

NRL Report 5952

Surface Activity of Fluorinated Organic Compounds at Organic-Liquid/Air Interfaces

Part V - The Effect of Partially Fluorinated Additives on the Wettability of Solid Polymers

N. L. JARVIS AND W. A. ZISMAN

*Surface Chemistry Branch
Chemistry Division*

and

R. B. FOX AND L. G. ISAACS

*Organic and Biological Chemistry Branch
Chemistry Division*

August 9, 1963



U.S. NAVAL RESEARCH LABORATORY
Washington, D.C.

PREVIOUS REPORTS IN THIS SERIES

"Part I - Surface Tension, Parachor, and Spreadability,"
N.L. Jarvis and W.A. Zisman, NRL Report 5244, Jan. 20, 1959

"Part II - Surface Tension vs Concentration Curves, Adsorption Isotherms, and Force-Area Isotherms for Partially Fluorinated Carboxylic Esters," N.L. Jarvis and W.A. Zisman, NRL Report 5364, Oct. 8, 1959

"Part III - Equation of State of Adsorbed Monolayers and Work of Adsorption of a Fluorocarbon Group," N.L. Jarvis and W.A. Zisman, NRL Report 5401, Nov. 17, 1959

"Part IV - Effect of Structure and Homology," M.K. Bennett, N.L. Jarvis, and W.A. Zisman, NRL Report 5705, Dec. 18, 1961

Copies available from Office of Technical Services
Department of Commerce - \$.50

CONTENTS

Abstract	1
Problem Status	1
Authorization.....	1
INTRODUCTION	1
EXPERIMENTAL MATERIALS AND METHODS	2
EXPERIMENTAL RESULTS	6
Polystyrene	6
Poly(methyl methacrylate)	7
Polyvinylidene Chloride Copolymer.....	8
Polyacrylamide	9
DISCUSSION	10
REFERENCES	11

Surface Activity of Fluorinated Organic Compounds at Organic-Liquid/Air Interfaces

Part V - The Effect of Partially Fluorinated Additives on the Wettability of Solid Polymers

N. L. JARVIS, R. B. FOX, L. G. ISAACS, AND W. A. ZISMAN

Chemistry Division

The surface properties of polymeric solids have been successfully modified by the adsorption of appropriate fluorinated compounds at polymer/air interfaces during the formation of the polymer surfaces. It was found that certain fluorocarbon derivatives would adsorb at polymer/air interfaces when added directly to the monomer before polymerization or when placed in a solution of the polymer, in which case the polymer surface was formed by the slow evaporation of the solvent. As expected, the amount of adsorption in either case was found to be dependent upon the organophilic/organophobic balance in the solute, which depends upon its fluorine content, molecular structure, and solubility in the bulk polymer phase.

The surface activity of the fluorinated compounds at each polymer/air interface was determined from the changes in wettability of the smooth, solid polymer surfaces brought about by their adsorption. It was demonstrated that additives developed previously to be surface active in organic liquids markedly decreased the critical surface tension of wetting (γ_c) of polymer surfaces. Values of γ_c of poly(methyl methacrylate) and a polyvinylidene chloride copolymer (containing 20 percent polyacrylonitrile) were reduced from approximately 39 dynes/cm to between 19 and 21 dynes/cm, when concentrations of about 1 percent by weight of suitable surface-active agents were dissolved in the polymers. An even lower value of γ_c of 10.4 dynes/cm was observed for polyacrylamide containing a surface-active additive. These low values of γ_c correspond to surfaces containing closely packed CF_2 and CF_3 groups, respectively.

INTRODUCTION

The wettability and adhesiveness of solid, smooth polymeric surfaces are strongly dependent upon the chemical constitution of the surface layer of molecules (1-3); therefore, in order to modify these surface properties it is necessary to alter the chemical composition of the surface in some way. One example of such a modification is the commercial use of controlled oxidation of the surface of polyethylene foil to insure wetting by and adhesion of polar printing inks (4). A series of studies of surface activity of soluble and insoluble compounds at organic-liquid/air interfaces have been reported by Zisman, Ellison, Bernett, and Jarvis (5-10). The most surface-active compounds were found to be various fluorocarbon derivatives having the proper organophilic/organophobic balance. If one considers a plastic solid to be either a supercooled liquid or a liquid of very high viscosity, then one would expect many of these partially fluorinated compounds to

manifest great surface activity when dissolved in various polymers, provided sufficient time is allowed for diffusion of the solute to the interface and for adsorption equilibrium to occur. The extent to which a surface-active solute adsorbs at a polymer surface will be determined by essentially the same properties that are responsible for their effectiveness in organic liquids, namely their concentration, ability to lower the surface energy of the system, fluorine content, and their solubility, or extent of association with the polymeric substrate. By analogy with aqueous systems, one might briefly call the combination of these properties in a fluorocarbon derivative its organophilic/organophobic balance.

The rate at which one of these surface-active agents will adsorb at the polymer/air interface will be primarily determined by the rate of diffusion in the bulk polymer phase. If added to a molten polymer or to a solution of the polymer in a volatile solvent, the surface-active agent will be able to diffuse sufficiently rapidly to adsorb at the surface as the polymer solidifies or as the solvent evaporates. The rate of adsorption will necessarily be much slower if the surface-active

NRL Problem C02-10; Subproject RR 001-01-43-4751. This is an interim report; work on this problem is continuing.

molecules do not have time to reach adsorption equilibrium at the polymer surface while the polymer is still in the fluid state. Once the polymer film is solid it may take hours or days for a significant amount of the additive to migrate to the surface, depending upon the concentration of the additive and the nature of the polymer.

Obviously the presence of adsorbed and oriented fluorocarbon groups at the polymer/air interface not only will decrease the surface-free energy of the polymer, and thus its wettability, but also should modify its coefficient of friction and decrease its adhesive properties. It is the purpose of this report to demonstrate the effectiveness of a small concentration of a partially fluorinated additive in changing the surface constitution and reducing the wettability of various polymer surfaces.

EXPERIMENTAL MATERIALS AND METHODS

The partially fluorinated compounds used in this investigation as the surface-active additives are listed in Table 1. Additives 1 through 6, which were prepared in high purity at NRL (11,12), have been used in the previous studies of surface activity at organic-liquid/air interfaces (5-10). Additives 7 and 8 are research preparations donated by the Organic Chemical Department of E.I. du Pont de Nemours and Company and by the Minnesota Mining and Manufacturing Company, respectively. The carefully purified liquids used in the determination of the critical surface tension of wetting, γ_c , were selected to give a wide range of surface tensions and a variety

of structural types. Sources, methods of purification, and surface tensions of the majority of these liquids (Tables 2-5) have been given in previous reports from NRL (13, 14). The 1,1-diphenylethane used, a product of Eastman Organic Chemicals, had been freed from polar impurities by several percolations through a column of Florisil.

Four polymers with different surface compositions were used in this study: polystyrene (PS), poly(methyl methacrylate) (PMMA), polyacrylamide (PAM), and a polyvinylidene chloride (PVeC) copolymer (containing 20 percent polyacrylonitrile). Polystyrene has essentially a hydrocarbon surface, whereas the surfaces of poly(methyl methacrylate) and polyacrylamide contain ester and amide groups, respectively. The surface of the polyvinylidene chloride copolymer, on the other hand, will contain a relatively large number of chlorine atoms. The presence of acrylonitrile in the polyvinylidene chloride copolymer improved the solubility characteristics of the polymer for the purposes of this study, but did not appreciably alter γ_c . Values of γ_c of these polymers ranged from 30 to 33 dynes/cm for polystyrene to approximately 40 dynes/cm for the polyvinylidene chloride copolymer.

The poly(methyl methacrylate) (PMMA) used in these experiments was obtained from freshly distilled degassed monomer by bulk polymerization to 30 percent conversion at 60°C with azodiisobutyronitrile as initiator. The polymer was purified by two reprecipitations from tetrahydrofuran solution with methanol. After drying at room temperature under vacuum for 24 hours, the material had average molecular weight $\bar{M}_v = 7.76 \times 10^5$. Mass spectroscopic analysis of the volatile

TABLE 1
Partially Fluorinated Compounds Used as
Surface-Active Additives

Number	Surface - Active Solute
1.	Tris(1H,1H-pentadecafluorooctyl) tricarballylate
2.	3-(hydroxymethyl)-1,5-pentanediol tris(heptafluorobutyrate)
3.	Bis(1H,1H-undecafluorohexyl) 3-methylglutarate
4.	Bis(1H,1H-pentadecafluorooctyl) tetrachlorophthalate
5.	1H,1H-pentadecafluorooctyl ethanesulfonate
6.	Bis(1H,1H-heptafluorobutyl) adipate
7.	18,18,19,19,20,20,21,21,22,22,22-undecafluorodocosanoic acid
8.	<u>N,N,N</u> -dimethyl 3-(<u>n</u> -perfluoroheptanecarboxamido) propyl-3-aminopropionic acid, inner salt

TABLE 2
Contact Angles for Various Liquids on Polystyrene

Liquid	Surface Tension (dynes/cm)	Contact Angles θ (degrees)			
		Pressed Disc No Additive	Surface by Solvent Evaporation		
			No Additive	4% Additive 3	10% Additive 2
Water	72.6	93	96	96	97
Glycerol	63.4	82	84		
Formamide	58.2	76	80		
Thiodiglycol	54.0		63		
Methylene iodide	50.8	*	*		
Arochlor 1242 (trichlorobiphenyl)	45.3	18	16		
α -Bromonaphthalene	44.6	18	15		
Tricresyl phosphate	40.9	14	18	16	18
Hexachloropropylene	38.1	11	14		
1,1-Diphenylethane	37.7	12	12		
t-Butyl naphthalene	33.7	Spr.†	Spr.		
Dicyclohexyl	32.8	Spr.	Spr.		
Bis(2-ethylhexyl) orthophthalate	31.3	7	10	12	14
Squalane	29.5		6		
Hexadecane	27.6	Spr.	Spr.	6	9
Tetradecane	26.7	Spr.	Spr.	Spr.	Spr.

*Polymer dissolved in methylene iodide.

†Contact angle less than 5 degrees; spreading.

material obtained by heating 0.1-g film samples of the polymer at 110°C for four hours showed 7.4×10^{-7} moles of monomer and traces of methylene chloride solvent, no other volatile material having been evolved. Films of PMMA about 15 μ thickness, with and without additives, were prepared in shallow rectangular Pyrex glass dishes by slow evaporation (for 24 hours or more), at room temperature, of methylene chloride solutions of about 0.1 g of the polymer and appropriate amounts of additive. During most of this time the surface-active compounds were free to diffuse to the polymer/air interface. Traces of solvent were removed by continuous pumping at room temperature an additional 16 hours. Finally, samples were stored in the evacuated desiccator until the contact-angle measurements could be made, usually within three days.

Polystyrene was prepared from freshly distilled and degassed styrene by bulk polymerization at 50°C under nitrogen with benzoyl peroxide as the initiator; conversion was about 50 percent. After precipitation with methanol, the polymer was purified by two reprecipitations from tetrahydrofuran solution with methanol, exhaustively extracted with methanol, and finally vacuum dried at room temperature. The polymer had $M_v = 1.8 \times 10^5$. Films of this material were prepared from methylene chloride solution in the same way as the PMMA films.

Acrylamide, melting point 85°C (from ethyl acetate), was polymerized in aqueous solution at about 75°C in the presence of 2-propanol and potassium persulfate as described by Sorenson and Campbell (15). The polyacrylamide (PAM) was further purified by an additional precipita-

TABLE 3
Contact Angles of Various Liquids on Poly(methyl methacrylate)

Liquid	Surface Tension (dynes/cm)	Contact Angles θ (degrees)						
		Pressed Disc No Additive	Surface Formed by Solvent Evaporation					
			No Additive	No Additive (after cleaning)	0.2% Additive 1	0.5% Additive 1	0.5% Additive 2	1.0% Additive 2
Water	72.6	80	94	76	96	96	96	97
Glycerol	63.4	69	88	69	89	91	96	
Formamide	58.2	64	75	63	79	85	85	
Thiodiglycol	54.0	47	63	46	59	59	61	
Methylene iodide	50.8	41	43	42	42	46	45	51
α -Bromonaphthalene	44.6	16	16	18	17	18	15	
Tricresyl phosphate	40.9	19	20	24	24	26	32	
Hexachloropropylene	38.1	Spr.	Spr.	Spr.	Spr.	Spr.	Spr.	
1,1-Diphenylethane	37.7	Spr.	Spr.	Spr.	Spr.	Spr.	10	
<i>t</i> -Butylnaphthalene	33.7	Spr.	Spr.	Spr.	10	11	8	
Dicyclohexyl	32.8	Spr.	Spr.	Spr.	41		6	40
Bis(2-ethylhexyl) orthophthalate	31.3	Spr.	8	6	19	18	20	
Squalane	29.5	Spr.	26		44	44	21	47
Hexadecane	27.6	Spr.	14	Spr.	48	52	19	39
Tetradecane	26.7		11	Spr.	45	48	15	36
Dodecane	25.4		Spr.	Spr.	43	44	9	33
Decane	23.9				37	39	Spr.	31
Octane	21.8				23	29		23

tion from aqueous solution with methanol and dried in vacuum. Films were prepared by the slow evaporation of water from aqueous solutions of the polymer and additive.

The polyvinylidene chloride copolymer kindly furnished by the Dow Chemical Company contained 80 percent polyvinylidene chloride and 20 percent polyacrylonitrile. A small amount of carbonyl was the only impurity detected by the infrared spectra of a thin film of the copolymer. Films were prepared by the slow evaporation of tetrahydrofuran solutions; otherwise they were handled in the same manner as the PMMA samples.

Smooth surfaces of each polymer were also prepared (without additives) by pressing samples of the powdered polymers against a highly polished stainless steel surface in a Carver press at 16,000 psi. Circular discs weighing several grams and measuring an inch in diameter were formed in this way. PS and PVeC copolymer were compressed at room temperature, PAM at 120°C and PMMA at 150°C. The pressure was maintained until smooth polymer surfaces were obtained. The mold and stainless steel piston were cleaned prior to use so that contact angles could be measured on the polymer surfaces without further surface treatment.

TABLE 4
Contact Angles of Various Liquids on Polyvinylidene Chloride Copolymer

Liquid	Surface Tension (dynes/cm)	Contact Angles θ (degrees)			
		Pressed Disc No Additive	Surface by Solvent Evaporation		
			No Additive	1.0% Additive 1	1.0% Additive 4
Water	72.6	81	85	86	100
Glycerol	63.4	67	72	72	92
Formamide	58.2	65	70	71	82
Thiodiglycol	54.0	42			
Methylene iodide	50.8	27	27	29	50
Arochlor 1242 (trichlorobiphenyl)	45.3	11	Spr.	8	23
α -Bromonaphthalene	44.6	9	9	Spr.	
Tricresyl phosphate	40.9	10	11	12	30
Hexachloropropylene	38.1	Spr.	Spr.	Spr.	
1,1-Diphenylethane	37.7	Spr.	Spr.	Spr.	
t-Butylnaphthalene	33.7	Spr.	Spr.	Spr.	
Dicyclohexyl	32.8	Spr.	Spr.	Spr.	
Bis(2-ethylhexyl)orthophthalate	31.3	Spr.	Spr.	Spr.	20
Hexadecane	27.6	Spr.	Spr.		44
Tetradecane	26.7				41
Dodecane	25.4				36
Decane	23.9				27
Octane	21.8				11

Contact angles on each polymer surface for the various liquids in Tables 2 - 5 were determined while increasing the volume of the drop, and thus slowly advancing its periphery over the surface. The contact angles of each polymer surface prepared by solvent evaporation were measured through the plane ends of the rectangular glass dishes using the method and improved goniometer telescope described previously (16). All contact angles on PMMA, PS, and PVeC copolymer were measured in air, but to prevent the adsorption of water by the water-soluble polymer, contact-angle measurements on PAM were made in a dry nitrogen atmosphere. Every contact angle reported is the average of the values obtained on at least three different drops on that plastic surface, and at least two independent

samples of each surface were prepared. Contact angles for successive drops on a given polymer surface seldom varied more than 4 degrees; however, somewhat larger differences were sometimes observed between independently prepared samples of the same polymer containing small amounts of certain additives. These variations may be a function of the age of the solid; *i.e.*, the longer the polymer specimen ages the greater the amount of additive that may diffuse to the surface. Due to the difficulty involved in measuring small contact angles through the plane ends of the glass sample dishes, contact angles of 5 degrees or less will be considered as essentially zero and indicative of spreading for the purposes of this study. Each prepared sample containing an additive was allowed to stand no longer than four days before

TABLE 5
Contact Angles of Various Liquids on Polyacrylamide
(values obtained in a dry N₂ atmosphere)

Liquid	Surface Tension (dynes/cm)	Contact Angles θ (degrees)			
		Surface by Solvent Evaporation			
		No Additive	0.6% Additive 8	1.2% Additive 8	1.0% Additive 8*
Water	72.6				
Glycerol	63.4				
Formamide	58.2				
Thiodiglycol	54.0	28		84	
Methylene iodide	50.8	47	91	93	95
Arochlor 1242 (trichlorobiphenyl)	45.3	33	87	86	83
α -Bromonaphthalene	44.6	33	86	87	85
Tricresyl phosphate	40.9	31	87	87	85
Hexachloropropylene	38.1	Spr.	39	42	59
1,1-Diphenylethane	37.7	22	82	82	82
t-Butylnaphthalene	33.7	20	80	78	78
Dicyclohexyl	32.8	19			
Bis(2-ethylhexyl) orthophthalate	31.3	20	78	77	76
Squalane	29.5		76	74	74
Hexadecane	27.6	14	71	71	70
Tetradecane	26.7	11	68	68	67
Dodecane	25.4		66	65	64
Decane	23.9		62	62	60
Octane	21.8		57	56	54

*Additive 8 added to monomer prior to polymerization.

contact-angle measurements were made. All measurements were made at $25^\circ \pm 1^\circ\text{C}$ with the relative humidity varying from 15 to 30 percent.

EXPERIMENTAL RESULTS

Polystyrene

Contact angles of the various pure liquids on polystyrene are given in Table 2 for surfaces of pure polystyrene prepared by solvent evaporation as well as by compression of the powdered polymer. Values of θ obtained in each case agree well with those reported by Ellison and Zisman (17), as shown in Fig. 1 of this report. This agreement indicates that the polystyrene surfaces formed by

solvent evaporation are essentially free of contamination, for the presence of a modest fraction of a monolayer of residual methylene chloride solvent at the interface would significantly decrease the contact angles (18) below those reported in Table 2. The plot in Fig. 1 of $\cos \theta$ vs surface tension (γ_{LV}^0) for various pure liquids indicates that γ_c for polystyrene is between 30 and 35 dynes/cm, the same range that has been previously reported as the best estimate of the critical surface tension of polystyrene (17, 19).

The fluorocarbon additives 1 through 7 listed in Table 1 were added in varying concentrations to solutions of polystyrene in methylene chloride.

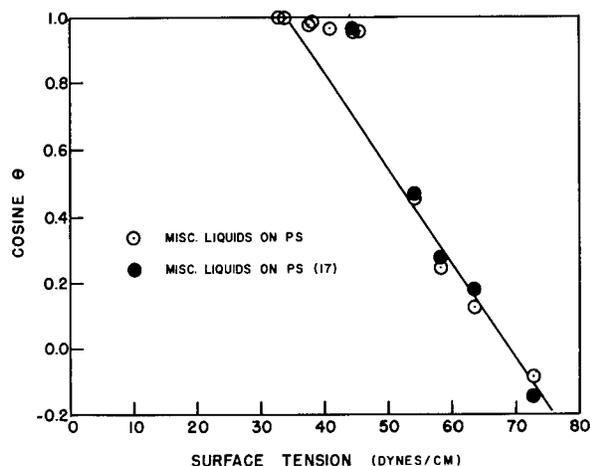


Fig. 1 — $\text{Cos } \theta$ vs γ_{LV} for various pure liquids on polystyrene surfaces

Each was added in concentrations up to at least 1 percent by weight of polymer, while the pentanediol (additive 2) and 3-methylglutarate (additive 3) derivatives were added in concentrations up to 10 percent and 4 percent respectively. In every case where only 1 percent additive was present there was no perceptible change in the wetting behavior of the polystyrene surface. Even at the higher concentrations, additives 2 and 3 had only a slight effect on the wettability of polystyrene, the most significant change being that hexadecane now gave definite, measurable contact angles. The ineffectiveness of these additives in polystyrene is a result of their low solubilities in the polymer. Each additive contains one or more highly polar ester or acid groups, which in combination with the high fluorine content of the molecule tends to cause low solubility in nonpolar liquids. In fact, in most instances the additives were so insoluble in the polystyrene that they either separated as another phase as the solvent evaporated or else formed cloudy, opaque films. Evidently, in order to modify the surface of polystyrene by adsorption of surface active molecules, it will be necessary to find more soluble partially fluorinated compounds.

Poly(methyl methacrylate)

The contact angles of the various liquids on PMMA surfaces are given in Table 3. The surfaces of PMMA (without additives) prepared by the two

independent techniques were initially studied exactly as prepared, without any attempt to clean the newly formed surfaces. Significant differences were observed between contact angles on these two surfaces, the specimen prepared by solvent evaporation exhibiting much higher contact angles with some liquids than the pressed discs. However, after the surface prepared by solvent evaporation was washed with detergent, rinsed profusely with distilled water, and dried, contact angles were obtained which agreed within the limits of experimental error with those measured on the pressed disc and were in better agreement with values reported in the literature. Craig and coworkers (20) have reported a contact angle of 78 degrees for water on clean PMMA, in very good agreement with that reported here for a clean surface. Therefore, the surface of the PMMA prepared by solvent evaporation had been contaminated by an easily removed film. It is unlikely the contamination came from the solvent, for samples of polystyrene prepared from the same batch of solvent and by the same technique did not show evidence of such contamination. It is concluded that the film removed by cleaning originated from a small amount of impurity in the PMMA sample which had adsorbed at the polymer/air interface as the solvent evaporated. A similar accumulation of impurity would not be expected to occur at the surface of the pressed disc due to the slower rate of diffusion in the solid polymer.

From the contact angles in Table 3, $\text{cos } \theta$ vs γ_{LV} was plotted in Fig. 2 for clean PMMA. From the intercept it is seen that γ_c is approximately 39 dynes/cm, well within the range of 33 to 44 dynes/cm recently reported by Wolfram (19). Ellison and Zisman (17) also obtained a critical surface tension of between 39 and 40 dynes/cm for polyethylene terephthalate, another polymer containing a large number of carboxylic ester groups.

The following fluorinated compounds were added to PMMA: tricarballylate (additive 1), pentanediol (additive 2), and 3-methylglutarate (additive 3) derivatives. Additive 1 was added in concentrations up to 0.5 percent by weight of polymer, while 2 and 3 were added in concentrations up to 1.0 and 2.0 percent, respectively. Contact angles of the surfaces prepared from PMMA containing fluorinated additives were studied without prior cleaning, as it was found that in many cases washing with a detergent would

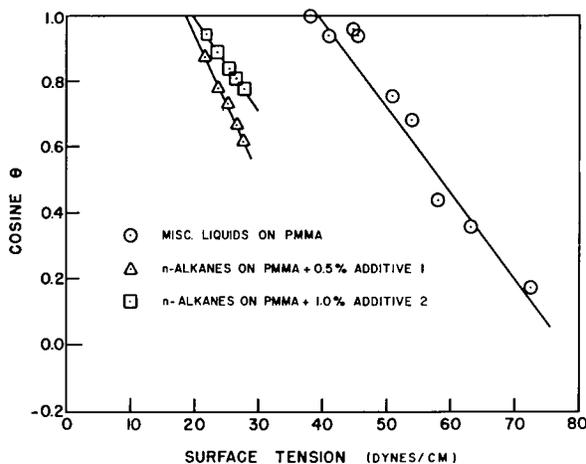


Fig. 2 — $\cos \theta$ vs γ_{LV} for various pure liquids on poly(methylmethacrylate) surfaces

remove significant amounts of the adsorbed additive. The trace of impurity in the PMMA discussed in the previous paragraph was not considered important here, since in the competitive adsorption between it and one of the highly surface-active fluorinated solutes, it would probably be the latter that would be the dominant specie adsorbed. Therefore, an additive was considered effective only if it increased θ above the values reported in Table 3 for PMMA prepared without additives by solvent evaporation. Additive 3 appeared to be so soluble in the PMMA that even a 2.0 percent concentration caused essentially no change in the wetting properties of the polymer. However, additives 1 and 2 brought about significant changes in the wettability.

The fluorinated tricarballylate (additive 1) was quite surface active in PMMA and at a concentration of only 0.2 percent had apparently reached its maximum adsorption at the polymer/air interface. As is shown in Table 3 there was no further increase in θ when the concentration was increased to 0.5 percent. However, significant changes in θ occurred only for the high-surface-tension polar liquids and the low-surface-tension nonpolar liquids, those having intermediate properties exhibiting contact angles identical to those of the additive-free PMMA. Previous work on the behavior of these additives when dissolved in organic liquids (8) indicates that the observed effect arises from the ability of the sessile drop to dissolve the film of additive accumulated in the

surface of the polymer. Even if the entire fluorocarbon monolayer beneath a drop was dissolved, the concentration within the drop would still be too low to reduce the liquid surface tension. Essentially then we would have a situation analogous to a pure liquid drop resting on the additive-free PMMA.

Additive 2 did not show the same surface activity in PMMA as the tricarballylate (additive 1), for 0.5 percent caused only moderate changes in θ , and only when 1.0 percent had been added did θ approach values obtained with additive 1. At the higher concentrations the polymer films containing the pentanediol derivative (additive 2) tended to wrinkle badly and pull away from the bottom of the glass dish; reliable measurements of θ were difficult to make, and hence fewer are reported. Again, the most significant changes in θ occurred for the very polar and nonpolar liquids.

In many studies of wettability Zisman and co-workers have used the contact angles of a series of n-alkanes as a convenient means for determining γ_c for low-energy solid surfaces (13, 16, 21, 22). In Fig. 2 are plotted the $\cos \theta$ vs γ_{LV} curves for the n-alkanes on PMMA surfaces containing 0.5 percent additive 1 and 1.0 percent additive 2. The critical surface tensions for 1 and 2 are 19 and 20 dynes/cm, respectively, which represents a decrease of about 20 dynes/cm from the value of γ_c obtained with the additive-free surface. Since the former values of γ_c are very close to that of 18 dynes/cm that Fox and Zisman (16) found for the n-alkanes on polytetrafluoroethylene surfaces, it is considered good evidence that a number of perfluoroalkane groups are present in the outermost part of the surface phase with the principal axis of the carbon-carbon chain parallel to the surface.

Polyvinylidene Chloride Copolymer

Contact angles observed on polyvinylidene chloride copolymer surfaces prepared by solvent evaporation are given in Table 4, along with the values obtained on highly polished surfaces of compressed discs of the additive-free powdered polymer. Values of θ exhibited by the various liquids on each type of PVeC copolymer surface are in good agreement, generally within the limits of experimental error. These values of θ are very similar to those reported previously by Ellison and Zisman (18) on a polyvinylidene chloride

surface, which for comparison are plotted in Fig. 3 along with the present results. The plot of $\cos \theta$ vs γ_{LV} in Fig. 3 shows the critical surface tension of the additive-free PVeC copolymer surface to lie between 38 and 44 dynes/cm.

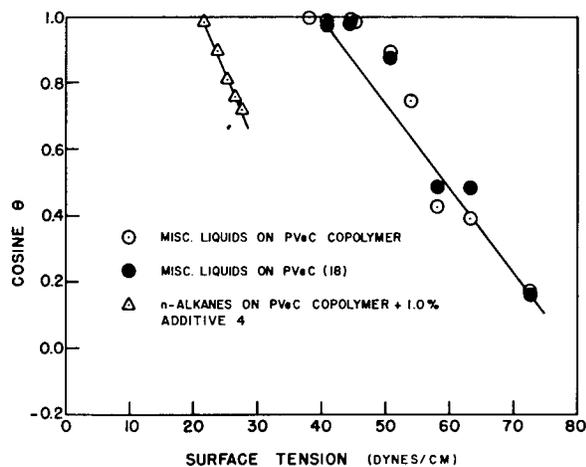


Fig. 3 — $\cos \theta$ vs γ_{LV} for various pure liquids on surfaces of polyvinylidene chloride copolymer (containing 20% polyacrylonitrile)

Fluorinated compounds 1, 3, 4, and 5 were dissolved in tetrahydrofuran solutions of the PVeC copolymer in concentrations up to 1 percent by weight of the polymer. Of these additives, the 3-methylglutarate (additive 3), ethanesulfonate (additive 5), and the tricarallylate (additive 1) derivatives failed to modify the wettability of the polymer surface. However, the tetrachlorophthalate derivative (additive 4) caused a marked decrease in the wettability of the polymer (see Table 4, last column). In Figure 3 the graph of $\cos \theta$ vs γ_{LV} for the n-alkanes on the resulting surface shows that γ_c is between 20 and 21 dynes/cm, which is close to the characteristic γ_c value of polytetrafluoroethylene, 18 dynes/cm. It is apparent that the polymer surface is rich in the fluorinated aliphatic chains of the solute and that the presence of the chlorine atoms in the tetrachlorophthalate molecule has served to increase the solubility of the additive in the highly chlorinated PVeC copolymer. The presence of the chlorine groups in the tetrachlorophthalate derivative thus gave it a more suitable organophilic/organophobic balance than was present in additives 1, 3, and 5.

Polyacrylamide

In Table 5 are listed the contact angles of the various liquids on polyacrylamide. On account of the high water solubility of this polymer, extremely low contact angles were observed for water, the values approaching zero with time. Glycerol and formamide also appeared to interact with PAM and failed to give reproducible contact angles. Contact angles of the remaining liquids, obtained in a dry nitrogen atmosphere, were reproducible and are therefore given in Table 5. The contact angles observed on the clean PAM surface are somewhat larger than might have been predicted on the basis of the polymer's chemical composition. If the amide groups are exposed at the surface one would expect the polymer to have a critical surface tension about as high as PMMA or nylon (17), whose γ_c values are about 40 dynes/cm. On the other hand, if the amide groups are not exposed the γ_c for PAM would be closer to that of polyethylene, approximately 31 dynes/cm. The plot of $\cos \theta$ vs γ_{LV} for the pure liquids on additive-free surfaces does not give a well-defined γ_c . If a line is drawn through the points representing the liquids with surface tensions greater than 35 dynes/cm and is drawn parallel to corresponding lines in Figs. 1-3, a γ_c is shown somewhere between 35 and 40 dynes/cm. However, if this is the true γ_c of the surface, then the liquids with surface tensions below 35 dynes/cm should have spread.

This anomalous wetting behavior of the low-surface-tension liquids on additive-free PAM may indicate that the polymer surface is contaminated. The most probable contaminant on the surface of this water-soluble polymer would be a layer of strongly adsorbed water which is not removed by drying under vacuum at room temperature. To determine whether or not adsorbed water will influence the contact angle, surfaces of PAM prepared by solvent evaporation and by pressing the dried powder into discs were exposed for several hours to atmospheres of varying relative humidity. The contact angles of methylene iodide on both surfaces were observed to increase from 47 to 58 degrees as the relative humidity rose from 0 to 99 percent, while the contact angles of hexadecane increased from 14 to 31 degrees over the same relative-humidity range. This behavior is analogous to the increase in methylene iodide contact angle with increasing hydration of a

silicate surface that was observed by Shafrin (23). On the basis of these experiments, the finite contact angles of the low-surface-tension liquids on additive-free PAM surfaces may be explained by the presence of adsorbed water.

The incorporation of a fluorocarbon additive in PAM presents a somewhat different problem than the previous polymers, inasmuch as it requires a fluorinated additive that has some solubility in water. The partially fluorinated additives 1 - 7 are each quite insoluble in water and fail to disperse in the polymer when added to aqueous solutions; rather they form a separate phase and settle to the bottom of the sample dish. Additive 8 was therefore selected for use in this polymer, since Guenther and Vietor (24) have shown that it was soluble in water up to 1 percent by weight. Each of the samples containing the additives was handled in the same manner as the additive-free surface, so that all would have about the same exposure to water vapor. In this way differences in wettability were observed, even though the precise critical surface tension could not be determined for the polymer itself. It subsequently was found that the contact angles on the films containing additive 8 did not seem to be susceptible to the presence of the small amounts of water vapor in the atmosphere and did not change significantly upon standing in the room at 15 to 20 percent RH up to several hours. The contact angles on PAM containing 0.6 and 1.2 percent of additive 8 given in Table 5 show that even 0.6 percent additive dramatically increased the contact angles of the liquids on the polymer surfaces. Contact angles for the n-alkanes approached those reported for surfaces consisting largely of $-CF_3$ groups (13, 14, 22, 25). A plot of $\cos \theta$ vs γ_{LV}° (Fig. 4) using the data for the n-alkane shows that for this surface γ_c is 10.4 dynes/cm. There was no further decrease in γ_c when the additive concentration was increased from 0.6 to 1.2 percent, indicating that even at the lower concentration maximum adsorption of the additive had developed at the interface.

Besides being added to aqueous solutions of PAM, additive 8 was also added to a solution of the acrylamide monomer prior to polymerization. After polymerization, the PAM was purified as described earlier and films were prepared by solvent evaporation with no further addition of surface-active additive 8. The contact angles given in the last column of Table 5 for the organic liq-

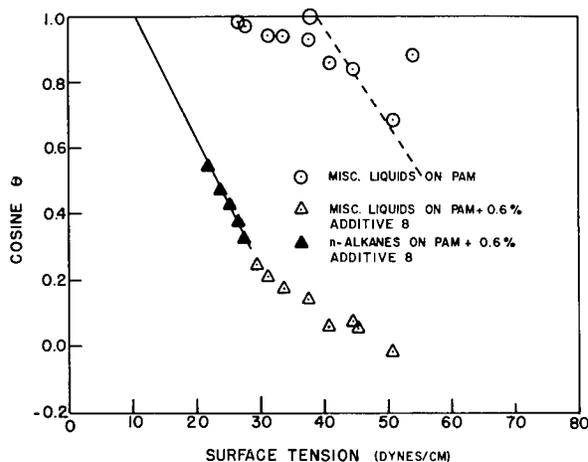


Fig. 4 — $\cos \theta$ vs γ_{LV}° for various pure liquids on polyacrylamide surfaces

uids on this film correspond, within the limits of experimental error, to those obtained when the additive was added to an aqueous solution of the polymer just prior to formation of the film.

DISCUSSION

Small amounts of appropriate fluorine-containing compounds, 1 percent by weight or less, were found to modify significantly the wetting properties of several polymer surfaces. The fluorine-containing surface-active agents were observed to be equally effective when added to the monomer prior to polymerization or when added to solutions of the polymer in a volatile solvent. If one considers the polymer as a liquid of very high viscosity, then it should be immaterial how the additives are incorporated into the polymer, provided sufficient time is allowed for diffusion of the solute to the interface. The less viscous the polymer the more rapidly adsorption equilibrium will be attained. One further property of a film formed by this technique is that it should be self-healing; that is, any surface-active molecules lost from the film will be replaced by the diffusion of additional material into the interface. The rate of self-healing will be dependent upon the rate of diffusion of the fluorocarbon derivatives in the bulk polymer and may be accelerated by heating the solid polymer or otherwise lowering its viscosity.

It is apparent from this study that in many ways the problems involved in selecting surface-active

agents for polymeric systems are quite analogous to those of finding surface-active agents for any organic liquid, the primary difference being the slow rate of diffusion of the additives in the polymer. The problem of surface activity in a polymeric system is thus a logical extension of the previous studies of surface activity in organic liquids, with the effectiveness of a specific additive in a polymer being dependent upon its organophilic/organophobic balance with respect to that polymer. In the present study only fluorocarbon derivatives were used as surface-active additives, but many hydrocarbon as well as silicone compounds would also be expected to show some surface activity in many polymers. The primary advantage of a fluorine-containing compound is that it will cause a much greater decrease in surface free energy, and thus give a polymer surface a lower wettability. A critical surface tension of 10 to 11 dynes/cm was observed for PAM containing only 0.6 percent by weight of a fluorinated additive, while PMMA and the PVEc copolymer had γ_c values of approximately 20 dynes/cm when small amounts of appropriate additives were present at the interface. The critical surface tensions of PMMA and the PVEc copolymer were thus reduced 20 dynes/cm, while that of PAM lowered at least 25 dynes/cm. These large decreases in critical surface tension reflect the change in surface composition which has taken place, the polymer molecules being replaced in the interface by closely packed CF_2 and CF_3 groups.

The presence of a closely packed layer of adsorbed molecules at a polymer surface will have a marked effect on many of its surface properties, such as friction, adhesiveness, and wettability. These properties of an adsorbed film have already found some application in industry. Allan (26) has demonstrated that small amounts of oleylamide incorporated in polyethylene foil will diffuse to the surface of the foil and greatly reduce the friction and adhesion between sheets of the plastic. A committee from the Piedmont Section of the American Association of Textile Chemists and Colorists in a recent report (27) described the incorporation of small amounts of fluorocarbon derivative in a polymeric material normally used to treat textiles for water repellency. They observed that the fluorocarbon preferentially adsorbed at the interfaces and decreased the γ_c values to 16 to 18 dynes/cm. Their films clearly showed the

ability to self-heal, for when the initially adsorbed layer was deliberately scraped off, additional molecules quickly adsorbed at the interface when the polymer matrix was recured at an elevated temperature. The usefulness of adsorbed films of surface-active molecules is thus apparent, and one may expect wide application of this technique to specific problems. The present study, in combination with previous investigations of wettability and surface activity in organic liquids, forms an excellent guide for the design and synthesis of further surface-active agents for polymeric systems.

REFERENCES

1. Zisman, W.A., "Relation of Equilibrium Contact Angle to Liquid and Solid Constitution," presented at the Kendall Award Symposium of the Colloid and Surface Chemistry Division of the A.C.S., Los Angeles, California, Apr. 2, 1962
2. Zisman, W.A., "Relation of Chemical Constitution to the Wetting and Spreading of Liquid on Solids," NRL Report 4932, May 15, 1957; presented at ONR Decennial Symposium, "A Decade of Basic and Applied Science in the Navy," Washington, D.C., Mar. 19, 1957
3. Zisman, W.A., "Constitutional Effects on Adhesion and Abhesion," presented at General Motors Research Symposium on Adhesion and Cohesion, July 25, 1961 (to be published)
4. Allan, A.J.G., *J. Polymer Sci.* 38:297 (1959)
5. Ellison, A.H., and Zisman, W.A., *J. Phys. Chem.* 63:1121 (1959)
6. Ellison, A.H., and Zisman, W.A., *J. Phys. Chem.* 60:416 (1956)
7. Jarvis, N.L., and Zisman, W.A., *J. Phys. Chem.* 63:727 (1959)
8. Jarvis, N.L., and Zisman, W.A., *J. Phys. Chem.* 64:150 (1960)
9. Jarvis, N.L., and Zisman, W.A., *J. Phys. Chem.* 64:157 (1960)
10. Bennett, M.K., Jarvis, N.L., and Zisman, W.A., *J. Phys. Chem.* 66:328 (1962)
11. Faurote, P.D., Henderson, C.M., Murphy, C.M., O'Rear, J.G., and Ravner, H., *Ind. Engr. Chem.* 48:445 (1956)
12. O'Rear, J.G., and Sniegoski, P.J., "New Partially Fluorinated Compounds," NRL Report 5795, July 18, 1962

13. Schulman, F., and Zisman, W.A., *J. Colloid Sci.* 7:465 (1952)
14. Shafrin, E.G., and Zisman, W.A., *J. Phys. Chem.* 66:740 (1962)
15. Sorenson, W.R., and Campbell, T.W., "Preparative Methods of Polymer Chemistry," New York: Interscience Publishers, p. 179, 1961
16. Fox, H.W., and Zisman, W.A., *J. Colloid Sci.* 5:514 (1950)
17. Ellison, A.H., and Zisman, W.A., *J. Phys. Chem.* 58:503 (1954)
18. Ellison, A.H., and Zisman, W.A., *J. Phys. Chem.* 58:260 (1954)
19. Wolfram, E., *Koll. Zeit.* 182:75 (1962)
20. Craig, R.G., Berry, G.C., and Peyton, F.A., *J. Phys. Chem.* 64:541 (1960)
21. Bennett, M.K., and Zisman, W.A., *J. Phys. Chem.* 64:1292 (1960)
22. Bennett, M.K., and Zisman, W.A., *J. Phys. Chem.* 66:1207 (1962)
23. Shafrin, E.G., private communication
24. Guenther, R.A., and Vietor, M.L., *Ind. Eng. Chem. Product Res. and Dev.* 1:165 (1962)
25. Hare, E.F., Shafrin, E.G., and Zisman, W.A., *J. Phys. Chem.* 58:236 (1954)
26. Allan, A.J.G., *J. Colloid Sci.* 14:206 (1959)
27. American Association of Textile Chemists and Colorists, Piedmont Section, *Am. Dyestuff Repr.* 52:25 (1963)