Critical Surface Tension of Blends of Thermosetting Fluorochemical Methacrylate Polymers with Thermosetting Hydrocarbon Acrylate Polymers

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Synopsis

Critical surface tensions (γ_c) for blends of thermosetting fluorochemical methacrylates and thermosetting acrylate polymers are measured in their cured thermoset condition. Values of γ_c depend on (1) the nature of the fluorochemical side chain and (2) the ratio of fluorochemical containing polymer to hydrocarbon polymer. The minimum value for γ_c is found to occur at a fluorocarbon to hydrocarbon polymer ratio of 0.10 to 0.001. At higher and lower ratios (>0.1 and <0.001), the value for γ_c increased. Thus, certain blends of fluorochemical methacrylate copolymer with hydrocarbon acrylate copolymer give lower γ_c than either the hydrocarbon acrylate or the fluorochemical methacrylate copolymer.

INTRODUCTION

Commercial acceptance of fluorochemical polymers in protective coating application has been based on several factors, among them are (a) their chemical inertness to solvent swelling and (b) their oleophobic nature. These attributes are based in part on the fact that these polymers have low critical surface tension and are not wetted by common organic solvents. Typical of these materials is Teflon, the homopolymer of tetrafluoroethylene. The value of γ_c for this polymeric material has been determined to be 18 d/cm.[1] Commercial use of this polymeric system in the coatings industry is limited because of its insolubility in polar solvents,[2] although powder sintering is one commercial mode of application.[3]

Our approach to preparing a fluorochemical coating surface was through use of blends containing thermosetting fluorochemical acrylates. Since the fluorine containing copolymers are expensive, the goal was to produce less expensive mixtures that contain the advantages of the fluorine containing polymers alone.

The critical surface tension of a solid surface, which is indicative of the oleophobic and low staining characteristics of the surface, was used to measure the improvement.

The relationship between the contact angle of a sessile drop and surface tensions at the liquid–solid–vapor interfaces was recognized by Young[4] to be related as follows:

$$\gamma_{SV^0} - \gamma_{SL} = \gamma_{LV^0} \cos e$$

where the subscripts SV^0 and LV^0 refer respectively to the solid and liquid in equilibrium with the saturated vapor.

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Fox and Zisman[1,5,6] in a series of studies established an empirical relationship between the cosine of the contact angle, cos θ, and the surface tension of the liquid, γ_{LV}, for a series of homologous liquids. They defined the critical surface tension for wetting as the intercept of the cos $\theta = 1$ line with the extrapolated plot of cos θ versus γ_{LV}.

We have used this empirical procedure to determine the γ_c for a series of thermoset fluorochemical acrylate/hydrocarbon acrylate blends. We also used Chan's graphical method for determining γ_c.[7] According to Chan,

$$\gamma_c = \left[\frac{\gamma_L(1 + \cos\theta_L)^2}{4}\right]\theta_L = 0.$$

From a plot of $\frac{1}{4}\gamma_L(1 + \cos\theta_L)^2$ versus γ_L, the value of $[\gamma_L(1 + \cos\theta_L)^2]/4$ at the intercept of the diagonal, where $\theta_L = 0$, is defined as the critical surface tension. The details are discussed in the experimental section.

We first prepared a low molecular weight fluorochemical containing N-methylolacrylamide reactive thermosetting copolymer soluble in n-butanol. Very high levels of n-dodecyl mercaptan were used as chain-transfer agent. When high levels of mercaptan were not used, the polymer phase separated from the n-butanol solvent. We assumed that each molecule of copolymer will have one mercaptan fraction. The elemental sulfur analysis of a vacuum-dried, noncrosslinked sample was used to calculate the molecular weight of the fluorochemical containing copolymer.

EXPERIMENTAL

Procedure

A typical thermosetting hydrocarbon acrylate polymer was prepared by a method detailed by Christenson and Hart.[8] It was used as the base hydrocarbon acrylate polymer. This is detailed in Example 1. A series of thermosetting fluorochemical acrylates was prepared by a procedure detailed in Example 2 using perfluorocyclohexyl carbinol acrylate.

TABLE I
Comparison of Data for Determination of γ_c Fluorochemical Copolymer OMA/A.
Concentration of Fluorochemical Copolymer 87.9%

Hydrocarbon test solvent	Surface tension, of test solvents, d/cm	Contact angle of liquid–solid interface θ, degrees	cos θ [a]	$\dfrac{\gamma_L(1 + \cos\theta)^2}{4}$ [b]
C_{16}	27.4	68	.374	12.94
C_{14}	26.4	67	.390	12.77
C_{12}	25.1	63	.454	13.27
C_{10}	23.7	59	.515	13.60
C_8	21.7	49	.656	14.88
C_7	19.3	35	.819	15.96
C_6	18.2	30	.866	15.84

[a] Method of Zisman.
[b] Method of Chan.

TABLE II
Tabulation of Critical Surface Tension
Versus Concentration of Fluorochemical Copolymer

Mixture 1 CMA containing copolymer		Mixture 2 OMA containing copolymer		Mixture 3 ω H-C$_5$MA containing copolymer		Mixture 4 6FKMA containing copolymer	
%	γ_c, d/cm	%	γ_c, d/cm	%	γ_c, d/cm	%	γ_c, d/cm
100.	19	100	17	100	23.8	100	21.0
88	18.5	87.9	16.4	91.9	23.4	82.9	20.0
19	16.8	14.1	14.8	45.5	23.0	46.9	18.5
8.8	16.8	2.92	14.5	25.4	21.0	11.9	17.8
0.94	16.8	1.57	14.5	5.83	18.8	3.24	17.8
0.20	16.8	0.436	14.5	4.14	18.8	1.72	17.8
0.073	16.8	0.101	14.5	0.61	18.3	0.428	18.0
0.050	17.5	0.0061	23.0	0.26	21.0	0.093	19.0
0.0068	22.6			0.044	24.5	0.0024	22.2
0	>28	0	>28	0	>28	0	>28

Fluorochemical acrylate and hydrocarbon acrylate polymers were blended and coated on clean glass slides and cured in a forced-draft oven at 150°C for 15 min. Contact angles were measured for a homologous series of linear saturated hydrocarbons running from C$_{16}$ to C$_6$ in length. Hydrocarbon test liquids were purified according to a method detailed by Chan.[7] The γ_L for these hydrocarbon liquids are noted in Table I. Contact angle measurements were obtained with an optical goniometer manufactured by Rame'-hart, Inc., Mountain Lakes, New Jersey. Contact angle measurements were made on at least two drops of liquid advanced to constant angle readings on the left and right interface of the drop.

Graphical determinations of γ_c were made using Zisman and Chan procedures.[1,5,6,7] In the former method values for cos θ versus γ_L were plotted to the intercept of the cos θ = 1. The Chan graphical procedure is discussed above.

Materials

All commercial monomers and chemicals were used as received:

1. Ethyl acrylate, Rohm and Haas Chemical Company, 15 ppm MEHQ added.

2. Styrene, Polysciences.

3. Acrylamide, Polysciences, 97% active.

4. n-Butanol, J. T. Baker, "Baker" grade.

5. n-Dodecyl mercaptan, Phillips Petroleum Company (Sulfole B-12).

6. Cumene Hydroperoxide, Hercules Chemical Company, 50% active.

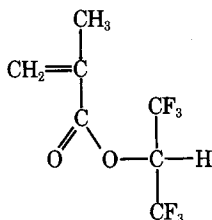7. Butyl Formcel, Celanese Chemical Company, 40% formaldehyde in n-butanol.

The following fluorochemical methacrylates were synthesized from the parent fluoroalcohols by an esterification of the alcohol with methacrylyl chloride in the presence of triethylamine:

$$CH_2{=}\!\!\underset{\displaystyle \underset{O}{\overset{\displaystyle C}{\|}}}{\overset{\displaystyle \overset{CH_3}{|}}{C}}\!\!-OCH_2{-}C_6F_{11}$$
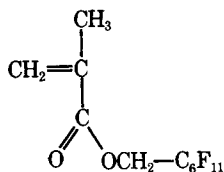
I (CMA) 1,2,2,3,3,4,4,5,5,6,6-undecafluorocyclohehyl carbinol methacrylate

$$CH_2{=}\!\!\underset{\displaystyle \underset{O}{\overset{\displaystyle C}{\|}}}{\overset{\displaystyle \overset{CH_3}{|}}{C}}\!\!-OCH_2{-}C_7F_{15}$$
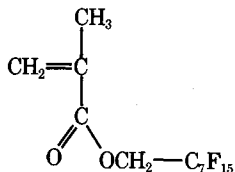
II (OMA) 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl methacrylate

$$CH_2{=}\!\!\underset{\displaystyle \underset{O}{\overset{\displaystyle C}{\|}}}{\overset{\displaystyle \overset{CH_3}{|}}{C}}\!\!-OCH_2{-}(CF_2)_4{-}H$$
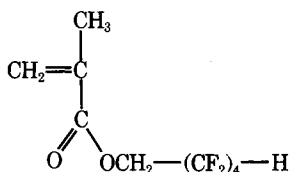
III (ω H-C$_5$MA) 2,2,3,3,4,4,5,5-octafluoropentyl methacrylate

$$CH_2{=}\!\!\underset{\displaystyle \underset{O}{\overset{\displaystyle C}{\|}}}{\overset{\displaystyle \overset{CH_3}{|}}{C}}\!\!-O{-}\underset{CF_3}{\overset{CF_3}{C}}{-}H$$

IV (6FKMA) 2,2,2,3,3,3-hexafluoroisopropyl methacrylate

The monomer IV was purchased from Allied Chemical. Trival abbrevia-
tions shown in parentheses are used below.

Example 1—Preparation of Thermosetting Hydrocarbon Acrylate Polymer

The following materials were placed in a 2-liter, three-neck round-bottom
flask equipped with a mechanical stirrer, reflux condenser, and thermometer:
ethyl acrylate, 225 g; styrene, 200 g; acrylamide, 75 g; n-butanol, 500 g; and
n-dodecyl mercaptan 12 ml. The mixture was heated with an oil bath to re-
flux condition (117°C). While stirring the heated mixture, a 50% solution of
cumene hydroperoxide was added incrementally. The conversion of mono-
mers to copolymer was followed and tabulated as follows:

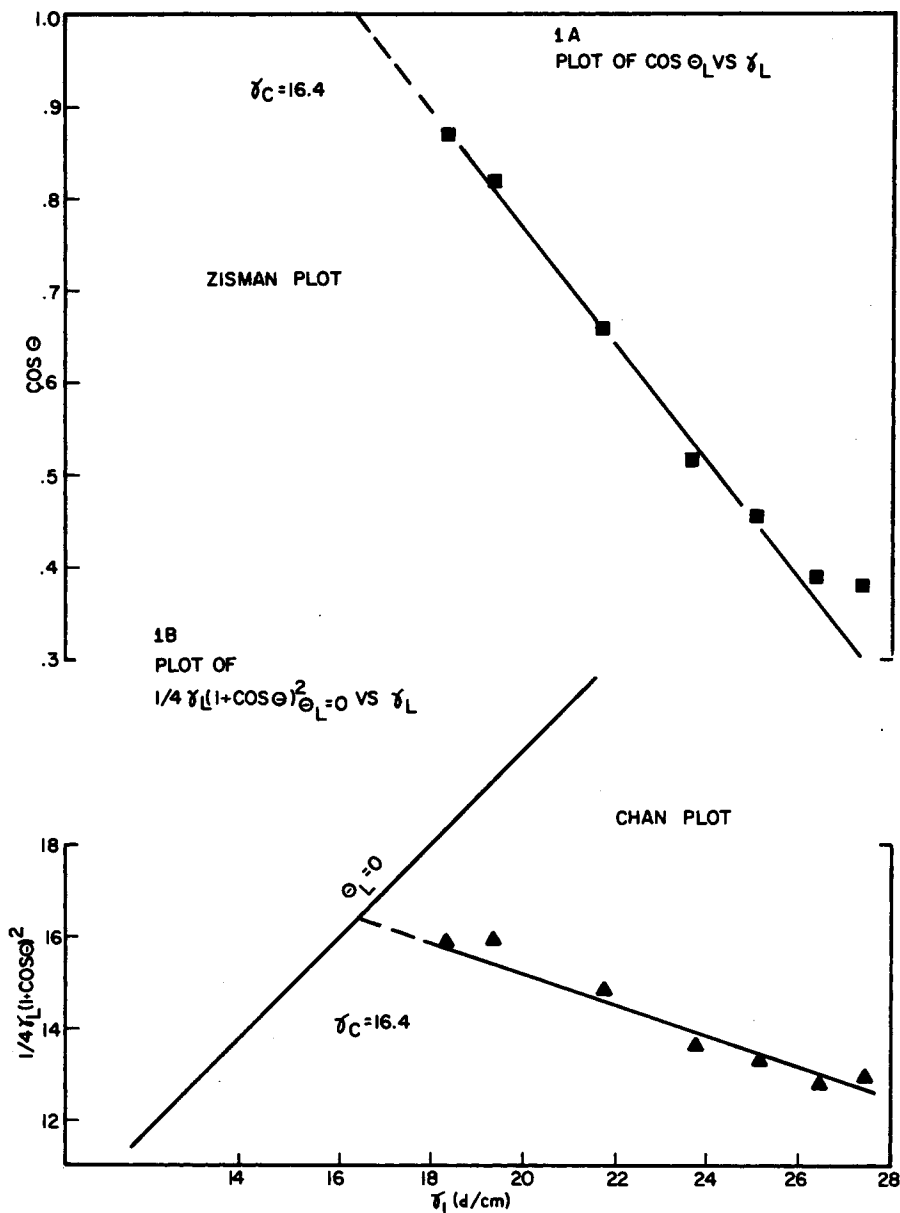| Time, hours	0	1.5	3.0	4.5	6	7.5
Cumene hydroperoxided added, ml	2	2	2	2	2	0
Conversion, %	0	46.2	59.2	67.6	81.3	90.1

Fig. 1. Determination of critical surface tension by the method of Zisman and Chan. Performed for a mixture based on 87.9 wt-% of copolymer II with 12.1 wt-% of the thermosetting hydrocarbon acrylate copolymer. Method of Zisman, by a plot of cos θ_L vs. γ_L; method of Chan, by a plot of $\frac{1}{4}\gamma_L(1 + \cos\theta)^2_{\theta_L=0}$ vs. γ_L.

After 9 hr, the mixture was cooled to 90°C and the following material was added to the mixture: maleic anhydride, 0.75 g; butyl Formcel, 225 ml. The mixture was heated to 105°C for 3 hr. At the end of that time, 200 ml n-butanol and 25 ml water were collected in a Dean-Stark trap. The material was then cooled. The material weighed 1077 g and had a polymer total solids content of 50.2%.

Example 2—Preparation of Thermosetting Fluorochemical Methacrylate Polymers. Copolymer of CMA and Acrylamide

The following materials were added to a 250-ml three-necked round-bottom flask equipped with a mechanical stirrer, reflux condenser, and thermometer: CMA, 42.5 g; acrylamide, 7.5 g; and n-butanol, 100.0 g. The mixture was heated to reflux, and n-dodecyl mercaptan and cumene hydroperoxide were added to the reaction mixture according to the following time schedule:

Time, hours	0	1	2	3	4	5
n-Dodecyl mercaptan, ml	5	2	2	0	0	0
Cumene hydroperoxide, ml	1	1	1	1	1	0

After 6 hr, the total solids on the reaction mixture reached a polymer total solids of 31.3%.

The material was then cooled to 90°C and the following methylolating ingredients were added to the reaction mixture: maleic anhydride, 0.20 g; and butyl formcel, 20 ml. The mixture was heated to 105°C for 1 hr. Twenty milliliters organic solvent and 2.0 ml water were collected in a Dean-Stark trap.

The material was cooled to 25°C. All the polymeric material remained soluble in n-butanol.

In similar manner, the 85/15 copolymers of three fluorochemical methacrylates (II, III, IV) with acrylamide were prepared. Elemental analyses are summarized below. Molecular weights are estimated from sulfur analyses.

Copolymer	Component	MW	Elemental changes				
			C	H	N	F	S
I	CMA acrylamide	1200	45.5	4.7	4.0	30.7	2.6
II	OMA-acrylamide	900	46.0	5.4	3.9	32.3	3.6
III	ωHC_5MA-acrylamide	1400	44.8	5.5	2.8	23.1	2.2
IV	6FKMA-acrylamide	650	51.5	6.5	3.6	18.8	4.4

$-OCH_2-(CF_2)_7-F$	$OCH_2-C_6F_{11}$	$-OCH\genfrac{}{}{0pt}{}{CF_3}{CF_3}$	$-CH_2-(CF_2)_4-H$
II	I	III	IV
14.5	16.8	17.8	18.8

RESULTS AND DISCUSSION

Contact angle data for the four thermoset fluorochemical methacrylate blends are noted in Table II. Critical surface tension (γ_c) for these blends were determined by graphical methods of Zisman[1,5,6] or Chan.[7] Both require graphical extrapolation. Both approaches offer similar results as shown in Figure 1.

Figure 2 is a plot of γ_c versus the concentration of fluorochemical methacrylate copolymer in the hydrocarbon matrix for the four systems. In general, these four blends display the same general shape with the following common features:
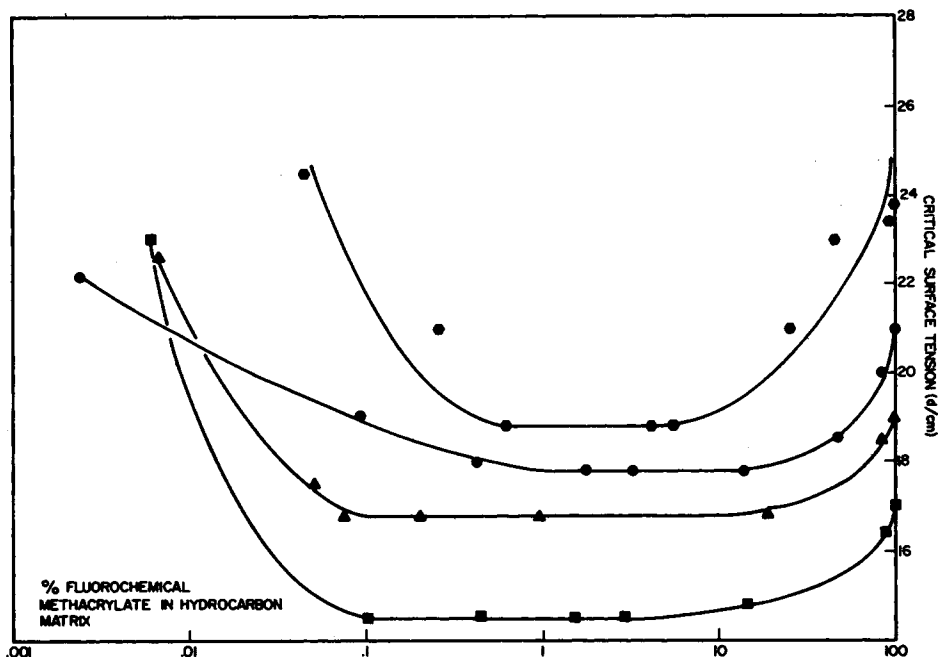
Fig. 2. Critical surface tension vs. concentration of fluorochemical methacrylate. Copolymer blends of: (▲) CMA copolymer with thermosetting hydrocarbon acrylate; (■) OMA copolymer with thermosetting hydrocarbon acrylate; (●) 6FKMA copolymer with thermosetting hydrocarbon acrylate; (C) ωHC_5MA copolymer with thermosetting hydrocarbon acrylate.

1. The undiluted fluorochemical containing copolymers have a γ_c which, depending on the nature of the fluorochemical side chain, varies from 17 to 23.8 d/cm.

2. The addition of small amounts of a hydrocarbon acrylate copolymer to the fluorocarbon containing copolymer reduces the γ_c of the overall mixture. The minimum value of γ_c for these mixtures occurs over the range of 10% to 0.1% fluorocarbon copolymer in the mixture.

3. As the level of fluorocarbon containing copolymer in mixture is reduced below 0.1%, the γ_c of the mixture increases.

The decrease in γ_c from the initial value at 100% fluorochemical methacrylate to the minimum value seen in all four cases probably reflects an increase in packing of fluorochemical side chains and concurrent submergence of the hydrocarbon backbone chain portions.

TABLE III
Minimal γ Value for Fluorochemical Methacrylate Copolymer Blends

Fluorochemical monomer	Structure of fluoro-chemical side chain	γ_c, d/cm	Range of minimum value
CMA	O—CH$_2$—C$_6$F$_{11}$	16.8	10% to .1%
OMA	O—CH$_2$—(CF$_2$)$_7$F	14.5	10% to .1%
ω HC$_5$MA	OCH$_2$(CF$_2$)$_4$—H	18.8	5% to .6%
6FKMA	O—CH(CF$_3$)(CF$_3$)	17.8	10% to 1%

The minimum values of γ_c achieved for these four systems are noted in Table III. These values of γ_c reflect the structure of the fluorochemical side chain. Both Chan[7] and Zisman[9] have reported a value of 10.6 d/cm for γ_c for the homopolymer of OMA. As a copolymer diluted in a hydrocarbon acrylate matrix, we achieved a value of 14.5 d/cm. Copolymers based on CMA diluted in a hydrocarbon acrylate matrix have a minimum value for γ_c of 16.8 d/cm, which is similar to literature value of 16.2 d/cm.[7]

Differences in minimum values of γ_c in fluoro copolymers and their blends follow fluorochemical structural differences noted by Shafrin and Zisman[10] and others. Minimum γ_c achieved are in systems of close packed —CF_3 groups. In the four systems studied here, the order of increasing γ_c is as follows:

The relative low value of γ_c for the fork tailed structure in system III can be attributed to the packing of the relatively short CF_3 tail. The high value of γ_c for the structure IV is due to the hydrogen in the ω position. Zisman[10] noted that an omega hydrogen in the terminal position of a fluorochemical side chain increases γ_c by approximately twofold.

CONCLUSIONS

Mixtures of nonfluorine-containing polymers with small amounts of fluorine-containing polymers can be prepared which are as effective as the more effective fluorine containing copolymers in the production of nonwettable and low-staining surfaces.[11] By blending 0.1% to 1.0% of certain fluoropolymer materials with hydrocarbon acrylate polymers, it is possible to produce a mixture having a γ_c value of 18.8 to 14.5 d/cm as compared to the γ_c value of 18 d/cm for a fluorochemical copolymer Teflon.

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