

# Influence of Casting Substrate on the Surface Free Energy of Various Polyesters

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**ABSTRACT:** The surface free energies of various polyester surfaces have been determined from contact angle measurements using several liquid types. The geometric mean, the harmonic mean, and Fowkes' methods for obtaining the components of surface free energy have been compared for poly(L-lactic acid) (PLLA), poly(DL-lactic acid) (PDLLA), poly(hydroxybutyrate) (PHB), and poly(hydroxybutyrate-hydroxyvalerate) (PHB–HV) copolymers. Polymer films were obtained by solution casting onto a number of smooth substrates, ranging from high-energy surfaces (aluminum, mercury, glass, and freshly cleaved mica) to low-energy surfaces [poly(ethyleneterephthalate) (PET), polytetrafluoroethylene (PTFE), and air]. Results show that the dispersion and polar surface free energy components of polyester surfaces cast against high surface energy (hydrophilic) substrates decrease with aging time toward a stable value. However, when cast against low surface energy substrates, the surface free energy of the resulting polymer/substrate-contacting surface was independent of aging time. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 997–1008, 2002

**Key words:** surface energy; degradable polymers; geometric mean; harmonic mean; Fowkes' method

## INTRODUCTION

The surface properties of polymers are important in many applications, for example, interfacial adhesion, friction, and wear.<sup>1,2</sup> In the biomedical field, the biocompatibility of polymers is critically dependent on surface properties, particularly when in contact with blood. Processes such as cell adhesion and protein adsorption on polymer surfaces are generally accepted to be influenced by polar and dispersion components of surface free energy.

Contact angle measurements have been widely used to determine physicochemical properties of solid surfaces. Indeed, these measurements can

be employed to monitor the surface properties of polymers, for example, degree of wetting, critical surface tension, dispersive and polar surface free energies, acid–base surface interactions, surface crystallinity, surface orientation of functional groups, surface roughness, and surface contamination.

A number of spectroscopic techniques such as X-ray photoelectron spectroscopy (XPS or ESCA), secondary ion mass spectroscopy (SIMS), ion-scattering spectroscopy (ISS), and Fourier transform infrared–multiple internal reflection spectroscopy (FTIR–MIR) are commonly employed to characterize solid surfaces. The disadvantage of techniques such as XPS or SIMS is that information regarding the orientation of functional groups at the surface is lost because reorientation may occur during sample preparation or in the instrument vacuum chambers, especially under

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bombarding X-rays, electrons, or ions. Thus, such surface analytical techniques, although invaluable as surface characterization tools, are generally less suited to study the orientation of organic functional groups at surfaces. Contact angle measurements, however, probe the first molecular layer of a solid surface and, indeed, have been used to monitor the reorientation of molecules at polymer surfaces.<sup>3-5</sup>

The aim of the present work was to characterize a number of solution-cast polyester film surfaces in terms of surface free energy and to relate this to the surface free energy of the casting substrate. These films were then evaluated in terms of their potential use in guided tissue regeneration in the periodontal field.<sup>6</sup> The polar and dispersive surface free energies were estimated using three different methods: geometric mean, harmonic mean, and Fowkes' methods.

### Estimation of Surface Free Energy of Polymers

The work of adhesion between a liquid and a solid surface is given by the combined Young-Dupre equation<sup>7,8</sup>:

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

where  $\gamma_L$  is the surface tension of the liquid and  $\theta$  is the equilibrium (Young) contact angle of the liquid on the solid surface.

In eq. (1), the equilibrium spreading pressure of the vapor adsorbed on the solid surface was neglected, which is generally true for liquids with finite contact angles on smooth, homogeneous, low-energy surfaces such as polymers.<sup>1,2</sup>

A number of methods are available for converting contact angle data into surface free energy. Those used in this study—geometric mean, harmonic mean, and Fowkes' methods—are commonly used to obtain estimates of the surface free energy of low-energy solids.

### Fowkes' Method

Provided only London dispersion forces operate between two contacting phases *S* and *L* then, according to Fowkes,<sup>9</sup> the work of adhesion is given by eq. (2):

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

Clearly, expressions (1) and (2) are equivalent, so that

$$\gamma_S^d = \frac{\gamma_L^2(1 + \cos \theta)^2}{4\gamma_L^d} \quad (3)$$

Hence, the dispersion component of surface free energy of a solid surface  $\gamma_S^d$  can be estimated from expression (3) through a single contact angle measurement, provided only dispersion interactions act between solid and liquid. This method is, therefore, applicable only in cases where nonpolar liquids ( $\gamma_L^d \approx \gamma_L$ ) are used on polar solids or polar liquids are used on nonpolar solids ( $\gamma_S^d \approx \gamma_S$ ).

### Geometric Mean Method

According to Owens and Wendt<sup>10</sup> and Kaelble,<sup>1</sup> the work of adhesion between a solid and liquid is given by

$$W_{SL} = 2(\gamma_S^d \gamma_L^d)^{1/2} + 2(\gamma_S^p \gamma_L^p)^{1/2} \quad (4)$$

where both dispersion (*d*) and polar (*p*) forces operate.

It can be seen that expressions (4) and (1) are equivalent, so that

$$\gamma_L(1 + \cos \theta) = 2(\gamma_S^d \gamma_L^d)^{1/2} + 2(\gamma_S^p \gamma_L^p)^{1/2} \quad (5)$$

Using this method it is necessary to measure the contact angle  $\theta$  of two liquids (with known dispersion and polar components) on a particular solid so that simultaneous equations are obtained, which can be solved for the dispersion and polar components of the surface energy of the given solid.

For two dissimilar liquids (*i*) and (*j*) on a particular solid, eq. (5) may be solved to yield the dispersion and polar components of the surface free energy of the solid. Kaelble<sup>1</sup> solved these equations by a determinant method:

$$D = \begin{vmatrix} (\gamma_L^d)_i^{1/2} & (\gamma_L^p)_i^{1/2} \\ (\gamma_L^d)_j^{1/2} & (\gamma_L^p)_j^{1/2} \end{vmatrix} \quad (6)$$

$$\gamma_S^d = \left[ \begin{vmatrix} \left(\frac{W_{SL}}{2}\right)_i & (\gamma_L^p)_i^{1/2} \\ \left(\frac{W_{SL}}{2}\right)_j & (\gamma_L^p)_j^{1/2} \end{vmatrix} \right]^2 / D^2 \quad (7)$$

$$\gamma_S^p = \left[ \begin{vmatrix} \left(\frac{W_{SL}}{2}\right)_i & (\gamma_L^d)_i^{1/2} \\ \left(\frac{W_{SL}}{2}\right)_j & (\gamma_L^d)_j^{1/2} \end{vmatrix} \right]^2 / D^2 \quad (8)$$

and found that the solution of eq. (5) was dependent on the value of  $D$  obtained from eq. (6). For example, when  $0 < D < 1$ , then  $D^2$ , the denominator in eqs. (7) and (8) is also small, leading to absurdly high values for surface free energy components.

### Harmonic Mean Method

The solid–liquid work of adhesion, where both dispersion and polar forces operate, can be predicted by the following harmonic mean<sup>2</sup>:

$$W_{SL} = \gamma_L(1 + \cos \theta) = \frac{4(\gamma_S^d \gamma_L^d)}{\gamma_S^d + \gamma_L^d} + \frac{4(\gamma_S^p \gamma_L^p)}{\gamma_S^p + \gamma_L^p} \quad (9)$$

As in the geometric mean method, it is necessary to measure the contact angle  $\theta$  of two different liquids on a particular solid so that simultaneous equations are obtained.

In this study, all three of the preceding methods were used, utilizing six different liquids, to obtain surface free energies of a number of polyester films. These films were obtained by solution casting against several substrates, which themselves had a range of different surface free energies. For comparison, commercial polyester films were also included and values obtained were compared to literature values.

## EXPERIMENTAL

The polyesters used in the present investigation were: poly(DL-lactic acid) (PDLLA), poly(L-lactic acid) (PLLA), poly(hydroxybutyrate) (PHB; Marlborough Biopolymers), poly(hydroxybutyrate-hydroxyvalerate) copolymers (PHB–HV), and poly(ethylene terephthalate) (PET; Melinex and Mylar) films.

All glassware was cleaned and dried at 100°C prior to use. Polymer films were prepared by casting from a 2 to 7% (w/v) solution of polyester in chloroform against the following clean, smooth surfaced substrates: glass, freshly cleaved mica (muscovite), aluminum, mercury, PET (Melinex or Mylar), and PTFE. After controlled evaporation of the solvent, all films were dried *in vacuo* at room temperature for 1 week to ensure removal of residual chloroform. The film was removed from its substrate immediately prior to contact angle measurement. Extreme care was taken to avoid tearing the film. The two sides of the resulting films will be referred to as the interfacial surface

(substrate side) and the free surface (air 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 onto the polyester surface with the aid of a micrometer syringe. The drop volume was gradually increased up to 0.1 to 0.5  $\mu\text{L}$  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. The temperature during measurements was  $22.5 \pm 1.0^\circ\text{C}$ . After measurements with a particular liquid, the syringe was carefully cleaned with acetone (analytical grade) and dried in an oven. To avoid contamination of one liquid by another, just prior to measurements, the syringe was cleaned with the test liquid at least 10 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 1 degree. 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. (10):

$$\tan\left(\frac{\theta}{2}\right) = \frac{2h}{D} \quad (10)$$

where  $h$  is the drop height,  $D$  is the base diameter, and  $\theta$  is the contact angle.

**Table I** Surface Tension Data of Liquids Used for Contact Angle Measurements

Number	Liquid	Surface Free Energy (mJ/m <sup>2</sup> )		
		Dispersion	Polar	Total
1	Water <sup>1,2</sup>	21.8	51.0	72.8
2	Glycerol <sup>1</sup>	37.0	26.4	63.4
3	Formamide <sup>1,2</sup>	39.5	18.7	58.2
4	Diiodomethane <sup>1,2</sup>	48.5	2.3	50.8
5	Ethylene Glycol <sup>11</sup>	29.3	19.0	48.3
6	1-Bromo-naphthalene <sup>12</sup>	44.6	0	44.6

**Table II Absolute Values of  $|D|$  for Liquid Pairs**

Liquid Pairs (i-j)	$ D $ (mJ/m <sup>2</sup> )
1-2	19.45
1-3	24.69
1-4	42.65
1-5	18.30
1-6	47.69
2-3	5.99
2-4	26.56
2-5	1.30
2-6	34.31
3-4	20.58
3-5	3.99
3-6	28.88
4-5	22.15
4-6	10.13
5-6	29.11

The liquids used for contact angle measurements were distilled water, glycerol, formamide, diiodomethane, ethylene glycol, and 1-bromonaphthalene; organic liquids were Gold Label (>99%) and were stored in the dark prior to commencement of experiments. The dispersion and polar components of surface tension of these liquids are listed in Table I. Liquid pairs that gave rise to values of  $D$  less than 10 mJ/m<sup>2</sup> [where  $D$  is the determinant in eq. (6)] were rejected. Absolute values for  $D$  are presented in Table II.

## RESULTS AND DISCUSSION

For comparative purposes, contact angle measurements were obtained from commercial samples of poly(ethyleneterephthalate) film, both Mylar and Melinex. The results, given in Table III, show good correlation with previously reported values.

An example of detailed surface energy results (for PHB cast against mica) are presented in Table IV. As can be seen, there was little variation in surface energy values obtained from different liquid pairs; however, the harmonic mean method gave higher values of the polar component compared to those of the geometric mean method. The surface free energies of each polymer studied, cast against all substrates used, are given in Table V. These values were obtained by the geometric mean method and represent what will be referred to as an "equilibrium" value. This equilibrium value was obtained from measurements taken several days after the dry film had been removed from its substrate.

For all three methods (geometric mean, harmonic mean, and Fowkes') and a particular casting substrate, the equilibrium dispersion component of surface free energy, a measure of hydrophobicity, increases in the order: PDLA; PLLA (MW = 50,000); PLLA (MW = 200,000); PHB; PHB-20%HV.

Contact angle measurements taken shortly after the films had completely dried showed an in-

**Table III Surface Free Energy Results for Commercial Samples of PET**

Method <sup>a</sup>	Smooth PET Surface	Equilibrium Surface Free Energy (mJ/m <sup>2</sup> )		
		Dispersion	Polar	Total
GM	Melinex	37.3 ± 3.5	3.6 ± 0.9	40.9 ± 2.8
GM	Mylar	39.4 ± 3.1	3.3 ± 1.0	42.7 ± 2.2
GM	Literature <sup>9</sup>	43.2	4.1	47.3
GM	Literature <sup>9</sup>	37.8	3.5	41.3
GM	Literature <sup>1</sup>	36.5 ± 3.0	2.9 ± 1.1	39.5 ± 1.9
GM	Literature <sup>13</sup>	41.8 ± 6.8	3.3 ± 2.8	45.1 ± 4.3
HM	Melinex	34.8 ± 3.2	8.4 ± 1.4	43.2 ± 2.0
HM	Mylar	35.8 ± 2.9	6.8 ± 1.2	42.6 ± 1.8
HM	Literature <sup>2</sup>	32.8	9.3	42.1
FM	Melinex	42.4 ± 2.1		
FM	Mylar	43.3 ± 2.2		
FM	Literature <sup>13</sup>	44.4		
FM	Literature <sup>2</sup>	43.1		

<sup>a</sup> GM = geometric mean; FM = Fowkes' method; HM = harmonic mean.

**Table IV Surface Energy Results for PHB Cast Against Mica<sup>a</sup>**

Liquids	Geometric Mean (mJ/m <sup>2</sup> )			Harmonic Mean (mJ/m <sup>2</sup> )		
	$\gamma_s^d$	$\gamma_s^p$	$\gamma_s$	$\gamma_s^d$	$\gamma_s^p$	$\gamma_s$
1-2	35.3	5.1	40.4	34.1	8.0	42.1
1-3	34.8	4.9	39.7	35.3	8.5	43.8
1-4	35.6	4.6	40.2	36.4	8.3	44.7
1-5	36.2	4.4	40.6	36.6	8.0	44.6
1-6	36.7	4.1	40.8	36.9	7.7	44.6
2-4	37.0	3.7	40.7	37.5	7.4	44.9
2-6	36.5	3.9	40.4	37.8	7.2	45.0
3-4	37.7	3.6	41.3	38.2	6.9	45.1
3-6	37.4	3.4	40.8	36.8	6.6	43.4
4-5	36.8	3.1	39.9	37.3	6.2	43.5
4-6	37.9	3.8	41.7	38.5	5.7	44.2
5-6	38.1	3.0	41.1	37.6	5.9	43.5
Mean	36.6	4.0	40.6	36.9	7.2	44.1
$\pm\sigma$	1.1	0.7	0.6	1.2	1.0	0.9

<sup>a</sup> Measurements taken at 22.5 ± 1.0°C.

interesting time-dependency phenomenon. Films cast against high surface energy substrates initially showed a relatively high value for both dispersion and polar components of surface free energy (for the interfacial surface). These values decreased over a period of about 12 h to a value that remained unchanged, even after several weeks, referred to previously as an equilibrium value. Films obtained from low surface energy substrates, however, showed no such time dependency—the initial values were the same as the “equilibrium” values. This was observed for all polymers in this study. Figures 1–3 clearly show this phenomenon for PDLLA, in which the graphs show individual components of surface free energy as well as a total value. Figures 4–11 represent data obtained on all other polymers studied;

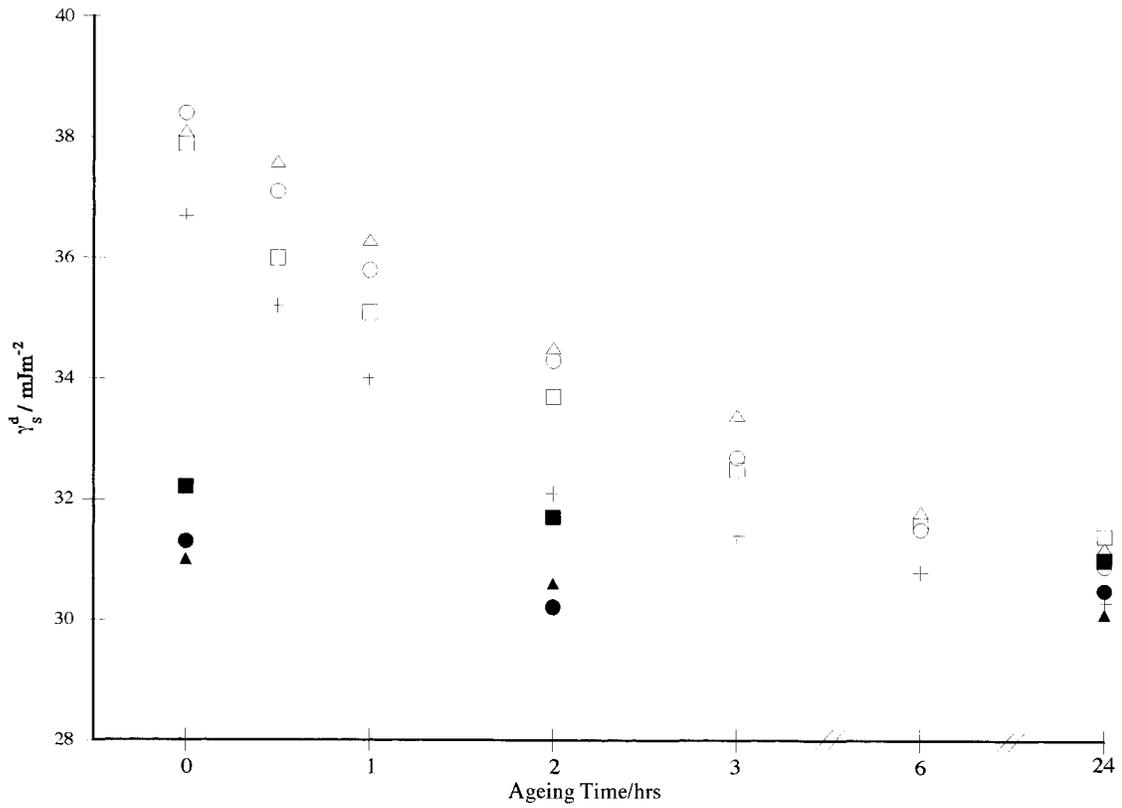
in these graphs, only the components of surface free energy are plotted. These graphs show that, in general, the greater the surface free energy of the substrate, the greater the initial value of surface free energy obtained for the interfacial polymer surface. It can also be seen that values for both polar and dispersion components obtained for interfacial polymer surfaces fall in decreasing order of substrate surface energy, that is, aluminum > mercury > glass > mica. In the majority of cases this order is retained throughout the period of time dependency.

It thus appears that the interfacial polymer surface retains an “imprint” of the substrate from which the film was obtained. This imprint slowly fades as molecules at the surface translate and rotate, eventually arriving at an equilibrium. It is

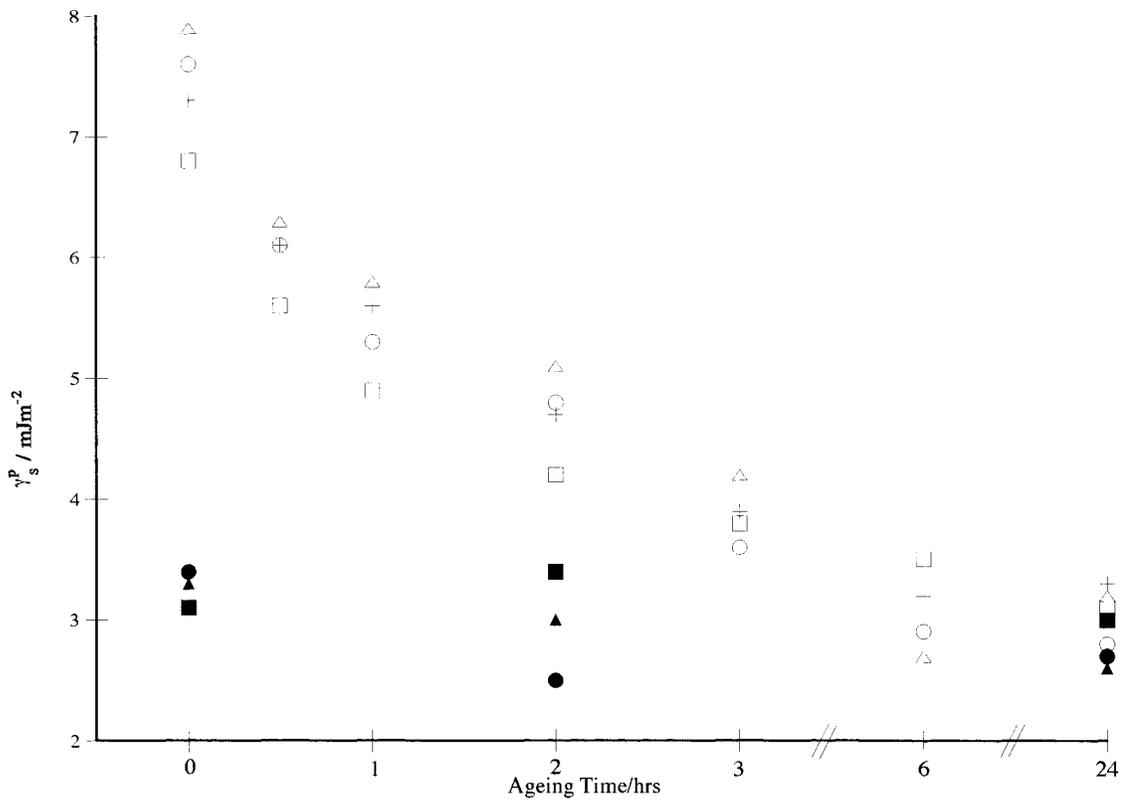
**Table V Surface Free Energy Results (mJ/m<sup>2</sup>) for All Polymers Cast Against All Substrates**

Polymer	Aluminum			Mercury			Glass			Mica			PET			PTFE		
	$\gamma_s^d$	$\gamma_s^p$	$\gamma_s$															
PDLLA	31.2	3.2	34.4	30.9	2.8	33.7	31.4	3.1	34.5	30.3	3.3	33.6	31.0	3.0	34.0	30.5	2.7	33.2
PLLA <sup>a</sup>	33.2	4.6	37.8	32.1	5.3	37.4	33.6	5.1	38.7	32.5	5.0	37.5	33.0	5.4	38.4	32.7	4.9	37.6
PLLA <sup>b</sup>	34.5	5.6	40.1	34.2	5.7	39.9	33.9	5.4	39.3	33.7	5.2	38.9	34.3	4.9	39.2	33.5	4.7	38.2
PHB	36.2	3.6	39.8	37.3	4.5	41.8	36.8	3.9	40.7	36.6	4.0	40.6	36.4	4.4	40.8	35.6	3.7	39.3
PHB/HV	37.7	2.7	40.4	38.1	3.8	41.9	37.0	3.2	40.2	36.9	3.4	40.3	36.8	3.1	39.9	36.5	2.9	39.4

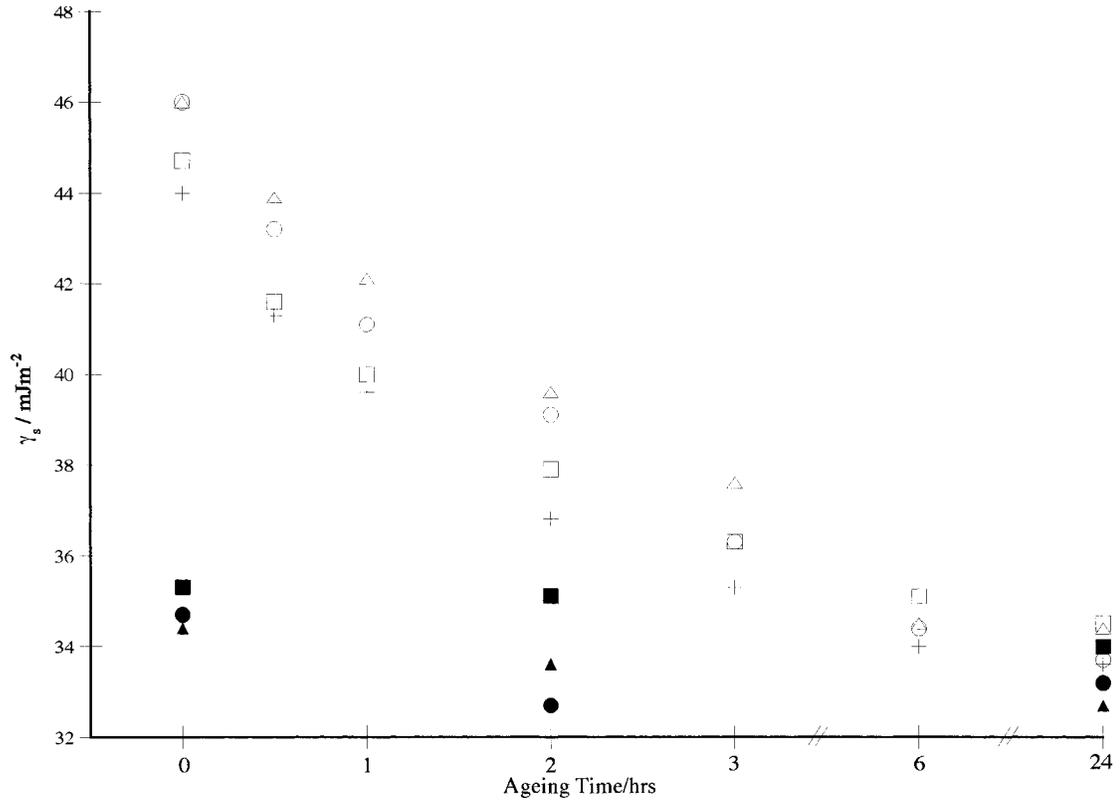
<sup>a</sup> MW = 50,000.<sup>b</sup> MW = 200,000.



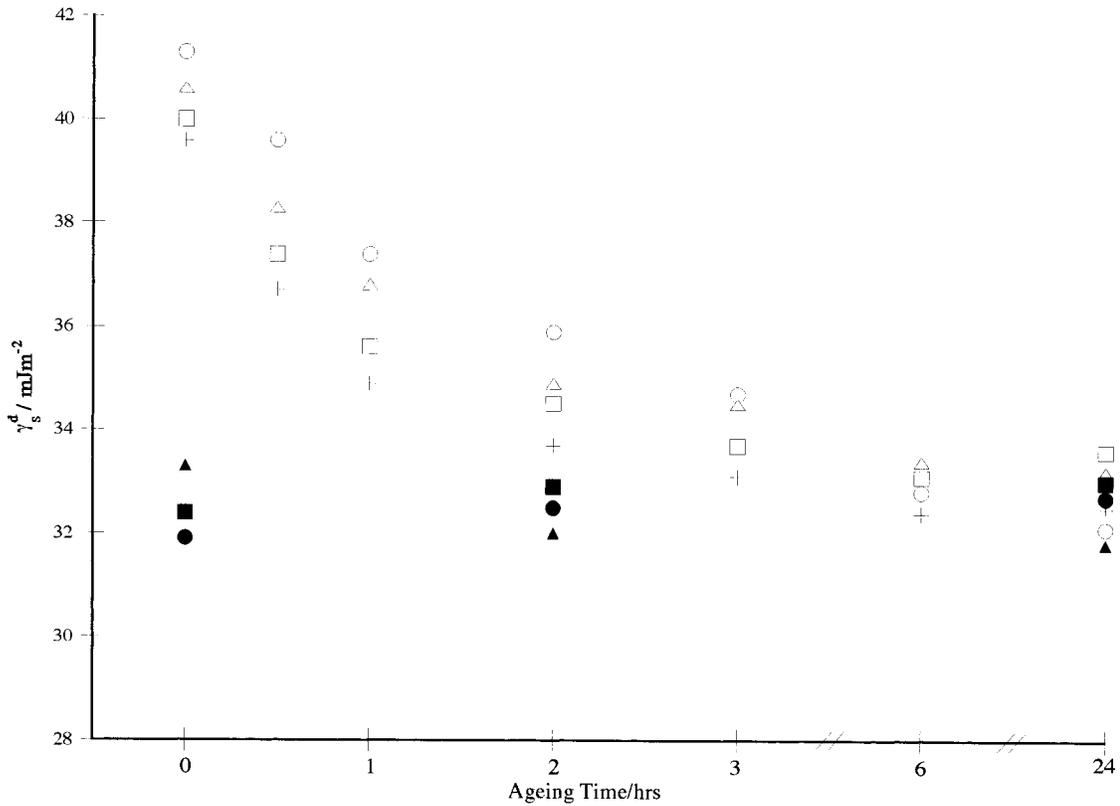
**Figure 1** Dispersion component of surface free energy versus aging time for PDLLA cast against: aluminum ( $\Delta$ ), mercury ( $\circ$ ), glass ( $\square$ ), mica ( $+$ ), PET ( $\blacksquare$ ), PTFE ( $\bullet$ ), and air ( $\blacktriangle$ ).



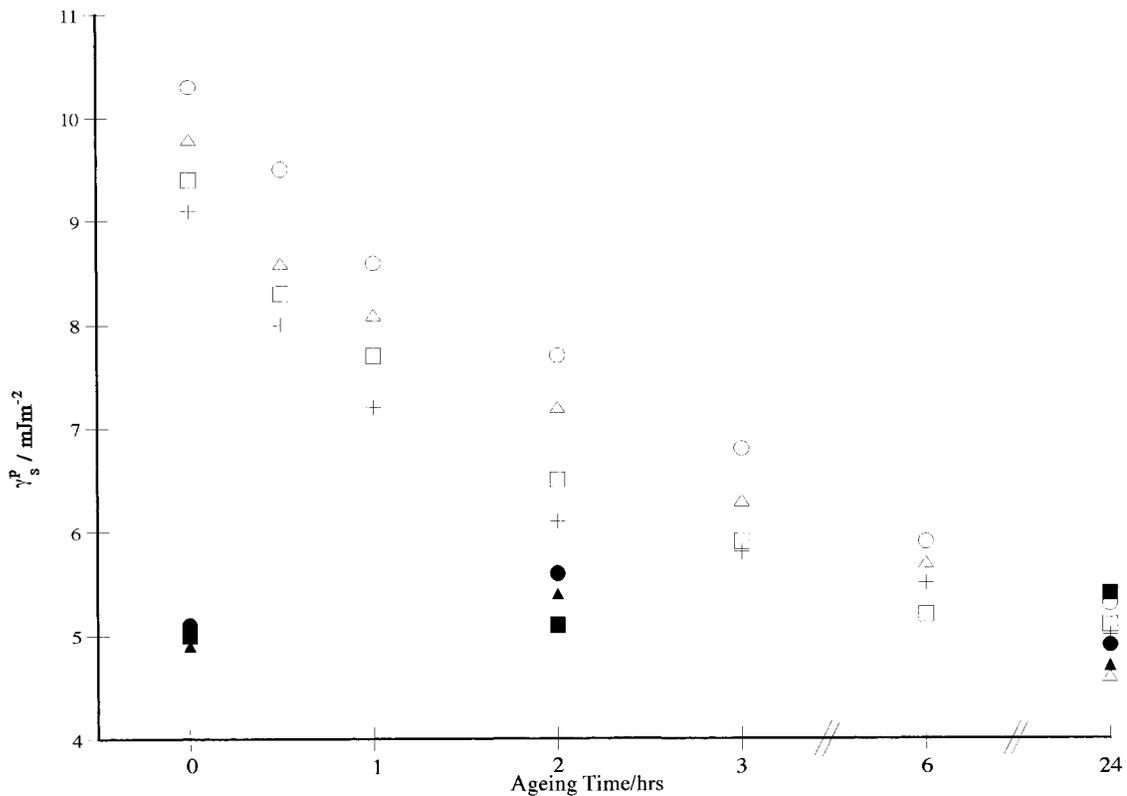
**Figure 2** Polar component of surface free energy versus aging time for PDLLA cast against: aluminum ( $\Delta$ ), mercury ( $\circ$ ), glass ( $\square$ ), mica ( $+$ ), PET ( $\blacksquare$ ), PTFE ( $\bullet$ ), and air ( $\blacktriangle$ ).



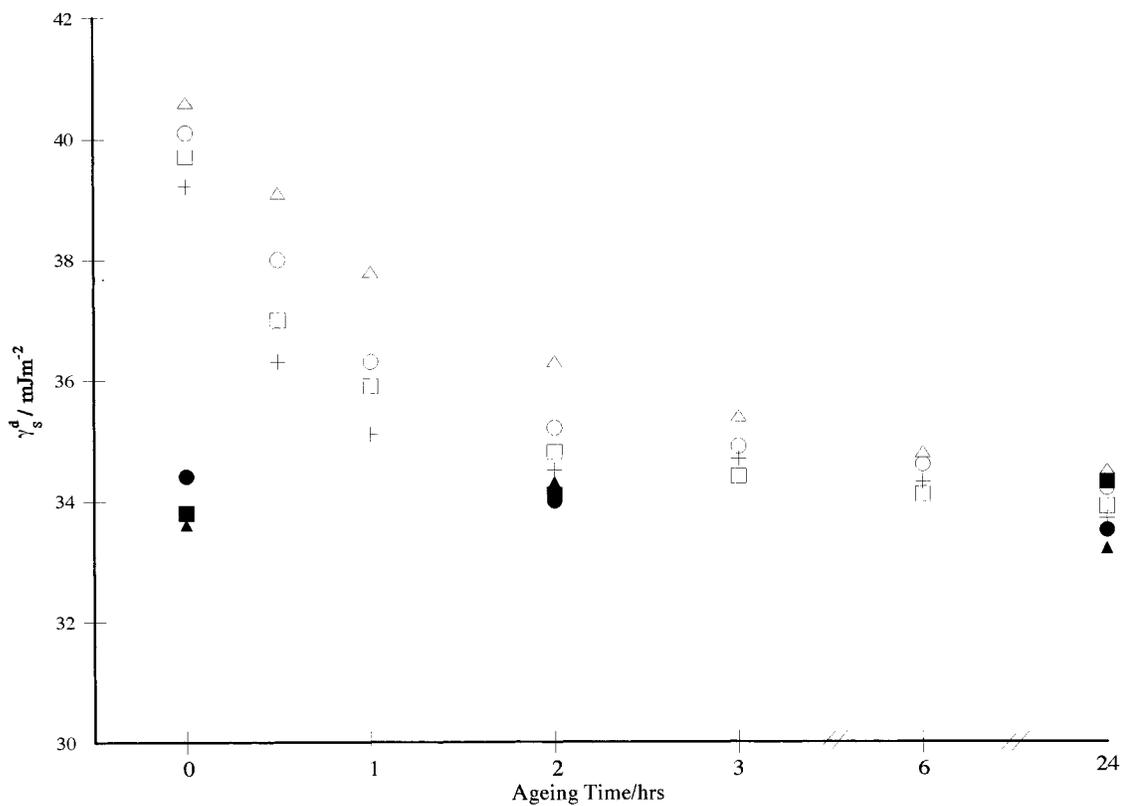
**Figure 3** Total surface free energy versus aging time for PDLLA cast against: aluminum ( $\Delta$ ), mercury ( $\circ$ ), glass ( $\square$ ), mica ( $+$ ), PET ( $\blacksquare$ ), PTFE ( $\bullet$ ), and air ( $\blacktriangle$ ).



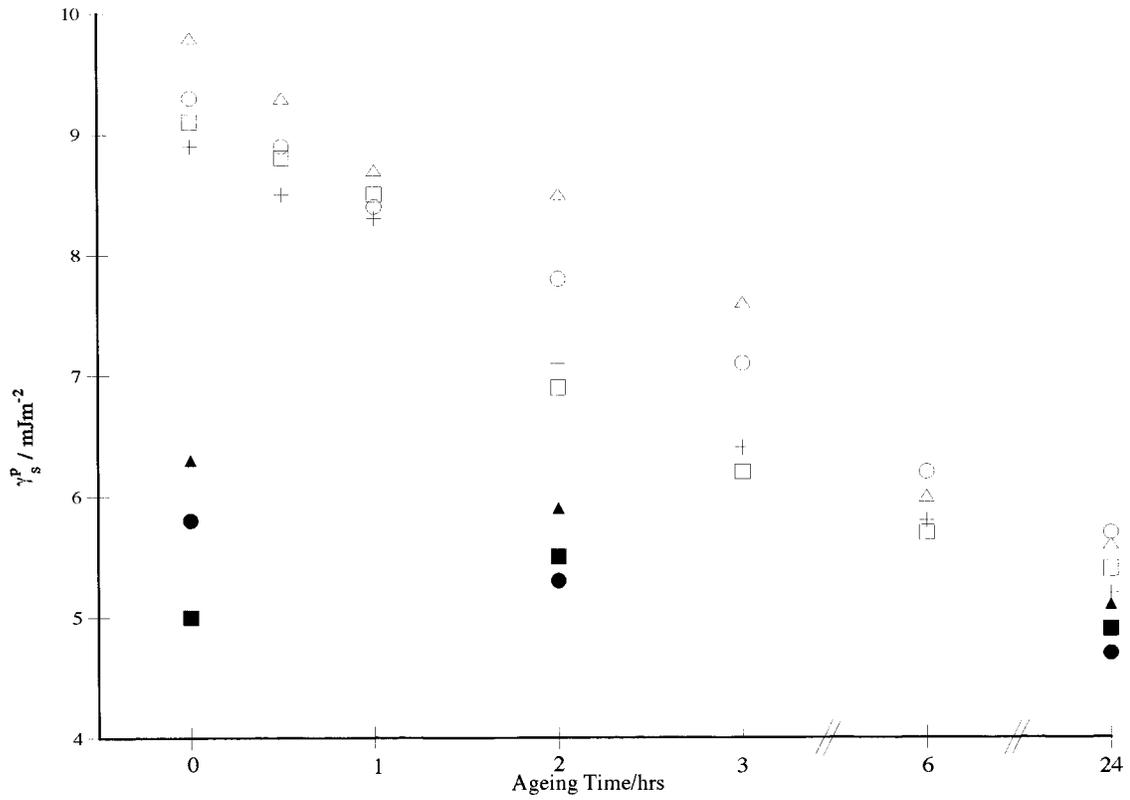
**Figure 4** Dispersion component of surface free energy versus aging time for PLLA (MW = 50,000) cast against: aluminum ( $\Delta$ ), mercury ( $\circ$ ), glass ( $\square$ ), mica ( $+$ ), PET ( $\blacksquare$ ), PTFE ( $\bullet$ ), and air ( $\blacktriangle$ ).



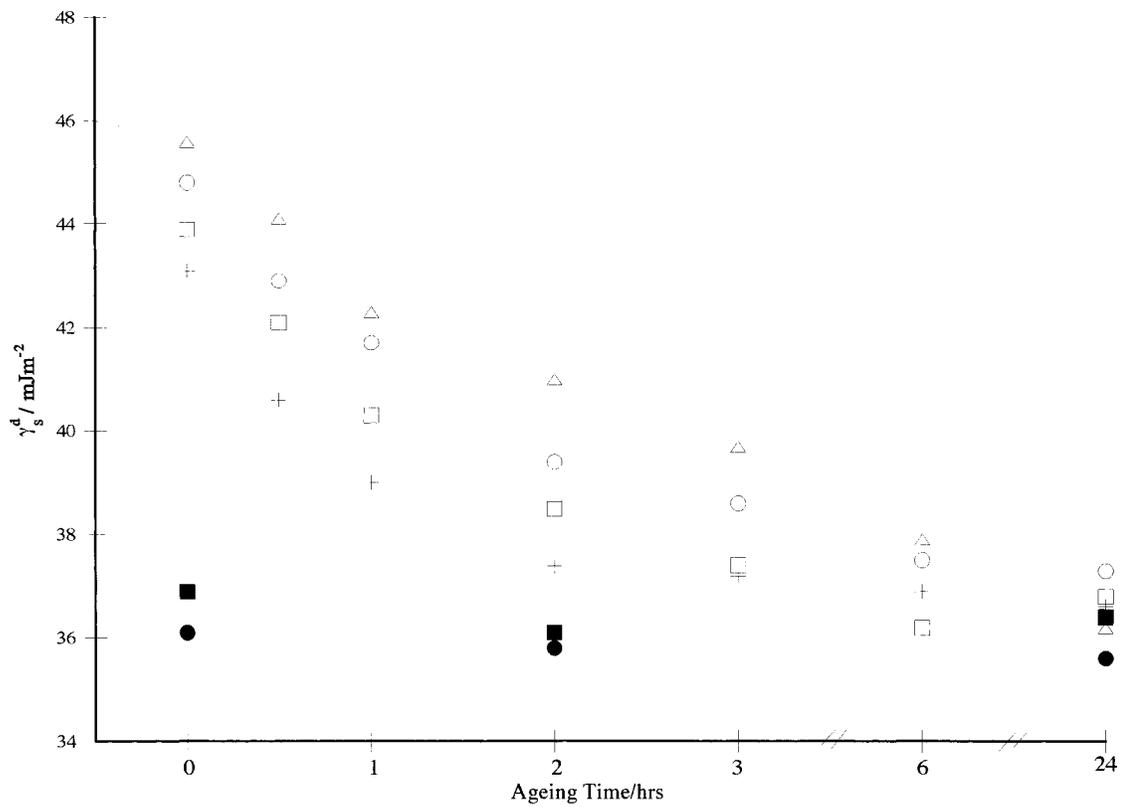
**Figure 5** Polar component of surface free energy versus aging time for PLLA (MW = 50,000) cast against: aluminum ( $\Delta$ ), mercury ( $\circ$ ), glass ( $\square$ ), mica ( $+$ ), PET ( $\blacksquare$ ), PTFE ( $\bullet$ ), and air ( $\blacktriangle$ ).



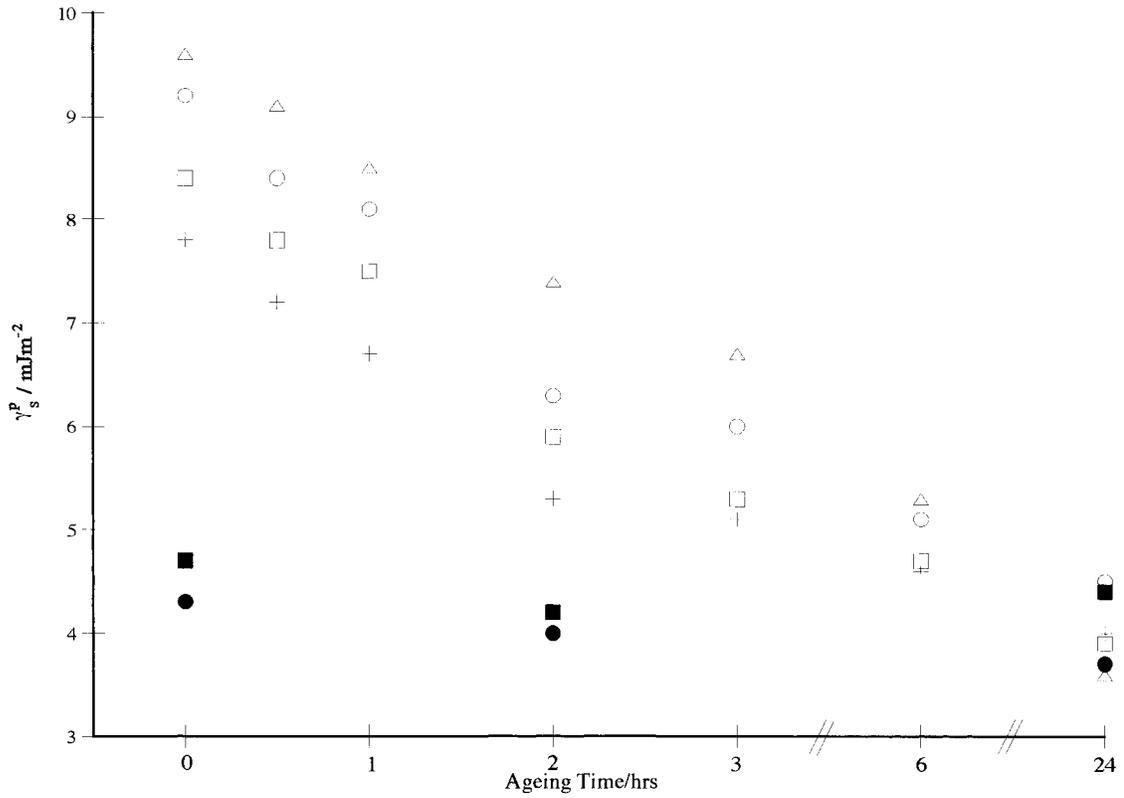
**Figure 6** Dispersion component of surface free energy versus aging time for PLLA (MW = 200,000) cast against: aluminum ( $\Delta$ ), mercury ( $\circ$ ), glass ( $\square$ ), mica ( $+$ ), PET ( $\blacksquare$ ), PTFE ( $\bullet$ ), and air ( $\blacktriangle$ ).



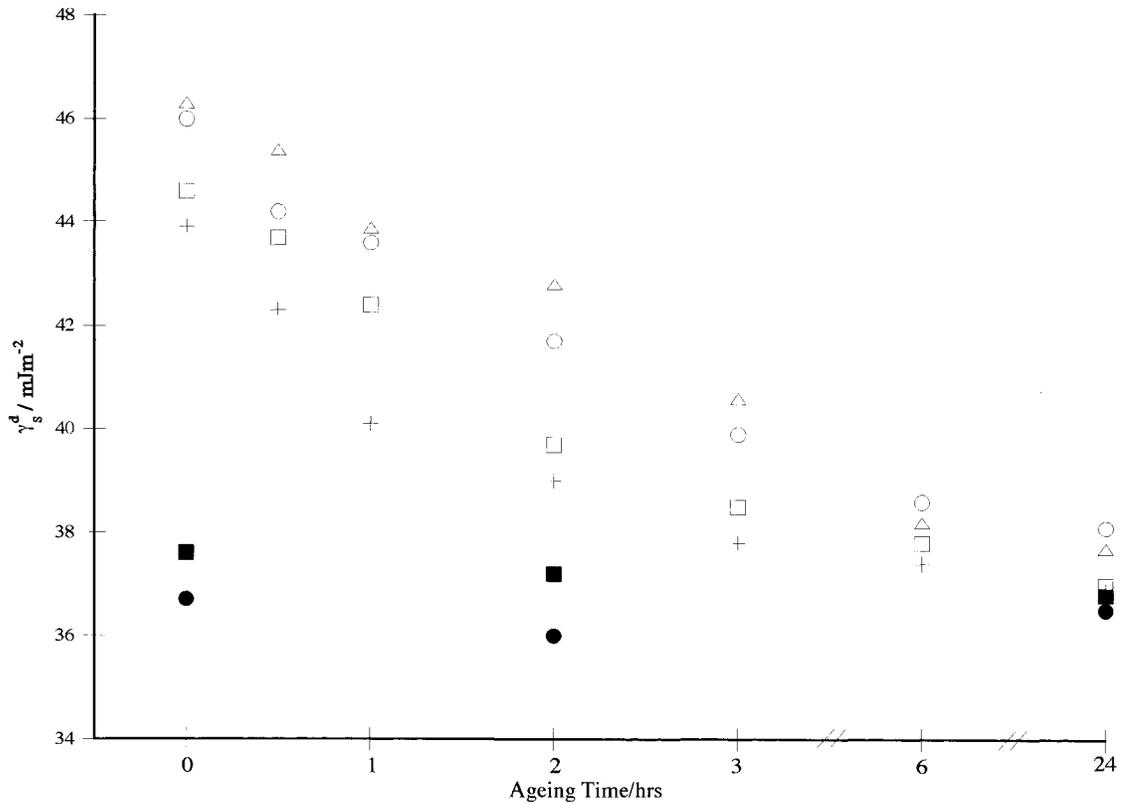
**Figure 7** Polar component of surface free energy versus aging time for PLLA (MW = 200,000) cast against: aluminum ( $\Delta$ ), mercury ( $\circ$ ), glass ( $\square$ ), mica ( $+$ ), PET ( $\blacksquare$ ), PTFE ( $\bullet$ ), and air ( $\blacktriangle$ ).



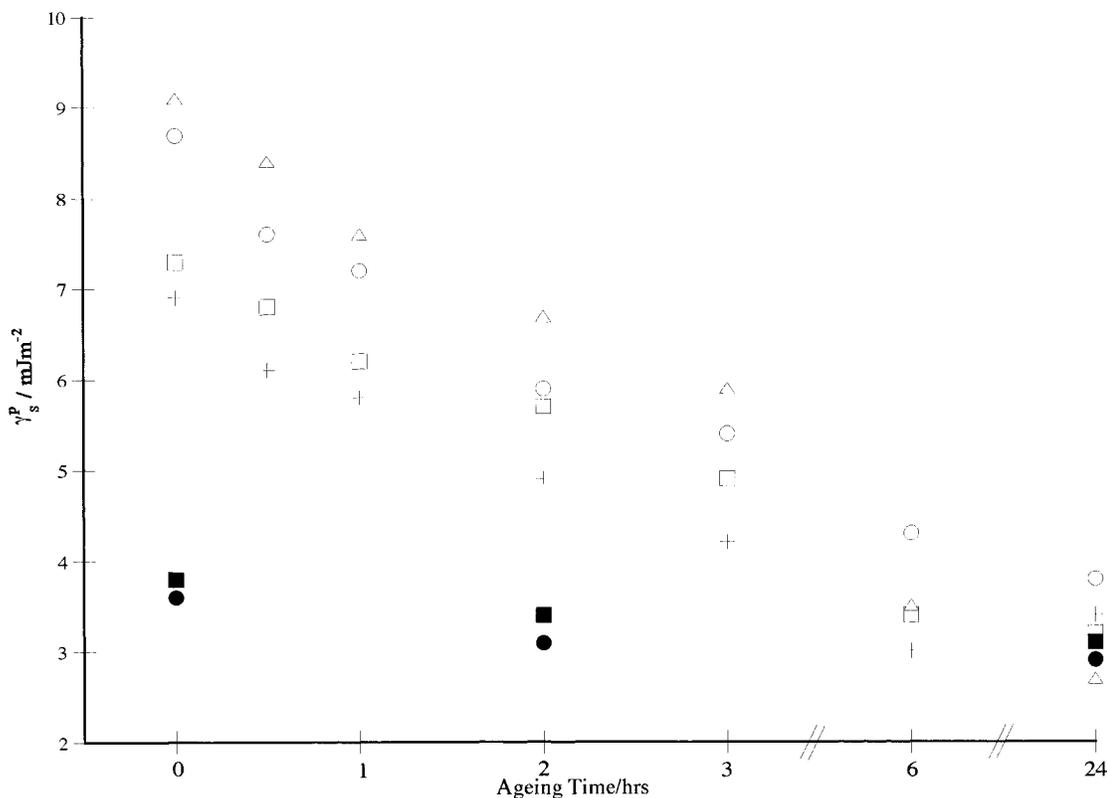
**Figure 8** Dispersion component of surface free energy versus aging time for PHB cast against: aluminum ( $\Delta$ ), mercury ( $\circ$ ), glass ( $\square$ ), mica ( $+$ ), PET ( $\blacksquare$ ), and PTFE ( $\bullet$ ).



**Figure 9** Polar component of surface free energy versus aging time for PHB cast against: aluminum ( $\Delta$ ), mercury ( $\circ$ ), glass ( $\square$ ), mica (+), PET ( $\blacksquare$ ), and PTFE ( $\bullet$ ).



**Figure 10** Dispersion component of surface free energy versus aging time for PHB-HV cast against: aluminum ( $\Delta$ ), mercury ( $\circ$ ), glass ( $\square$ ), mica (+), PET ( $\blacksquare$ ), and PTFE ( $\bullet$ ).



**Figure 11** Polar component of surface free energy versus aging time for PHB-HV cast against: aluminum ( $\Delta$ ), mercury ( $\circ$ ), glass ( $\square$ ), mica ( $+$ ), PET ( $\blacksquare$ ), and PTFE ( $\bullet$ ).

not clear from this study which part of the polymer molecule gives rise to this phenomenon, although from inspection of the repeat unit it is highly probable that the carbonyl group is implicated.

The wettability and measured adhesion of chemically oxidized polyethylene was previously investigated by Baszkin et al.,<sup>14-16</sup> who observed a decrease in wettability and joint strength at temperatures sufficiently high to permit some molecular mobility. This effect was attributed to surface reorientation of polar groups (mainly carbonyls) into the bulk, leading to a less hydrophilic polyethylene surface. Similarly, a loss of surface polarity and self-adhesion was observed upon heating corona-treated PET film,<sup>17</sup> presumably attributed to reorientation 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.<sup>18</sup> observed a contact angle change of about  $15^\circ$  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 behavior was observed by Pike et al.<sup>19</sup> 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 poly vinyl alkylates, Kasemura et al.<sup>20</sup> observed large contact angle hysteresis for polymers with side chains of between 6 and 12 carbon atoms long, explained by surface molecular mobility.

A study in our laboratories (reported elsewhere)<sup>21</sup> into acid/base interactions also gives strong evidence for reorientation of surface groups after removal of a polyester film from various substrates.

## CONCLUSIONS

The surface free energy of various polyester surfaces has been elucidated from contact angle mea-

surement on solution-cast films. The values obtained utilizing different mathematical approaches were compared and found to be similar. Time dependency was observed for films cast against high surface energy substrates, the surface free energy of the film in contact with the substrate diminishing in value to an equilibrium value.

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