Influence of casting substrate on the acid–base interaction energies of various polyesters

R. Smith[*], R. Pitrola

IRC in Biomedical Materials, Queen Mary and Westfield College, Mile End Road, London E1 4NS, UK

Abstract

The acid–base surface characteristics of four polyesters: poly(L-lactic acid) (PLLA), poly(DL-lactic acid) (PDLLA), polyhydroxybutyrate (PHB) and copoly(hydroxy butyrate–20% hydroxyvalerate)P(HB–20% HV) have been determined from contact angle and surface tension experimental data. Smooth surfaced polyester films were prepared by solution casting against a number of substrates ranging from high surface energy (aluminium, mercury, glass and freshly-cleaved mica) to low surface energy (poly(ethyleneterephthalate)(PET), poly(tetra-fluoroethylene)(PTFE) and dry nitrogen gas).

Results show that the acid–base interaction energy of the polyester surface is dependent on the casting substrate and ageing time. For a particular casting substrate, the equilibrium acid–base interaction energy between a polyester surface and an acidic liquid decreases in the order: PDLLA; PLLA; PHB; P(HB–20%HV).

The time dependence of the acid–base interaction energy is interpreted in terms of orientation of surface acidic or basic sites. Furthermore, detailed results suggest that the initial acidic or basic character of the cast polyester surface is influenced by the acid/base surface properties of the casting substrates. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Surface characterisation; Degradable polymers; Contact angle

1. Introduction

The tissue compatibility of synthetic polymers is highly dependent on surface properties. It is generally established that the adhesion and spreading of cells against polymer surfaces is related to the polar and dispersion surface free energies [1–5].

Recently, acid–base interactions (which include hydrogen bonds) have been considered more important than surface free energy in determining interfacial reactions and may play a dominant role in the changing acidity/basicity of the local tissue response.

Clearly, a detailed investigation relating to the surface mobility of chemical groups or molecular re-orientation would lead to a better understanding of the observation that some polymers (and other materials) become particularly well integrated into living systems.

According to the Lewis acid–base concept[6], acids are electron acceptors and bases are electron donors. Fowkes and co-workers [7–9] have found that Lewis acid–base interactions occur between the so called "polar" groups in liquids and solids and that these interactions are generally independent of the "polarity" as measured by the dipole moment.

Acid–base surface properties of synthetic materials can be investigated using a number of techniques, the most common being contact angle measurements, using acidic or basic liquids and Fourier Transform Infrared Spectroscopy (Attenuated Total Internal Reflectance (ATR) or grazing angle techniques) [7–9].

Contact angle measurements, particularly with acidic or basic liquids, are generally more sensitive to chemical and structural surface modification compared to other surface techniques, such as XPS, since a contacting liquid interacts with the outermost molecular layer of a solid surface, providing no impurities are present and no absorption by the solid occurs.

The aim of the present work was to assess the acid–base surface properties of various polyesters, some of which are currently used as biomaterials, for subsequent periodontal experiments [10].

1.1. Estimation of acid/base work of adhesion

The work of adhesion between a liquid and a solid-surface is given by the combined Young–Dupre equation

---

* Corresponding author.

[11–13]:

$$W_{SL} = \gamma_L(1 + \cos \theta) \qquad (1)$$

where, γ_L, is the surface tension of the liquid and, θ, is the equilibrium (Young) contact angle of the liquid on the solid surface. In Eq. (1), the equilibrium spreading pressure of the vapour absorbed on the solid surface has been neglected; this is generally true for liquids with finite contact angles on smooth, homogeneous, low energy surfaces, such as polymers [14,15].

It has been suggested by Fowkes [7–9] that the work of adhesion between two phases, solid, (S), and liquid, (L), could be divided into London dispersive, (d), and acid–base, (ab), components:

$$W_{SL} = W_{SL}^{d} + W_{SL}^{ab} \qquad (2)$$

According to Fowkes, provided only London dispersion forces operate between the two contacting phases, S and L, the dispersion component of the work of adhesion, W_{SL}^{d}, is given by:

$$W_{SL}^{d} = 2(\gamma_S^{d}\gamma_L^{d})^{1/2} \qquad (3)$$

γ_S^{d}, and γ_L^{d}, are dispersion components of surface free energies of solid and liquid, respectively.

Eqs. (1) and (3) can be solved to determine the dispersion surface energy component of a polymer, provided liquids with only dispersion force interactions (e.g. n-alkanes, di-iodomethane or 1-bromonaphthalene) are used in the contact angle measurements. The acid–base component of the work of adhesion is given by:

$$W_{SL}^{ab} = W_{SL} - W_{SL}^{d} = \gamma_L(1 + \cos \theta) - 2(\gamma_S^{d}\gamma_L^{d})^{1/2} \qquad (4)$$

where, θ, is the measured contact angle of a test liquid (acidic or basic) on a particular polymer surface, γ_L, is the surface tension of the test liquid, (the superscript (d) indicates a London dispersion force component and (ab) refers to the acid–base interactions).

The surface tensions of test liquids used in this study are listed in Table 1. The dispersion surface energy components of polyester surfaces employed in this investigation have already been calculated in a recent publication [16].

2. Materials and methods

The liquids used for contact angle measurements were distilled dimethylsulphoxide (DMSO), dimethylformamide (DMF), pyridine and 48% phenol in tricresylphosphate (TCP); these organic liquids were the best grade available and were stored in the dark prior to commencement of experiments.

The polyesters employed in this study were: poly (DL-lactic acid) (PDLLA), poly(L-lactic acid (PLLA), poly (hydroxybutyrate) (PHB), and copoly(hydroxybutyrate–20%hydroxy valerate) P(HB–20%HV).

Polymer films were cast from a 2–8%(w/v) solution in

Table 1
Surface tension of liquids used

Liquid	Surface tension (mN m^{-1})	
	Dispersion component	Total
Dimethylsulphoxide	34.9	43.6
Dimethylformamide	32.4	37.3
Pyridine	37.2	38.0
48% Cresol in tricresylphosphate	34.8	39.5

chloroform against the following clean, smooth surfaced substrates: glass, freshly-cleaved mica (muscovite), aluminium, mercury, poly(ethyleneterephthalate)(PET) (Melinex or Mylar) and polytetrafluoroethylene (PTFE). The environment during casting experiments was clean air or dry nitrogen gas. After controlled evaporation of the solvent, all films were dried under vacuum at room temperature for one week to remove residual chloroform. Immediately prior to testing, the films were carefully removed from the substrate by gently lifting one edge with the aid of a scalpel and peeling back. Care needed to be taken at this point to avoid tearing or damaging the films, especially from the more brittle polymers.

The two sides of the resulting films will be referred to as the interfacial surface (substrate side) and free surface (air or nitrogen side), all interfacial polyester surfaces were optically smooth whereas the free surfaces were generally less smooth.

Contact angles were measured by placing a small drop of liquid on to the polyester surface with the aid of a micrometer syringe. The drop volume was gradually increased up to 0.1–0.5 μl by small increments. During drop formation, care was taken to ensure that the tip of the syringe needle never touched the solid surface and the three phase contact line. An optical microscope was used to observe the well-resolved contact line, which appeared to be almost circular for all drops on all specimen surfaces. During this procedure it is essential to eliminate vibration. After measurements with a particular liquid, the syringe was carefully cleaned with acetone (analytical grade) and dried in an oven. In order to avoid contamination of one liquid by another, just prior to measurements, the syringe was cleaned with the test liquid at least ten times. For each liquid on a given polymer, the contact angle was the mean of at least eight independent measurements; the standard deviation in contact angle was about one degree. Contact angle measurements were made at 22.5 ^ 1°C. It should be noted that all contact angle/surface free energy results were independent of thickness of polymer film. The contact angle was calculated from Eq. (5):

$$\tan\left(\frac{\theta}{2}\right) = \frac{2h}{D} \qquad (5)$$

where (h) is the drop height, (D) is the base diameter and (θ) is the contact angle.

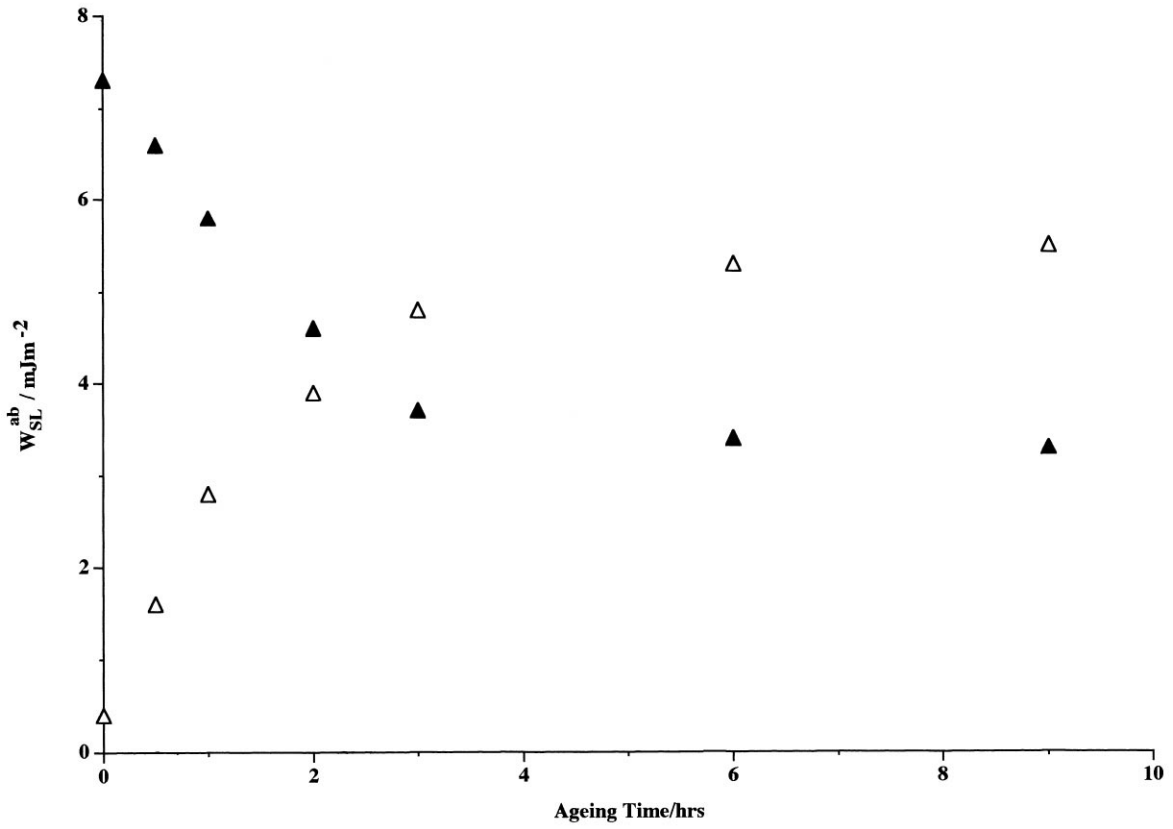Fig. 1. Acid–base work of adhesion of DMSO (▲) and TCP (△) on PDLLA cast against aluminium, as a function of polymer ageing time.
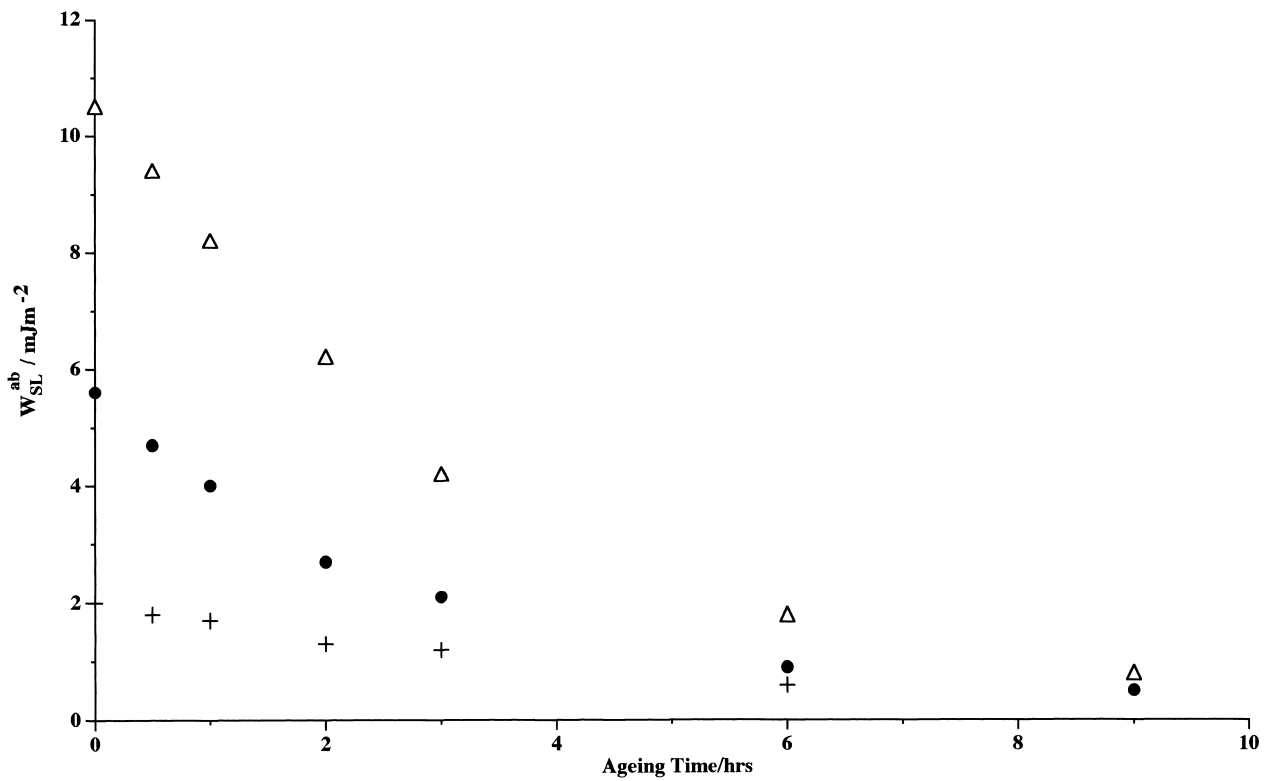

Fig. 2. Acid–base work of adhesion of DMSO (▲), DMF (●) and Pyridine (+) on PDLLA cast against mica, as a function of polymer ageing time.
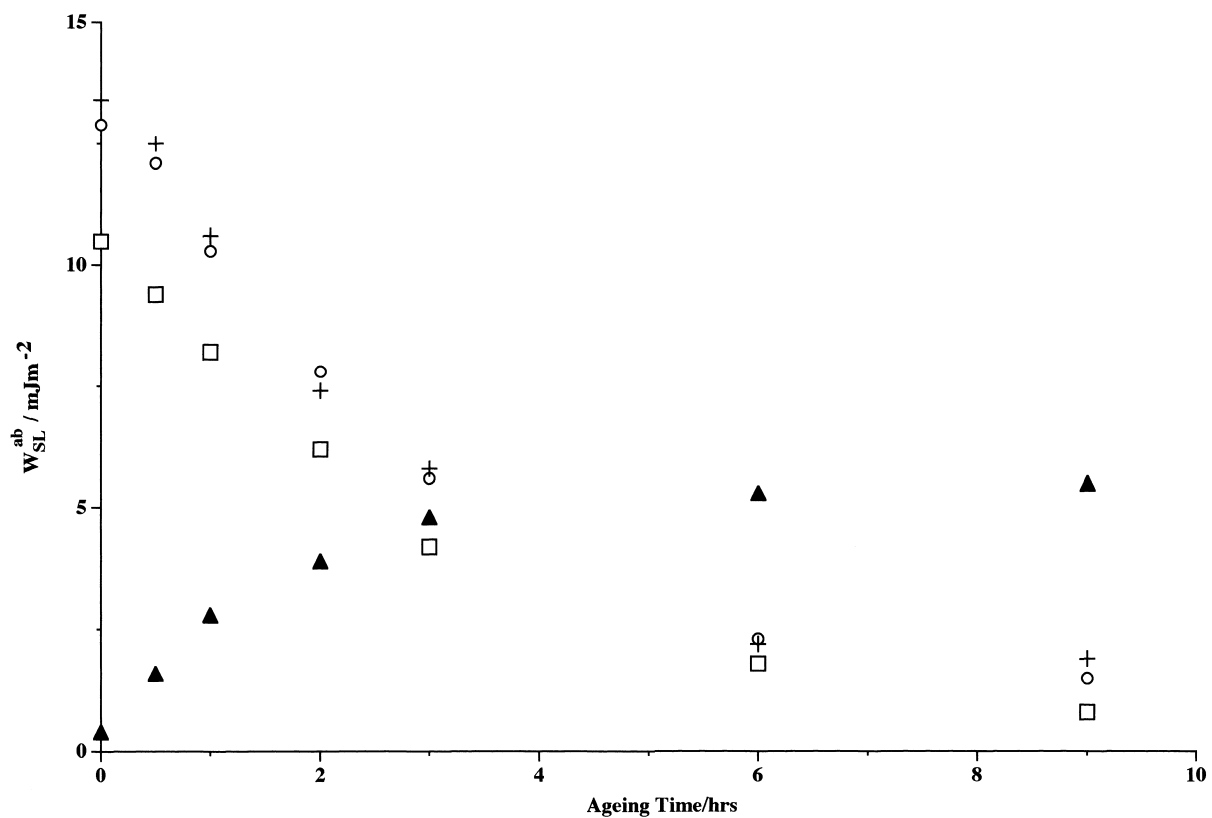
Fig. 3. Acid–base work of adhesion of DMSO on PDLLA cast against PET (+), glass (■), mica (▲) and aluminium (○), as a function of polymer ageing time.
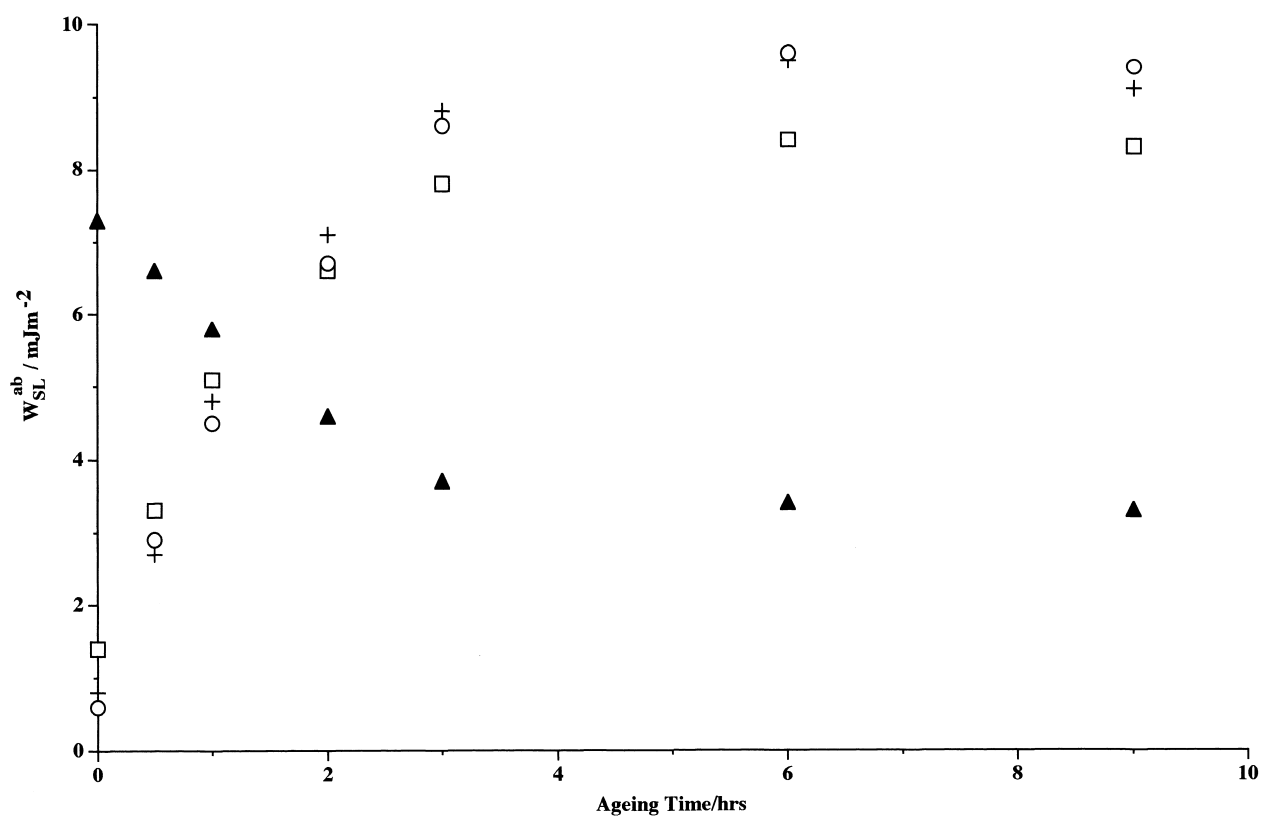

Fig. 4. Acid–base work of adhesion of TCP on PDLLA cast against PET (+), glass (■), mica (▲) and aluminium (○), as a function of polymer ageing time.
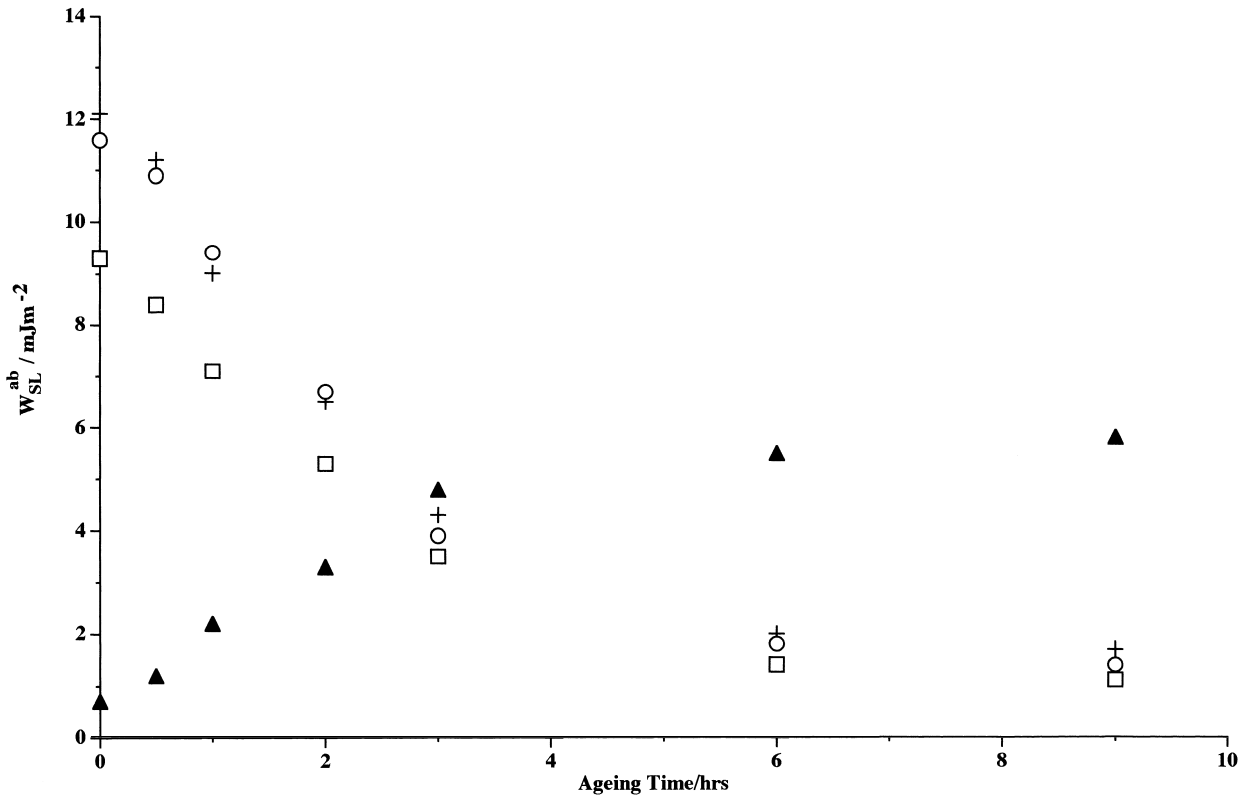
Fig. 5. Acid–base work of adhesion of DMSO on PLLA cast against PET (+), glass (W), mica (A) and aluminium (O), as a function of polymer ageing time.
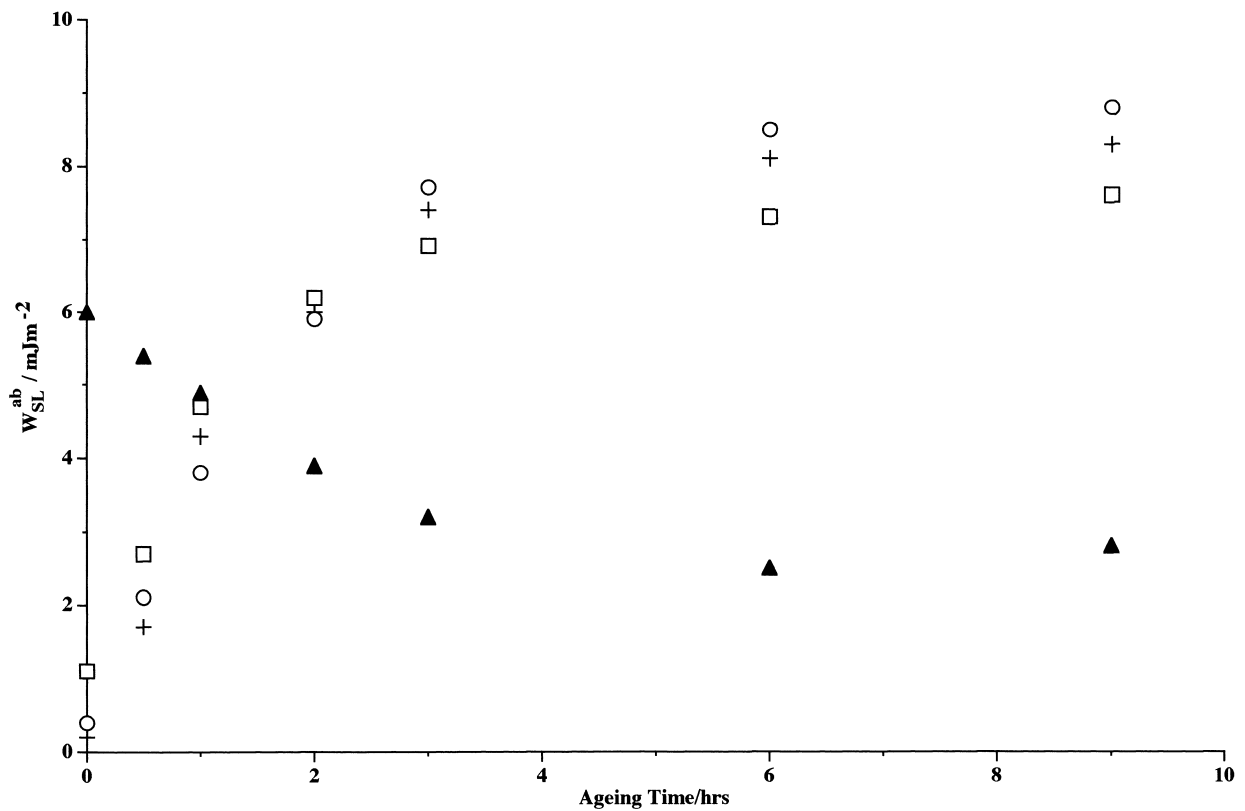

Fig. 6. Acid–base work of adhesion of TCP on PLLA cast against PET (+), glass (W), mica (A) and aluminium (O), as a function of polymer ageing time.
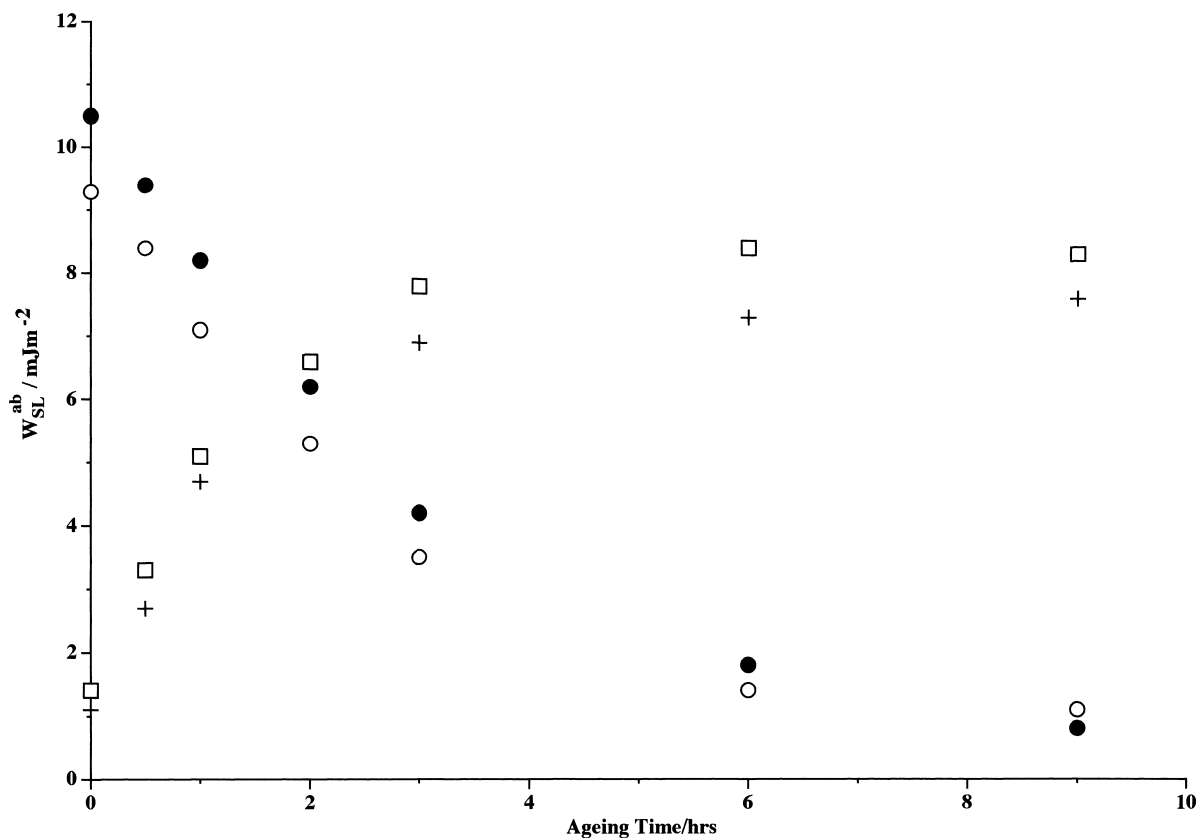
Fig. 7. Comparison of the acid/base work of adhesion of PDLLA and PLLA cast against mica. PDLLA/DMSO (X), PLLA/DMSO (W), PDLLA/TCP (A), PLLA/TCP (+).

3. Results and discussion

The detailed acid–base results of all polyesters studied are presented in Figs. 1–13. These results demonstrate that the acid–base work of adhesion (interaction energy) between a particular polyester surface and an acidic or basic liquid is dependent on the casting substrate and ageing time of the polymer surface, where ageing time refers to the time elapsed after removal of the film from the substrate. Furthermore, the detailed results suggest that the initial acidic or basic character of the polyester surface (substrate side) is strongly influenced by the acid/base surface properties of the casting substrate itself. For example, a substrate which has a surface that is acidic in character, in contact with a polyester produces an initially basic polyester surface, which changes with ageing time, toward an equilibrium, more acidic surface. This effect is demonstrated in Fig. 1 where PDLLA cast against an aluminium (acidic) substrate has an initially high value of interaction with TCP, an acidic liquid, indicating an essentially basic polymer surface. This initial value decays over about 4 h to a lower value. The value obtained for DMSO, a basic liquid, on the same polyester surface is initially very small, again indicating a basic surface. This value increases (in line with the above decrease) with time. Fig. 2 shows the results obtained from PDLLA cast against mica, an essentially

basic substrate. This results in the polymer having an essentially acidic surface. The acid/base interaction of three different basic liquids, DMSO, DMF and pyridine with this polymer surface again shows time dependant behaviour. The differing basicities of the test liquids are also reflected in the three curves, DMSO having the highest values of acid/base interaction energy and pyridine the lowest. Figs. 3 and 4 show the detailed results for PDLLA cast against aluminium (acidic), and mica, glass and PET (basic) substrates tested with DMSO (basic) and TCP (acidic) liquids. These curves again show time dependent behaviour and clearly show the influence that the acid/base nature of the substrate has in determining the characteristics of the resulting polymer surface. Figs. 5 and 6 show a similar set of results for PLLA, cast against the same substrates and tested with the same liquids. Fig. 7 shows that there is a difference in behaviour between PDLLA and PLLA. Mica is a basic substrate that would give rise to an acidic polyester surface, Fig. 7 indicates that the acidic nature of the PDLLA surface is greater than that observed for PLLA, presumably associated with the greater mobility of polymer chains in amorphous PDLLA.

Figs. 8–11 show the results obtained from PHB and PHB/HV cast against mercury (acidic), and glass, mica and PET (basic) substrates, tested with DMSO (basic) and TCP (acidic) liquids. Once again, similar behaviour is observed,
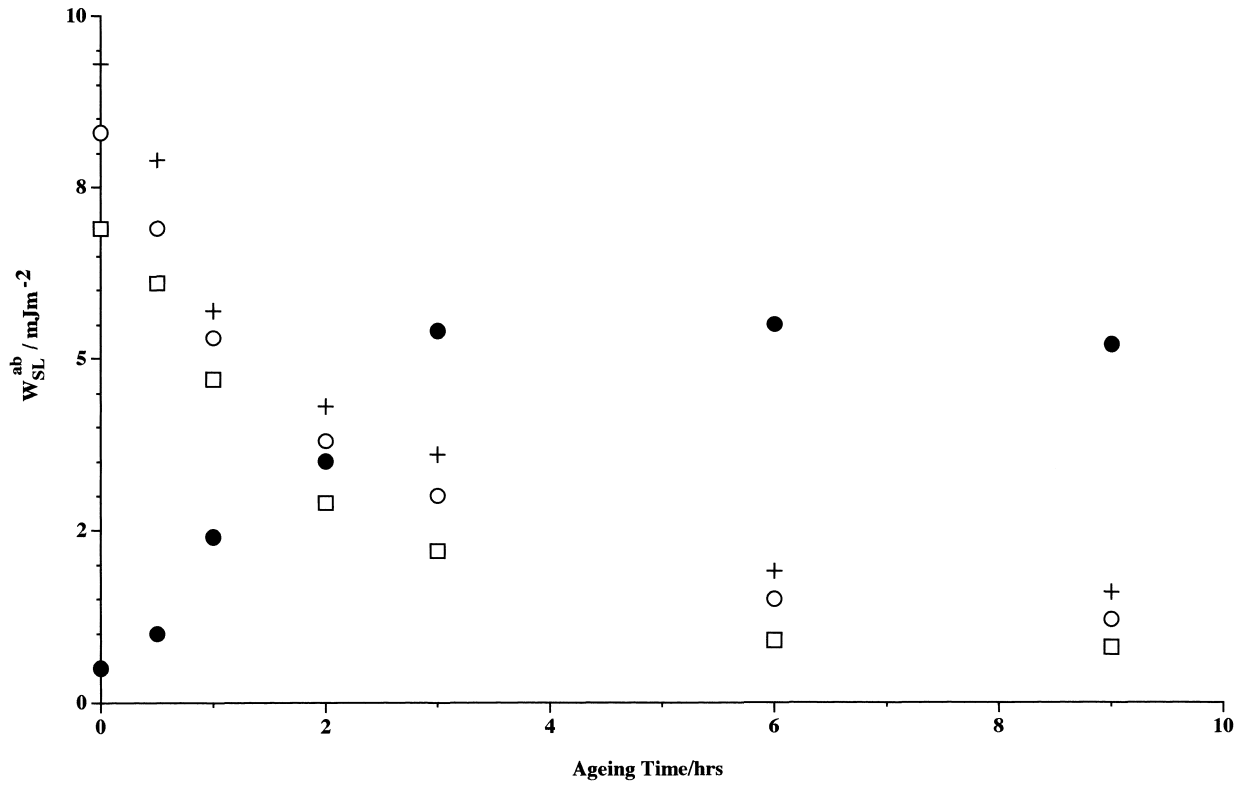
Fig. 8. Acid–base work of adhesion of DMSO on PHB cast against PET (+), glass (W), mica (A) and mercury (X), as a function of polymer ageing time.
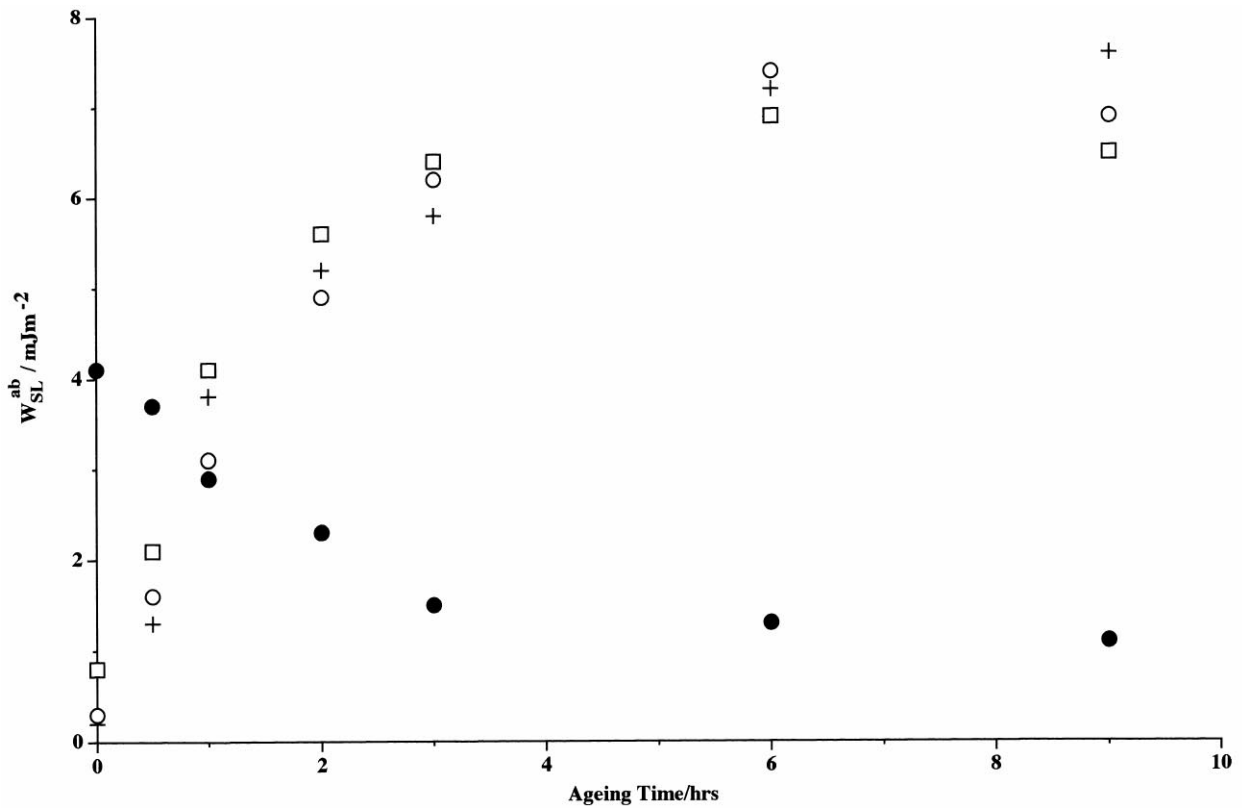

Fig. 9. Acid–base work of adhesion of TCP on PHB cast against PET (+), glass (W), mica (A) and mercury (X), as a function of polymer ageing time.

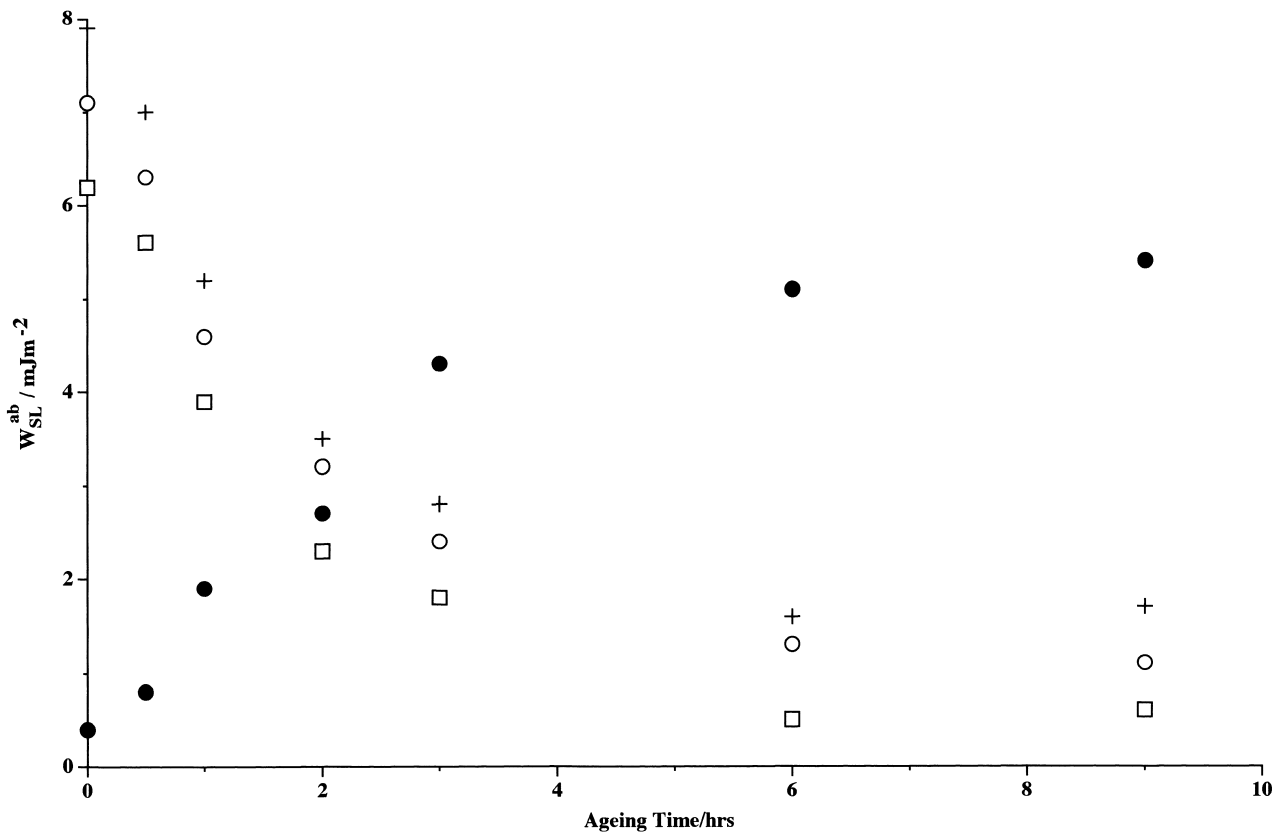*R. Smith, R. Pitrola / Polymer 41 (2000) 9111–9122*

Fig. 10. Acid–base work of adhesion of DMSO on PHB–HV cast against PET (+), glass (☐), mica (○) and mercury (●), as a function of polymer ageing time.
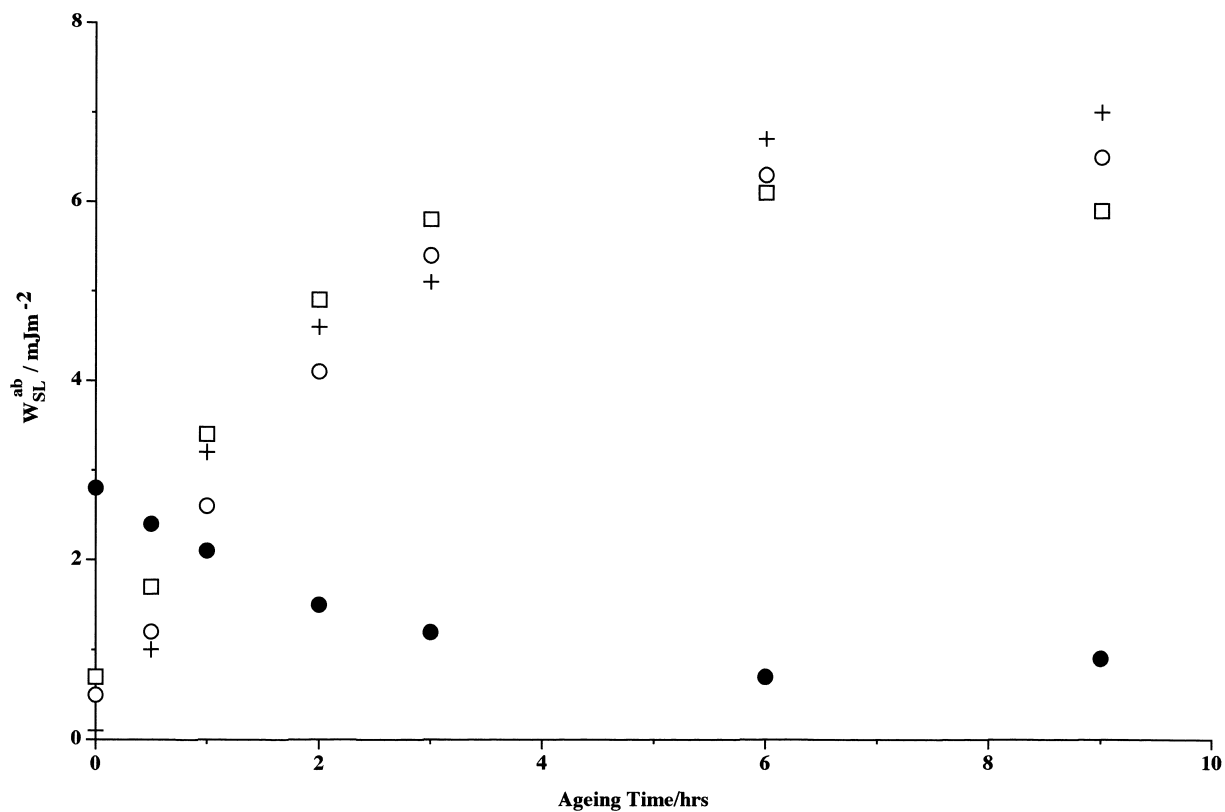

Fig. 11. Acid–base work of adhesion of TCP on PHB–HV cast against PET (+), glass (☐), mica (○) and mercury (●), as a function of polymer ageing time.
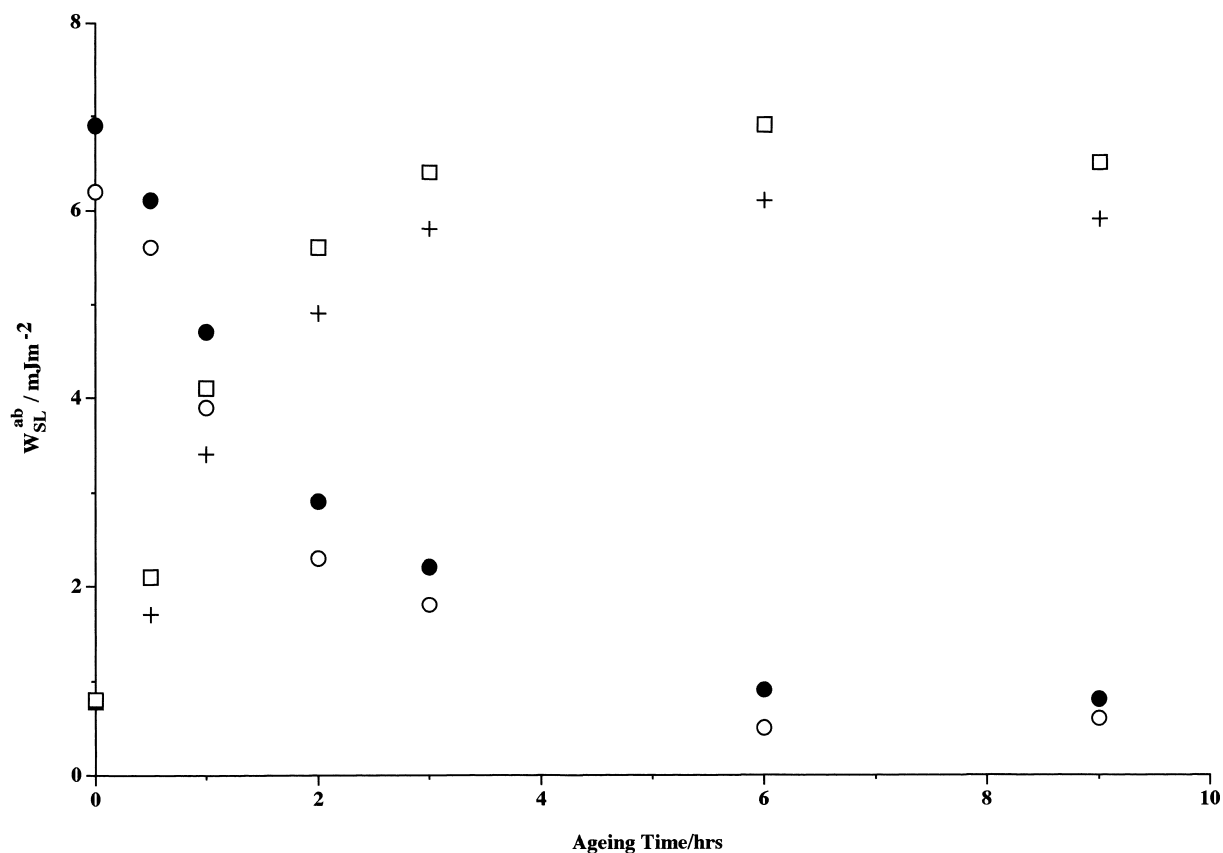
Fig. 12. Comparison of the acid/base work of adhesion of PHB and PHB–HV cast against mica. PHB/DMSO (X), PHB–HV/DMSO (W), PHB/TCP (A), PHB–HV/TCP (+).

in particular, time dependency and the influence that the acid/base nature of the substrate has in determining the characteristics of the resulting polymer surface. Fig. 12 shows that there is a difference in behaviour between PHB and PHB/HV. As indicated above, mica is a basic substrate that would give rise to an acidic polyester surface, Fig. 12 indicates that the acidic nature of the PHB surface is greater than that observed for PHB/HV. This may be associated with the larger side chain present in the HV moiety.

As an example, typical of all the polyesters in this study, Fig. 13 shows the acid/base behaviour of PHB cast against PTFE. As can be seen there is no evidence of time-dependent behaviour but the substrate still influences the acid/base character of the polyester surface.

Fig. 14 shows typical behaviour resulting from casting against nitrogen (free surface)

The acid/base nature of the equilibrium polyester surface can be determined from these results and values are given in Tables 2 and 3. For a particular casting substrate it can be seen that the equilibrium acid/base work of adhesion between a polyester surface and an acidic liquid decreases in the order PDLLA; PLLA; PHB; P(HB–20%HV). However, the equilibrium acid–base interaction energy with basic liquids (DMSO and DMF) shows little change along the above polymer series.

For a particular polyester surface/test liquid pair, the equilibrium acid/base work of adhesion depends on the substrate type used during solution casting (Tables 2 and 3). That is, the long term acid/base nature of the polyester surface is influenced by the acid–base surface characteristics of the original casting substrate.

It is generally accepted that polymer molecules with sufficient molecular mobility will change their surface orientation in response to the environment to minimise interfacial free energy. Surface molecular orientations leading to relaxation and re-equilibration of some polymer surface properties such as contact angle, surface free energy and work of adhesion have been generally demonstrated [17–25]. Furthermore, rigid polymers such as poly(methyl methacrylate) and polystyrene also display some surface re-orientation at the polymer–water interface[26], presumably due to segmental chain mobility activated near room temperature with water plasticisation of the interfacial region.

The wettability and measured adhesion of chemically oxidised polyethylene has been investigated by Baszkin et al. [18–20] who observed a decrease in wettability and joint strength at temperatures sufficiently high to permit some molecular mobility. This effect was attributed to surface re-orientation of polar groups (mainly carbonyls) into the
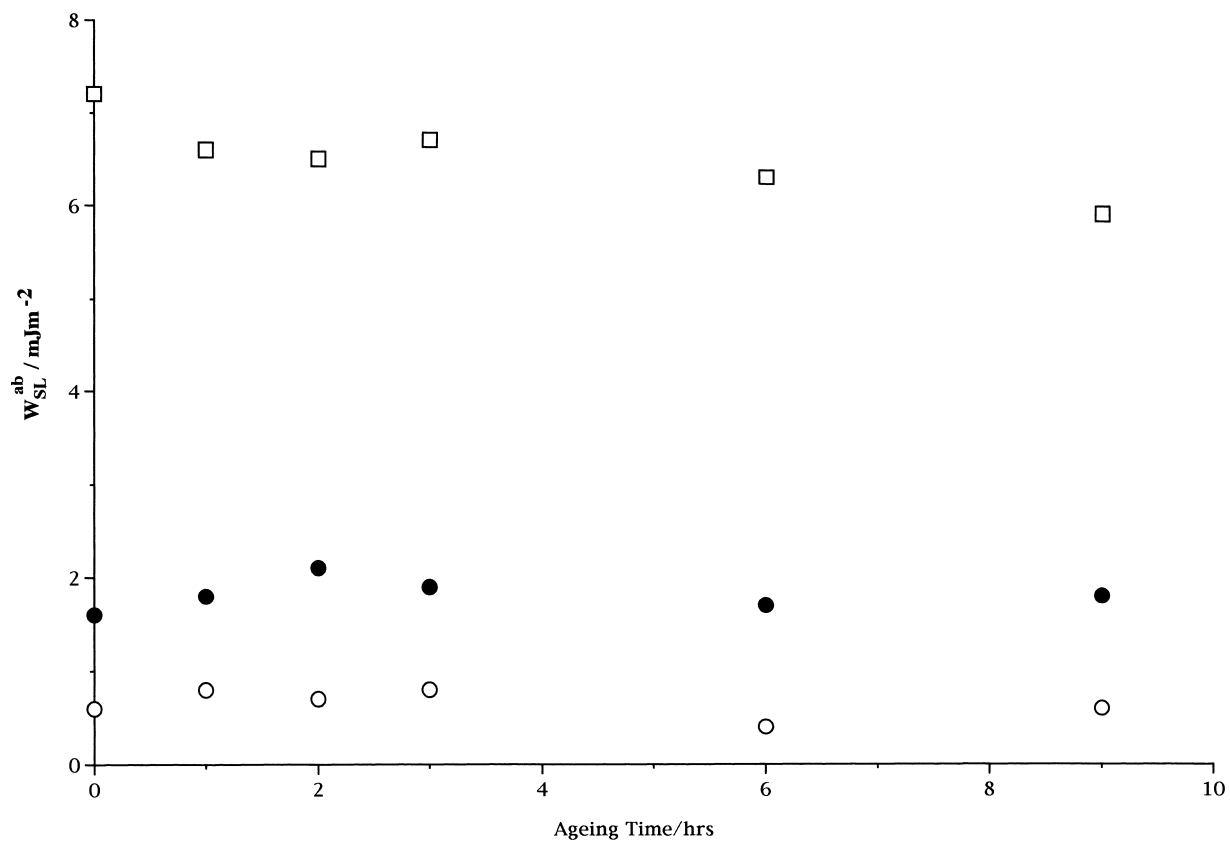
Fig. 13. Acid/base work of adhesion of DMSO (X), DMF (W) and TCP (A) on PHB cast against PTFE, as a function of ageing time.
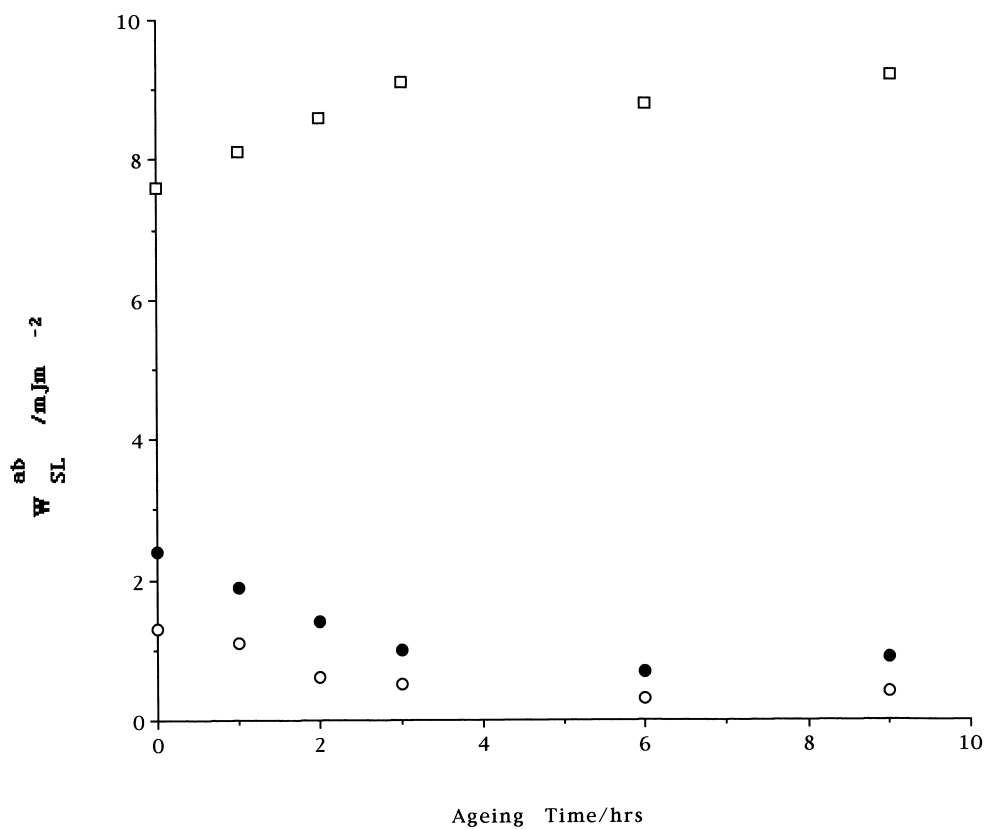

Fig. 14. Acid/base work of adhesion of DMSO (X), DMF (W) and TCP (A) on PHB cast against nitrogen, as a function of ageing time.

Table 2
Equilibrium acid/base work of adhesion between a polyester surface, cast against a number of substrates and TCP

Polyester surface	Equilibrium values of W_{SL}^{ab} (mJ m^{-2})						
	Al	Hg	Glass	Mica	PET	PTFE	N$_2$
PDLLA	3.3	3.6	9.4	8.3	9.1	7.4	10.2
PLLA	2.8	2.7	8.8	7.6	8.3	6.5	9.2
PHB	1.4	1.1	6.9	6.5	7.6	5.9	7.3
PHB/HV	0.5	0.9	6.5	5.9	7.0	5.3	6.8

bulk, leading to a less hydrophilic polyethylene surface. Similarly, a loss of surface polarity and self adhesion has been observed upon heating corona treated PET film [27], presumably due to re-orientation of surface polar groups. It is clear that polymer interfacial adhesion (and cell adhesion) is influenced by polar groups changing their orientation at the polymer surface.

Zhang et al. [28] observed a contact angle change of approximately 15° for a polyurethane surface after immersion in water over a period of 25 h, indicating surface restructuring in response to a change in environment. Similar behaviour was observed by Pike et al. [29] using dynamic contact angle measurements where hysteresis was observed indicating that the polymer surface rearranged in response to prolonged contact with water. They also observed that the molecular weight of the soft block (the flexible segment) had a controlling influence on the degree of hysteresis. In a study on a series of polyvinyl alkylates, Kasemura et al. [30] observed large contact angle hysterisis for polymers with side chains of between 6 and 12 carbon atoms long, explained by surface molecular mobility.

The present work demonstrates that polymer surface re-orientation can be monitored by contact angle/work of adhesion measurements using model acidic and basic liquids. A polyester molecule contains both acidic and basic sites due to the presence of the ester group itself. Our study has shown that an initially acidic polyester surface, obtained by casting against a basic glass surface, would interact strongly with basic test liquids. As expected, this acidic polyester surface showed negligible acid–base interactions with acidic test liquids, however, the equilibrium polyester surface showed strong acid–base interactions with acidic liquids but low acid–base interaction energies were observed against basic test liquids. This

suggests that the equilibrium polyester surface in air is naturally basic in character, an observation borne out in Fig. 14, where the surface of PHB cast against nitrogen showed an essentially high interaction energy with an acidic liquid (TCP). Basic liquids (DMSO and DMF) both showed very low interaction energies with this surface.

The glass transition temperatures of all the polyesters used in this study were close to room temperature, suggesting the possibility of chain mobility, particularly at the surface. The observed time dependence of the acid–base work of adhesion is thus interpreted in terms of orientation of surface acidic or basic sites along the polyester chain.

In summary, the results of this study suggest that the surface properties of polyesters, and perhaps polymers in general, are time and environment dependent. The surface characteristics of the casting substrate are very important including both chemical and structural properties.

4. Conclusions

The acid–base interaction energies of a number of simple polyesters have been calculated from contact angle measurements using acidic and basic liquids on solution cast films. The acid–base nature of the substrate has been shown to influence the acid–base characteristics of the polymer surface. The acid–base nature of the polymer surface changes with time reaching an equilibrium value in approximately 10 h, providing evidence of polymer surface mobility and re-orientation.

Table 3
Equilibrium acid/base work of adhesion between a polyester surface, cast against a number of substrates and DMSO

Polyester surface	Equilibrium values of W_{SL}^{ab} (mJ m^{-2})						
	Al	Hg	Glass	Mica	PET	PTFE	N$_2$
PDLLA	5.5	4.8	1.5	0.8	1.9	1.0	1.1
PLLA	5.8	4.9	1.4	1.1	1.7	1.2	0.9
PHB	6.0	5.2	1.2	0.8	1.6	1.7	1.3
PHB/HV	6.3	5.4	1.1	0.6	1.7	1.4	1.5

References

[1] Baier RE. Surface properties influencing biological adhesion. In: Manly RS, editor. Adhesion in biological systems, New York: Academic Press, 1970. p. 15–48.

[2] Grinnell F. Cellular adhesiveness and extracellular substrata. Int Rev Cytol 1978;53:65–144.

[3] Birdi KS. Cell adhesion on solids and the role of surface forces. J Theor Biol 1981;93:1–5.

[4] Van der Valk P, van Pelt AWJ, Busscher HJ, de Jong HP, Wildevuur CRH, Arends J. Interaction of fibroblasts and polymer surfaces: relationship between surface free energy and fibroblast spreading. J Biomed Mater Res 1983;17:807–17.

[5] Lyndon MJ. Synthetic hydrogels as substrates for cell adhesion studies . Br Polym J 1986;18:22–7.

[6] Lewis GN. Valence and the structure of atoms and molecules. New York: Chemical Cataloguing Co, 1923 (p. 142).

[7] Fowkes FM. In: Mittal KL, editor. Acid base interactions in polymer adhesion, Physicochemical aspects of polymer surfaces, vol. 2. New York: Plenum Press, 1983. p. 583–603.

[8] Fowkes FM. Interface acid–base/charge transfer properties. In: Andrade JD, editor. Surface chemistry and physics, Surface and interfacial aspects of biomedical polymers, vol. 1. New York: Plenum Press, 1987. p. 337–72.

[9] Fowkes FM, Tischler DO, Wolfe JA, Lannigan LA, Ademu-John CM, Halliwell MJ. Acid base complexes of polymers. J Polym Sci: Polym Chem 1984;22:547–66.

[10] Calgut P, Pitrola R, Waite I, Doyle C, Smith R. Histological

evaluation of bio-degradable and non-degradable membranes placed transcutaneously in rats. J Clin. Periodontol 1991;18:581–6.

[11] Young T. Proc R Soc London 1804.

[12] Young T. Philos Trans R Soc London 1805;95:65.

[13] Dupre A. Theorie mecanique de la chaleur. Paris, 1869. p. 368.

[14] Kaelble DH. Physical chemistry of adhesion. New York: Wiley/Interscience, 1971.

[15] Wu S. Polymer interface and adhesion. New York: Marcel Dekker, 1982.

[16] Smith R, Pitrola R. Influence of casting substrate on the surface free energy of various polyesters. Submitted for publication.

[17] Holly FJ, Refojo MF. Wettability of hydrogels. I. Poly(2-hydroxyethyl methacrylate). J Biomed Mater Res 1975;9:315–26.

[18] Baszkin A, Nishino M, Ter-Minassian-Saraga L. Solid liquid adhesion of oxidised polyethylene films:effect of temperature. J Colloid Interface Sci 1976;54:317–28.

[19] Baszkin A, Nishino M, Ter-Minassian-Saraga L. Solid liquid adhesion of oxidised polyethylene films: effect of temperature on polar forces. J Colloid Interface Sci 1977;59:516–24.

[20] Baszkin A, Ter-Minassian-Saraga L. Effect of surface polarity on self adhesion of polymers. Polymer 1978;19:1083–8.

[21] Pennings JFM, Bosman B. Relaxation of the surface energy of solid polymers. Colloid Polym Sci 1979;257:720–4.

[22] Briggs D, Rance DG, Kendall CR, Blythe AR. Surface modification of poly(ethyleneterephthalate) by electrical discharge treatment. Polymer 1980;21:895–900.

[23] Yasuda H, Sharma AK, Yasuda T. Effect of orientation and mobility of polymer molecules at surfaces on contact angle and its hysteresis. J Polym Sci: Polym Phys 1981;19:1285–91.

[24] Rance DG. Thermodynamics of wetting from its molecular basis to technological application. In: Brewis DM, editor. Surface analysis and pretreatment of plastics and metals, London: Applied Science, 1982. p. 121–52.

[25] McCarthy TJ. Polymer surface modification by diffusion of functional groups from the bulk to the surface. Org Coat Appl Polym Sci Proc 1983;48:520–2.

[26] Good RJ, Kotsidas ED. The contact angle of water on polystyrene:a study of the cause of hysteresis. J Colloid Interface Sci 1978;66: 360–2.

[27] Owens DK. The mechanism of corona and ultra violet light induced self adhesion of poly(ethyleneterephthalate) film. J Appl Polym Sci 1975;19:3315–26.

[28] Zhang D, Ward RS, Shen YR, Somorjai GA. Environment induced surface structural changes of a polymer: an in situ spectroscopic study. J Phys Chem B 1997;101:9060–4.

[29] Pike JK, Ho T, Wynne KJ. Water induced surface rearrangements of (PDMS-urea urethane) segmented block polymers. Chem Mater 1996;8:856–60.

[30] Kasemura T, Takahashi S, Nakame N, Maegawa T. Surface dynamics for poly(vinyl alkylates) via dynamic contact angle and surface tension relaxation. Polymer 1996;37:3659–64.