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SURFACE ENERGY OF FLUORINATED SURFACES

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SUMMARY

By fluorinating the surface of a polymer, the hydrogen bonding energy of a polar surface has been defined. The contact angles for three solvent classes; nonpolar, polar and hydrogen bonding, on a polar surface results in the separation of dispersion, polar, and hydrogen bonding energies. Both critical surface tension plots and theoretical calculations were used to define the surface energy for fluorinated polyethylene.

INTRODUCTION

Schonhorn and Hansen have reported that the adhesion to fluorinated polyethylene is improved even though the surface tension was reduced [1]. Based on these results they concluded that wetting is less important in adhesion than previously considered.

Zisman and co-workers have shown that surface tension of a surface can be obtained by measuring contact angles of various solvents on the surface [2]. By plotting the cosine of the angle versus the surface tension of the liquid, extrapolation to complete wetting (angle $\theta = 0$ or cosine $\theta = 1$) yields the surface tension of the surface.

The surface tensions of the solvents, γ_L, can be separated into dispersion and polar terms [3].

$$\gamma_L = \gamma_D + \gamma_P$$

the γ_D term can be determined by measuring the interfacial tension between the solvent and water or some other material in which γ_D is known [4]. According to the "constitutive law of wettability," wettability of organic surfaces is determined by the nature and packing of the surface atoms or exposed groups of atoms of the solid and is otherwise independent of the nature and arrangements of the underlying atoms or molecules [5].

The dispersion surface tension (γ_D) of a polymer has been stated to be independent of both crystallinity and mechanical strains [3]. Fowkes has assumed that the forces between polar and nonpolar molecules is due only to dispersion forces and therefore relates $\gamma_1^D = \gamma_C$ [3,4]. More recently, it has been shown that in fact $\gamma_1^D \neq \gamma_C$ when polar and nonpolar molecules interact [6-9].

Owens and Wendt [7] have shown that the following cases exist:

1. Nonpolar solvent on nonpolar solid: $\gamma_S^D = \gamma_C$;

2. Polar solvent on nonpolar solid: $\gamma_S^D > \gamma_C$;

3. Nonpolar solvent on polar solid: $\gamma_S^D > \gamma_C$
   where γ_S^D = dispersion force of the solid and
   γ_C = critical surface tension of the solid.

Both Dann [8] and Good [9] give excellent discussions on the polar forces effect on contact angles. To date there is no adequate prediction of hydrogen bonding solvents contact angle on polar surfaces. This is presumably due to a rather complex interaction not only between the solid and the solvent, but also between solvent molecules. In addition, there is no good theoretical separation of polar forces from hydrogen bonding forces [10]. Thus in almost all contact angle measurements and subsequent surface energy phenomena explanation, hydrogen bonding solvents are ignored. One of the possible explanations for this lack of theoretical agreement to hydrogen bonding liquids is that entropy factors are ignored [11].

Several attempts to measure the polar forces (nondispersion forces) for various surfaces have been made [7,8,12-14]. For instance, Dann [8b] has defined a nondispersion interaction term, I_{SL}^P, as

$$I_{SL}^P = S_C(\mathrm{obs}) - Sc(\mathrm{calc})$$

where $Sc(\mathrm{obs}) = (\cos\theta - 1)\gamma_1$ for the observed spreading coefficient and $Sc(\mathrm{calc}) = 2\sqrt{\gamma_1^D \gamma_S^D} - 2\gamma_1$ for the calculated spreading coefficient. Thus, I_{SL}^P is the stabilization due to nondispersion interactions and is a measure of the polarity of the surface.

Since there is adequate precedent to use contact angle measurements to study the surface tension of a polymer, we have used this approach to define the action of fluorine on a polymer surface.

EXPERIMENTAL

The procedure used to prepare the samples for contact angle measurements was to treat the samples using fluorine/nitrogen and fluorine/nitrogen/oxygen blends of various concentrations of fluorine. In all cases the reaction time was held constant at ten minutes under a static reaction condition (no gas flow during the ten minute reaction). No special sample preparation such as surface cleaning, solution casting or melting of the polymer to generate "smooth" surfaces was performed.

Polyethylene bottles that were used in this study are composed of high density polyethylene resin. Polyethylene tubular film, density = 0.920, from Boyertown Packaging Service Corp. were also used and only the inside portion of the film was studied. Polypropylene bottles, Nalgene, were purchased from Sargent Welch. The polyester film was Mylar 1S from duPont.

Contact angle measurements were carried out using a Rame'-Hart goniometer in which only advancing contact angles were measured. All solvents were either reagent grade, spectro-grade, or their purity was checked by refractive index measurements. For those solvents of unknown surface tension, surface tension measurements were carried out using a Fisher surface tensiometer.

RESULTS

Contact angle measurements were obtained using a variety of solvents: hydrocarbons, alkyl halides, and hydrogen bonding solvents. Table 1 compares literature contact angles for selected liquids on untreated polyethylene and polyester with contact angles obtained in this study. We found that at least 15 minutes were required for the glycerol to reach equilibrium on the polyethylene surface. All the remaining solvents were also checked for equilibrium prior to contact angle measurements. As Table 1 shows, our contact angles agree within reason to accepted literature values. Thus, the lack of a cleaning

TABLE 1

Contact angles for untreated polymers

Polymer	Solvent	Contact Angle This Work	 Literature	Lit. Ref.
Polyethylene	water	94°	94.0°	27
	glycerol	89°	79.0°	27
	formamide	74.6°	77.0°	27
	diiodomethane	53.9°	52.0°	27
	1-bromonaphthalene	35.1°	35.0°	27
	1,1,2,2-tetrachloroethane	14.0°	10.0°	27
Polyester	water	80.4°	81°	28
	glycerol	64.0°	65°	28
	formamide	59.1°	61°	28
	thiodiglycol	37.1°	46°	28
	methylene iodide	36.8°	38°	28
	1-bromonaphthalene	14.8°	15°	28

procedure or a smoothing of the surface step has not affected the accuracy of these measurements.

Polyethylene

Polyethylene was treated at 1.5 x 10^{-4}M and 5 x 10^{-3}M fluorine concentration. The "critical surface tension" for the treated polyethylene was determined by using three solvent classes: alkanes, alkyl halides and hydrogen bonding solvents.

Table 2 gives the contact angles and work of adhesion for the two treatment levels. Work of adhesion (W_A) is defined by the following [15].

$$W_A = \gamma_L(1 + \cos \theta)$$

where γ_L = surface tension of the liquid

θ = contact angle of the liquid on the polymer.

As can be seen from Table 2, adhesion generally decreased for hydrocarbon and alkyl halide solvents, but increased for hydrogen bonding solvents. This points to the fact that the surface energy of the polymer increased towards hydrogen bonding solvents but decreased towards polar and nonpolar solvents. Increased surface tension by oxidation is expected to increase adhesion for polar groups [15].

TABLE 2

Contact angle data and work of adhesion for PE

Solvent	γ_L	Control θ	Control $\cos\theta$	Control W_A	1.5×10^{-4}M F_2 θ	1.5×10^{-4}M F_2 $\cos\theta$	1.5×10^{-4}M F_2 W_A	5.0×10^{-3}M F_2 θ	5.0×10^{-3}M F_2 $\cos\theta$	5.0×10^{-3}M F_2 W_A
Octane	21.8	0	1.00	43.6	0	1.00	43.6	6.0	0.995	43.5
Decane	23.9	0	1.00	47.8	0	1.00	47.8	33.5	0.833	43.8
Dodecane	25.4	0	1.00	50.8	16.75	0.958	49.7	46.4	0.690	42.9
Tetradecane	26.7	0	1.00	54.4	19.4	0.943	51.9	52.4	0.610	42.9
Hexadecane	27.6	0	1.00	55.2	19.0	0.946	53.7	50.1	0.641	45.3
Toluene	28.5	0	1.00	57.0	5.3	0.996	56.9	39.9	0.767	50.4
O-xylene	30.1	0	1.00	60.2	10.3	0.984	59.8	40.5	0.760	53.0
Decahydronaphthalene	33.5	0	1.00	67.0	38.23	0.785	59.8	60.9	0.486	49.8
Carbon Tetrachloride	26.95	2.8	0.999	53.9	4.5	0.997	53.8	25.1	0.905	51.3
1,1,2,2-Tetrachloroethane	36.03	14.0	0.970	71.0	29.0	0.875	67.6	53.1	0.60	57.7
1-bromonaphthalene	44.6	35.1	0.818	81.1	55.1	0.572	70.1	69.3	0.354	60.4
Diiodomethane	50.8	53.9	0.590	80.8	65.3	0.371	69.6	80.0	0.174	59.6
Water	72.8	94	0.072	67.6	70.5	0.334	97.1	80.4	0.167	84.9
Glycerol	63.4	80	0.017	64.5	80	0.171	74.2	96.8	-0.118	55.9
Formamide	58.2	74.6	0.265	73.5	45.5	0.701	98.9	63.8	0.441	83.9
2,2'-Thiodiethanol	54.0	67.3	0.387	74.3	58.0	0.530	82.6	77.9	0.21	65.3
1,4-Butanediol	49.11	64.5	0.431	70.3	44.6	0.718	84.7	62.8	0.458	71.6
N,N-Dimethylacetamide	37.37	39.8	0.769	66.1	0	1.00	74.7	2.9	0.999	74.7
2,2'-oxydiethanol	47.8	68.0	0.375	65.7	31.5	0.853	88.6	57.1	0.543	73.8
Triethylene glycol	49.69	67	0.391	69.1	34.6	0.823	90.6	59.3	0.511	75.1

An explanation for this phenomenon is seen when the "critical surface tension" plots for the treated polymer is carried out. Using Zisman's approach to estimating surface tensions of surfaces by plotting cosine θ versus the liquid's γ_L and extrapolating to cosine θ = 1, where θ = 0, the "critical surface tension" is found. Figure 1 shows the result of this type of plot.

When the contact angle for the fluorinated polyethylene is compared to Teflon, it is seen that Teflon prohibits wetting of both polar and hydrogen bonding solvents as well as alkanes [16-18]. In fact a smooth plot is obtained for all the fluorinated olefinic polymers

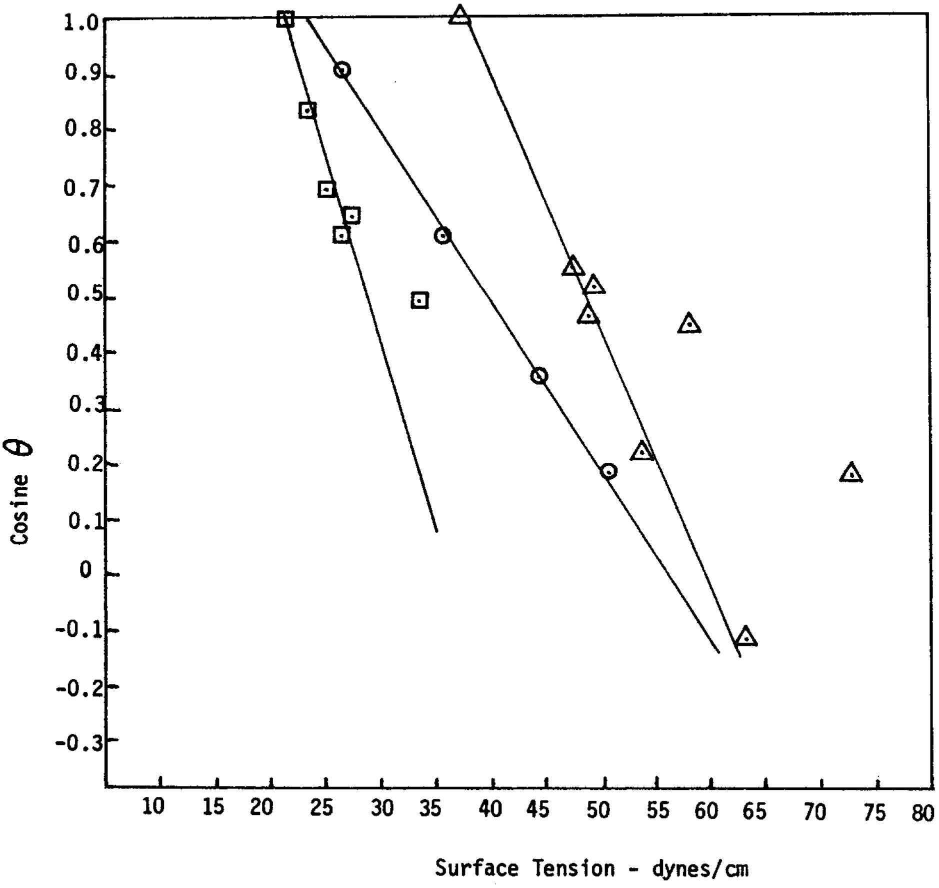

Figure 1. Fluorinated polyethylene: (□) non-polar; (○) polar; (△) hydrogen bonding.

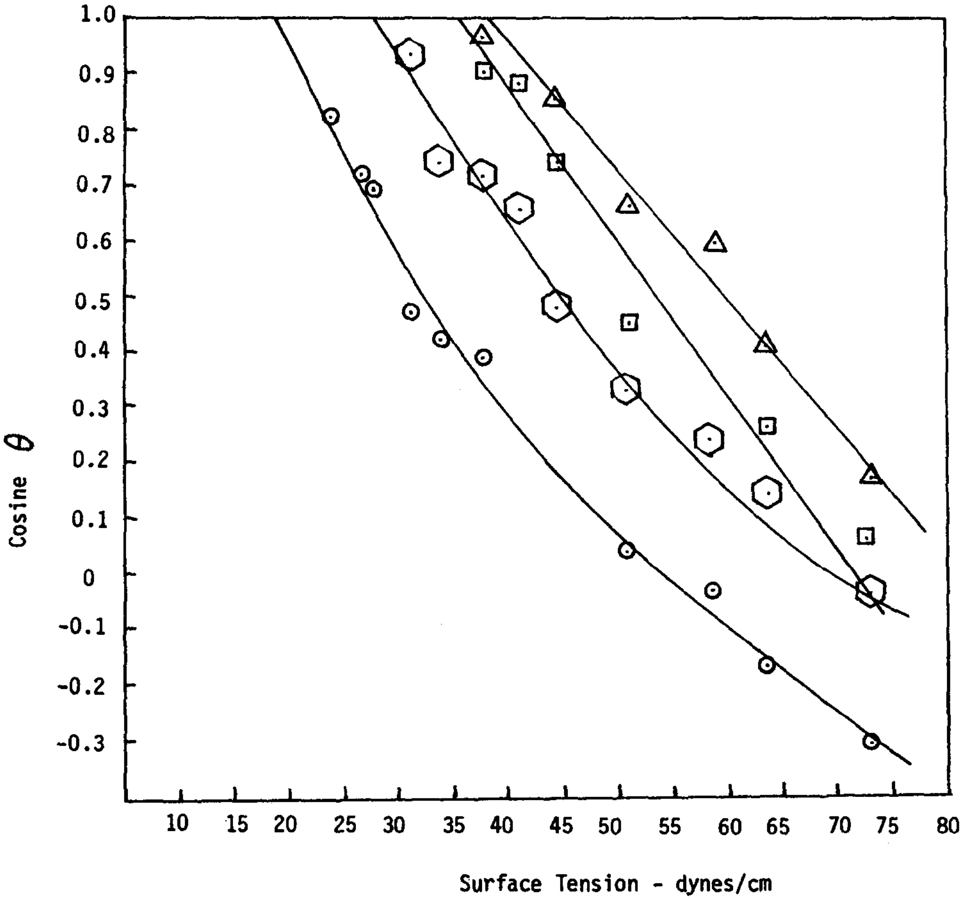

Figure 2. Polyfluoroolefins. (△) polyvinyl fluoride; (□) polyvinylidene fluoride; (⬡) polytrifluoroethylene; (○) polytetrafluoroethylene.

independent of solvent type, Figure 2 [18]. Therefore, it is believed that the deviation from linearity according to solvent type is not a result of fluorine incorporation, but rather accompanying oxidation of the surface. This is in disagreement with Clark who has studied fluorination of polyethylene by ESCA and states oxidation does not accompany fluorination [19]. The hydrogen bonding ability for fluorine is considered very low so that the fluorine atom alone does not account for the increased wetting.

To further substantiate this view, polyethylene film was subjected to various oxyfluorination conditions, since the presence of

TABLE 3

Contact angle data and work of adhesion for oxyfluorinated PE

Solvent	γ_L		10% F_2			10% F_2/1% O_2			10% F_2/5% O_2	
		θ	cos θ	W_A	θ	cos θ	W_A	θ	cos θ	W_A
Water	72.8	77.99	0.208	87.94	64.0	0.438	104.68	57.1	0.543	112.3
Glycerol	63.4	62.03	0.469	39.13	54.6	0.580	100.17	39.3	0.774	112.5
Formamide	58.2	34.9	0.820	105.92	15.5	0.964	114.31	0	1.00	116.4
2,2'-Thiodiethanol	54.0	43.4	0.727	93.26	27.1	0.890	102.06	18.9	0.946	105.1
1,4-Butanediol	49.11	30.0	0.866	91.64	16.5	0.959	96.21	3.3	0.998	98.1
2,2'-Oxydiethanol	47.82	18.7	0.947	93.11	0	1.00	95.64	5.0	0.996	95.5
1-Octanol	27.53	0	1.00	55.06	0	1.00	55.06	-	-	-
Octane	21.8	0	1.00	43.6	-	-	-	-	-	-
Decane	23.9	-	-	-	0	1.00	47.8	21.8	0.929	46.1
Dodecane	25.4	40.27	0.763	44.78	0	1.00	50.8	39.4	0.773	45.03
Tetradecane	26.7	39.10	0.776	47.42	0	1.00	53.4	26.3	0.897	50.6
Hexadecane	27.6	44.03	0.719	47.44	25.2	0.905	52.58	36.3	0.806	49.85
Toluene	28.5	-	-	-	0	1.00	57.0	20.6	0.936	55.2
n-propylbenzene	28.5	-	-	-	19.5	0.943	55.38	-	-	-
n-heptylbenzene	29.1	-	-	-	18.0	0.956	56.92	-	-	-
1,1,2,2-tetrachloroethane	36.03	43.53	0.725	62.15	30.5	0.862	67.09	38.3	0.785	64.31
1-bromonaphthalene	44.6	64.60	0.429	63.73	5.2	0.614	71.98	51.0	0.629	72.65
Diiodomethane	50.8	70.67	0.331	67.61	66.75	0.395	-	67.8	0.379	70.1
Carbon Tetrachloride	26.95	13.59	0.972	53.15	0	1.00	53.9	8.5	0.989	53.6
Chlorobenzene	33.56	-	-	-	16.75	0.958	65.71	34.0	0.829	61.38
Chloroform	27.14	-	-	-	0	1.00	54.28	0	1.00	54.28
Decahydronaphthalene	33.5	-	-	-	38.5	0.783	59.73	50.4	0.638	54.87
N,N-dimethylacetamide	37.37	-	-	-	0	1.00	74.74	0	1.00	74.74
Bis(2-methoxyethl)ether	-	-	-	-	0	1.00	-	0	1.00	-
Tetrachloroethylene	31.74	-	-	-	0	1.00	63.48	0	1.00	63.48
Trichlorotrifluoroethane	-	-	-	-	0	1.00	-	0	1.00	-
Triethylene glycol	40.60	6	1.00	00.03	00.03	00.03	00.03	00.03	00.03	00.03

oxygen has been shown to induce oxidation during fluorinations [20]. The polyethylene film was treated at 10% F_2, 10% F_2/1% O_2 and 10% F_2/5% O_2; the contact angles and work of adhesion are found in Table 3. It can be seen that the addition of oxygen allows hydrogen bonding and polar solvents to wet better. The extent of the nonpolar solvents ability to wet is also increased. This is probably due to the fact that less fluorine is incorporated and thus the dispersion force is also higher. Figure 3 plots the γ_L values versus cosine θ for a typical oxyfluorination treatment. The $\gamma_S{}^H$ term for the treated sam-

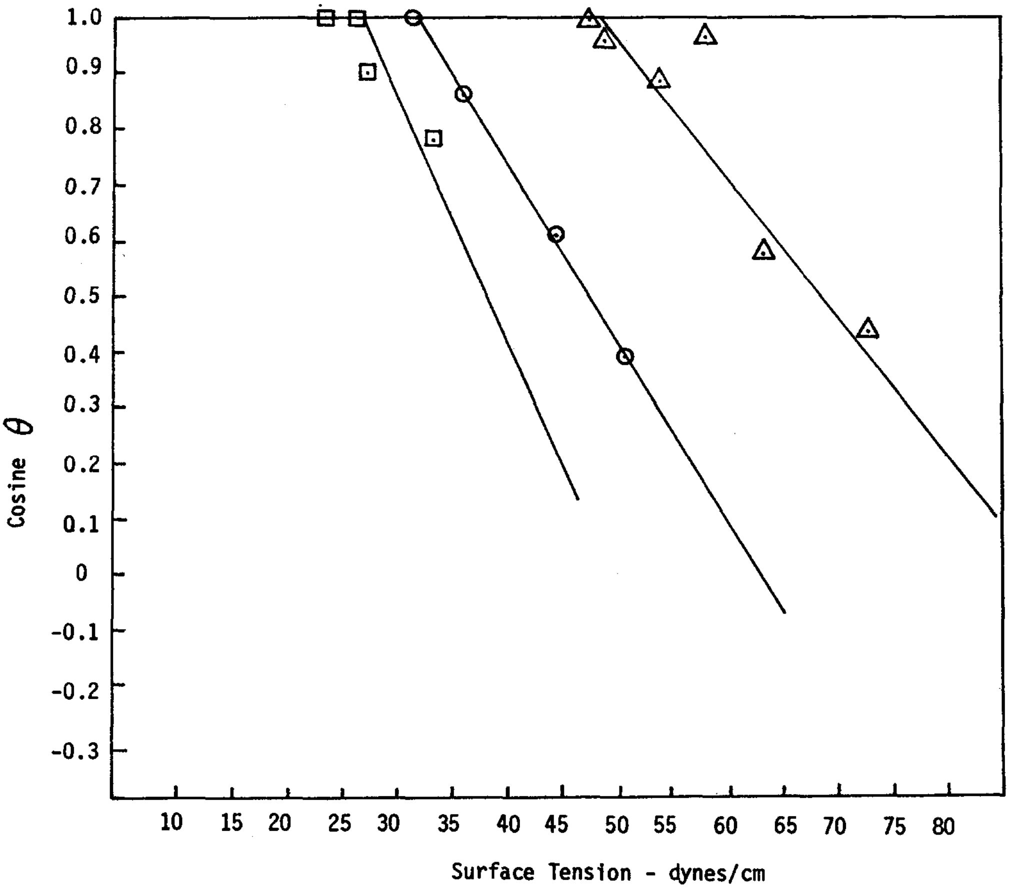

Figure 3. Oxyfluorinated polyethylene: (□) non-polar; (○) polar; (△) hydrogen bonding.

ples increases with increased oxygen concentration, Table 4. Also both γ_S^D and γ_S^P increase with the addition of oxygen. The cause for the 5% O_2 experiment to have slightly decreased γ_S^D and γ_S^P

TABLE 4

Comparison of surface energies for PE and PP - dynes/cm

Reaction Condition	Sample	γ_S^D	γ_S^P	γ_S^H	γ_c
Control	PE	33.5 (35^1)	35.0	35.0	31.0^2
	PP	33.5 (28.5^1)	32.0	27.5	29.8^3 (29^2)
10% F_2	PE	22.0	27.0	45.0	-
	PP	24.5	27.5	44.5	-
10% F_2/1% O_2	PE	27.0	32.0	48.5	-
	PP	29.0	32.0	47.5	-
10% F_2/5% O_2	PE	23.5	28.0	49.0	-
	PP	26.0	32.0	47.5	-

1 - See Ref. 4. 2 - See Ref. 21. 3 - Average of γ_S^P and γ_S^H.

terms is not known. However, the fact that γ_S^H goes from 45 to 48 to 49 dynes/cm with the addition of oxygen, proves that oxidation does in fact cause the increased wetting of hydrogen bonding liquids. The γ_S^P term also showed an increase upon the addition of oxygen, but not to the same degree as γ_S^H.

If the γ_S values for various fluoro polymers are plotted against the number of fluorine atoms per repeating unit, a straight line relationship exists, Figure 4 [21,22]. Assuming the carboxyl groups present in the fluorinated polyethylene samples do not affect the magnitude of the γ_S^D term, then a fluorinated polyethylene surface having a γ_S^D term of 22 dynes/cm has a carbon to fluorine ratio of 0.67. The carbon to fluorine ratio is similar to Clark's estimation of the degree of fluorination on the surface layer [19].

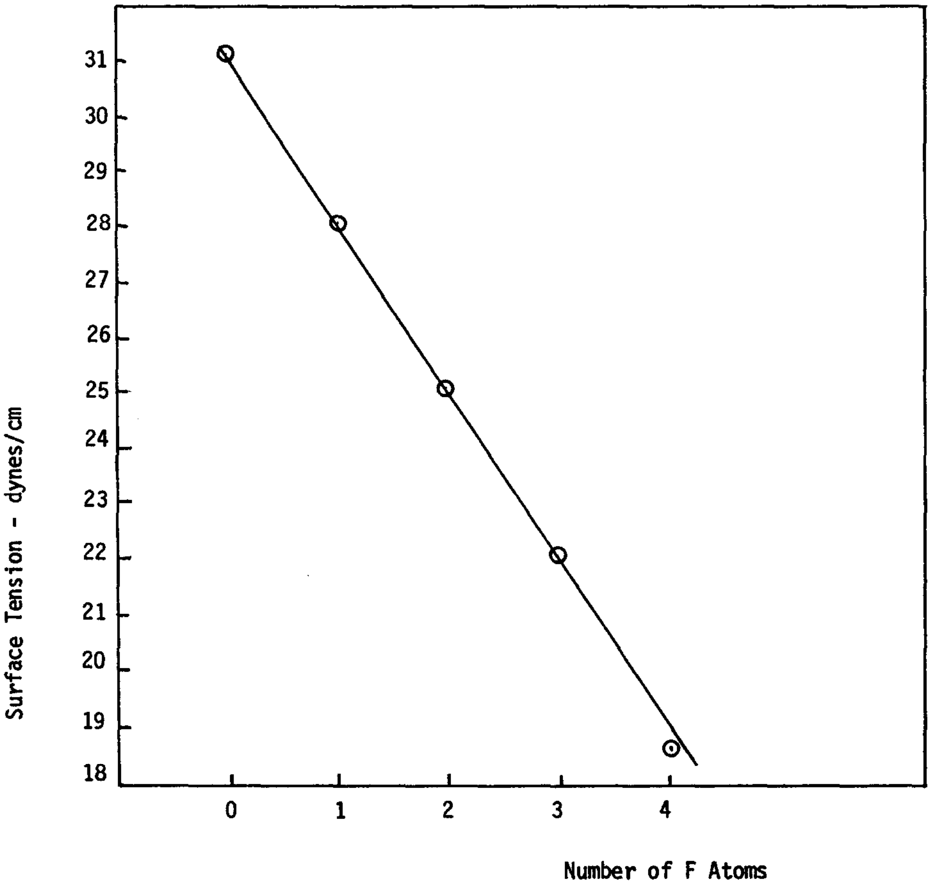

Figure 4. Surface Energy Versus Fluorine Substitution

Polypropylene

Since poly (hexafluoropropylene) has a surface energy lower than poly (tetrafluoroethylene), 17 and 18.5 dynes/cm, respectively, it was of interest to see if the surface energy of fluorinated polypropylene would be lower than fluorinated polyethylene.

Table 5 gives the contact angles and work of adhesion for the various liquids used for both fluorinated and oxyfluorinated surfaces. For both polar and nonpolar liquids the contact angles increased upon both fluorination and oxyfluorination. However, the extent of in-

TABLE 5

Contact angle data and work of adhesion for teated PP bottles

Solvent	γ_L		Control			10% F_2			10% F_2/1% O_2			10% F_2/5% O_2	
		θ	$\cos\theta$	W_A	θ	$\cos\theta$	W_A	θ	$\cos\theta$	W_A	θ	$\cos\theta$	W_A
1-Bromonaphthalene	44.6	44.6	0.712	76.4	54.6	0.579	70.4	48.1	0.668	74.4	46.5	0.688	74.4
Carbon Tetrachloride	26.95	0	1.00	59.9	0	1.00	59.9	0	1.00	59.9	0	1.00	59.9
Chlorobenzene	33.6	14.1	0.97	66.2	26.9	0.892	63.6	19.6	0.942	65.3	21.3	0.932	64.9
Chloroform	27.14	0	1.00	54.3	0	1.00	54.3	0	1.00	54.3	0	1.00	54.3
Decahydronaphthalene	33.5	0	1.00	67.0	10.9	0.756	58.8	34.6	0.823	61.1	34.5	0.824	61.1
Decane	23.9	0	1.00	47.8	0	1.00	47.8	0	1.00	47.8	0	1.00	47.8
Diiodomethane	50.8	54.3	0.584	80.5	65.9	0.409	71.6	55.6	0.565	79.5	52.1	0.614	82.0
N,N-Dimethylacetamide	37.37	39.1	0.776	66.4	0	1.00	74.7	0	1.00	74.7	0	1.00	74.7
Dodecane	25.4	0	1.00	50.8	21.4	0.931	49.1	0	1.00	50.8	0	1.00	50.8
Formamide	58.2	85.9	0.072	62.4	34.8	0.822	106.0	19.3	0.944	113.0	12.9	0.975	114.9
Hexadecane	27.6	0	1.00	35.2	27.8	0.885	52.0	0	1.00	55.2	30.4	0.863	51.4
Bis(2-methoxyethyl)ether	-	0	1.00	-	0	1.00	-	0	1.00	-	0	1.00	-
1,1,2,2-Tetrachloroethane	36.03	19.5	0.943	70.0	39.3	0.774	63.9	10.5	0.983	71.5	27.3	0.889	68.1
Tetrachloroethylene	31.7	0	1.00	63.4	25.8	0.901	60.3	0	1.00	63.4	6.0	0.995	63.2
Tetradecane	26.7	0	1.00	53.4	15.8	0.962	52.4	0	1.00	53.4	20.5	0.937	51.7
2,2'-Thiodiethanol	54.0	68.4	0.369	73.9	40.4	0.762	95.1	34.6	0.823	98.4	26.3	0.897	102.4
Trichlorotrifluoroethane	-	0	1.00	-	0	1.00	-	0	1.00	-	0	1.00	-
Toluene	28.5	0	1.00	57.0	12.5	0.976	56.3	0	1.00	52.0	9.4	0.987	56.6
Water	72.8	93.6	-0.063	-4.6	54.9	0.425	103.7	56.3	0.556	113.3	50.6	0.634	118.9
1,4-Butanediol	49.11	62.5	0.462	71.8	29.0	0.875	92.1	23.9	0.914	94.0	15.1	0.965	96.5
Glycerol	63.4	85.8	0.074	68.1	56.9	0.546	98.0	43.5	0.725	109.4	39.3	0.774	112.5

crease for oxyfluorination was less than that for straight fluorination. Again this may be due to the fact that less fluorine atoms are present when the polymer is oxyfluorinated. The contact angles were consistently reduced for hydrogen bonding liquids upon oxyfluorination or fluorination. In fact, on oxyfluorination the contact angles decreased even more when 5% oxygen was substituted for 1% oxygen.

The plots of γ_L versus cosine θ for the various treatments are similar to that for polyethylene. Contact angles for the control polymer could not be compared to literature values but if the γ_c value found in this work is compared to γ_c from the literature, agreement exists [21].

Table 5 compares the results for PE and PP treated under the same reaction conditions. Fluorination reduces the dispersion energy of the polypropylene surface to 24 dynes/cm; slightly higher than for fluorinated polyethylene. The polar energy is reduced to the same extent as polyethylene, PP = 27.5 and PE = 27.0, as is the hydrogen bonding energy, PP = 47.5 and PE = 49 dynes/cm. With the addition of oxygen to the reaction medium, the trends found for polyethylene were also found for polypropylene.

Polyester

Since surface energy studies have allowed a better description of the treated polyolefin surfaces, the contact angle measurements were extended to polyester substrates. Both the contact angles and the work of adhesion can be found in Table 6. The same familiar trend is found for fluorinated polyester surfaces as was found for the polyolefin surfaces. Increased wetting of hydrogen bonding liquids and decreased wetting of both polar and nonpolar liquids occur for the treated surfaces.

The control yields a surface energy of 43 dynes/cm which is independent of the liquid series used. The mild fluorination was not enough to cause non-wetting for the alkane series, but did lower the polar energy of the surface to 36 dynes/cm. The hydrogen bonding energy was only slightly raised to 48 dynes/cm. The heavily treated surface is now more similar to a heavily fluorinated polyolefin surface. Compare Tables 4 and 7. The dispersion energy is close to 22 dynes/cm, the polar energy almost 32 dynes/cm and the hydrogen bonding energy 49 dynes/cm for the fluorinated polyester film.

TABLE 6

Contact angle data and work of adhesion for treated PET

Solvent	γ_L	Control θ	 $\cos\theta$	 W_A	1.5×10^{-4}M F_2 θ	 $\cos\theta$	 W_A	5×10^{-3}M F_2 θ	 $\cos\theta$	 W_A
Water	72.8	80.4	0.167	84.9	64.1	0.436	104.5	37.1	0.797	130.8
Glycerol	63.4	64.0	0.438	91.2	61.5	0.427	93.6	54.5	0.581	100.2
Formamide	58.2	59.1	0.513	88.1	21.3	0.932	112.4	34.5	0.824	106.2
2,2'-Thiodiethanol	54.0	37.1	0.797	97.0	32.6	0.842	99.5	27.3	0.889	102.0
Diiodomethane	50.8	36.8	0.801	91.5	50.5	0.636	83.1	69.4	0.352	68.7
1-Bromonaphthalene	44.6	14.8	0.967	87.7	45.0	0.707	76.1	60.9	0.487	66.3
Xylene	30.1	0	1.00	60.2	0	1.00	60.2	19.6	0.942	58.5
Hexadecane	27.6	0	1.00	55.2	3.1	0.999	55.0	36.8	0.781	49.2
Carbon Tetrachloride	26.95	0	1.00	53.9	0	1.00	53.9	15.0	0.966	53.0
Tetradecane	26.7	0	1.00	53.4	0	1.00	53.4	34.0	0.829	48.8
Dodecane	25.4	0	1.00	50.8	0	1.00	50.8	21.6	0.930	49.0
Decane	23.9	0	1.00	47.8	4	0.998	47.7	17.9	0.952	46.7
Octane	21.8	0	1.00	43.6	2.4	0.999	43.6	13.5	0.972	43.0
1,4-Butanediol	49.11	41.3	0.752	86.0	16.6	0.958	96.2	23.6	0.916	94.1

TABLE 7

Surface energy for treated PET - dynes/cm

Sample	γ_s^D	γ_s^P	γ_s^H	γ_c
Control	43[1]	-	-	43[2]
1.5×10^{-4} M F_2	28	37	49	-
5×10^{-3} M F_2	22.5	32.5	48.5	-

1 - See Ref. 8b. 2 - See Ref. 21.

DISCUSSION

Contact angle measurements have been used to define the surface chemistry of fluorinated polymers. Fluorinated polyethylene has been shown to have a carbon to fluorine ratio of 0.67 for a well treated surface. This is based on the assumption that the surface energy as found from the contact angles for the hydrocarbons is independent of the polar forces on the polymer surface. This is in agreement with Schonhorn and Hansen if it is assumed that only nonpolar liquids were used for contact angle measurements. Owens and Wendt have predicted that this is really not the case and thus the surface may be even more heavily fluorinated [7]. However, it is not expected to have a carbon to fluorine ratio of 0.5 since Clark has shown that the surface layer of a fluorinated polyethylene film when heavily fluorinated approaches the ratio 0.5 very slowly [19].

The obvious choice if the polar energy of the surface interferes with the measurement of the dispersion energy is to study the surface energies of fluorinated acids to ascertain the effect of carboxyl groups on dispersion energy. However, Zisman [23] and Fox [24] have studied fluorinated acids extensively and found that the trifluoromethyl group at the terminal end of the molecule results in extremely reduced surface energy for the monolayer. This is explained by the fact that the molecules orient themselves perpendicular to the surface with the best bonding group next to the surface. This results in a trifluoromethyl surface and prevents the carboxyl groups from participation in the interaction with the solvent. See also Pittman's review of surface properties of fluorocarbon polymers [25].

It has been found that fluorine atoms along the molecule's chain do not have a profound affect over the terminally fluorinated molecule [23]. The effect of fluorine along the chain of a fluorinated polymer, as well as the carboxyl group formation obtained in this study, would be expected to interact with the solvent. For these polymer surfaces the molecules cannot orient themselves perpendicular to the surface and thus both the fluorine atoms and carboxyl groups will affect the wetting phenomena of the surface. This seems to be the first case in which both the fluorine atoms and the carboxyl group have simultaneous interaction with the wetting liquid and thus permit an interaction affect to be studied in detail.

When a comparison between the various polymer resins studied is made, the effect of fluorine on the surface of the polymer seems to be the same in all cases. Only the degree of change is different for the various resins.

The dispersion energy is reduced to less than 25 dynes/cm, the polar energy is also reduced but not to the same degree as the dispersion energy, and the hydrogen bonding energy is increased in all cases. Since hydrogen bonding surfaces show variations in wetting phenomena with solvent type and fluorinated surfaces do not, the surface of the treated polymers (direct fluorinated surfaces) must have both fluorinated and hydrogen bonding groups.

As we have seen for both a fluorinated and oxyfluorinated series of samples, both the polar and nonpolar forces vary with treatment condition. As a polyethylene sample is mildly treated then more heavily treated, the dispersion force continually decreases. At the same time hydrogen bonding force increases. This is believed due to both oxidation and fluorination occurring simultaneously. Upon longer fluorination exposure, the degree of fluorination continually increases to the limiting C:F of 0.67. This causes a continual lowering of the dispersion force to 22 dynes/cm and a reduction in the rate of hydrogen bonding force increase, since fluorinated surfaces have less wetting ability towards all solvents. This concept is in agreement with the data shown by Clark [19]. Although Clark states oxidation does not accompany fluorination, the data shows oxygen present on the surface of the fluorinated samples. The data also shows a leveling out of the percent oxygen upon longer fluorination times.

When a fluorinated polyethylene surface has a critical surface tension of 22 dynes/cm for nonpolar liquids, 30 dynes/cm for alkyl halides and 47 dynes/cm for hydrogen bonding liquids, the polar force is 8 dynes/cm and the hydrogen bonding force is 17 dynes/cm. This interprets to 38% dispersion force, 26% polar force and 36% hydrogen bonding force.

Using the approach of Owens and Wendt [7], the dispersion force and the hydrogen bonding force can be calculated using the following equation:

$$1 + \cos \theta = 2\sqrt{\gamma_S^D}\ \left(\frac{\sqrt{\gamma_L^D}}{\gamma_{LV}}\right) + 2\sqrt{\gamma_S^H}\ \left(\frac{\sqrt{\gamma_L^H}}{\gamma_{LV}}\right)$$

where θ = contact angle;

γ_S^D, γ_L^D = dispersion force for the solid and liquid, respectively;

γ_S^H, γ_L^H = hydrogen bonding force for the solid and liquid, respectively;

γ_{LV} = surface tension of the liquid.

When we use the respective values for hexadecane, methylene iodide and water, the dispersion force, the polar force and the hydrogen bonding force are calculated, Table 8. This approach estimates the surface energy to be between 20.3 and 24.9 dynes/cm; whereas, the experimental value ranges from 22 to 47 dynes/cm depending on the liquid series chosen. If the individual terms are considered, the γ_S^D term for treated polyethylene is between the γ_S^D terms for poly (trifluoroethylene) and poly (tetrafluoroethylene) surfaces, 19.9 and 12.5 ergs/cm^2, respectively. However, the γ_S^H term is higher than poly (vinylidene fluoride), 7.1 ergs/cm^2; it is more in line with a hydrogen bonding polymer such as nylon 6-6, 9.1 ergs/cm^2. It is interesting to note than when the hydrogen bonding solvent is used for this calculation, the hydrogen bonding term, γ_S^H, is 33% of the total surface energy. This agrees with our previous findings when we used the following equation:

$$\frac{\gamma_S^H - \gamma_S^D}{\gamma_S^H} \times 100 = \%\ \text{hydrogen bonding force}$$

TABLE 8

Components of surface energy for treated PE and other polymers

Sample	Water	Contact Angle, ° Methylene Iodide	Hexadecane	ergs/cm^2 γ_s^D	γ_s^H	γ_s	γ_c dynes/cm
Fluorinated Polyethylene	85	75.1	54.3	18.9^2 16.57^3	1.35^2 8.28^3	20.27^2 24.9^3	$22\text{-}47^4$
Polyethylene^1	94	52	-	32.0	1.1	33.1	31
Poly (vinyl fluoride)^1	80	49	-	31.3	5.4	36.7	28
Poly (vinyliden fluoride)^1	82	63	-	23.2	7.1	30.3	25
Poly (trifluoroethylene)^1	92	71	-	19.9	4.0	23.9	22
Poly (tetrafluoroethylene)^1	108	88	-	12.5	1.5	14.0	18.5
Nylon 6-6^1	70	41	-	34.1	9.1	43.2	46
Poly (ethylene terephthalate)^1	81	38	-	37.8	3.5	41.3	43.0

1 - See Ref. 7.

2 - Values using hexadedane/methylene iodide.

3 - Values using methylene iodide/water.

4 - See text.

TABLE 9

I_{SL}^{P} values for a treated PE bottle

Solvent	γ_L	γ_L^P	γ_L^D	θ	cos θ	I_{SL}^{P}
Water[1]	72.8	51.0	21.8	85	0.087	35.3
Formamide[2]	58.2	18.7 (26.2)[3]	39.5 (32)[3]	42.6	0.736	42.1
Methylene Iodide[2]	50.8	2.3	48.5	75.1	0.257	-1.47
Hexadecane[1]	27.6	0	27.6	49	0.656	-45.7
Toluene[4]	27.9	4.4	23.3	32.9	0.840	-6.05

1 - See Ref. 28.

2 - See Ref. 4.

3 - See Ref. 8a.

4 - See Ref. 14.

Dann [8b] has introduced a nondispersion term to indicate the polar character of a surface, I_{SL}^{P}. This term is calculated from the following equation:

$$I_{SL}^{P} = (\cos\theta + 1)\,\gamma_L - 2\sqrt{\gamma_S^D\,\gamma_L^D}$$

Using this equation and 22 dynes/cm as γ_S^D, I_{SL}^{P} has been calculated for several liquids, Table 9. Again the nondispersion term approximates nylon 6-6 ($I_{SL}^{P} = 38.7$) when water is used as the liquid. As the polarity of the solvent decreases, the nondispersion interaction also decreases.

In conclusion, the present study has shown that a polar surface may be studied by contact angle measurements using three series of solvents; nonpolar, polar, and hydrogen bonding. By this method, the dispersion energy, polar energy, and hydrogen bonding energy of the surface can be determined. In addition, not only can the dispersion energy and polar energy be calculated from theoretical considerations but is has been shown that the hydrogen bonding energy also can be calculated using these methods.

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