Surface Free Energy Analysis of Polystyrene–Poly(β-hydroxynonanoate) Graft Copolymers

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SYNOPSIS

Polystyrene–poly(β-hydroxynonanoate) (PS–PHN) graft copolymers having 12, 17, 27, 31, 37, 60, 89, and 94% PS contents were prepared using active PS synthesized from styrene and oligododecandioyl peroxide initiator. Then the copolymer films were cast from chloroform, toluene, cyclohexanone, and butyl acetate. PS and PHN homopolymer blends were also prepared as films having 8, 12, 28, 34, 44, and 64% PS in the same casting solvents. The contact angles of water, glycerol, ethylene glycol, formamide, *trans*-decaline, and paraffin oil drops were measured on these cast films. The contact angle results were evaluated in terms of surface free energy components using Van Oss–Good methodology. It was determined that the Lifshitz–van der Waals component (γ_s^{LW}) of the graft copolymers and blend of homopolymers did not differ so much with the copolymer composition. However, the electron donor component of the surface free energy (γ_s^-) decreased with the decrease of PHN content to a considerable extent. It was observed that this decrease is more linear than that of homopolymer blends. The effect of the nature of the casting solvents on the surface properties of the polymers was also investigated in terms of their solubility parameter values and it was found that the more H-bonding solvents resulted in higher (γ_s^-) surfaces. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The determination of the surface free energy properties of the polymers is especially important for their use in biomedical applications. The indirect determination of the surface free energy of polymers by the one-liquid contact angle method (the air–liquid–solid system) was proposed by Fowkes,[1] Dahlquist,[2] Girifalco–Good,[3] Wu,[4] and Owens–Wendt.[5] The change of the surface free energy properties with the copolymer composition was determined by applying some of these semiempirical approaches.[6-8] Later, the use of nonlinear programming methods was adopted.[9,10]

Recently, Van Oss and coworkers introduced a theory and practical methodology to estimate the interfacial tensions between apolar and electron ac-

ceptor/electron donor molecules.[11-13] They assume that surface and interfacial free energies consist of two components: an apolar or a Lifshitz–van der Waals component (indicated by superscript LW) of electrodynamic origin and a polar component (indicated by superscript AB) caused by acid–base interactions. This methodology was successfully applied to polymer and protein interactions with liquids, surface free energy determination of polymers, polymer solubility predictions of solvents, and critical micelle concentration of surfactants.[11-15] This methodology was also tested with liquid–liquid interactions[16] and the calculated results agreed well with independent interfacial tension data from mercury interactions.[17]

Poly(β-hydroxynonanoate) (PHN) is a biopolyester and is accumulated by microorganisms. The poly(β-hydroxy alkanoate) series of biopolyesters including PHN are biodegradable, biocompatible, and of interest for biomedical application.[18,19] Very recently, a new grafting technique onto PHN was reported.[20] A vinyl polymerization initiated by oligoperoxides[21,22] yields active polymers having un-

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Table I   Surface Free Energy Components of PS-C and PHN-C Homopolymer Films Calculated by Methods I and II (mJ/m²)

Polymer	Method	γ_s^{LW}	γ_s^+	γ_s^-	γ_s^{AB}	γ_s^{TOT}
PS-C	I	23.50	0.20	3.37	1.64	25.14
	II	27.86	0.09	1.00	0.60	28.46
PHN-C	I	8.10	3.10	11.90	12.15	20.25
	II	22.04	0.02	11.78	0.97	23.01

decomposed peroxide groups. Active polystyrene (PS) obtained in this way can be grafted onto the biopolyester PHN via macropolystyrene radicals occurring from the decomposition of peroxygen bonds of thermally active polystyrene.[20]

In the present study, contact angle measurements and the evaluation of the surface free energy components by Van Oss–Good methodology was carried out to analyze the surface free energy properties of the PS–PHN graft copolymer films cast from chloroform (C), toluene (T), cyclohexanone (CH), and butyl acetate (BA). The surface free energy analysis of PS and PHN homopolymer blends was also carried out for comparison.

EXPERIMENTAL

Materials

PHN was prepared by growing *Pseudomonas oleovorans* with 20 mM nonanoic acid in 12 L of fermentation solution according to the procedure in the cited literature.[23] The pure PHN yield was 5 g and M_w was 182,000 g/mol (by GPC according to PS standards).

Oligo(dodecandioyl peroxide) (ODDP) was synthesized by the reaction between dodecandioyl chloride and sodium peroxide according to the procedure in the literature[24] (M_w = 1270 g/mol by cryoscopy). Peroxygen content of ODDP was found to be 15.1 wt % by iodometric analysis.

Synthesis of Active PS

A given amount of styrene and the oligoperoxide were charged separately in a Pyrex tube. Argon was introduced through a needle to expel the air into the tube for about 3 min. The tightly capped tube was put in an oil bath at 80°C. After 40 min of polymerization time, the content of the tube was coagulated into methanol. The active PS sample was dried overnight under vacuum at 40°C. The yield was 2.56 g, peroxygen percentage was 0.1, and the

intrinsic viscosity of the active PS in benzene at 30°C was 0.32 dL/g.[21,24]

Graft Copolymerization

The same procedure[20] was applied to obtain graft copolymers. A given amount of active PS and PHN were dissolved in chloroform and poured on a watch glass. The solvent was evaporated and the polymer mixture film was obtained. Then it was dried and transferred into a Pyrex tube. The tube was capped with a rubber septum and put into a thermostatted oil bath at 80°C. After a given period of time, the polymer product was removed by cracking the glass tube. Then the fractional precipitation method was carried out to separate pure PS–PHN graft copolymers from the corresponding homopolymers. The volume ratios of nonsolvent (methanol) to the polymer solution in chloroform are 1.3–1.9 for graft copolymers, 1.1–1.2 for homo-PS, and > 2.4 for PHN. Pure graft copolymers were obtained in moderate yield (e.g., 30–68%). Typical characterization measurements including FTIR, NMR spectra, and DSC curves of the graft copolymers were reported in Hazer.[20] Styrene content of the copolymer fractions was determined by a Varian 635D UV-VIS spectrometer. This method is based on measuring the absorbance of the phenyl group of the PS at 269 nm.[25]

Formation of Copolymer and Blend Films

The graft copolymers were dissolved in C, T, CH, and in BA. The films were formed on thin glass slides by slowly evaporating the solvent from the dipped slide at room temperature. Then the films were dried in a vacuum oven at 30°C.

To obtain blends of PS and PHN homopolymers, stock solutions of each polymer in C, T, CH, and BA (2% by wt) were prepared and the required amounts of solutions mixed. The solvents were evaporated and the dried films were obtained on the glass slides with the previous procedure for graft copolymers.
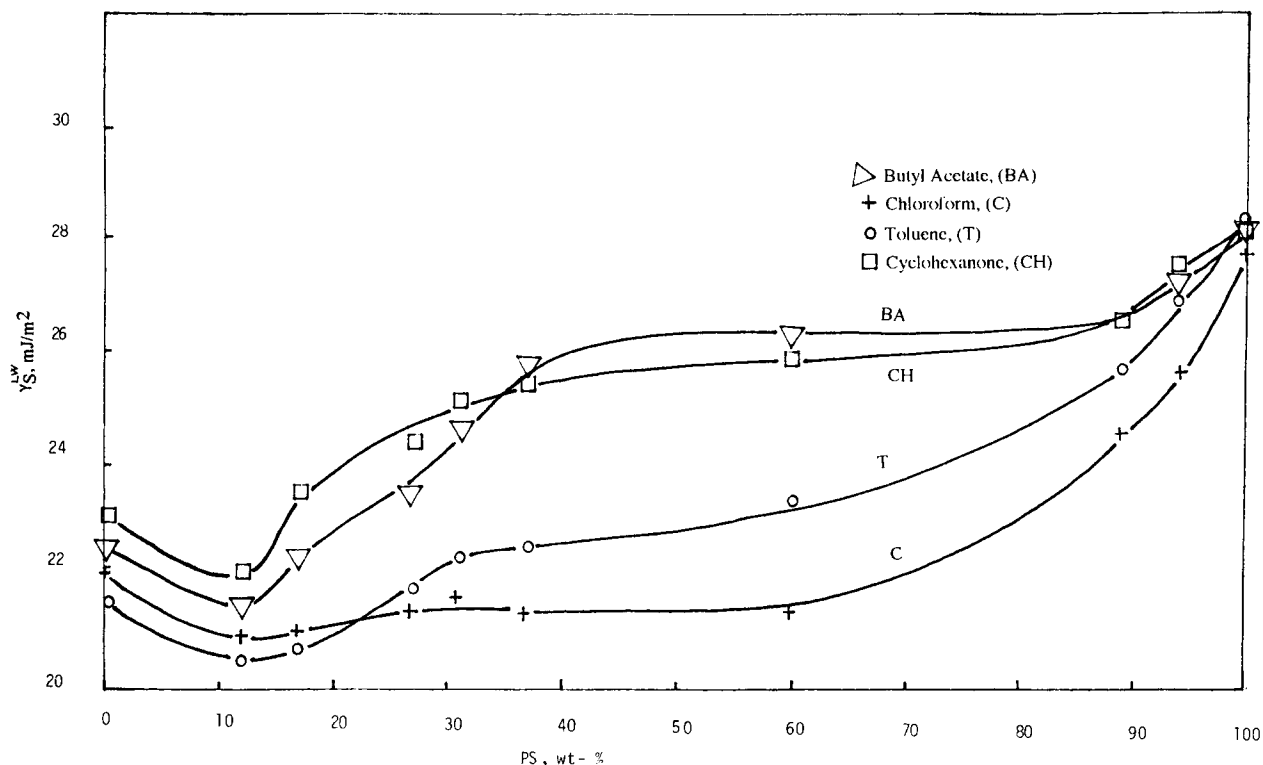
Figure 1 Change of γ_S^{LW} with the PS content of PS–PHN graft copolymers.

Contact Angle Measurements

The advancing contact angles of water, glycerol, ethylene glycol, formamide, paraffin oil and decaline drops were measured with a Model G-III Contact Angle Meter (Kernco Instrument Co. Inc., El Paso, TX). The one-liquid method (air–liquid drop-polymer system) was used. All the measured contact angles were an average of three measurements and deviated within ±2°.

THEORY

Surface Free Energy Components

The Young's equation[26] describes the thermodynamic equilibrium of the three surface tensions. γ_{SV}, γ_{SL}, and γ_{LV} existing at the phase boundries of a drop of liquid at rest on a solid surface.

$$\gamma_{LV}\cos \theta = \gamma_{SV} - \gamma_{SL} \qquad (1)$$

where γ_{LV}, γ_{SV}, and γ_{SL} are, respectively, the free energies of liquid (L), solid (S) against their saturated vapor (V), and of the interface between solid and liquid. In this equation, the phases are supposed to be mutually in equilibrium and the spreading film

pressure of the absorbed vapor of the liquid on the solid (π_e) is neglected.

The work required to pull the liquid away from the surface leaving the equilibrium-absorbed film (i.e., the total work of adhesion) is given by the Dupré equation[27]:

$$-\Delta G_A = W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \qquad (2)$$

Eliminating γ_{SL} from eqs. (1) and (2), the well-known Young–Dupré equation is obtained:

$$W_A = \gamma_{LV}(1 + \cos \theta) \qquad (3)$$

According to Van Oss–Good theory,[11–15] the surface and interfacial tensions consist of two components, an apolar or an LW component of electrodynamic origin and an AB polar component caused by Lewis acid–base interactions. The two components are additive.

$$\gamma_{ij} = \gamma_{ij}^{LW} + \gamma_{ij}^{AB} \qquad (4)$$

They suggested that LW forces include not only the London dispersion forces (d) but also the Keesom orientation (p) and Debye induction (I) forces:
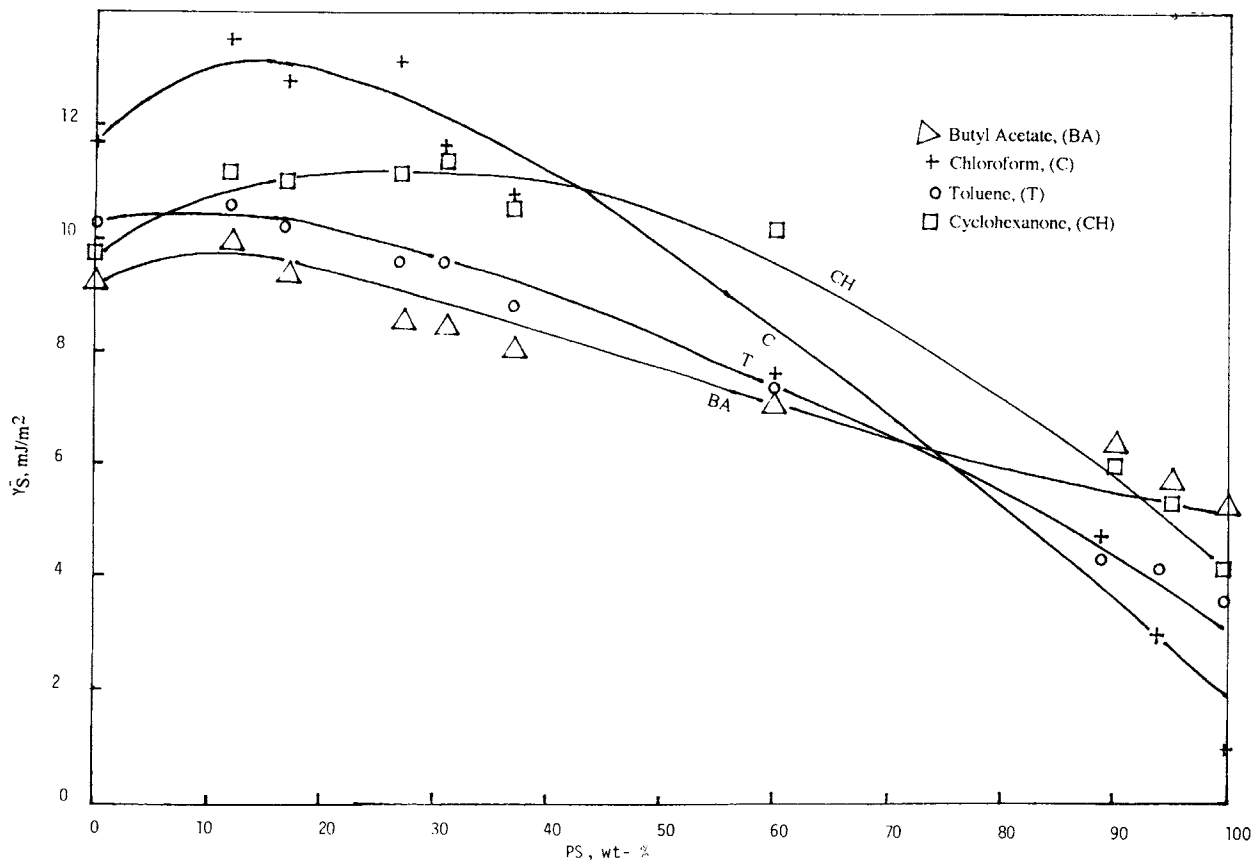
Figure 2   Change of γ_S^- with the PS content of PS–PHN graft copolymers.
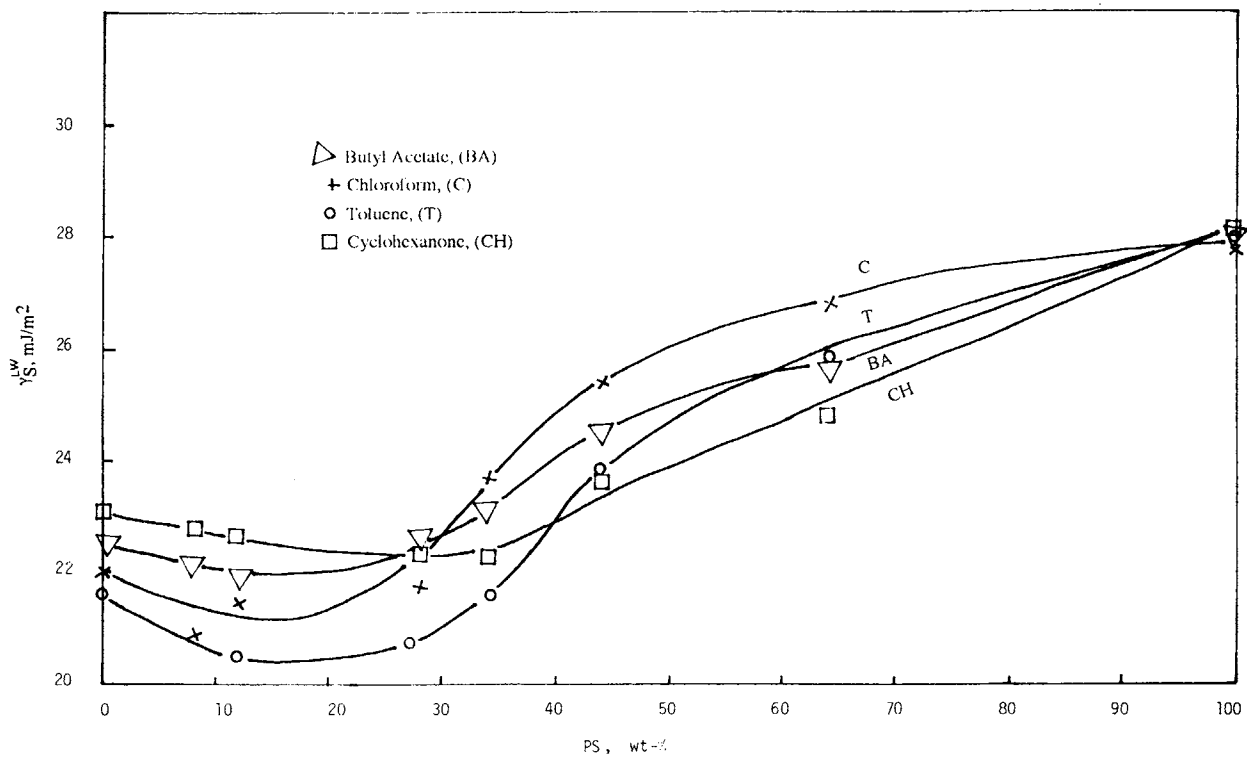

Figure 3   Change of γ_S^{LW} with the PS content of PS and PHN homopolymer blends.

$$\gamma_{ij}^{LW} = \gamma_{ij}^{d} + \gamma_{ij}^{p} + \gamma_{ij}^{I} \qquad (5)$$

For all exclusively LW interactions, that is, interactions between two completely apolar compounds, the Good–Girifalco–Fowkes combining rule is applicable:

$$\gamma_{ij}^{LW} = (\sqrt{\gamma_i^{LW}} - \sqrt{\gamma_j^{LW}})^2 \qquad (6)$$

Between many liquid–solid interfaces, in addition to LW interactions, polar interactions of the hydrogen-bonding type often occur. All electron acceptor/electron donor interactions or Lewis AB interactions are this type. Unlike LW interactions, AB interactions are essentially asymmetrical and can only be satisfactorily treated by taking that asymmetry into account.[12] The γ^{AB} component comprises two nonadditive parameters. These are the electron-acceptor surface free energy component (designated as γ^+) and the electron-donor component (designated as γ^-). These two parameters can be combined so that in the AB interaction between polar materials i and j, the electron acceptor of i interacts with the electron donor of j, and the electron donor of i interacts with the electron acceptor of j. Thus, the free energy

Table II Solubility Parameters at 25°C in Hildebrand Units[33]

Solvent	δ^d	δ^p	δ^H
Chloroform	8.7	1.5	2.8
Toluene	8.8	0.7	1.0
Cyclohexanone	8.7	3.1	2.5
Butyl acetate	7.7	1.8	3.1
Styrene	9.1	0.5	2.0

of interaction between polar materials of i and j is expressed as

$$-\Delta G_{ij}^{AB} = 2(\sqrt{\gamma_i^+ \gamma_j^-} + \sqrt{\gamma_i^- \gamma_j^+}) \qquad (7)$$

Now because by definition

$$W_A = -\Delta G_A = (-\Delta G_{ij}^{LW}) + (-\Delta G_{ij}^{AB}) \qquad (8)$$

and one may obtain by combining eqs. (2) and (6) in LW form that

$$-\Delta G_{ij}^{LW} = 2\sqrt{\gamma_i^{LW}\gamma_j^{LW}} \qquad (9)$$
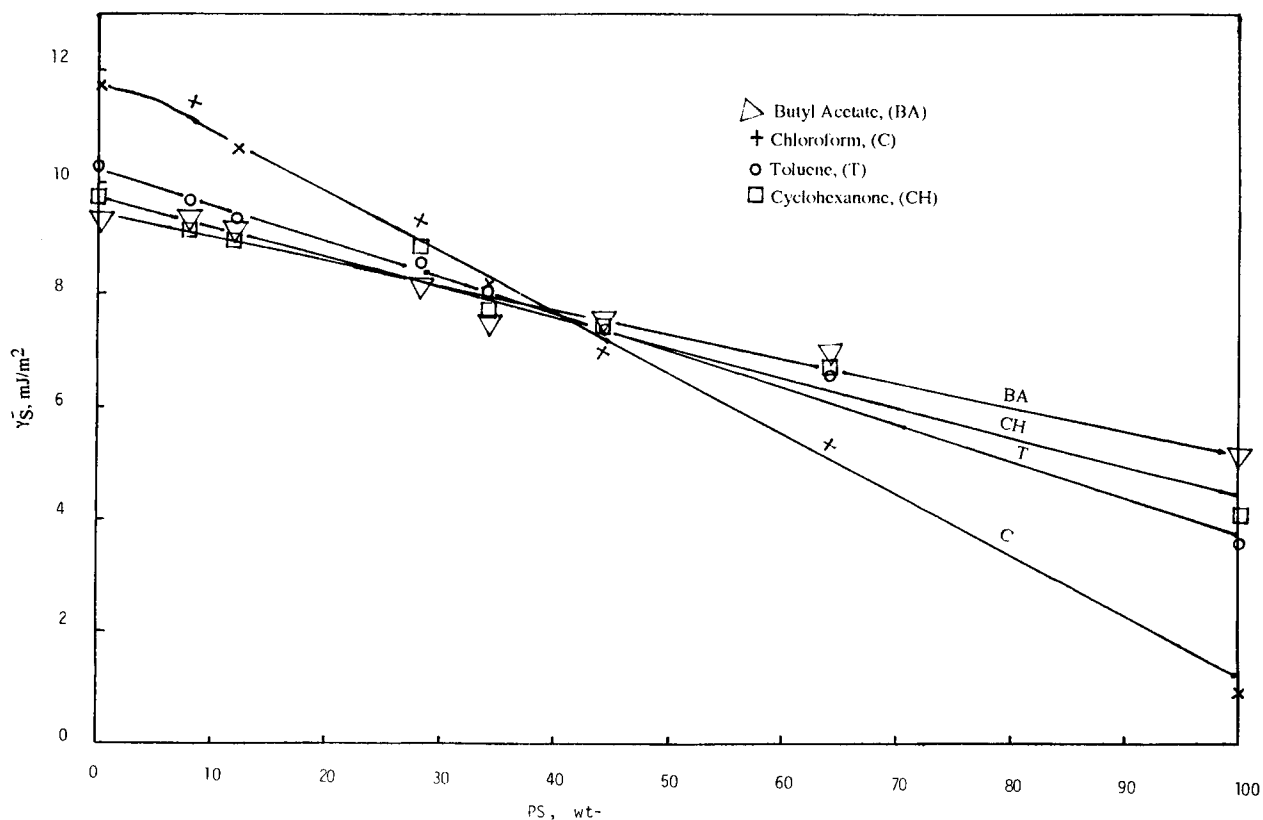

Figure 4 Change of γ_S^- with the PS content of PS and PHN homopolymer blends.

then, by combining eqs. (7), (8), and (9) one obtains

$$-\Delta G_A = W_A$$
$$= 2(\sqrt{\gamma_i^{LW}\gamma_j^{LW}} + \sqrt{\gamma_i^+\gamma_j^-} + \sqrt{\gamma_i^-\gamma_j^+}) \quad (10)$$

Combining eqs. (3) and (10) and taking $\gamma_{LV} = \gamma_L$ as usual, the complete Young equation, comprising both the apolar and polar interactions, becomes

$$\gamma_L(1 + \cos\theta)$$
$$= 2(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^+\gamma_L^-} + \sqrt{\gamma_S^-\gamma_L^+}) \quad (11)$$

Now, one has to find the relation between γ^{AB} and its components γ^+ and γ^-. Dupré showed that the free energy of cohesion is

$$-\Delta G_{ii}^{coh} = 2\gamma_i \quad (12)$$

For AB interactions eq. (12) becomes

$$-\Delta G_{ii}^{AB} = 2\gamma_{ii}^{AB} \quad (13)$$

If we express eq. (7) in terms of i only,

$$-\Delta G_{ii}^{AB} = 4\sqrt{\gamma_i^+\gamma_i^-} \quad (14)$$

From eqs. (13) and (14) it follows that

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^+\gamma_i^-} \quad (15)$$

Now if we apply eq. (2) to AB components and combine it with eqs. (7) and (15), we obtain the AB interfacial free energy between i and j materials:

$$\gamma_{ij}^{AB} = 2(\sqrt{\gamma_i^+\gamma_i^-} + \sqrt{\gamma_j^+\gamma_j^-}$$
$$+ \sqrt{\gamma_i^+\gamma_j^-} + \sqrt{\gamma_i^-\gamma_j^+}) \quad (16)$$

Equation (16) describes the polar interactions between two condensed phase materials in the same manner as used earlier by Small[28] to describe the contribution of hydrogen bonding to the heat of mixing of polar molecules in solvents that are capable of hydrogen bonding.

Combining eqs. (6) and (16) the total interfacial free energy between solid and liquid materials is

$$\gamma_{SL} = (\sqrt{\gamma_S^{LW}} - \sqrt{\gamma_L^{LW}})^2 + 2(\sqrt{\gamma_S^+\gamma_S^-}$$
$$+ \sqrt{\gamma_L^+\gamma_L^-} + \sqrt{\gamma_S^+\gamma_L^-} + \sqrt{\gamma_S^-\gamma_L^+}) \quad (17)$$

Clearly, the total interfacial free energy γ_{SL} can have a positive or negative value according to the magnitude of the components.

Computation of Surface Free Energy Components

There are two methods proposed by Van Oss and coworkers[11-15,29] that could be employed to compute the surface free energy components of either the solid or liquid.

Method I

In view of eq. (11) the solid properties γ^{LW}, γ^+, and γ^- can be calculated by simultaneous solution of three equations if the measurement of contact angles with respect to three different polar liquids is known on the solid substrate. However, γ^{LW}, γ^+, and γ^- for these liquids must be known *a priori*. Equation (11) can be written in the form of

$$A = B\sqrt{\gamma_S^{LW}} + C\sqrt{\gamma_S^+} + D\sqrt{\gamma_S^-} \quad (18)$$

where

$$A = \gamma_L(1 + \cos\theta)$$
$$B = 2\sqrt{\gamma^{LW}}$$
$$C = 2\sqrt{\gamma^-}$$
$$D = 2\sqrt{\gamma^+} \quad (19)$$

Three equations of the form of eq. (18) constitute a set of three simultaneous equations that can be solved for the three unknown properties of the solid, γ_S^{LW}, γ_S^+, and γ_S^-.

Method II

Alternatively γ_S^{LW} can be determined first by using an apolar liquid. Then two other polar liquids can be used to determine the remaining properties of the solid.

For an apolar liquid, $\gamma_L^+ = \gamma_L^- = 0$ and $\gamma_L = \gamma_L^{LW}$, then eq. (11) can be written in the form of

$$\gamma_L(1 + \cos\theta) = 2(\sqrt{\gamma_S^{LW}\gamma_L}) \quad (20)$$

Therefore, the γ_S^{LW} value can be determined directly and can subsequently be used. For a second polar liquid, eqs. (11) can be written as

$$E = C\sqrt{\gamma_S^+} + D\sqrt{\gamma_S^-} \quad (21)$$

where

$$E = \gamma_L(1 + \cos\theta) - 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}} \quad (22)$$

C and D are defined as in eq. (19). Two equations of the form of eq. (22) constitute a set of two si-

multaneous equations that can be solved for the two unknown properties of the solid γ_S^+ and γ_S^-. All γ_S^{LW}, γ_S^+, and γ_S^- results were averaged for a single value.

RESULTS AND DISCUSSION

Graft Copolymers

The polymerization of styrene with ODDP produced active PS capable of thermally produced polymer radicals.[21,22,25] These polymer radicals can lead to a grafting reaction with the biopolyester, PHN. We might say that the active PS radicals cut some ester bonds of PHN and bound to the PHN macromolecules as pendant segments during the course of the grafting reaction.[20] Characteristic bands of the polymer segments in their FTIR and NMR spectra were observed as reported in Hazer.[20] The characteristic band of the phenyl group of PS at 269 nm in the UV spectrum of the copolymers was used to determine PS content of the copolymer and the results are in good agreement with the results obtained from the PS contents calculated from their NMR spectra.

Surface Free Energy Analysis

First of all, the consistency of the results obtained from methods I and II of the Van Oss approach was tested. The contact angle results of PHN-C and PS-C were used in the calculations of surface free energy components of these homopolymers by using the method I and method II routes. The surface free energy components of the used liquids are taken from Van Oss et al.[30] Mathematica program Version 2 was used to solve the simultaneous equations, eqs. (18)–(22). The results of these calculations are presented in Table I. We realized that method I gives inconsistent results when compared with the previously published data for PS homopolymer, and it is also impossible to obtain 8.1 mJ/m² for the γ_S^{LW} value and 12.15 mJ/m² for the γ_S^{AB} value of PHN-C if we consider the pendant groups of this homopolymer. The results obtained from method II seems to be reasonable and it was decided to use only method II for all other calculations. The inconsistent results of method I were probably due to the unnegligible spreading pressure effect.[31,32]

The apolar Lifshitz–van der Waals component of surface free energy (γ_S^{LW}) change with the PS content of PS–PHN graft copolymer films cast from C, T, CH, and BA, calculated by method II are shown in Figure 1. The apolar component values were be-

tween 20.5 and 28.3 mJ/m², that is, these values deviated only ±16% from the mean. An increase of γ_S^{LW} was seen with the increase of PS content as expected due to the interactions of the bulky phenyl group. The electron donor component of surface free energy (γ_S^-) change with the PS content of graft copolymers are shown in Figure 2. These values changed a considerable extent; they were between 1.00 and 13.61 mJ/m² and deviated ±86.3% from the mean. A decrease of γ_S^- values was exhibited with the increase of PS content as expected. Because PHN have two oxygen atoms in the backbone chain, these cause the electron acceptor–donor interactions with the used solvents in the testing systems. The electron donor component of PS homopolymer is between 1.0 and 5.3 mJ/m², which is nearly 3.4 times less than that of PHN homopolymer (9.2–11.8 mJ/m²).

The change of γ_S^{LW} with the PS content of PS-PHN homopolymer blends cast from C, T, CH, and BA, calculated by method II are shown in Figure 3. The apolar component values were between 20.5 and 28.3 mJ/m², that is, these values also devated within ±16% from the mean. A linear increase of γ_S^{LW} was seen between 30 and 100% PS content in Figure 3, contrary to the large plateau of graft copolymers as seen in Figure 1 between 30 and 80% PS content.

The electron donor component (γ_S^-) change with the PS content increase of PS–PHN homopolymer blends are shown in Figure 4. The values were between 1.0 and 11.8 mJ/m² and deviated within ±84.4% from the mean. A nearly linear decrease of γ_S^- with PS increase was exhibited in Figure 4 for homopolymer blends; however, for the graft copolymers the linear decrease was seen only after 30% PS content.

Effect of Casting Solvent

The casting solvents were removed during vacuum drying. However, they had an effect on the copolymer or blend homopolymer surface free energies during the drying step due to their interaction with the pendant groups of the polymer. Some of the pendant groups are buried in the bulk polymer; some other groups are present on the surface more than the bulk polymer. The solvents used for the casting help to localize these groups. We try to explain the interactions between the solvents and the polymer surface free energies using their solubility parameter values[33] given in Table II. As seen in this table, the dispersion solubility parameters of all four solvents are close to each other. The main changes are present in polar and hydrogen-bonding solubility parameters. As γ_S^- is re-

lated to the H-bonding solubility parameter, using a solvent having a high H-bonding parameter should result in a high γ_S^- of the polymer indicating that the casting solvent molecules increase the H-bonding pendant group population of the polymer at the surface during evaporation from the surface. This thesis is well supported by the CH and C effect as seen in Figure 2. However, BA casting resulted in unexpectedly low γ_S^- values that remain unexplained for the graft copolymers. The same thesis worked well for BA and CH for a blend of homopolymers but failed for C for this case as seen in Figure 4. However, we should note that chloroform resulted in the highest γ_S^- values up to 40% PS content, then decreased sharply for high PS values. We should also point out that CH, which is the leading γ_S^- producing solvent, also has the highest polar solubility component and T, which is the lowest γ_S^- producing solvent, has the lowest H-bonding and polar solubility components. The effect of the casting solvents on γ_S^{LW} is low, within ±8% from the mean. This is expected due to the close dispersion solubility component values (±6.7% from the mean) of all the used solvents.

CONCLUSIONS

γ_S^{LW} values of PS-PHN graft copolymers did not differ so much with the increasing PS contents. The values deviated within ±16% from the mean and an increase of γ_S^{LW} with PS content was detected due to the interactions of the bulky phenyl group. For the PS–PHN homopolymer blends a linear increase of γ_S^{LW} was seen between 30 and 100% PS content.

γ_S^- values of PS-PHN graft copolymers changed to a considerable extent and deviated ±86.3% from the mean. The decrease of the electron donor component of surface free energy (γ_S^-) with the decrease of the PHN content was seen because of the lessening of the oxygen atom interactions present only in the PHN backbone chain. For the PS–PHN homopolymer blends a linear decrease of γ_S^- values with the PHN content decrease was exhibited.

It was determined that the casting solvents had an effect on localizing the remaining polymer concentrations on the surface of the films different from the bulk polymer itself. The effect of casting solvents was explained in terms of their solubility parameter component properties, that is, the more H-bonding solvents resulted in higher γ_S^- surfaces.

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