

Wetting Properties of Homopolymers and Copolymers of Pentafluorostyrene and Methylacrylate and Homopolymer Blends

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Synopsis

Poly(pentafluorostyrene) (PPFS), polymethylacrylate (PMA), and poly(pentafluorostyrene-co-methylacrylate), poly(PFS-co-MA) were prepared and the wetting characteristics of polymer blends of PPFS and PMA were compared with that of poly(PFS-co-MA) via contact angle measurements. The critical surface tension of poly(pentafluorostyrene) was found to be 22.6 dyne/cm, which is comparable to the value reported for poly(trifluoroethylene) (22 dyne/cm). The critical surface tension of poly(PFS-co-MA) is not linearly related to its composition. The polymer blends of PPFS and PMA exhibit significant surface enrichment of the fluoropolymer. The harmonic-mean method¹ was employed to determine surface tensions of these polymers and many known polymers. It is found that the method produces useful surface tension data provided the contact angle values are derived from testing liquids of dissimilar polarity.

INTRODUCTION

The structural and chemical nature of solid surfaces as well as morphology are important in determining many physical properties such as adhesion,² polymer wear,³ wetting,^{1,4} and catalysis.⁵ Polymeric films with a desirable nonspreading or poor wetting characteristic usually are materials of low surface energy such as siloxane polymers⁶ and fluoropolymers.⁶ The former class of materials, except for the cross-linked ones, usually have a low glass transition temperature⁷ and normally exist in the form of liquid at room temperature. They are not easily employed for surface modification. The commercial fluoropolymers (e.g., polytetrafluoroethylene) typically are not solvent soluble, therefore, they are not readily available for solution coating to modify the wetting characteristics of different substrates.

In an attempt to modify surface properties of a substrate, we have engaged in studying the wetting phenomenon of a solvent-soluble fluoropolymer system namely, poly(2,3,4,5,6-pentafluorostyrene) (PPFS). Copolymers of 2,3,4,5,6-pentafluorostyrene (PFS) and methylacrylate (MA) with varying monomer composition and polymer blends of poly(pentafluorostyrene) and polymethylacrylate were prepared and their wetting properties were examined. In this paper we would like to report the results of wetting studies of these materials.

EXPERIMENTAL

Homopolymers and copolymers of 2,3,4,5,6-pentafluorostyrene and methylacrylate were synthesized by solution polymerization with a free radical

initiator and purified by precipitation. The detailed synthesis and characterizations of these materials will be reported elsewhere.⁹ Polystyrene equivalent molecular weights of these polymers were obtained by gel permeation chromatography (GPC) analysis using a series of μ -styragel columns and tetrahydrofuran (THF) eluent (1.0 mL/min flow rate). The polymer compositions were derived from the elemental analysis data.

The poly(dimethyl siloxane) was General Electric SE-33 containing 0.2 mole % of methyl vinylsiloxane which was used without further purification.

The samples for contact angle measurements were prepared on clean glass substrates by spin-coating at 1500 rpm from 10 mg/mL solutions in tetrahydrofuran except the poly(dimethyl siloxane) which was 15 mg/mL in toluene. The coated samples were first air dried and then dried under vacuum at 50°C for 2.5 h. Methylene iodide, formamide, and a series of hydric liquids (including water, *n*-butanol, 1-octanol, polyglycol P-1200, polyglycol 15-200, and ethylene glycol) were employed in the contact angle measurements.

Contact angle measurements were made by the sessile drop method using an apparatus manufactured by Rame-Hart Inc. (Model No. A-100). The measurements of advancing angle were made at $24.5 \pm 1.5^\circ\text{C}$ with the sample chamber saturated with the vapor of a test liquid to avoid any possible error due to liquid evaporation. For each polymer sample, at least four equilibrium contact angles were recorded and averaged to obtain a final value which was employed in the surface tension calculation.

Critical surface tensions were calculated by Zisman's method⁸ using standard linear regression. The harmonic-mean¹ calculations were carried out on a microcomputer with a program written in BASIC.

RESULTS AND DISCUSSION

The average molecular weights and compositions of the polymers and copolymers used in this study are shown in Table 1.

TABLE I
Molecular Weight^a and Composition Data of Various Polymers and Copolymers

Polymer	\bar{M}_w	\bar{M}_N	MWD	Composition ^c	
				PFS %	MA %
Poly(pentafluorostyrene) ^b	5.2×10^5	2.7×10^5	1.9	100	0
Poly(methylacrylate) ^b	1.1×10^6	3.5×10^5	3.2	0	100
Poly(pentafluorostyrene-co-methylacrylate)	1.0×10^6	3.5×10^5	2.8	8.9	91.1
Poly(pentafluorostyrene-co-methylacrylate)	9.4×10^5	2.6×10^5	3.6	25.8	74.2
Poly(pentafluorostyrene-co-methylacrylate)	4.2×10^5	2.2×10^5	1.9	58.0	42.0
Poly(pentafluorostyrene-co-methylacrylate)	3.0×10^5	1.3×10^5	2.3	67.8	32.2

^aMolecular weight is polystyrene equivalent molecular weight determined by GPC.

^bThe polymers were prepared by AIBN initiator and used in the polymer blend study.

^cMole percentages were calculated from elemental analysis data.

TABLE II
Critical Surface Tension Data Obtained by the Zisman's Method

Sample/Description	W	F	MI	E	P/15-200	P/P-1200	1-Oct.	n-But.	CST
	(deg) Cos θ	(deg) Cos θ	(deg) Cos θ	(deg) Cos θ	(deg) Cos θ	(deg) Cos θ	(deg) Cos θ	(deg) Cos θ	
1) Poly(methyl-acrylate)	73.0	51.2	47.4	49.1	22.4	16.1			31.0
2) Poly(PFS-co-MA)	80.3	68.6	54.5	61.6	36.6	26.4	5.75		28.0
8.9% PFS	0.168	0.365	0.581	0.476	0.803	0.896	0.995		
3) Poly(PFS-co-MA)	86.0	71.5	59.1	66.0	42.6	36.5	17.9		25.7
25.8% PFS	0.070	0.317	0.514	0.407	0.736	0.804	0.952		
4) Poly(PFS-co-MA)	91.9	75.7	63.1	72.2	48.0	42.1	22.3		24.8
58.0% PFS	-0.033	0.247	0.452	0.306	0.669	0.742	0.925		
5) Poly(PFS-co-MA)	94.2	78.1	66.0	75.2	50.3	45.1	26.0		24.1
67.8% PFS	-0.073	0.206	0.407	0.255	0.639	0.706	0.899		
6) Poly(Pentafluoro-styrene)	99.1	82.0	70.1	76.1	53.3	46.3	31.3	~ 6.0	22.6
	-0.158	0.139	0.340	0.240	0.598	0.691	0.854	0.995	
7) 1.1 mole% PPFS in PMA	97.5	71.1	62.4	70.8	44.0	43.1	20.4		25.3
	-0.131	0.324	0.463	0.329	0.719	0.730	0.937		
8) 5.0 mole% PPFS in PMA	96.5	81.2	68.1	75.9	52.8	45.6	25.6		23.9
	-0.113	0.153	0.373	0.244	0.605	0.700	0.902		
9) 10.1 mole% PPFS in PMA	97.9	81.6	70.0	75.1	53.0	45.5	29.9		22.9
	-0.137	0.146	0.342	0.357	0.602	0.701	0.867		
10) Poly(dimethyl-siloxane) ^a	105.5	98.5	79.1	92.8	70.3	57.4	39.5	26.9	21.2
	-0.267	-0.148	0.189	-0.049	0.337	0.539	0.772	0.892	

^a Contains 0.2M% methylvinylsiloxane (GE-SE-33)

W = water ($\gamma = 72.8$ dyne/cm)

F = formamide ($\gamma = 58.2$ dyne/cm)

MI = methylene iodide ($\gamma = 50.8$ dyne/cm)

E = ethylene glycol ($\gamma = 47.7$ dyne/cm)

P/15-200 = polyglycol 15-200 ($\gamma = 36.5$ dyne/cm)

P/P-1200 = polyglycol P-1200 ($\gamma = 31.8$ dyne/cm)

1-Oct. = 1-Octanol ($\gamma = 27.8$ dyne/cm)

n-but. = n-Butanol ($\gamma = 24.2$ dyne/cm)

CST = Critical surface tension (4 pts(dyne/cm))

These polymers and copolymers are believed to be atactic due to the nature of free radical polymerization. The polymer films of homopolymers and copolymers prepared by the spin-casting method have fairly smooth surfaces and are void of volatile impurities which may influence contact angle measurements. Critical surface tensions of all the polymers, copolymers, and polymer blend samples were obtained by Zisman's method⁶ using a linear regression method. The critical surface tension of each polymer sample was calculated based on largest $\cos \theta$ values recorded by four testing liquids of low surface tension. The results are shown in Table II.

The critical surface tensions of polypentafluorostyrene and polymethylacrylate were found to be 22.6 dyne/cm and 30.4 dyne/cm, respectively. The critical surface tension of polypentafluorostyrene is comparable to the data reported for polytrifluoroethylene (22 dyne/cm)^{8d} and polydimethylsiloxane 21.2-24 dyne/cm¹⁰ but is significantly lower than the value of polystyrene (30-35 dyne/cm). As expected, substitution of aromatic hydrogen atoms of

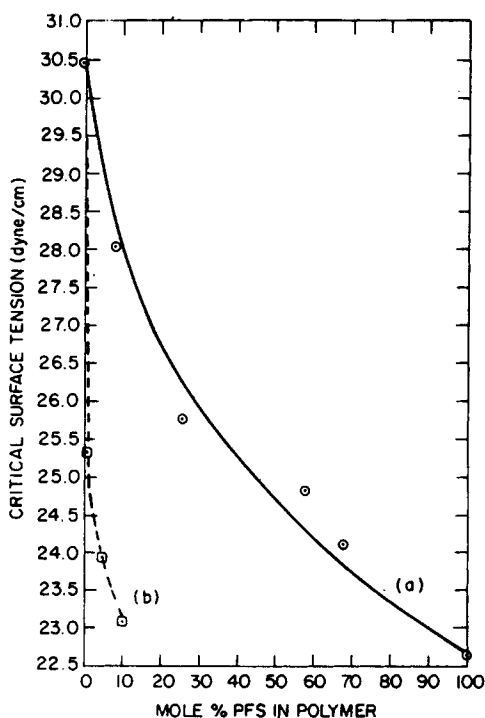


Fig. 1. The plot of critical surface tension vs. polymer's composition (mole%): (a) —poly(PFS-co-MA) and (b) ----polymer blends of PPFs and PMA.

polystyrene with fluorine atoms greatly decreases the wettability of the polymer's surface.

For the copolymers of pentafluorostyrene and methylacrylate the critical surface tension decreases as the monomer content of pentafluorostyrene in the copolymers increases. The data agree with the general expectation that incorporation of the low surface energy component, pentafluorostyrene, in the copolymers decreases the polymer's wettability. A plot of critical surface tension as a function of copolymer composition of poly(pentafluorostyrene-co-methylacrylate) produces a nonlinear curve (Fig. 1). All the data are situated below the straight line connecting the critical surface tensions of two homopolymers. For an ideal situation where wettability of a polymer surface is determined solely by the chemical constituents and area of coverage on the outermost surface, the critical surface tension (γ_c) of a random copolymer may be estimated by adding the products of mole fraction of each component and the surface tension of its homopolymer (i.e., $\gamma_c = \gamma_A M_A + \gamma_B M_B$)¹¹ provided that surface and bulk compositions are the same and there are no preferred surface orientation and neighboring group effect as well as no coverage area difference between two monomers on the polymer's surface. In this ideal case, the critical surface tension of a random copolymer is probably linearly related to the molar composition of each component. However, a nonlinear relationship between the critical surface tension of a copolymer and its composition normally exists because factors such as molecular orientation, sequence distri-

bution of monomer units, surface morphology, surface area, and phase transition usually influence γ_c . The ideal linear relationship has been reported for a certain range (0–59 mole% of propylene oxide) of random copolymers of ethylene oxide and propylene oxide.¹² However, if one considers the entire range of copolymer composition (0–100 mole% of propylene oxide), a nonlinear curve is obtained when the surface tension of the random copolymer is plotted against the mole% of propylene oxide in the copolymer. A nonlinear relationship between γ_c and composition was also reported by Toyama et al. for the copolymer system of styrene and methyl methacrylate.¹³

Nuclear magnetic resonance (NMR) study of the copolymers of PPFS and PMA suggests that most of the copolymers are random. However, the existence of a very small amount of block-like copolymers cannot be completely ruled out. In the copolymerization of pentafluorostyrene and methylacrylate, it is possible that two monomer units with different reactivity are not ideally distributed in the polymer chain in a random fashion. Due to possible reactivity ratio difference pentafluorostyrene may form block copolymers toward the end of polymerization especially when a reactive monomer's concentration is depleted and the polymer's yield is high. This may lead to a preferred molecular sequence in the polymer chain, some phase separation, and possible orientation of low surface energy pentafluorostyrene units on the polymer surface. Thus, the calculated γ_c data are somewhat lower than the values expected for an ideal random copolymer system. However, in the composition range of 25–100 mole% of pentafluorostyrene, the copolymer's critical surface tension (γ_c) appears to be somewhat linearly related to its molar composition (Fig. 1).

For the polymer blends of PPFS and PMA large differences in critical surface tension was observed suggesting a significant surface enrichment. A polymer blend of 1.1% of PPFS in PMA gives a critical surface tension of 25.3 dyne/cm, which is substantially lower than the value (30.4 dyne/cm) obtained for PMA. Critical surface tensions of polymer blends containing 5% and 10% of PPFS in PMA are 23.9 and 23.1 dyne/cm, respectively, and approach γ_c of pure PPFS (22.6 dyne/cm). Apparently, the low surface energy PPFS can easily separate from PMA during the casting process and diffuses to the polymer surface resulting in a reduced wettability. The results clearly indicate that these two polymers are incompatible. Differential scanning calorimetry (DSC) measurement⁹ of a polymer blend sample containing 10% PPFS in PMA showed two distinct glass transition temperatures attributed to phase-separated PPFS and PMA. Formation of low surface energy PPFS domains in the PMA matrix was also observed at the surface by transmission electron microscopy (TEM).

Although critical surface tensions (γ_c) obtained by Zisman's method have been widely reported in the literature,⁶ the data obtained by Zisman's plot ($\cos \theta$ vs. γ_l) is often influenced by the types of liquids used in the measurements. A wide range^{14,15} of γ_c values can be obtained for a given solid if a large difference in polarity exists between the testing liquids and the solid.¹ Furthermore, the equilibrium spreading pressure, π_c , also varies with the nature of testing liquids and can be fairly large when the measured contact angle on a solid is small. Generally, the critical surface tension (γ_c) of a polymer is smaller than the surface tension (γ_s) by an amount of γ_{sl} and π_c ;

that is $\gamma_c = \gamma_s - (\gamma_{sl} + \pi_c)$ where γ_{sl} is the surface tension between a solid and a liquid and π_c is the equilibrium spreading pressure.¹

The abnormality of γ_c can be avoided in characterizing the wettability of a polymer surface by using the harmonic-mean method proposed by Wu.¹⁶

$$(1 + \cos \theta_1) \gamma_1 = 4 \left(\frac{\gamma_1^d \gamma_s^d}{\gamma_1^d + \gamma_s^d} + \frac{\gamma_1^P \gamma_s^P}{\gamma_1^P + \gamma_s^P} \right)$$

$$(1 + \cos \theta_2) \gamma_2 = 4 \left(\frac{\gamma_2^d \gamma_s^d}{\gamma_2^d + \gamma_s^d} + \frac{\gamma_2^P \gamma_s^P}{\gamma_2^P + \gamma_s^P} \right)$$

where $\gamma = \gamma^d + \gamma^P$ (dispersion and polar components of surface tension) and subscripts s, 1 and 2 refer to the solid and the testing liquids 1 and 2, respectively. θ_1 and θ_2 are contact angles measured by liquids 1 and 2, respectively. This method considers both the polar and the dispersive (non-polar) interactions between a solid and a testing liquid and produces data in good agreement with the values derived from polymer melt method,^{1,16} liquid homolog method^{1,16} and the equation of state method.^{1,16}

We have used Wu's harmonic-mean method to calculate surface tension data of our polymers, copolymers, and polymer blends and the results are listed in Table III. It is noted that the total surface tension values (γ_H^T) derived from the liquid pairs, water/methylene iodide and formamide/methylene iodide, agree very well. However, these values deviate significantly from the data derived from the liquid pair, water/formamide, which consists of two liquids of similar polarity. The latter liquid pair probably heavily weights the contribution from the polar term without proper consideration of the dispersive term. Based on these results it is concluded that the harmonic-mean surface tension data derived from solvents of similar polarity (please see the data within heavy line in Table III) are typically less accurate than those obtained from solvents of very different polarity. Dalal¹⁷ recently has mathematically analyzed this discrepancy and may have shown that the pair-wise solution of testing liquids with similar polarity is ill conditioned and intrinsically produces poor results.

In order to demonstrate the generality of our conclusion we have carried out harmonic-mean surface tension calculations on a wide variety of commercial polymers including poly(chlorotrifluoroethylene), poly(ethylene terephthalate), polystyrene, polyvinylchloride, polyvinylfluoride, polymethylmethacrylate, paraffin wax, poly(tetrafluoroethylene), and poly(hexamethylene adipamide). Again, the calculated surface tension results obtained from solvents of different polarity (please see the data outside the heavy line in Table IV) are more consistent than the data derived from solvent pairs of similar polarity. The calculated surface tension data of these commercial polymers are shown in Table IV. The results are in good agreement with our earlier conclusion and the data compare favorably with the literature values obtained by the polymer melt method^{1,16,18} (Table V). The data clearly indicate that the harmonic-mean method can be properly employed to obtain very useful surface tension data for many polymers.

TABLE III
Surface Tension Data Determined by the Harmonic-Mean Method

Polymer	W		F		MI		W/F		W/MI		F/MI		Ave.		St. Dev.
	θ	γ^d	θ	γ^d	θ	γ^d	γ_H^P	γ_H^T	γ_H^d	γ_H^P	γ_H^d	γ_H^P	γ_H^d	γ_H^T	
Poly(methylacrylate)	73.0	51.2	47.4	24.2	15.7	39.9	26.9	14.7	41.6	27.4	12.8	40.2	40.9	0.7	
Poly(PFS-co-MA) 8.9% PFS	80.3	68.6	54.5	14.6	16.5	31.1	24.6	11.9	36.5	28.3	4.9	33.2	34.9	1.7	
Poly(PFS-co-MA) 25.8% PFS	86.0	71.5	59.1	16.0	12.8	28.7	23.3	9.7	33.0	26.0	5.0	31.0	32.0	1.0	
Poly(PFS-co-MA) 58.0% PFS	91.9	75.7	63.1	16.8	9.6	26.4	22.6	7.4	30.0	25.0	4.0	29.0	29.5	0.5	
Poly(PFS-co-MA) 67.8% PFS	94.2	78.1	66.0	16.5	8.7	25.2	21.6	6.7	28.3	23.8	3.8	27.6	28.0	0.4	
Poly(Pentafluoro- styrene)	99.1	82.0	70.1	17.2	6.4	23.6	20.8	5.1	25.9	22.5	3.1	25.6	25.8	0.2	
1.1 mole% PPFS in PMA	97.5	71.1	62.4	30.2	3.3	33.5	24.8	4.5	29.3	23.3	6.7	30.0	29.7	0.4	
5.0 mole% PPFS in PMA	96.5	81.2	68.1	15.4	8.2	23.6	21.1	6.0	27.1	23.9	2.7	26.6	26.9	0.3	
10.1 mole% PPFS in PMA	97.9	81.6	70.0	16.3	7.2	23.5	20.5	5.6	26.1	22.3	3.3	25.6	25.9	0.3	
Poly(dimethyl- siloxane) ^a	105.5	98.5	79.1	6.6	9.9	16.5	17.9	3.7	21.6	—	—	—	21.6	—	

^aPartially cross-linked poly(dimethylsiloxane) which contains 0.2 M% methylvinylsiloxane (GE-SE-33).

W = Water, F = Formamide, MI = Methylene Iodide.

θ = Measured contact angle

γ_H^d = Dispersive component of surface tension

γ_H^P = Polar component of surface tension,

γ_H^T = Total surface tension determined by Harmonic-Mean method.

Ave. = Average value for surface tension data derived from water/CH₂I₂ and formamide/CH₂I₂ pairs.

St. dev. = Standard deviation (population method).

TABLE IV
Effect of Testing Liquid Pair on Surface Tensions of Various Polymers

Polymer	Solvent Pair		W/G	W/F	G/F	MI/TCP	W/MI	W/TCP	G/MI	G/TCP	F/MI	F/TCP	Avg.	St. Dev
	θ	γ												
Polystyrene	θ		91/80	91/74	80/74		91/35		80/35		74/35		38.5	
	γ_H^d	γ_P^d	16.00		17.7		38.4						4.2	
	γ_H^T	γ_H^T	10.4		9.6		4.2						42.6	
Poly(chlorotrifluoroethylene)	θ		90/82	90/82	82/82	64/44	90/64	90/44	82/64	82/44	82/64	82/44	26.7	4.4
	γ_H^d	γ_P^d	13.4	9.8			21.6	28.4		30.0			5.3	4.0
	γ_H^T	γ_H^T	12.2	14.7			8.5	6.5		0.8			32.0	2.6
Poly(ethylene terephthalate)	θ		81/65	81/61	65/61		81/38		65/38		61/38		36.3	3.0
	γ_H^d	γ_P^d	22.8	21.8	31.3		32.8		38.4		37.6		5.4	3.3
	γ_H^T	γ_H^T	12.2	12.6	6.2		9.3		3.2		3.8		41.7	0.4
Poly(vinylchloride)	θ		87/67	87/66	67/66	36/14	87/36	87/14	67/36	67/14		66/14	38.7	3.5
	γ_H^d	γ_P^d	26.3	22.3			35.8	37.0	45.5	37.5		37.8	3.6	2.2
	γ_H^T	γ_H^T	8.3	9.6			6.2	5.9	0.6	2.9		2.2	42.3	2.2
Poly(vinylfluoride)	θ		80/66	80/54	66/54	49/28	80/49	80/28	66/49	66/28	54/49	54/28	30.8	3.3
	γ_H^d	γ_P^d	21.1	28.1			27.2	33.6	29.4	34.0		33.6	8.6	2.7
	γ_H^T	γ_H^T	13.3	10.9			11.2	9.5	6.8	4.6		7.7	39.4	2.4
Poly(methyl methacrylate)	θ		80/69	80/64	69/64	41/19	80/41	80/19	69/41	69/19	64/41	64/19	36.5	3.2
	γ_H^d	γ_P^d	18.3	18.2	19.2		31.2	35.8	41.1	36.7		36.5	4.8	3.8
	γ_H^T	γ_H^T	14.6	14.7	13.5		10.1	9.1	1.2	2.5		3.2	41.3	2.1
Paraffin wax	θ		108/96	108/91	96/91	66/62	108/66	108/62	96/66	96/62	91/66	91/62	22.5	
	γ_H^d	γ_P^d	14.6	16.9			21.6	22.5					1.5	
	γ_H^T	γ_H^T	4.1	3.2			6.7	1.5					24.0	
													18.7	20.1
													28.3	24.0

TABLE IV. (Continued from the previous page.)

Polymer	Solvent Pair		W/G	W/F	G/F	MI/TCP	W/MI	W/TCP	G/MI	G/TCP	F/MI	F/TCP	Avg.	St. Dev
Poly(tetrafluoro ethylene)	θ	108/100	108/92	100/92	77/75	108/77	108/75	100/77	100/75	92/77	92/75	92/75		
	γ_H^d	10.3	15.6		16.9	20.5	17.2	18.3	18.3	17.3	18.3	17.3	18.3	1.6
	γ_H^P	6.2	3.7		6.7	2.1	3.1	0.5	0.5	2.6	2.1	2.6	2.1	1.1
	γ_H^T	16.5	19.3		23.6	22.6	20.3	18.8	18.8	19.9	20.4	19.9	20.4	1.7
Poly(hexamethylene adipamide)	θ	72/60	72/50	60/50		72/28		60/28		50/28				
	γ_H^d	21.0	24.5			35.0		42.3		38.2			38.5	3.0
	γ_H^P	17.6	16.1			12.9		3.6		7.1			7.9	3.8
	γ_H^T	38.6	40.6			47.9		45.9		45.3			45.8	1.8

W = water, G = glycerine, F = formamide, MI = methylene iodide, T = tricresylphosphate.

θ is equilibrium contact angle obtained from Ref. 1 pp. 162-163.

γ_H^d = dispersive component, γ_H^P = polar component, γ_H^T = total surface tension as determined by harmonic-mean method.

^a Obtained from Ref. 1 p. 153.

Italic numbers are unreliable results due to poor selection of a testing liquid pair.

TABLE V
Surface Tension Data of Polymers Determined by Different Methods

Polymer	Harmonic-mean ^a method W/MI dyne/cm	Harmonic-mean ^b method average value dyne/cm	Polymer melt ^a method dyne/cm
Polystyrene	42.6	42.6	40.1
Poly(chlorotrifluoroethylene)	30.1	32.0	30.9
Poly(ethylene terephthalate)	42.1	41.7	44.6
Poly(vinylchloride)	41.9	42.3	—
Poly(hexamethylene adipamide)	42.1	45.8	46.5
Poly(vinylfluoride)	38.4	39.4	—
Poly(methyl methacrylate)	41.2	41.3	41.1
Poly(tetrafluoroethylene)	22.6	20.4	—
Poly(pentafluorostyrene)	25.9	25.8	—

^aData from Ref. 1; W/MI = water/methylene iodide pair.

^bData of different liquid pairs are used in the calculation of average surface tensions. (This work, please see Table IV for details.)

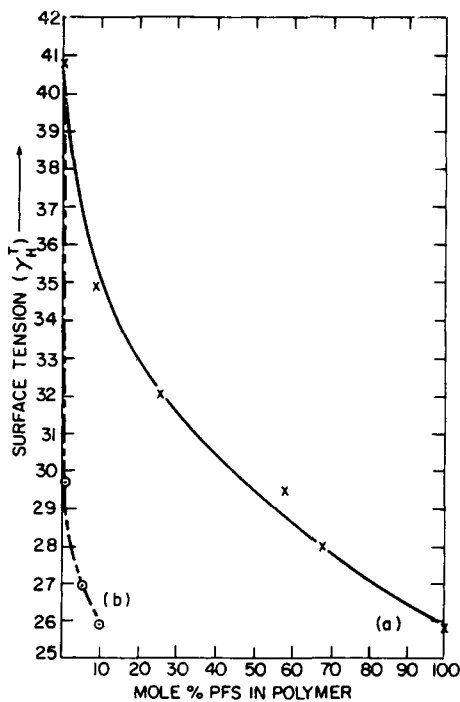


Fig. 2. The plot of average surface tension calculated by the Harmonic-Mean method using the data of various testing liquid pairs vs. polymer's composition (mole%): (a) — poly(PFS-co-MA) and (b) ---- polymer blends of PPFS and PMA.

Table III shows that the calculated average surface tension of PMA is 40.9 dyne/cm, which is in excellent agreement with the surface tension data obtained directly by the polymer melt method ($\gamma = 41.0$ dyne/cm).¹⁸ Similarly, the calculated surface tension of the poly(dimethylsiloxane) is 21.6 dyne/cm which compares favorably with the data ($\gamma = 19.8$ – 19.9 dyne/cm) obtained directly by the polymer melt method.^{16,19} A nonlinear curve (Fig. 2) is also observed when γ_H^T , the surface tension obtained from the harmonic-mean method, instead of γ_c , the critical surface tension, is plotted against mole% of pentafluorostyrene in the copolymer. However, the average surface tension data points in Figure 2 seem to give a better curve fit than the critical surface tension data shown in Figure 1. The plot of γ_H^T data versus polymer blend composition also indicates a significant surface enrichment of the low surface energy component, PPFS, due to a phase-separation phenomenon in the coating process. Mixing 1 mole% of PPFS with 99 mole% of PMA causes a significant phase separation and the observed surface tension of the polymer blend is dominated by the minor component of low surface energy polymer ($\gamma_H^T = 25.8$ dyne/cm for PPFS vs. $\gamma_H^T = 40.9$ dyne/cm for PMA). The occurrence of the phase separation is clearly due to incompatibility of PPFS in PMA. The results of this study also suggest that the soluble PPFS can be used either alone or together with PMA or other soluble polymers in solution coating to produce a nonspreading low surface tension surface.

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