Surface Tension Versus Barrier Property for Fluorinated Surfaces

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Synopsis

The barrier property of fluorinated surfaces was compared to the surface tension measurements. A relationship between barrier property and the solvent's surface tension was developed. However, other properties of both the solvent and the polymer contribute to barrier property. The surface tension of the polymer surface was separated into nonpolar, polar, and hydrogen bonding forces. By estimating the % $\gamma_L{}^D$ of various solvent mixtures, the % $\gamma_S{}^D$ was estimated for the polymer surface.

INTRODUCTION

Recently, it has been reported that fluorinated polyethylene bottles have improved barrier property toward various solvents.[1] In order to better understand the chemistry behind this phenomenon, the surface tensions of these bottles were compared to the barrier property observed.

It has been shown that in order for a solvent to permeate a polymer substrate, the solvent must first dissolve in the polymer, diffuse through the resin, and finally evaporate.[2] As the solubility of the solvent increases, permeation through the polymer will increase. Diffusion depends mainly on solubility and diffusivity of the vapor. This means that a surface treatment of a polymer resin will only affect the first step of permeation, namely, solution formation.

Solubility depends on the surface tension of both the polymer and the solvent.[3] If a solvent does not permeate a polymer resin, then a surface treatment will have no effect on its permeation rate. If, however, the solvent does dissolve in the polymer, then the permeation rate will be dependent on the solubility of the solvent in the surface coating.

According to the activated diffusion theory of permeation, it is assumed if a solvent is not dissolved readily in the solute (polymer), it will not permeate it easily.[4] In order to determine if a solvent will dissolve in a polymer, the solvent's solubility parameter is compared to the polymer's solubility parameter. Those solvents with solubility parameters close to, or identical with, that of the polymer will be soluble in the polymer.[5] There are several ways to determine a polymer's solubility parameter, one of which is to estimate it from the surface tension of the polymer[5-7]:

$$\delta_s = 4.1(\gamma_c/V^{1/3})^{0.43}$$

where δ_s = solubility parameter of the polymer, γ_c = critical surface tension of the polymer, and V = molar volume of the polymer. Hansen has shown that spreading or wetting of a solvent on a polymer surface is analogous to dissolving and has used this relationship to assign solubility parameters to surfaces.[8]

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Zisman and coworkers have shown that the critical surface tension of a surface can be obtained by measuring the contact angle of a solvent on a surface.[9] 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 critical surface tension. A recent report has used this approach to define the surface of fluorinated polyethylene.[10]

Since there is adequate precedent to use contact angle measurements to study the surface tension of a polymer, this approach has been used to define the action of fluorine on a polymer surface and its relationship to permeation.

EXPERIMENTAL

Polyethylene bottles were fluorinated using a modification of the procedure reported by Schonhorn and Hansen.[11] The bottles were treated both at various fluorine concentrations and at various reaction times in order to obtain a range of fluorine incorporation. Since different methods were used to treat the bottles, variations in surface chemistry is expected. In addition, variations occur depending on the location of the bottle in the reactor within a given experiment. However, the general trend obtained in this work is accurate.

Experiments were conducted on determining the effect of various processing agents and other similar additives on the surface chemistry of the fluorinated bottles. There were no significant changes in surface chemistry due to these additives. During the course of this work, a variety of commercial resins were fluorinated. No significant differences were noted for the various resins. Therefore, the relationship between surface chemistry and barrier property was restricted to natural polyethylene bottles containing normal processing chemicals.

Surface energy measurements were obtained by the method of Hayes.[10] Permeation data were also obtained as reported earlier.[1]

DISCUSSION

In order to correlate surface energy to permeation studies, the polyethylene bottles were treated so that the fluorine incorporation ranged from 0.018% to 0.041% F. Table I gives the permeation data of toluene for the four bottles, the fluorine incorporation, and the surface tension. The surface tensions were obtained by using three series of solvents: nonpolar, polar, and hydrogen bonding. Table II gives the contact angles and work of adhesion for the various solvents on these samples. Work of adhesion, W_A, is defined by[12]

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

where γ_l = surface tension of the liquid and θ = contact angle of the liquid on the polymer. As can be seen from Tables I and II, there is an increase in surface tension on going from sample 2 to sample 3. This variation probably results in the differences in reaction conditions or in the lack of complete control of the reaction parameters in this process.

The Young equation relates the various parameters involved at the liquid–solid–vapor interfaces when a drop of liquid is placed on a planar horizontal surface[13]:

$$\gamma_{lv}\cos\theta = \gamma_{SV} - \gamma_{Sl} - \pi_e$$

TABLE I
Surface Tensions for Various Treatment Levels of PE Bottles

Sample	$\gamma_S{}^D$, dynes/cm	$\gamma_S{}^P$, dynes/cm	$\gamma_S{}^H$, dynes/cm	% Wt loss at 50°C toluene (4 days)	% F incorporated
Control	31.0[a]	35.0[b]	35.0[b]	12.0	0.0
Sample 1	29.0	33.5	40.0	0.60	0.018
Sample 2	24.5	29.5	40.0	0.15	0.020
Sample 3	25.5	30.5	44.5	0.08	0.028
Sample 4	22.0	30.5	47.0	0.04	0.041

[a] Zisman's γ_c, reference 14.
[b] Our data for polar and hydrogen bonding solvents.

where γ = interfacial tension and subscripts refer to the phases (s, solid; l, liquid; v, vapor), θ = contact angle between the liquid drop and the solid surface, and π_e = equilibrium spreading pressure = 0. By plotting the cosines of the contact angles of various liquids against their surface tensions, then extrapolating to cos $\theta = 1$, the intercept is defined as the critical surface tension of wetting, γ_L. Therefore, from the Young equation γ_c is equal to $\gamma_{SV} - \gamma_{SL}$ at cos $\theta = 1$.

When this technique was applied to the contact angle data obtained on the four polyethylene bottles that had been fluorinated at different treatment levels, three distinct surface tensions were obtained for each bottle depending on the solvent series used. When these same liquids were applied to an untreated polyethylene surface, only one plot was obtained. Since nonpolar (hydrocarbons), polar (halocarbons), and hydrogen bonding (alcohols and amides) solvents were the three solvent classes used, these three distinct surface energies measure the dispersion, polar, and hydrogen bonding energies of the surface.[10]

Thus, the surface obtained by fluorination is one of lower dispersion energy, lower polar energy, and higher hydrogen bonding energy than the untreated polyethylene surface. Fluorination would be predicted to lower the surface energy since fluorocarbons have lower surface energies than the corresponding hydrocarbon.[14] However, the increased surface tension for hydrogen bonding solvents is unexpected in view of the work by Clark indicating oxidation does not accompany fluorination.[15] It has since been shown that, in fact, oxidation does accompany fluorination.[10]

The hydrogen bonding ability for fluorine is considered very low so that the fluorine atom alone does not account for the increased wetting. Miller[16] and Shinohara[17] have shown that if oxygen is present during the fluorination reaction, oxidation can occur.

In order to test this theory, polyethylene was fluorinated in the presence of added oxygen. The polar energy increased 3.5 dynes/cm over a surface that had been treated in the absence of added oxygen. Therefore, the trace amounts of oxygen present in the reactor during the fluorination are enough to allow for oxidation of the polyethylene surface.

The source of oxygen could be as an impurity in the treatment gases, as a residue in the reactor, or as absorbed oxygen in the polymer. There are presently no adequate methods to accurately determine the oxygen concentration in fluorine gas. There are several methods by which the oxygen content can be estimated. However, this has little effect on the utility of the fluorination process

TABLE II
Contact Angle Data and Work of Adhesion

Solvent	γ_L	Sample 1			Sample 2			Sample 3			Sample 4		
		θ	$\cos\theta$	W_A	θ	$\cos\theta$	W_A	θ	$\cos\theta$	W_A	θ	$\cos\theta$	W_A
Decane	23.9	0	1.00	47.8	0	1.00	47.8	0	1.00	47.8	33.0	0.839	43.95
Dodecane	25.4	0	1.00	50.8	20.0	0.94	49.3	12.0	0.978	50.2	42.4	0.739	44.17
Tetradecane	26.7	0	1.00	53.4	20.5	0.937	51.7	17.0	0.956	52.2	33.5	0.834	48.9
Hexadecane	27.6	0	1.00	55.2	24.3	0.918	52.9	14.5	0.968	54.3	49.0	0.656	45.7
Decahydronaphthalene	33.5	43.5	0.725	57.8	46.4	0.69	56.6	43.8	0.722	57.7	57.4	0.539	51.6
Carbon tetrachloride	26.95	0	1.00	53.9	0	1.00	53.9	0	1.00	53.9	10.8	0.982	53.4
Chloroform	27.14	0	1.00	54.28	0	1.00	54.28	4.8	0.997	54.2	0	1.00	54.28
Tetrachloroethylene	31.74	0	1.00	63.5	19.1	0.945	61.7	19.0	0.946	61.8	15.5	0.964	62.3
Chlorobenzene	33.56	26.5	0.895	63.6	34.3	0.827	61.3	29.4	0.871	62.8	40.3	0.763	59.2
1,1,2,2-Tetrachloroethane	36.03	24.5	0.910	68.8	36.3	0.806	65.1	34.5	0.824	65.7	31.5	0.853	66.8
1-Bromonaphthalene	44.6	49.5	0.649	73.5	64.1	0.436	64.0	64.0	0.438	64.1	69.4	0.352	60.3
Diiodomethane	50.8	64.0	0.438	73.1	79.4	0.184	60.1	78.6	0.197	60.8	75.1	0.257	63.8
Toluene	28.5	0	1.00	57.0	10.3	0.984	56.5	0	1.00	57.0	32.9	0.84	52.4
Water	72.8	70.0	0.342	97.7	89.1	0.015	73.9	79.8	0.178	85.6	85.0	0.087	75.1
Formamide	58.2	36.3	0.806	105.1	53.8	0.591	92.6	47.3	0.679	97.7	42.6	0.736	101.0
2,2'-Thiodiethanol	54.0	49.0	0.656	89.4	68.3	0.371	74.0	52.3	0.612	87.1	46.1	0.693	91.4
N,N-Dimethylacetamide	37.37	0	1.00	74.5	0	1.00	74.5	0	1.00	74.5	0	1.00	74.5

as a barrier treatment other than to indicate a desire to have no oxygen present during the reactions.

From the activated diffusion theory of permeation, it could be predicted that since the nonpolar and polar surface energies decreased and the hydrogen bonding surface energy increased, the permeation rates for many solvents through the treated polyethylene surface would be different. Further, it could be predicted that many hydrocarbons would be retained since the nonpolar surface energy was similar to trifluoroethylene and yet more polar than the hydrocarbons. Solvents with intermediate polarity could not be predicted as to permeation rate.

Even though the dispersion force continually decreases upon higher fluorination levels, not until the surface tension $\gamma_S{}^D$ is significantly lowered with respect to the control (γ_S control = 31 to γ_S treated < 26 dynes/cm) does the barrier property of the treated bottle improve greatly. The polar force decreases to a constant value, $\gamma_S{}^P \sim 30$ dynes/cm, while the hydrogen bonding force continually increases upon treatment.

The significance of these results is found when barrier property improvement for a treated bottle is compared to the surface tension of the solvent, Table III. When a polyethylene bottle is treated with fluorine to increase the barrier property of the container, it must be treated such that the dispersion force is less than 25 dynes/cm and preferably 22 dynes/cm. When this is accomplished,

TABLE III
Solvents Used in Permeability Study

Solvent	γ_L	% Wt loss F_2-PE (11 days)	% Wt loss PE control (11 days)
n-Pentane	—	0.21	98.10
n-Hexane	18.43	0.19	61.29
n-Heptane	—	0.08	24.26
Isooctane	—	0.03	4.54
Cyclohexane	25.5	0.15	22.34
Carbon tetrachloride	26.95	0.05	28.26
Benzene	28.85	3.65	36.68
Toluene	28.5	1.80	41.23
o-Xylene	30.1	0.54	59.20
Mesitylene	—	0.18	15.83
Chlorobenzene	33.56	5.41	32.05
Glyme	—	13.20	12.37
Diglyme	—	1.73	2.14
Tetrahydrofuran	—	45.66	53.93
Dioxane	—	3.04	4.23
Chloroform	27.14	38.17	44.93
Methylene chloride	26.52	46.26	50.81
1,2-Dichloroethane	24.0	8.09	8.54
Acetone	23.7	2.58	2.51
Methyl ethyl ketone	24.6	2.68	2.81
Ethyl acetate	23.9	3.39	3.57
DMSO	—	0.12	0.09
Methanol	22.61	0.66	0.75
n-Propanol	23.78	0.35	0.34
Isopropanol	—	0.19	0.32
n-Butanol	24.6	0.27	0.30

barrier property toward hydrocarbon solvents is improved. As was seen from contact angle measurements, aromatic solvents still wet readily and thus are not retained as well. Aromatic compounds are also more polar than the saturated hydrocarbons, thus the surface tension for these solvents must be higher in order to be retained.

The higher surface tension requirement for polar solvents is due to the polar force of the treated surface. In order to prevent wetting by the polar liquids, the surface tension of the liquid must be greater than 30 dynes/cm. This explains why no improvement is noted for chloroform (γ_L = 27.14 dynes/cm) and methylene chloride (γ_L = 26.5 dynes/cm). Carbon tetrachloride (γ_L = 26.95 dynes/cm) is retained because the molecule is nonpolar and thus it needs only a surface tension greater than 22 dynes/cm to be held.

When solvent mixtures are considered, the surface tension of the mixture is estimated from the partial surface tensions of the components. That is, a 50–50 mixture of a polar and a nonpolar solvent of, say, 50 and 20 dynes/cm, respectively, would have a surface tension of 35 dynes/cm. When this approach is used for the solvent mixtures of toluene/ethyl acetate and toluene/acetone, the surface tensions can be estimated (Table IV). Since toluene is not as polar as the solvents used to obtain the polar force of the polyethylene surface, the surface tension of toluene need not be above 30 dynes/cm to show reduced permeation. However, when it is mixed with a highly polar solvent, acetone or ethyl acetate, the surface tension of the mixture must be higher to show reduced permeation.

As can be seen from Table IV, the solvent mixtures do not show increased surface tensions but rather reduced surface tensions and subsequently higher permeation rates than the pure solvent. This series of solvents also show how the polarity of the solution affects permeation. When the % dispersion force of the solvent is estimated by summing the individual dispersion, polar, and hydrogen bonding terms,[4] the permeation rate is highest between 75% and 80% $\gamma_L{}^D$ for the treated bottles. However, the absolute permeation rate declines as the polarity increases, % $\gamma_L{}^D$ decreases. This is because the solvent is more polar than the control portion of the bottle and thus the overall rate decreases. This maximum permeation between 75% and 80% $\gamma_L{}^D$ also indicates that $\gamma_S{}^D$ should be between 75% and 80% of the surface energy. From Table I it can be seen that, in fact, $\gamma_S{}^D$ is 75%–80% of the $\gamma_S{}^P$ term for a treated surface.

TABLE IV
Permeation of F_2-PE with Solvent Mixtures

Solvent system	Surface tension, dynes/cm	F_2-PE bottle % weight loss (20 days, 122°F)	Control % weight loss (20 days, 122°F)	% $\gamma_L{}^D$ [a]
Toluene	28.5	6.7	85.5	83.8
Toluene/EtOAc 10:1	28.08	35.1	83.8	80.53
Toluene/EtOAc 5:2	27.19	45.2	56.6	74.17
Toluene/EtOAc 1:1	26.2	43.2	41.9	67.9
Toluene/EtOAc 2:5	25.2	16.0	20.5	62.28
EtOAc	23.9	7.5	8.8	55.8
Toluene/acetone 10:1	28.06	68.1	89.1	79.9
Toluene/acetone 5:2	27.13	47.9	51.0	69.95
Toluene/acetone 1:1	26.1	34.4	35.1	61.65
Toluene/acetone 2:5	25.07	16.7	13.0	54.65
Acetone	23.7	5.0	5.0	47.21

[a] See reference 4.

If the treated and control permeation rates are compared, the maximum relative permeation rate for the treated bottle occurs at 67.9% $\gamma_L{}^D$ for toluene/ethyl acetate and at 54.7% $\gamma_L{}^D$ for toluene/acetone. This probably arises from the best combination of solvent properties to allow for maximum permeation rates through both the treated and control molecules.

It could be argued that when the dispersion energy is less than 80% of the total energy of the solution, then the control portion of the bottle determines the rate of solvent permeation.

Finally, it is noted that several hydrocarbon solvents are retained even though the surface tension of the liquid is less than 22 dynes/cm. This results from the fact that both the fluorine atoms and the polar groups on the treated surface cause the surface to be so unlike the hydrocarbon solvents, e.g., more polar than the alkanes, that even though these solvents may wet the surface, they do not dissolve in the surface layer readily. Without solution formation, penetration is not possible.

Thus, it has been shown that the surface of a fluorinated polymer can be described by both surface tension measurements and solvent barrier properties. These physical measurements will be correlated to chemical changes as determined by ESCA studies at a later date.

References

1. D. D. Dixon and L. J. Hayes, *J. Appl. Polym. Sci.*, to appear.
2. C. W. Hall, *Mod. Packag.*, **46**, 53 (1973).
3. M. Salame and J. Pinsky, *Mod. Packag.*, **36**, 153 (1962).
4. J. H. Parliman, *Mod. Packag.*, **22**, 198 (1948).
5. J. L. Gardon, Cohesive-Energy Density, in *Encyclopedia of Polymer Science and Technology*, Vol. 3, Interscience, New York, 1965, p. 833.
6. J. H. Hildebrand and R. L. Scott, Evaluation of Solubility Parameters, in *The Solubility of Nonelectrolytes,* Reinhold, New York, 1950, p. 431.
7. C. M. Hansen, *Ind. Eng. Chem., Prod. Res. Dev.,* **8**, 2 (1969).
8. C. M. Hansen, *Chemtech.,* **2**, 547 (1972).
9. E. G. Shafrin and W. A. Zisman, *J. Phys. Chem.,* **61**, 1046 (1957).
10. L. J. Hayes, *J. Fluorine Chem.,* **8**(1), 69 (1976).
11. H. Schonhorn and R. H. Hansen, *J. Appl. Polym. Sci.,* **12**, 1231 (1968).
12. J. W. Swanson and J. L. Becker, *Tappi,* **49**(5), 198 (1966).
13. T. Young, *Trans. R. Soc. (London),* **95**, 65 (1805).
14. H. W. Fox and W. A. Zisman, *J. Colloid Sci.,* **7**, 428 (1952).
15. D. T. Clark, W. J. Feast, W. K. R. Musgrave, and I. Ritchie, *J. Polym. Sci.,* **13**, 875 (1975).
16. W. T. Miller, Jr., *Fluorine Free Radical Chemistry,* U.S. Army Report AD647471, 1966.
17. H. Shinohara, M. Iwasaki, and S. Tsujimura, *J. Polym. Sci. A-1,* **10**, 2129 (1972).