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ORIGINAL CONTRIBUTION

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Wettability of biodegradable surfaces

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Abstract The study of the interfacial characteristics of biodegradable polymers/copolymers is of importance from the point of view of both surface science and pharmaceutical/cosmetic applications. Films formed from biodegradable polymers allow systematic wettability studies on surfaces with a wide range of copolymer (chemical) compositions. The possibility of interchanging these drug carrier polymers, if their wetting characteristics are similar, could be beneficial to diverse applications. Low-rate dynamic contact angles on films (solvent cast on polar substrates, i.e. on silicon wafer) of poly(lactic acid), and its copolymers with poly(glycolic acid), (with four different copolymer ratios of 85/15, 75/25, 65/35 and 50/50) were measured by axisymmetric drop shape analysis-profile (ADSA-P) with four liquids: water, formamide, 2,2′-thiodiethanol and 3-pyridylcarbinol. The solid surface tensions, γ_{sv}, were calculated from the advancing contact angles, θ_A. The surface topography of the polymer films was investigated by atomic force microscopy (AFM). The surface composition of the polymer layers was analyzed by X-ray photoelectron spectroscopy (XPS). The advancing contact angles were found to be independent of the composition of the copolymers, while the receding angles, θ_R, did decrease with increasing ratio of the polar component [poly(glycolic acid)] in the copolymers. The solid surface tensions calculated from the advancing contact angles of the liquids for all homo- and copolymers were the same within the error limit; the mean value being $\gamma_{sv} = 35.6 \pm 0.2$ mJ/m^2. The surface roughness, which was obtained from AFM images, increased with increasing poly(glycolic acid) ratio, without affecting the advancing contact angles. The constancy of γ_{sv} is attributed to the effect of the surface activity of the nonpolar segments of the polymer chains, which oriented to form the outermost layer of the film. This was confirmed by XPS analysis.

Key words DL-Poly(lactic acid) · DL-poly(lactic/glycolic acid) copolymers · Axisymmetric drop shape analysis-profile (ADSA-P) · Contact angle · Surface tension

Introduction

Poly(lactic acid), DL-PLA, and its copolymers with poly(glycolic acid), DL-PLGA, (with different copolymer ratios) are widely recommended [1–5] as biodegradable drug carriers in the form of micro- and nanospheres. Both hydrophobic and hydrophilic drugs might be encapsulated in the polymers and the success in encapsulation as well as the drug release from the microspheres *in vitro* and *in vivo* might be influenced, among other parameters, by the suitable matching of the surface properties of the encapsulated drugs with those of the carrying polymers.

Poly(lactic/glycolic acid) copolymers have been studied for a wide range of applications, such as carrying anticancer drugs, using PLGA 50/50 copolymer [6], proteins in PLA 100 [7], PLGA 75/25, and PLGA 50/50 [8], peptides in PLA 100 and PLGA 75/25 [9], nonsteroidal anti-inflammatory drugs encapsulated in PLA 100 [10], hormone in PLGA 75/25 [11] or PLGA 50/50 loaded with drug for intraocular administration [12], just to give some examples. These polymeric drug delivery systems decompose in the human body due to hydrolysis, while releasing the encapsulated drug in the targeted area.

Many aspects of the physico-chemical characterization of polylactide-type biodegradable polymers can be found in the literature, although the information available regarding their hydrophobicity is inadequate. In practice, the *in vitro* surface characterization does not represent directly the wettability of such polymers *in vivo*. Nevertheless, the collection of reliable data of contact angles as well as the solid surface tensions allows prediction of the basic wetting behavior of these polymers.

The determination of the degree of surface modification also requires knowledge of the hydrophobicity of the polymer carrier. For example, if the drug delivery system is used as an implant and/or is intended to be intravenously administered [13–16], then the surface of the carrier should be more hydrophilic. From the examples given, it is evident that all of the commercially available homo- (PLA 100) and copolymers (most frequently PLGA 75/25 and 50/50) were applied randomly as potential drug carriers for the delivery of the different encapsulated substances. No systematic surface characterizations have been carried out for PLA and PLGA copolymers. Only a very limited number of static contact angle data for these copolymers were found in the literature [17–19]. All these contact angle data were obtained by goniometric methods with water only. Their results showed an increase in wettability with increasing poly(glycolic acid) ratio. This finding, however, contradicts our previous results [20], in which, surprisingly, the water contact angles measured on the different copolymers showed no significant dependence on polymer composition in the range studied. Since all of the commercially available poly(lactide) type homo- and copolymers are candidates for carrying drugs, it is important to know whether they are interchangeable from a surface chemistry point of view. In addition, the wettability study of these copolymer films is of interest from a surface science point of view, because the selected model surfaces allow variation of the film composition gradually from the 100% homopolymer [poly(lactic acid)] to a 50/50 copolymer ratio, by increasing the content of the poly(glycolic acid).

The purpose of the present work was to conduct a systematic wettability study on DL-poly(lactic acid) homopolymer and poly(lactic/glycolic acid) copolymer surfaces. The dynamic advancing and receding contact angles were measured using axisymmetric drop shape analysis-profile (ADSA-P) [21–25]. We selected the ADSA-P technique because it provides more information on the contact angle phenomena than can be gained by the goniometric method, such as the swelling and/or dissolution of the outermost layer of the solid by the measuring liquid [26, 27]. This technique is able to distinguish between the meaningful contact angles (i.e., those which can be used in the determination of solid surface tensions) and meaningless data (i.e., those which must be disregarded because they do not satisfy the prerequisites as discussed in references [28–32]). With those meaningful contact angle data, the solid surface tensions of the polymer films can be calculated by an equation-of-state approach [28, 33–35].

Atomic force microscopy (AFM), investigations were also performed to obtain insight into the topography of polymer surfaces [36–38]. In addition, X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical composition of the surface layer of the polymer films [39–41].

Materials and methods

Materials

Poly(DL-lactide), DL-PLA, (MW: 106,000) and four of its random copolymers with glycolic acid, poly(DL-lactide-co-glycolide), DL-PLGA, with 85/15 and 75/25 (MW: 90,000–126,000), as well as with 65/35 and 50/50 (MW: 40,000–75,000) component ratios of lactide/glycolide obtained from Sigma-Aldrich (Oakville, ON, Canada) were used. Structural compositions of the components, i.e., the poly(lactic acid) and poly(glycolic acid), are illustrated in Fig. 1. Dichloromethane (ACS reagent, HPLC grade) supplied by Sigma-Aldrich was used for sample film preparation. Doubly distilled water, formamide, 2,2′-thiodiethanol and 3-pyridylcarbinol were used as measuring liquids. Selected physical properties of these liquids are summarized in Table 1.

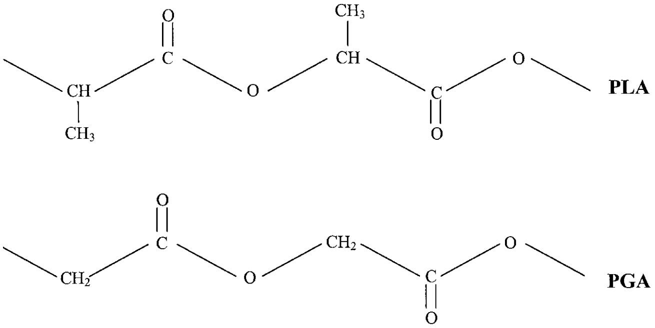

Fig. 1 Chemical composition of poly(lactic acid) (*PLA*) and poly(glycolic acid) (*PGA*)

Silicon wafers < 100 > (Silicon Sense, Naschua, N.H., USA) with a thickness of 525 ± 50 μm were used as substrates for the polymer films.

Methods (sample preparation)

Surface cleaning. The silicon wafers were cut into rectangular shapes of about 2.5 × 1.5 cm with a hole of 1 mm i.d. in the center of each wafer. The surfaces were then rinsed with ethanol to remove the impurities and were soaked in freshly prepared persulfuric acid (volume ratio of concentrated sulfuric acid: 30% w/v solution of hydrogen peroxide = 2:1) for at least 2 h. The samples were thoroughly washed and then soaked in distilled water for 1 h (with pH checked). Finally, the surfaces were dried under an infrared lamp for 15 min before the coating process.

Film preparation. The polymer films were prepared by a solvent casting technique; 2% (w/v) of polymer were dissolved in dichloromethane and 200 μl of each polymer solution was deposited onto the hydrophilic substrate with a pipette. To prevent fast evaporation of the solvent, which could lead to roughness of the film, the samples were covered for 20 min, allowing the solution to spread on the surface. Then the polymer films were dried at room temperature in a vacuum chamber overnight.

Measuring methods

ADSA-P investigation. In this study, the advancing and receding dynamic contact angles were measured with drops of four different liquids (distilled water, formamide, 2,2′-thiodiethanol and 3-pyridylcarbinol) on five polymer surfaces using ADSA-P. As described in references [25, 28, 35], ADSA-P allows determination of both liquid-vapour interfacial tension and contact angle from the shape of axisymmetric menisci of sessile drops. Details of the experimental procedures can be found elsewhere [25, 28, 35]. For each polymer with each liquid four to ten individual sessile drops were formed on freshly prepared surfaces. Different rates of advancing and receding (which can be determined from the slope by linear regression by plotting the data of drop radius over time) were studied for each liquid: velocities of the three-phase contact line in this study ranged from 0.1 to 1.0 mm/min for advancing measurements and from 0.3 to 2.0 mm/min for receding measurements. The experiments were performed at 23.0 ± 0.5 °C and approximately 45% relative humidity in a temperature controlled room. The surface tensions of liquids used in this study were determined independently with a pendant drop, also by ADSA-P.

AFM analysis. AFM measurements were carried out on DL-PLA 100, and DL-PLGA 75/25 and 50/50 films by means of a Nanoscope III (Digital Instruments, Calif., USA) atomic force microscope in an ambient environment. The instrument was operated in the contact mode, by using a $DISi_3N_4$ tip of 0.12 N/m force constant. Areas of different sizes (linear lengths of the studied area were 2, 5 and 10 μm) were scanned and the images gave characteristic morphological features of the studied surfaces. Cross section analysis of the surface topography was accomplished by the Nanoscope 4.23r6 software. The statistical values, R_a, and RMS, which can be obtained from this analysis, give information on the surface roughness of different polymer and copolymer films.

XPS analysis. Elemental and chemical analysis of polymer (DL-PLA 100) and selected copolymer films (DL-PLGA 85/15 and DL-PLGA 50/50) were performed by XPS. A monochromatized X-ray source (AlKα at 1486.6 eV) with a spot size 4 × 1 mm was used. A flood gun with characteristics of 3 eV and 30% emission was necessary for charge compensation. The samples were measured at 90° and 25° take-off angles. All spectra were calibrated to the position of the carbon (C) 1s peak.

Results

Contact angle measurements

A typical ADSA-P output illustrating advancing and receding angles of water on DL-PLA 100 is given in Fig. 2, where the contact angles, the drop radius, the volume and also the surface tension of the measuring liquid are plotted as a function of time. As shown in Fig. 2, from time zero, t_0, to time t_A, the advancing contact angle, θ_A, was formed by continuously pumping liquid into the droplet up to the point t_A. At time t_A the flow of liquid was reversed, the contact angle started to decrease and the three-phase line became stationary, i.e., the drop radius was constant. Meanwhile, the volume of the droplet decreased till time t_R. At time t_R the radius of the droplet started to decrease and the contact angle measured from that time represents the receding angle, θ_R. Both the rate of the advancing and receding radius, $rate_A$ and $rate_R$, and the relevant linear correlation coefficient, r, were given in the output. The measurements were performed at various $rates_A$ and $rates_R$ to demonstrate that both the advancing and the receding contact angles are independent of the rate of contact line motion within the range used here. It should also be noted that neither the advancing nor the receding angles of water show a time dependence on these polymer surfaces.

Figure 3 illustrates typical contact angles for water on the surface of poly(lactic acid) and its four

Table 1 Selected physical properties of measuring liquids. *Lit.* Literature value, *Meas.* measured value, γ_{lv} liquid/vapor interfacial tension

Liquid	Structural formula	Surface tension γ_{lv} mJ/m^2		MW g/mole	Boiling point °C	Density at 20 °C kg/m^3	Viscosity at 20 °C mPa s
		Lit.	Meas.				
3-Pyridylcarbinol	C_6H_7NO	49.73^{20}	49.30^{22}	109.13	154/28 mm	1.124	18.5^a
2,2′-Thiodiethanol	$C_4H_{10}O_2S$	54.00^{20}	54.00^{22}	122.19	164–166/20 mm	1.221	65.5^a
Formamide	CH_3NO	58.35^{20}	58.51^{22}	45.04	210	1.134	4.135
Water	H_2O	72.88^{20}	72.70^{22}	18.00	100	0.998	1.002

[a] Measured by capillary viscometer

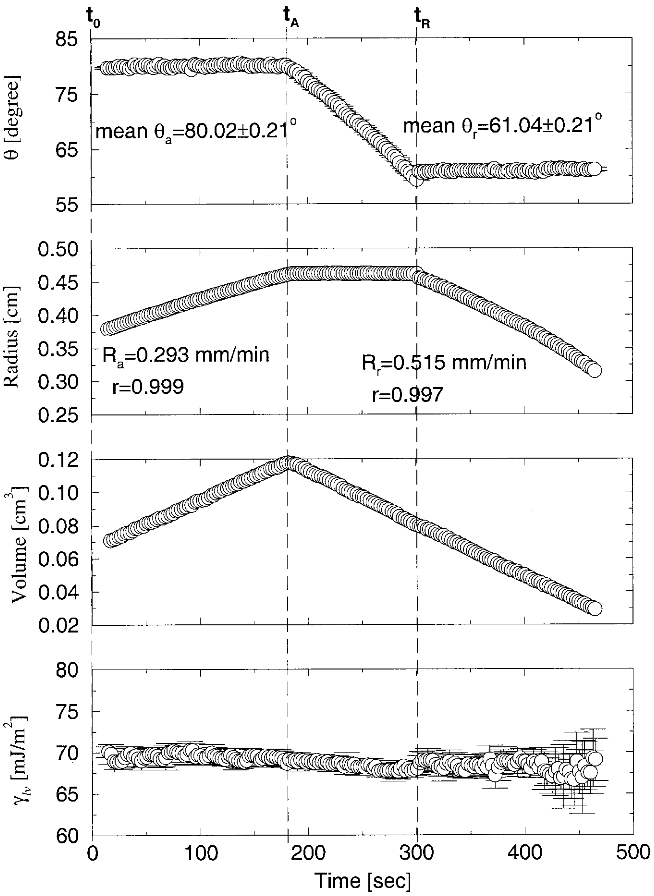

Fig. 2 Typical results obtained by axisymmetric drop shape analysis-profile (ADSA-P) for water drop on DL-PLA 100 homopolymer surface. θ_A Advancing contact angle, θ_R receding angle, R_a rate of advancing radius, R_r rate of receding radius, γ_{lv} liquid/vapor interfacial tension

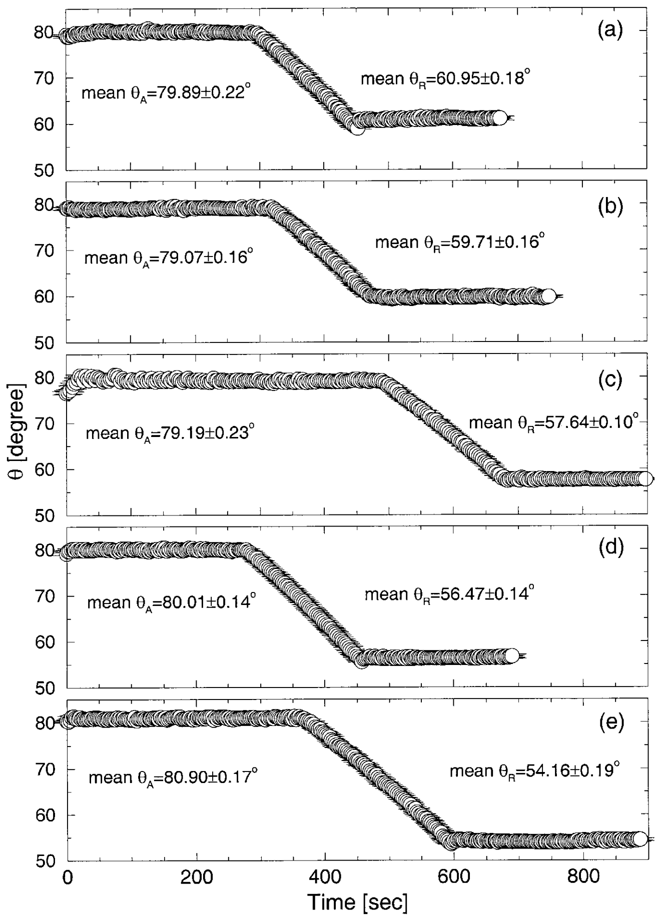

Fig. 3a–e Typical results obtained by ADSA-P for water drop on **a** DL-PLA 100 homopolymer, **b** DL-PLGA 85/15, **c** DL-PLGA 75/25, **d** DL-PLGA 65/35, and **e** DL-PLGA 50/50 copolymer surfaces

copolymers with poly(glycolic acid). It can be seen that the advancing contact angles obtained for the five polymers are essentially the same, but the receding contact angles decrease with increasing poly(glycolic acid) ratio. The results suggest that the polarity of the copolymers is not reflected in θ_A, but only in θ_R.

The contact angle patterns produced by 2,2′-thiodiethanol and formamide on the five polymer films are similar to those obtained for water in Fig. 3. However, the advancing contact angles of formamide on *some* DL-PLGA 50/50 surfaces show a pattern called "stick-slip" [30], as shown in Fig. 4. In that system the radius did not start to decrease after reversing the flow direction of the liquid, which means that receding angles were not measurable. In addition, an opaque spot was observed after removing the drop of formamide from the surface of those 50/50 copolymer samples which showed the "stick-slip" pattern. These observations imply that surface swelling and/or dissolution of solid by the liquid might occur during the solid/liquid contact. But even for those DL-PLGA 50/50 films which seemingly did not interact with formamide during the experiment and yielded constant advancing contact angles (not shown here), finite receding contact angles were not obtained (Table 2). It should be noted that for the formamide/DL-PLGA 50/50 system, only the constant advancing contact angles were averaged and used for subsequent solid surface tension, γ_{sv}, calculation.

The advancing contact angles for 3-pyridylcarbinol were essentially constant for both the homopolymer DL-PLA and the copolymer DL-PLGA surfaces, but all the receding contact angles were changing with time. It should be noted that opaque spots at the liquid/solid contact were visible after the experiment on all polymers. The spots were also inspected under a microscope (with 32 × magnification). It is believed that the films were changed by the liquid during the contact with 3-pyridylcarbinol. Therefore, the advancing contact angles measured on these systems were disregarded.

Table 2 summarizes both the mean advancing and receding contact angles (with 95% confidence limit) measured with the four liquids on the five polymer films, as well as the number of individual surfaces (*n*) used for each liquid/solid system. It can be concluded from Table 2 that the increasing ratio of the hydrophilic component [i.e. poly(glycolic acid)] of the copolymer does not influence the advancing contact angle values. This has been verified by a statistical analysis using ANOVA. On the other hand, all the receding angles measured with different liquids uniformly showed a decrease with increasing poly(glycolic acid) ratio, i.e. the receding angles do reflect the increasing polarity of the copolymers. It should be noted that the averaged advancing contact angles for systems where the liquids interacted with the solid, were marked in Table 2. These angles for 3-pyridylcarbinol were not used in the subsequent calculation of the solid surface tensions of the polymers.

The advancing contact angles of the remaining three liquids were used in the determination of surface tensions of the polymer films by the equation-of-state approach [28, 33, 34]. The surface tensions of the five polymers with different PLA/PGA ratio together with the contact angle are in Table 3. The γ_{sv} values calculated from the three liquids show constancy for all surfaces with an average value of 35.6 ± 0.2 mJ/m^2. The results indicate that the hydrophobicity of these copolymers does not change with their component ratio.

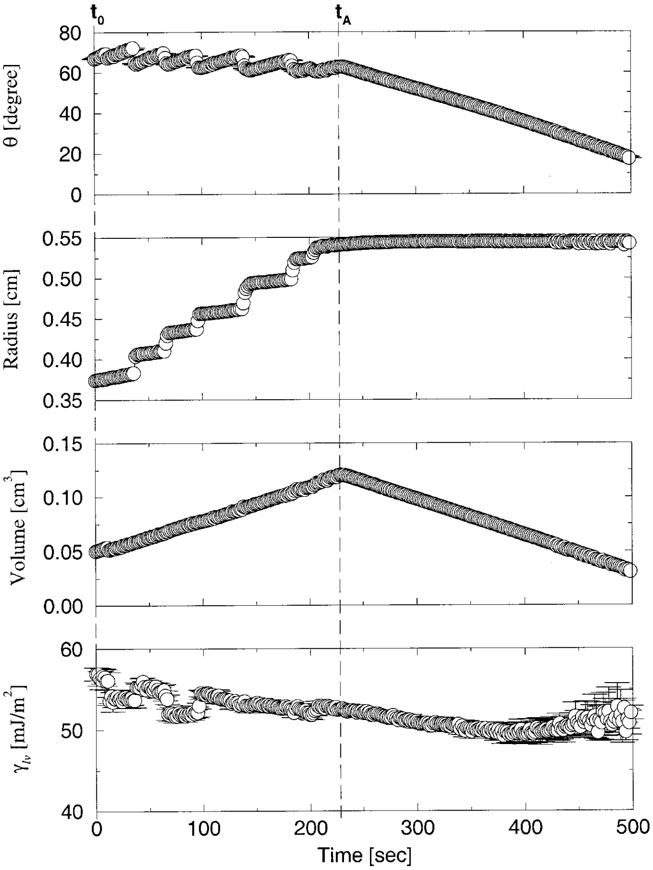

Fig. 4 Typical result, showing "stick-slip", obtained by ADSA-P for formamide drop on the DL-PLGA 50/50 copolymer surface

Table 2 Advancing, θ_A and receding, θ_R contact angles of different liquids on polymer films [with different poly(lactic acid)/poly(glycolic acid) (*PLA/PGA*) copolymer ratio] solvent cast on silicon wafer. θ measured by axisymmetric drop shape analysis-profile (ADSA-P) method. Surface tension γ_{lv} values: water, 72.70 mJ/m^2; formamide, 58.51 mJ/m^2; 2,2′-thiodiethanol, 54.00 mJ/m^2; 3-pyridylcarbinol, 49.30 mJ/m^2

Liquid	Copolymer ratio PLA/PGA	*n*	Mean θ_A ± 95%°	*n*	Mean θ_R ± 95%°
Water	100	5	79.82 ± 0.28	5	60.97 ± 0.31
	85/15	5	79.04 ± 0.07	5	59.81 ± 0.14
	75/25	4	79.96 ± 0.82	4	58.34 ± 0.92
	65/35	5	80.25 ± 0.18	5	56.35 ± 0.37
	50/50	5	81.05 ± 0.37	5	54.17 ± 0.07
Formamide	100	9	62.85 ± 0.26	9	39.57 ± 0.14
	85/15	6	61.76 ± 0.42	6	37.91 ± 0.70
	75/25	5	62.09 ± 0.34	4	34.75 ± 1.33
	65/35	7	61.51 ± 0.34	6	22.82 ± 0.38
	50/50	3	61.60 ± 1.98	–	–
2,2′-Thiodiethanol	100	5	56.87 ± 0.25	5	40.46 ± 0.43
	85/15	5	56.36 ± 0.24	5	38.84 ± 0.12
	75/25	6	55.77 ± 0.25	6	37.78 ± 0.31
	65/35	5	56.58 ± 0.09	5	36.53 ± 0.12
	50/50	5	56.68 ± 0.21	5	35.40 ± 0.14
3-Pyridylcarbinol	100	6	46.71 ± 0.41[a]	–	–
	85/15	10	43.51 ± 0.22[a]	–	–
	75/25	7	43.94 ± 0.81[a]	–	–
	65/35	5	42.53 ± 0.34[a]	–	–
	50/50	7	43.00 ± 0.65[a]	–	–

[a] Possible interaction at the solid/liquid interface

Table 3 Surface characteristics of polymer films (with different PLA/PGA ratios) solvent cast on silicon wafer. γ_{sv} solid/vapor interfacial tension

	γ_{lv} mJ/m^2	n	$\theta_A \pm 95\%°$	γ_{sv} mJ/m^2 Equation of state
DL-PLA 100				
2,2′-Thiodiethanol	54.00	5	56.9 ± 0.3	35.2
Formamide	58.51	9	62.9 ± 0.3	35.4
Water	72.70	5	79.8 ± 0.3	35.5
DL-PLGA 85/15				
2,2′-Thiodiethanol	54.00	5	56.4 ± 0.2	35.5
Formamide	58.51	6	61.8 ± 0.4	36.0
Water	72.70	5	79.0 ± 0.1	36.0
DL-PLGA 75/25				
2,2′-Thiodiethanol	54.00	6	55.8 ± 0.3	35.8
Formamide	58.51	5	62.1 ± 0.3	35.8
Water	72.70	4	80.0 ± 0.8	35.4
DL-PLGA 65/35				
2,2′-Thiodiethanol	54.00	5	56.6 ± 0.1	35.4
Formamide	58.51	7	61.5 ± 0.3	36.2
Water	72.70	5	80.3 ± 0.2	35.3
DL-PLGA 50/50				
2,2′-Thiodiethanol	54.00	5	56.7 ± 0.2	35.3
Formamide	58.51	3	61.6 ± 2.0	36.1
Water	72.70	5	81.1 ± 0.4	35.0

AFM analysis

Since surface morphology might influence contact angle measurements and hence the calculated surface tension values, the roughness of polymer films used in this study were examined by AFM. All of the films proved to be homogeneous on the microscopic scale but minor mechanical heterogeneity was observed by the AFM images, especially for copolymer surfaces. Section analyses, which provide the roughness information on an arbitrary cross section of the surface, are given for DL-PLA 100, DL-PLGA 75/25 and DL-PLGA 50/50 films. The height images (not attached here) for the homopolymer PLA 100 showed a smooth surface, the DL-PLGA 75/25 film had a smooth surface with occasional shallow craters, while the whole surface of the 50/50 film was uneven.

Typical roughness parameters were selected to characterize the surface roughness: R_a (in nanometers) represents the mean roughness, which means a mean value of a surface cross section relative to the center line. RMS (in nanometers) characterizes the standard deviation of roughness (z values) along a given line. The R_a values for DL-PLA 100, DL-PLGA 75/25 and DL-PLGA 50/50 are 0.267 ± 0.016, 0.565 ± 0.098 and 1.927 ± 0.570 nm, respectively (the data are given with 95% confidence limits). In addition, the RMS values for DL-PLA 100, DL-PLGA 75/25 and DL-PLGA 50/50 are 0.397 ± 0.074, 0.808 ± 0.148 and 2.517 ± 0.671 nm, respectively. These results show that the magnitude of surface roughness of these polymers is on the order of nanometers, as shown by the roughness profiles given in Fig. 5. Line tension considerations [42] suggest that this very small extent of surface roughness does not affect contact angles.

XPS study

For all copolymers, the elements detected on the surfaces were only carbon and oxygen. No other elements were detected, which means that the polymers formed continuous films on the substrates with a thickness larger than the analysis depth of XPS (approximately 10 nm). The peak synthesis has been performed for DL-PLA 100, DL-PLGA 85/15 and DL-PLGA 50/50 on C1s spectra with the following chemical shifts: C–C and C–H at 285.0 eV, C–O at 287.0 eV,and O–C = O at 289.0 eV. The results of peak synthesis are collected in Table 4. From the analysis performed at 90° detection angle, the carbon component values for poly(lactic acid) agree well with the theoretical composition. However, for the copolymers, the experimentally determined composition of the film reflects a higher C–C content than the theoretical one at the expense of the more polar C–O and O–C = O components in the surface layer. This effect became more pronounced as the poly(glycolic acid) content increased, with the highest effect at PLGA 50/50 ratio.

Discussion

Advancing contact angles obtained for the five polymers in this study do not change with the increase

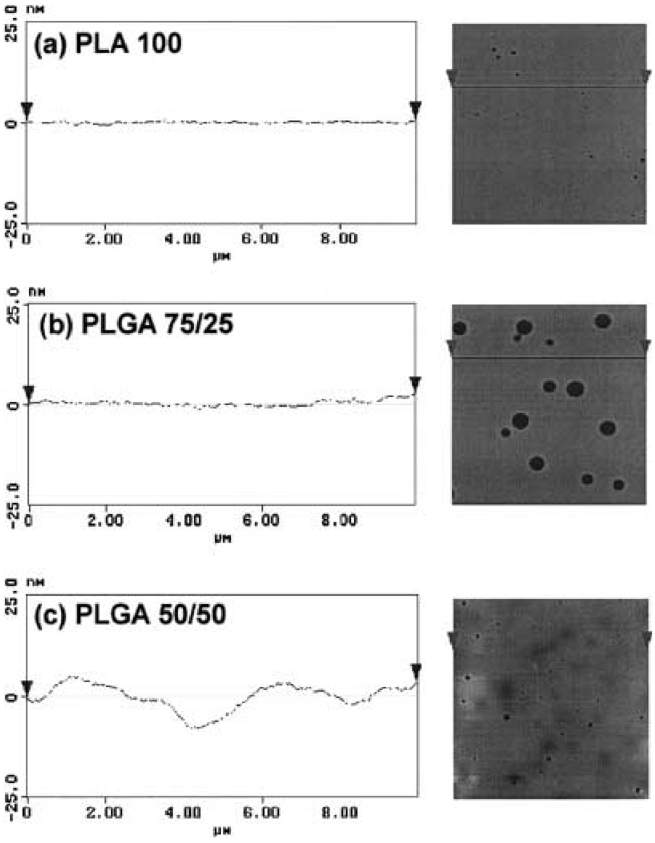

Fig. 5a–c Atomic force microscopy images of **a** DL-PLA 100 [mean roughness (R_A) 0.267 ± 0.016 nm, root mean square (RMS) 0.397 ± 0.074 nm], **b** DL-PLGA 75/25 (R_A 0.565 ± 0.098 nm, RMS 0.808 ± 0.148 nm) and **c** DL-PLGA 50/50 surfaces (R_A 1.927 ± 0.570 nm, RMS 2.517 ± 0.671 nm). The data are given with 95% confidence limits

of the poly(glycolic acid) ratio. This is plausible in the light of the XPS measurements. From the XPS analysis, it is inferred (Table 4) that the experimentally determined compositions of the copolymer films have a higher atomic C–C percentage in the surface layers at the expense of the more polar C–O and O–C = O components. The results from the two measuring depths (at 4.2 and 10 nm) of the film suggest that the hydrophobicity tends to decrease with increasing depth of the film. In view of this, the chemical composition results obtained at the two different depths were extrapolated back to the film surface (i.e. 0 nm). It was found that the compositions of the three different types of bonds for the three polymer films are generally near to the theoretical values of PLA 100. This result agrees well with our contact angle measurements, i.e. the θ_A results obtained for the five polymers are essentially the same. Apparently, segment orientation and adsorption occurred during film formation, forming an energetically favorable conformation. In other words, surface activity brings about the conformational changes of the copolymer chains, such that the less polar molecular segments turn towards the nonpolar air/film interface.

Table 4 The chemical composition of the surface layer of poly (lactic acid) and poly(lactic/glycolic acid) copolymer films determined by X-ray photoelectron spectroscopy (*XPS*). The thickness of surface layers analyzed at 90° and 25° detector position were about 10 and 4.2 nm, respectively

Polymer	C1s atom %		
	C–C	C–O	O–C = O
DL-PLA 100			
Theoretical	33.3	33.3	33.3
XPS at 90°	34.1	33.6	32.3
XPS at 25°	33.3	34.3	32.4
DL-PLGA 85/15			
Theoretical	28.4	35.8	35.8
XPS at 90°	31.4	34.2	34.4
XPS at 25°	32.8	34.1	33.1
DL-PLGA 50/50			
Theoretical	16.6	41.7	41.7
XPS at 90°	23.4	38.6	38.0
XPS at 25°	26.1	37.2	36.7

The contact angle results presented here confirm our previous results on water contact angle measurements [20]. The comparison of the water advancing contact angles obtained by ADSA-P and the static contact angles of water measured by a goniometer technique as found in the literature [17–19] is given in Table 5. While the literature data show a decrease in contact angles with increasing poly(glycolic acid) ratio, this trend is not confirmed by results from the ADSA-P measurements. Due to the lack of experimental detail in the literature, a

Table 5 Comparison of advancing contact angle θ_A of water measured by ADSA-P on polymer films (with varied copolymer ratios) with those of θ_A (measured by goniometeric method) obtained from the literature

Liquid	Copolymer PLA/PGA ratio	Mean θ_A ± 95%°			
		n	ADSA-P	*n*	Literature data
Water	100	5	79.8 ± 0.3		79.0 ± 4.0[18], 72[19]
	85/15	5	79.0 ± 0.1		
	75/25	4	80.0 ± 0.8	10	74.5 ± 0.4[17]
	65/35	5	80.3 ± 0.2	10	69.7 ± 0.3[17]
	50/50	5	81.1 ± 0.4	10	68.9 ± 0.7[17], 65 ± 4[18]

definitive explanation for the discrepancy between the literature results and the present data cannot be given. However, the most likely explanation is as follows: there is a considerable difference in the degree of sophistication between the present measurements and those reported in the literature. There, a drop of liquid is deposited on the surface and the contact angle is determined at some unspecified time later. In the ADSA experiments, the drop front advances slowly and constantly, producing a constant contact angle, which was found to be independent of the rate of motion of the three-phase line. This contact angle, constant at slow rates of advance of the drop front, is known to be equal to the proper static contact angle [28, 30].

However, measuring true static contact angles is not a trivial matter, as illustrated in Fig. 6, where a typical result obtained from a dynamic-static contact angle measurement with water on PLA 100 is given. One can see from this figure that the dynamic contact angle remains constant for the 200 s measuring time interval, but θ decreases with time immediately after the motor is stopped, while obtaining static contact angles, i.e., contact angles at constant contact radius. Similar patterns were obtained for all four copolymers. This result is presumably due to both liquid penetration into the polymer film and evaporation. Obviously, the slowly advancing liquid front eliminates the effect of all such processes. Therefore, it is necessary to measure contact angles dynamically in order to obtain reliable results. Caution should be exercised when measuring static contact angles and using these values in the determination of the solid surface tensions.

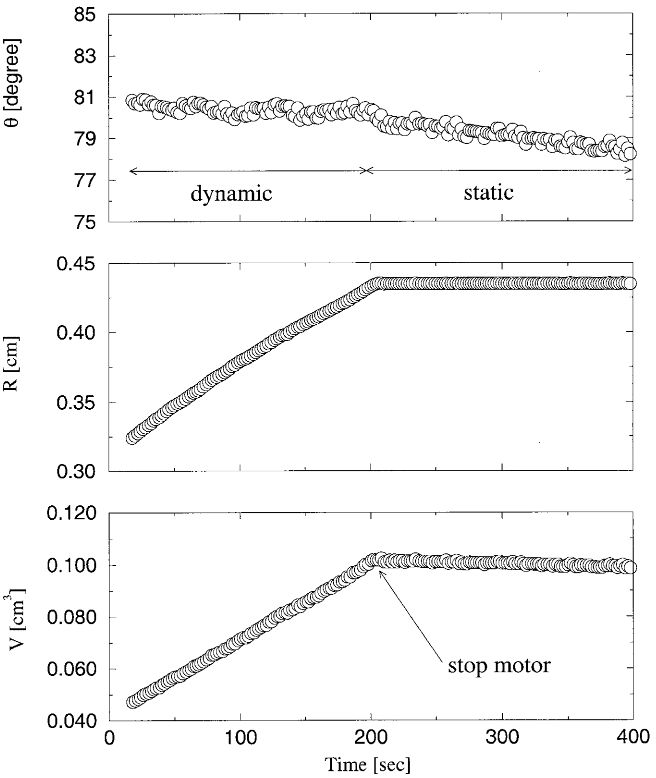

Fig. 6 Dynamic and static contact angles of water on DL-PLA 100-coated silicon wafer

Furthermore, the hydrophobicity of the polymer film can be affected by different film preparations. Since the nonpolar groups of the polymer do indeed have a preference to adsorb at the surface during film formation due to the evaporation of solvent, it is conceivable that the extent of this segment adsorption would depend on the film formation time. Alternate methods of surface preparation, say by microtoming a bulk polymer sample, would likely yield surfaces of very different properties. It would appear that contact angle measurements on polymer surfaces which have not been characterized, or produced under controlled conditions and for which the experimental methodology and procedure is not disclosed [17–19] are not useful.

Receding contact angles of these poly(lactic acid) and poly(lactic/glycolic acid) polymers, which have not been reported in previous studies, were also found to be informative: θ_R decreases with increasing poly(glycolic acid) ratio. Since receding angles were measured on surfaces which had been (by necessity) previously wetted and presumably changed by the polar liquids, they do not reflect the properties of dry polymer films but of modified films. These polymer films could be changed by polar liquids in two ways. (1) Liquid penetration and polar segment re-orientation: whereas during the formation of the film, adsorption of the hydrophobic polymer segments minimized the free energy of the system at the polymer/air interface, a re-orientation such that the polar chain segments constitute the outermost layer of the polymer next to the polar liquid might occur and (2) interfacial hydrolysis of the outermost layer of the film. Both mechanisms can result in a change in the composition of the polymer films at the liquid/solid interface. Thus, it is plausible that θ_R decreased with increasing poly(glycolic acid) content of the copolymers. The study of receding contact angles may be of importance from the biological point of view, because drug delivery will typically take place in an aqueous medium, not air.

Conclusions

The conclusions we have drawn are as follows:

1. The advancing contact angles measured by ADSA-P do not change with copolymer composition and the mean solid surface tension of the polylactide-type polymers was calculated as 35.6 ± 0.2 mJ/m^2.

2. The receding contact angles decrease with increasing poly(glycolic acid) ratio.
3. The surface roughness, which was characterized by AFM measurements, increases slightly with poly(glycolic acid) content in the polymer films. The magnitude of the surface roughness is within 20 Å and has no effect on the contact angles.
4. Finally, the XPS study suggests that the constant value of the surface tension of these polymers is due to the surface activity of the nonpolar segments in the copolymer chain during film formation.

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