appearance of the new polar functional groups on the PET surface (-OH, C-O, C=O, O=C–O and N-CO-N [19]), with which test liquids could interact by hydrogen bonding. Lower CA of water and formamide and higher CA of diiodomethane confirm the above conclusion (Figure 2A). Functionalisation of the polymer surface is crucial in terms of increasing its biocompatibility. It facilitates the attachment of lipids that build natural membranes. Then, such a biological coating constitutes a link between the artificial solid and living tissue, reducing the risk of a negative response of the body.

Deposition of the DPPC and/or Chol layers caused the decrease in γ_s^{LW} and γ_s^-, with the decreased observed for PET$_{air}$/DPPC – from 42.6 to 27.9 mJ/m² and from 52.3 to 20.1 mJ/m², respectively – for PET$_{air}$. The electron-acceptor parameter of PET$_{air}$/DPPC was higher than PET$_{air}$ and changed from 0.83 to 2.1 mJ/m². γ_s^{AB} remained almost the same (13.2 and 13.1 mJ/m²). The total SFE was lower in that case than for PET$_{air}$ because after deposition of the Langmuir-Blodgett layer γ_s^{LW} was lower than without it. On the other hand, the presence
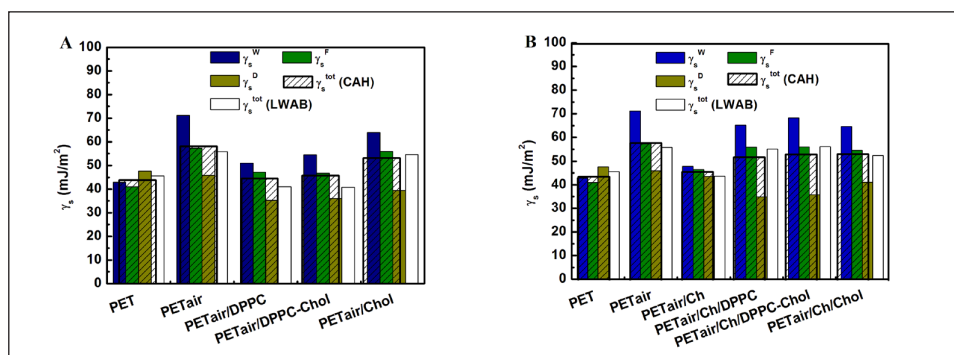
Figure 4 Total apparent surface free energy calculated from the contact angle hysteresis approach for the unmodified commercial and modified PET surfaces **(A)** without and **(B)** with chitosan layer

Figure 5 Total surface free energy and its components calculated from the Lifshitz-van der Waals acid-base (LWAB) approach for the unmodified commercial and modified polyethylene terephthalate (PET) surfaces **(A)** without and **(B)** with a chitosan (Ch) layer

of lipids increased the γ_s^+, with PET_{air}/Chol have the highest compared with PET_{air} (from 0.83 to 3.0 mJ/m²). Similarly, the greatest increase was for γ_s^{AB} (from 13.2 to 20.1 mJ/m²). This can be related to the structure of Chol, particularly to the presence of polar -OH groups, and it is due to an access of the liquids to the polar surface. Furthermore, there was a clear relation between γ_s^{tot} and the monolayer composition: the changes in γ_s^{tot} were dependent on the monolayer composition. γ_s^{tot} was 41.0, 40.8 and 54.6 mJ/m² for PET_{air}/DPPC, PET_{air}/DPPC--Chol and PET_{air}/Chol, respectively. Nevertheless γ_s^{tot} was highest for PET_{air} in every examined surface without Ch (Figure 5A). The presence of Ch increased γ_s^-, most prominently in the case of binary monolayer (Figure 5B), compared with the layers without Ch. Similarly, γ_s^{AB} also increased by 13.8 and by 14.8 mJ/m² for the DPPC and DPPC-Chol layers, respectively. These data confirm the presence of polar groups on the surface capable of interacting through hydrogen bonds. The γ_s^{LW} component was similar (28.2, 28.8 and 35.8 mJ/m² for the Ch-containing films and 27.9, 28.2 and 34.5 mJ/m² for the systems without a Ch layer). Additionally, the Ch film decreased γ_s^{LW} and γ_s^- compared with PET_{air}. PET_{air}/Ch/ DPPC showed the biggest changes in components values – a decrease in γ_s^{LW} from 42.6 to 28.2 mJ/m² and a decrease in γ_s^- from 52.3 to 37.7 mJ/m². On the other hand, the presence

of Ch molecules contributed to increase γ_s^+ and γ_s^{AB}. The largest changes in γ_s^+ occurred for PET$_{air}$/Ch/DPPC (from 0.83 to 4.8 mJ/m^2), and the largest changes for γ_s^{AB} occurred for PET$_{air}$/Ch/DPPC-Chol layer (13.2 to 27.3 mJ/m^2). PET$_{air}$/Ch/DPPC-Chol had the highest total SFE (56.1 mJ/m^2), which could promote the improved biosafety of the implant/tissue. By contrast, PET$_{air}$/Ch/Chol has the lowest γ_s^{tot} (52.4 mJ/m^2). Both correlate with the CA.

The smallest changes were obtained for the PET activated by plasma, coated with Ch and with mixed the DPPC-Chol layer (Figure 2B). The increased polar interactions (γ_s^{AB}) of the Ch/lipid layers with liquids confirms the characteristic arrangement of DPPC and/or Chol molecules, which reorganise on or within the Ch scaffold, directing their polar parts (heads) towards the air. Then, they are more accessible to the liquids (imitating the different character of a natural environment) and can interact by hydrogen bonds. The results indicate that modification of the Ch coating with lipids can improve its haemostatic properties. The positive charge of Ch at blood pH stimulates the attraction of negatively charged blood cells. This can lead to undesirable effects including the clot formation. By enhancing the electron-donor properties of the surface lipids alter the charge density of Ch, thereby increasing the probability of adopting a foreign body by the organism.

4. Conclusions

The PET surface wettability was modified by the low temperature air plasma action and deposition of Ch and/or lipid layers on to it. The wetting properties were determined by measurements of the water, formamide and diiodomethane CA. Based on them, the changes in total SFE were calculated from the CAH and LWAB approaches. The SFE calculated from both models was similar. The results indicate that the γ_s^{tot} depends on the PET surface modification and composition of the coatings. The presence of the Ch film changed the type of interactions between the PET surface and liquid molecules. Furthermore, Ch presumably provokes reorganisation of the lipid molecules during the monolayer deposition process. Namely, the polar heads of lipid molecules are exposed outwards. Hence, the surface polarity increased, particularly for PETair/Ch/DPPC-Chol χ_{Chol} = 0.25, which is characterised by the highest total SFE and electron-donor parameter. In addition to greater resistance to bacterial infections and a possible inflammatory process due to the presence of a Ch layer, such increased polarity gives a chance for greater adhesion of the artificial PET surface to human tissues and an easier process of implant acceptance. Such a property makes the above system the most promising for potentially innovative applications in vascular prosthesis engineering.

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