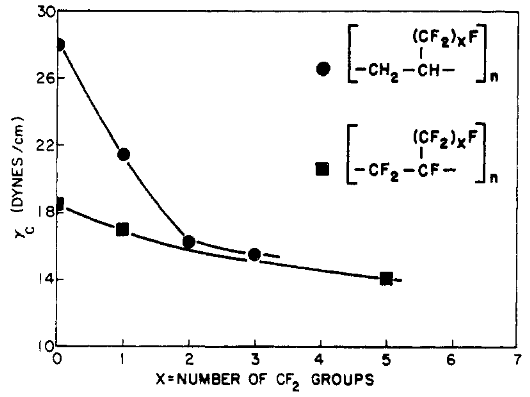

Figure 4. Effect of substituent chain length on γ_c.

the -CH_2CH< backbone and the $(CF_2)_xF$ side group was discussed by Hu and Zisman.[9] If one assumes that the side group is directed away from the polymer solid surface into the wetting liquid, the dipole is closer to the interface the lower the value of x. Results in their report and in the present study show that θ is lower with lower values of x. Thus, when x changes from 1 to 3, γ_c is lowered from 21.5 to 15.5 dyn/cm (Figure 4), with the larger decrease of 5.2 dyn/cm when $1 < x < 2$ and the smaller decrease of 0.8 dyn/cm when $2 < x < 3$. Shafrin and Zisman,[14] in their study of adsorbed monolayers of progressively fluorinated fatty acids of the general formula $F(CF_2)_x(CH_2)_{16}COOH$ and $F(CF_2)_x(CH_2)_{10}COOH$, showed that the uncompensated dipole has a large effect on wetting when $x \leq 7$ but becomes less significant when $x \geq 7$. They also noticed an abrupt reversal of the effect of homology at $2 < x < 3$ where the difference in γ_c was only 0.8 dyn/cm because of random tilting of the fluorocarbon group. The similar abrupt discontinuity at $2 < x < 3$ in the present study can be explained by restriction of rotation of the substituent and the subsequent shielding of the electrostatic dipole. The latter is accentuated by the fact that the ethylenic hydrocarbon, to which the perfluoroalkyl side groups are connected, imposes restrictions on the packing of these substituent groups, necessitating progressively larger intramolecular rotations and bending within the chain. This results in exposure of the CF_2 atomic grouping in an outermost surface of randomly oriented perfluoroethyl or -propyl groups. It would be interesting to study polymers with progressively longer perfluoroalkyl side groups to ascertain whether regular decreases in γ_c can be observed or whether a limiting value has been approached.

When the ethylene backbone is fully fluorinated, a gradual and uninterrupted decrease in γ_c is observed with increase in x (Figure 4), since no large uncompensated dipoles are present. The shape of the two curves in Figure 4 seems to point to an eventual asymptotic approach to the γ_c *vs.* x curve obtained from adsorbed monolayers of fully fluorinated carboxylic acids.[14] Since to date no curve of any other family or series of related compounds,[15] including the two present ones, has crossed or gone beyond the one of the perfluoro acids, it is suggested that the latter represents an envelope of limiting values.

It is obvious from the multitude of possible steric configurations and dipole contributions that we face the difficult problem of rationalizing how to compute the correct molecular conformation to arrive at a minimum surface energy for substituted ethylene fluoropolymers.

Acknowledgment. I wish to thank Dr. William A. Zisman for many helpful discussions.

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Critical Surface Tensions of Tetrafluoroethylene–Perfluoro(propyl vinyl ether) Copolymers

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Received October 5, 1973

ABSTRACT: An investigation of the wetting characteristics of random copolymers of tetrafluoroethylene with 1.5, 2.1, and 2.6 mol % perfluoro(propyl vinyl ether) has shown a rectilinear decrease in the critical surface tensions of wetting (γ_c) at 20° from 18.7 to 17.7 dyn/cm. Heat aging these thermoplastic resins, *e.g.*, at 260°, depresses γ_c by an additional 1.5 dyn/cm, so that an overall decrease in γ_c below that of the homopolymer of 1 dyn/cm for each mol % comonomer is achieved. The depression in γ_c resulting from heat treatment (8 to 8.5% of an already low-energy surface) is larger by an order of magnitude than what has been observed heretofore with other polymers.

Low-energy solid surfaces are characteristic of highly fluorinated polymers. Polytetrafluoroethylene (PTFE) was the first of such highly fluorinated polymers to have its hydrophobic and oleophobic properties carefully studied and defined.[1] Through the years PTFE has retained its appeal to the scientific, industrial, and military market by virtue of its many outstanding properties, such as very low-energy surface, low coefficient of friction, nearly total chemical in-

Table I
Changes in γ_c (dyn/cm) with Variations in Comonomer Content and Annealing Temperature

Code	Mol % perfluoro(propyl vinyl ether)[6]	Melt flow no., g/10 min[6]	γ_c (dyne/cm) at 20° as a function of heat treatment (24 hr)			
			None	200°	257°	284°
I	1.5	12	~18.9		16.6	
II	1.5	2	18.7	17.7	17.2	16.9
III	2.1	15	18.1		16.5	17.2
IV	2.6		17.7		16.2	16.8

Table II
Surface Tensions of Wetting Liquids at 20° and 40% Relative Humidity

Liquids	γ_{LV}, dyn/cm
n-Alkanes	
Octane	21.85
Nonane	23.1
Decane	23.9
Dodecane	25.4
Tetradecane	26.7
Hexadecane	27.6
Linear Dimethylpolysiloxanes	
Hexamer	18.58
Heptamer	18.95
Octamer	19.10
Nonamer	19.30
Decamer	19.48
Dodecamer	19.66

ertness, excellent dielectric properties, and high mechanical strength at temperatures as high as 300°.[2] PTFE, however, has two practical drawbacks: fabricating parts from it is difficult because it never becomes fluid, and making other substances adhere to it is possible only if rather drastic surface treatments are employed. In 1960 copolymers of hexafluoropropylene and tetrafluoroethylene were introduced. These resins are fluid enough beyond their melting points to be molded and extruded, but the price for achieving this advantage was a reduction in high-temperature mechanical strength.[3]

Recently fluorocarbon resins have become available which retain most of the desirable properties of PTFE while being moldable or extrudable, and also bondable. They are random copolymers of tetrafluoroethylene with perfluoro(*n*-propyl vinyl ether), $CF_2{=}CF(OCF_2CF_2CF_3)$.[4] The ability of these perfluorinated thermoplastic resins to adhere tenaciously to a diversity of surfaces is significant and is the subject of another paper.[5] The present paper deals with their wettability.

Experimental Section

Four different samples of the copolymer, supplied as 0.03 in. thick compression-molded sheets by the Plastics Department of the E. I. du Pont de Nemours and Co. are listed in Table I by comonomer content and melt flow number (ASTM D2116-66), an inverse function of viscosity.[6] Their melting points lay in the range 300–310°. Rectangular specimens 0.5 × 1.5 in. were cut from the smooth 0.03 in. thick sheets. Except for cleaning, some specimens were used as received. Most specimens, however, were prepared by melting copolymer into specular 0.006 in. thick sheets between Pyrex plates on a heated (320–330°) Carver hydraulic press. Before each use, specimens were bathed in hot Freon TF for a few hours in a Soxhlet apparatus, after which they were placed in a clean drying oven for a few hours at 70°.

In the course of this study we decided to investigate the effect of heat treatment upon the copolymer. For annealing up to 260°, specimens were placed in an oven with a carefully cleaned stainless-steel interior. Heat-aged specimens were returned to room temperature at the normal cooling rate of the oven, which was 3.0°C/min over the range 260–150° and increasingly slower thereafter. For annealing above 260° a Blue M inert-gas oven, also with an all stainless-steel interior, was used, in which was maintained a slight positive pressure of nitrogen (Air Products "Ultrapure," dried by passage through columns of activated alumina and Linde 4A molecular sieves). The ambient cooling rate of this oven was less than 2.5°C/min. An annealing time of 24 hr was chosen for reasonable assurance of molecular equilibrium in the resins, even though some of our data indicated that 8 hr or less would have sufficed.

Critical surface tensions of wetting (γ_c) were determined using as wetting liquids a series of pure *n*-alkanes.[1] In a few instances, linear methyl end-blocked dimethylpolysiloxanes, which provided a lower range of surface tensions than the alkanes, were employed to confirm these values of γ_c; agreement between the two series was good to a few tenths of a dyne per centimeter. The alkanes were purified of polar contaminants by slow percolation through columns of activated alumina and Florisil. The silicones were research grade liquids freshly received from the Dow Corning Corp. Their high purity was verified by gas chromatography. Surface tensions at 20° of the alkanes were measured on calibrated glass nozzles in a Cassel maximum-bubble-pressure tensiometer;[7] those of the silicones were measured by the drop-weight method using a platinum tip with an outer diameter of 1.034 mm. The values are given in Table II. The advancing contact angle (θ_A) of each wetting liquid was measured with a goniometer telescope using the drop-buildup method at 20° and 40 ± 5% relative humidity.[8] The variation in θ_A, at most ±2° from the mean, progressively decreased in going from the low to the high molecular weight members of a homologous wetting series. The cosines of the advancing contact angles of a homologous series of liquids were plotted against the surface tensions, γ_{LV}, of these liquids (Figure 1). The intercept of the resultant straight line at $\cos\theta_A = 1$ ($\theta_A = 0°$) gave γ_c, a characteristic property of the solid surface, corresponding to the maximum surface tension a liquid can possess and still spread on a particular solid surface.[1] The precision in γ_c, mainly as a result of the nature of graphical extrapolation, was about ±0.2 dyn/cm.

Receding contact angles (θ_R) were measured using a Gilmont model S 1100 micrometer syringe. The 0.025 in. wide tip of the syringe was immersed in the drop during the entire measurement,[9] after we had demonstrated to our own satisfaction that the presence of the syringe tip did not affect the value of the contact angle. Liquid was withdrawn from the drops in increments of 2 μl.

Results and Discussion

Table III gives γ_c of the copolymers, both untreated and annealed. (The code letters A, B, C, etc., specify separate specimens, each receiving exclusively the treatment named.) One notices that γ_c of the untreated specimens is close to that of PTFE and that annealing at 257° and above causes a permanent lowering of γ_c of about 1.5 dyn/cm. Moreover, as one might expect by analogy with the copolymers of tetrafluoroethylene and hexafluoropropylene,[10,11] there is a decrease in γ_c with increasing comonomer content among the untreated specimens which remains evi-

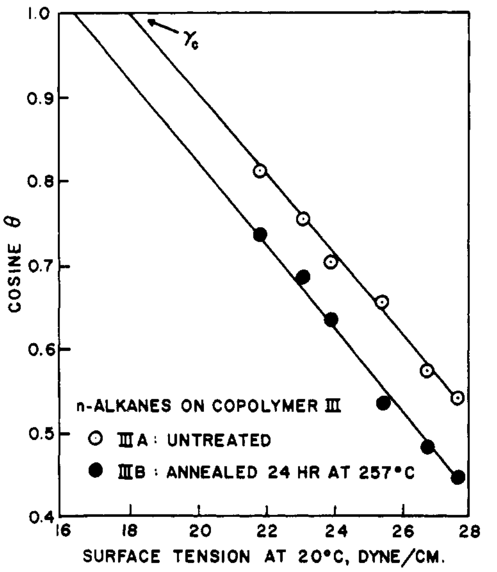

Figure 1. Typical plots of cos θ *vs.* γ_{LV} used to determine critical surface tensions of wetting of polymers.

Table III

Wettability of the Copolymers before and after Heat Treatment, as Measured with *n*-Alkanes

Specimen	Heat Treatment		Av θ_A of $C_{16}H_{34}$, deg	γ_c, dyn/cm, at 20°
	Temp, °C	Time, hr		
PTFE			46	18.5[1]
I A			55	~18.9[a]
I B	257	24	61	16.6
II A			59	18.7
II B	257	24	62	17.2
II C	284	24	63	16.9
II D[b]			52	18.8
II E[b]			53	18.7
II F[b]	170	24	55	17.6
II G[b]	198	24	56	17.7
II H[b]	257	24	60	17.3
II I[b]	257	64	60	17.8
III A			57	18.1
III B	257	24	64	16.5
III C	284	24	64	17.2
IV A			60	17.7
IV B	257	24	65	16.2
IV C	284	24	65	16.8

[a] Contact angle values were inexplicably poor (±3°) regardless of which of the two methods of preparing the samples was used. [b] As received.

dent among those annealed for 24 hr at 257°. The slight upturn in γ_c with extended annealing at 257° (specimen III) or with annealing at 284° (specimens IIIC and IVC) may reflect some slight degradation of the polymer surface, even though it has been found that other (bulk) physical properties of these copolymers, such as tensile strength, have not been adversely affected even after heat aging in air at 285° for as long as 2000 hr.[6] Apart from this slight increase in γ_c, there seems to be a linear decrease in γ_c with increasing annealing temperature, as indicated by the results for copolymer II.

The untreated specimens can be described as air quenched. This applies equally to the compression-molded sheets supplied by the Du Pont Co. and to the 0.006-in. sheets remolded by us, insofar as both types were cooled from the melt at the rather high ambient cooling rate of the respective hydraulic presses (>5 deg/min). Two such untreated specimens (1.5 mol %, melt flow number 6 g/10 min, copolymer not otherwise discussed in this paper) were compared with a specimen which had been water quenched by removing the molten material from a 380° muffle furnace and immediately plunging it into cool water. All three specimens were found to have essentially the same γ_c. For still another specimen of the same material, cooled from the melt at the relatively slow rate of 2.35 deg/min, γ_c was 1 dyn/cm lower.

The arrangement in Table I helps to illustrate how γ_c decreases with increasing comonomer content under the same conditions of annealing (top to bottom) as well as with higher annealing temperatures but constant comonomer content (left to right). The role of the comonomer in lowering the value of γ_c is involved with its ability to populate the surface with perfluoromethyl groups. Earlier work done in this laboratory clearly demonstrated the contribution of CF_3 groups to lowering the wettability of a surface. With the value of γ_c of PTFE (18.5 dyn/cm) taken as characteristic of a surface of close-packed $-CF_2-$ groups, a study was made of increasing CF_3 substitution. The copolymer of tetrafluoroethylene and hexafluoropropylene containing 23 mol % comonomer, for instance, had a γ_c of 17.8 dyn/cm,[10] whereas the homopolymer of hexafluoropropylene had a γ_c of 17.1–16.2 dyn/cm, depending on the molecular weight of the material.[11] The surface of lowest energy encountered was that of an adlineated close-packed monolayer of perfluorododecanoic acid adsorbed on smooth glass or platinum. Its γ_c of 5.6 dyn/cm was taken as characterizing a surface of close-packed CF_3 groups.[12] Perfluoroalkanoic acids of lower molecular weight do not pack quite so closely because of diminished intermolecular cohesive forces; γ_c of a monolayer of perfluorobutyric acid, for example, is a much higher value of 9.2 dyn/cm. Hence the packing of the CF_3 groups in a surface is critical in determining the γ_c of that surface.

In the present case, the molecular mobility brought about by the high temperature of the annealing process expedites the migration of perfluoromethyl terminal side chains to the copolymer surface, a process which occurs as a result of the surface's thermodynamic drive to attain its lowest energy state. A Stuart and Briegleb molecular model demonstrates how the side chain either hugs the polymer backbone or else protrudes upward away from it. The model indicates that the side chain would encounter considerable steric hindrance in shifting from one conformation to the other because bulky fluorine atoms immobilize the pendant side chain at both bonds to the ether oxygen. Such steric rigidity would account for the rather dramatic annealing conditions needed to affect γ_c.

The tendency for γ_c to decrease as comonomer content increases could probably be obtained as a well defined relationship provided various parameters were standardized. Chief among these would be molecular weight, on which several other properties such as viscosity and tensile strength are dependent. Thus the differences in γ_c between the annealed specimens of low viscosity copolymer I and high viscosity copolymer II are undoubtedly real, despite the fact that their comonomer content is the same. Lower viscosity in a polymer, as a manifestation of lower average molecular weight, indicates the ability to achieve a greater degree of molecular rearrangement (lower γ_c in the present case) than its higher viscosity counterpart at the same rate of cooling from the melt or under the same conditions of annealing.

It is interesting that in the copolymer of tetrafluoroethylene with hexafluoropropylene, 23 mol % of comonomer decreased γ_c by 1 dyn/cm below that of PTFE,[10] whereas the same decrease was achieved with as little as 2.6 mol % of the perfluoro(propyl vinyl ether) comonomer. Moreover, in the latter case, the small range of comonomer content, 1.5–2.6 mol %, also helps to account for the lack of definition in the relationship between γ_c and the copolymer composition. Increasing the levels of perfluoro(propyl vinyl ether) in the copolymer, if synthetically feasible, might yield increasingly lower energy surfaces, but probably at considerable expense to the high-temperature capability of these resins.

Referring again to Table III, one sees that contact angles of hexadecane tend to be a few degrees higher on the specular specimens than on the less smooth "as received" specimens. In going down the series of alkanes, however, this gap grows progressively smaller, the result being that the graphical extrapolations from the two sets of data for specimens having essentially the same thermal history converge at $\cos\theta_A = 1$. It thus appears that the slope of the $\cos\theta_A$ *vs.* γ_{LV} (or $\cos\theta_A/\gamma_{LV}$) curve, but not γ_c, is influenced by surface roughness.

Both surface roughness and heterogeneity contribute to contact angle hysteresis. In measuring receding contact angles of tetradecane on various specular specimens, we found that $\theta_A - \theta_R = 15 \pm 1°$. In light of Johnson and Dettre's observation that contact angles are not noticeably affected by rugosities as large as grooves left by typical machining operations,[13] such large hysteresis was surprising, for examination of the copolymer specimens under a 70× optical microscope failed to reveal any significant surface irregularities. Moreover, the technique we used to prepare specular specimens when employed in this laboratory on previous occasions on numerous polymers reliably reduced contact angle hysteresis to <2°. Perhaps a heterogeneous surface produced by clustering of CF_3 groups is responsible for the large hysteresis observed with these copolymers.

Irregularities on the "as received" specimens were easily visible under the microscope. The effect of surface roughness of this magnitude on contact angle hysteresis was obvious, for as liquid was withdrawn from a drop of tetradecane, instead of receding the drop would gradually flatten out with no shrinkage in area.

Summary and Conclusions

Our study has dealt with the wettability of copolymers of tetrafluoroethylene with 1.5, 2.1, and 2.6 mol % of perfluoro(propyl vinyl ether). The 1.5 mol % resin exhibited a γ_c roughly that of the homopolymer, but as comonomer content increased, γ_c decreased as much as 1 dyn/cm. When these copolymers were heat aged (*e.g.*, at 257°), their γ_c values were lowered by about 1.5 dyn/cm. The lowering of the surface energy caused by increasing comonomer content is attributable to the presence of CF_3 groups in the surface. The further lowering of γ_c by the annealing process is accounted for by conditions of enhanced molecular mobility during annealing, thus allowing more perfluoromethyl terminal side chains to find their way to the surface. The lowering of γ_c by annealing to the extent observed here (8–8.5%, a sizable decrease in already low surface energy material) is, to our knowledge, larger by nearly an order of magnitude than what other experimenters have observed with other polymers. This simple technique, however, may possibly prove to be of general utility with polymers containing surface-active groups pendant to the main chain.

Acknowledgments. The authors extend their thanks to the Advanced Research Department, Dow Corning Corp., for supplying the silicone wetting agents and to the Plastics Department of the Du Pont Co. for the copolymer samples and much helpful consultation.

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