

Connection of surface tension with multiple tribological properties in epoxy + fluoropolymer systems

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Abstract: Contact angles of free liquids on solid samples were measured and the van Oss–Good method was applied for evaluating surface tensions of the solids. A parachor method was used for comparison: in this case the respective values were calculated for the polymer solids from molecular and group contributions. Surface tensions were computed from the parachors and the two methods compared. Effects of varying the fluoropolymer added to the epoxy before curing are discussed. For a given fluoropolymer, effects of changing its concentration on surface tension have also been evaluated and compared to the changes in scratch resistance (scratch penetration depth, recovery depth) and in static and dynamic friction. Morphological and phase structure changes are reflected in all these properties, showing a strong connection between the surface tension and tribological properties.

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Keywords: polymer surface tension; wetting angle; polymer tribology; epoxy surface modification; fluoropolymers

INTRODUCTION

Epoxy resins are widely used and well known for their mechanical properties.^{1–3} Their structures are investigated by several techniques including positron annihilation spectroscopy.⁴ Each year industrial demand for advanced polymeric materials that can successfully substitute for metal parts is increasing dramatically. Given the importance of epoxy-based materials in the substitution process, they constitute one of the areas of activity for our group.^{5–12} In particular, we use peroxides for crosslinking epoxies,^{5–7,10,12} as do Seppälä and coworkers for crosslinking ϵ -caprolactone.¹³

Although very useful, epoxies have several disadvantages, including high friction and low resistance to scratch and abrasion. We have assumed that modification of the epoxy resins with a material exhibiting distinctly different properties might be a remedy for these problems. It appears that this modifier could be fully fluorinated poly(aryl ether ketone) (12F-PEK).^{14,15} Our goal is to obtain epoxy-based materials with high scratch resistance in particular, as well as endowed with specific chemical, electrical, magnetic and optical properties. Among many physical properties, surface tension is important when

wetting and adhesion of liquid on solid surface is involved.^{16–20}

This work has been preceded by a complementary study dealing with other surface properties of polymer blends—namely tribological properties. We have reported¹⁴ that both static and dynamic friction of samples cured at 24 °C decreases significantly by adding as little as 5% 12F-PEK, and remains practically constant above 10% 12F-PEK. Scanning electron microscopy (SEM) micrographs supported our explanation that the significant improvement at such a low concentration of fluoropolymer is due to the existence of two phases: fluoropolymer movement towards the surface and phase inversion; 12F-PEK becomes the matrix in spite of its low concentration. In the second paper¹⁵ we demonstrated that significant scratch recovery as well as a lower original penetration depth are obtained for blends cured at 24 °C with again only 5 wt% concentration of 12F-PEK.

These promising results encouraged us to investigate other surface properties of the above system. We now look for connections between friction and scratch resistance investigated previously and surface tension, which is the subject of the present paper. As already

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noted, the minor component, due to its low surface energy, travels to the surface and becomes the matrix; we expected that the surface tension would be highly dependent on the 12F-PEK concentration as well.

EXPERIMENTAL

Materials

The fluoropolymer (12F-PEK) was synthesized in the Department of Chemistry at Southwest Texas State University.^{21,22} The chemical formula is given in Fig 1. Its properties have been described before.¹⁴ The epoxy used was the diglycidyl ether of bisphenol A resin (Shell Chemicals, EPON™ 828), which was cured with an aliphatic amine (triethylenetetramine (TETA), Shell Chemicals—EPI-CURE™ 3234. Its most probable formula is shown in Fig 2.

Half of the samples was cured at 70 °C for 3 h while the other half was cured at 24 °C in order to simulate room temperature curing applications. The curing was performed in Teflon moulds; no mould release was used. Top and bottom surfaces of the samples were examined. The details of blend preparation were given in Reference 14.

Contact angle measurements

Contact angle measurements of liquid droplets on polymer were used to characterize surface wettability.

The contact angle is defined as the angle between the polymer support surface and the tangent line at the point of contact of the liquid droplet with the polymer (Fig 3). The surface of a drop of a liquid placed on a solid can be represented by a spherical cap; in such a case the contact angle θ is calculated from the height of the cap h and the radius of the solid–liquid contact area r . The height of the spherical cap is represented by the equation $h = R(1 - \cos \theta)$

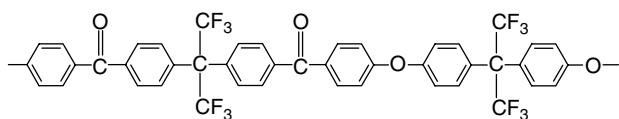


Figure 1. Chemical formula of 12F-PEK.

while the radius $r = R \sin \theta$. From these relationships we obtain

$$\theta = 2 \arcsin \frac{h}{R} \quad (1)$$

Precise measurements of h and r values are performed by means of an appropriate optical system. Geometric parameters of the drop are easy to determine on a magnified image. Details of this approach have been discussed by several authors.^{23–26}

In general, there is a variety of experimental techniques for determination of surface tension: measurements of the force needed to lift a ring from the liquid surface, capillary rise, Laplace's hanging droplet, and more. In our case, experiments were performed as follows. The container with a liquid was prepared and the syringe needle was immersed into the liquid. The syringe was then filled with the liquid and the excess liquid was wiped off. The air bubbles were eliminated by pointing the needle upwards and rotating the sleeve until the liquid started squirting out. Then the dispenser assembly was lowered along the guide and the locking knob tightened. This was

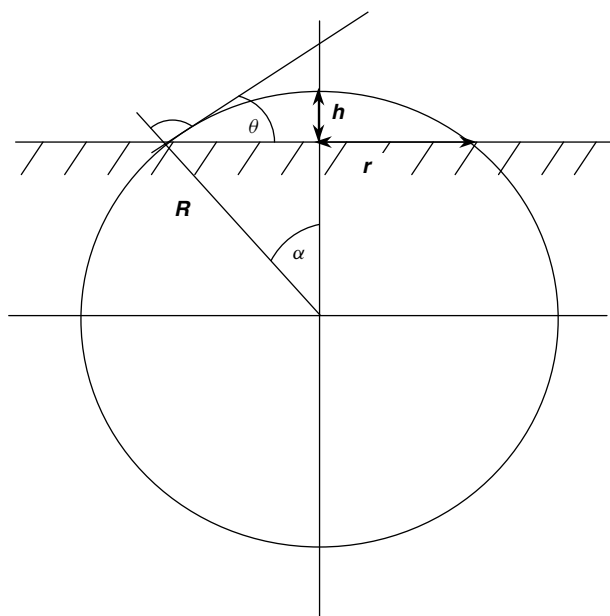


Figure 3. Contact angle determination.

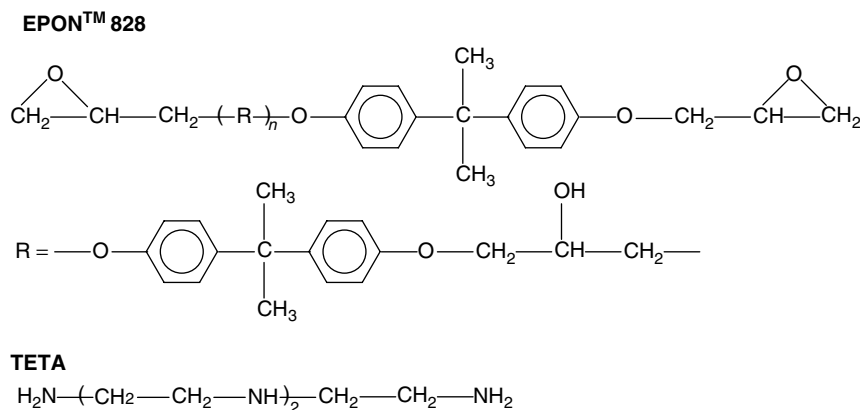


Figure 2. Chemical formula of diglycidyl ether of bisphenol A resin cured with an aliphatic amine, triethylenetetramine (TETA).

Table 1. Results of contact angle measurements

Weight % 12F-PEK	Curing temperature (°C)	Bottom of the samples			Top of the samples			
		θ (H ₂ O)	θ (Diiodomethane)	θ (Glycerol)	θ (H ₂ O)	θ (Diiodomethane)	θ (Glycerol)	
0	24	37	47	36	28	45	35	
5		54	46	57	51	47	58	
10		62	45	52	59	47	54	
15		70	70	44	62	69	48	65
20		72	72	55	55	72	58	53
0	70	63	47	62	61	47	63	
5		60	60	66	62	60	68	
10		74	61	65	67	62	66	
15		71	68	67	74	64	67	
20		83	54	57	84	54	62	

all done without disturbing the specimen table or the component to be tested. Then the illuminator was activated by switching on the power. The sample was placed in the specimen holder and secured with spring clamps. The testing surface was located precisely under the tip of the syringe needle and the knob of the micrometer syringe rotated clockwise to release the desirable amount (10 divisions on the screen) of the testing liquid. Then the specimen holder was brought up until the droplet touched the surface and the specimen holder was lowered to complete the transfer of the droplet. The contact angle was measured by rotating the clear protractor with a hairline on the measuring screen until the hairline crossed the apex. The contact angle measurements of sessile drops of pure liquid on smooth polymer surface were taken. This was repeated ten times for each polymer + liquid pair and then the mean value calculated.

The contact angles were measured at 25 °C on a contact angle meter Model CAM-MICRO manufactured by Tantec, Inc, Schaumburg, IL. All the experiments reported in this paper were performed at the Department of Chemistry, Southwest Texas State University, San Marcos. The results are listed in Table 1.

CALCULATION PROCEDURES

Parachor method

At least two methods are available for the evaluation of the surface tension γ of solids. The first consists in measuring the contact angle between the solid and several liquids. The second relies on calculation of the surface tension of the solid from the parachor.

The parachor is an additive function first introduced by Sugden in 1924 and discussed in some detail by van Krevelen.²⁷ Calculation of the molar parachor is believed to be a useful procedure for evaluating the surface tension. The parachor is defined as

$$P_s = \gamma^{1/4} \frac{M}{\rho} = \gamma^{1/4} V \quad (2)$$

Here M = molar mass, V = molar volume, and ρ = density.

If the group contributions to P_s and V are known, the surface tension γ can be obtained as

$$\gamma = \left(\frac{P_s}{V} \right)^4 \quad (3)$$

The conventional numerical values of the parachor and its contributions are expressed in (cm³ mol⁻¹) (erg cm⁻²)^{1/4} which is equivalent to (cm³ mol⁻¹) (mJ m⁻²)^{1/4}. Since the parachor is believed to be practically independent of temperature, Eqn (3) can be used to calculate the temperature dependence of the surface tension.

The surface tension of solid polymers may be calculated from the parachor of various functional groups of the repeat unit. The molar volumes in the amorphous state have to be used, because semicrystalline polymers usually have amorphous surfaces when prepared by cooling from the melt. There are several sets of group contributions provided by different authors. Usually, group contributions to parachor given by Sugden²⁷ show the best correspondence with experimental values for polymers. One needs to note that the parachor scheme is one of a number of group contribution schemes described by van Krevelen²⁷ and such schemes are used for a variety of purposes.^{28,29}

The van Oss–Good theory

Contact angles of different liquid drops on a solid surface are often used for surface tension measurements. This approach has been developed in particular by van Oss and Good.^{17,18,26} It has been used by a number of authors—for instance by Zukiene and her colleagues for polychloroprene and several copolymers.³⁰ The contact angle method is based on the following definition:

$$\gamma = \gamma^{LW} + \gamma^{AB} \quad (4)$$

γ^{LW} is the Lifshitz–van der Waals component of the surface tension due to the dispersion forces, also known as the van der Waals or London forces and studied in particular by Landau and Lifshits.³¹ γ^{AB} is the acid–base component of the surface tension.

If the substance exhibits both Lewis acid and Lewis base character, we have further

$$\gamma^{AB} = 2\sqrt{\gamma^+\gamma^-} \quad (5)$$

$\gamma^+ \equiv$ (Lewis) acid parameter of the surface tension while $\gamma^- \equiv$ (Lewis) base parameter of the surface tension.

If the substance is nonpolar, by definition

$$\gamma^{AB} = 0 \quad (6)$$

The general contact angle equation for a liquid *l* on a solid *s* (expressed in terms of the Gibbs function of adhesion) is

$$G_{sl}^a = -\gamma_l(1 + \cos \theta) = -2(\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + \sqrt{\gamma_s^+\gamma_l^-} + \sqrt{\gamma_l^+\gamma_s^-}) \quad (7)$$

If liquids l_1 , l_2 , and l_3 form non-zero contact angles on solid *s*, we can then use Eqn (7) to construct a set of three equations in terms of the three contact angles θ_1 , θ_2 and θ_3 :

$$\gamma_{l_1}(1 + \cos \Theta_1) = 2(\sqrt{\gamma_s^{LW}\gamma_{l_1}^{LW}} + \sqrt{\gamma_s^+\gamma_{l_1}^-} + \sqrt{\gamma_{l_1}^+\gamma_s^-}) \quad (8a)$$

$$\gamma_{l_2}(1 + \cos \Theta_2) = 2(\sqrt{\gamma_s^{LW}\gamma_{l_2}^{LW}} + \sqrt{\gamma_s^+\gamma_{l_2}^-} + \sqrt{\gamma_{l_2}^+\gamma_s^-}) \quad (8b)$$

$$\gamma_{l_3}(1 + \cos \Theta_3) = 2(\sqrt{\gamma_s^{LW}\gamma_{l_3}^{LW}} + \sqrt{\gamma_s^+\gamma_{l_3}^-} + \sqrt{\gamma_{l_3}^+\gamma_s^-}) \quad (8c)$$

To use equations (8a–c) and also (7), we need a set of values of γ^{LW} , γ^+ , and γ^- for a series of reference liquids. Various ways of determining surface tension of liquids are available.²³ For a nonpolar liquid γ^{LW} is the entire surface tension.

To obtain γ^{LW} values for polar liquids, one can follow the recommendation of Good:²⁶ measure first contact angles for apolar liquids on an apolar solid. We have in this case

$$\gamma_s^{LW} = \gamma_l^{LW}(\text{apolar liquid}) \frac{(1 + \cos \Theta)^2}{4} \quad (9)$$

Equation (9) is general. In other words, the value of γ_s^{LW} obtained in this way is valid regardless of whether there is an acid–base component of γ_s .

After γ_s^{LW} has been obtained from Eqn (9), it is possible to simplify the set of three equations to a set of two, namely Eqns (8b) and (8c). These can be recognized as a pair of simultaneous equations in the unknowns γ_s^+ and γ_s^- , with parameters that can be obtained from the $\gamma_{l_1}^+$ and $\gamma_{l_1}^-$ values of liquids 2 and 3.

To determine γ_s values for the components, Good²⁶ recommends a selection of three or more liquids, with

two of them being polar. In our measurements water, glycerol and diiodomethane have been used.

SURFACE TENSIONS

Results of calculations based on the van Oss–Good method are listed in Tables 2 and 3. Note that values in the Tables are expressed in $\text{erg cm}^{-2} = \text{dyn cm}^{-1} = \text{mJ m}^{-2} = \text{mN m}^{-1}$. Those results are also presented in graphical form in Figs 4 and 5. In these and also in the figures that follow the continuous curves have been obtained by polynomial fits. We see that in both cases—tops and bottoms of the samples—changes in the acid and base parameters of the surface tension appear earlier (at lower concentration) for samples cured at 24 °C than for those cured at 70 °C. This confirms the conclusion we have reached in Reference 14 that the phase separation process competes with the chemical crosslinking reaction between the epoxy and the curing agent. At the higher temperature of 70 °C, the crosslinking reaction is favoured and occurs faster. This causes phase separation of the 12F-PEK and epoxy-rich phases only at higher 12F-PEK contents than at 24 °C. The Lifshitz-van der Waals component of the surface tension changes only slightly with the concentration. This result should not be surprising since the dispersion forces it represents are weak and should be similar for particles of similar dimensions and atomic structures (both our components, fluoropolymer and epoxy, contain benzene rings and electronegative constituents).

After calculating the surface tensions from the parachor method we came to the conclusion that, in our case, this method does not give the expected results. This is probably due to the high molar volumes of our materials. Surface tension values from this method are 2.09 and 4.26 erg cm^{-2} for 12F-PEK and epoxy, respectively, thus one order of magnitude smaller than the values from contact angles. The examples listed by van Krevelen pertain to polymers with distinctively lower volumes with respect to molar mass.

Table 2. Surface tension components and total values calculated using the van Oss–Good method [erg cm^{-2}] for top surfaces of the samples

	wt%	γ^{LW}	γ^+	γ^-	γ^{AB}	γ Total
Curing temperature 24 °C	0	37.0	1.6	44.8	16.8	53.8
	5	35.9	0.1	34.7	3.6	39.6
	10	35.9	0.9	19.8	8.3	44.2
	15	35.4	0.2	15.0	3.2	38.6
	20	29.7	3.7	6.1	9.5	39.2
Curing temperature 70 °C	0	35.9	0.1	24.2	2.4	38.3
	5	28.6	0.1	28.7	3.1	31.7
	10	27.4	0.6	19.6	6.7	34.1
	15	26.3	1.1	11.7	7.1	33.4
	20	32.0	2.4	1.4	3.7	35.7

Table 3. Surface tension components and total values calculated using the van Oss–Good method [erg cm^{-2}] for bottom surfaces of the samples

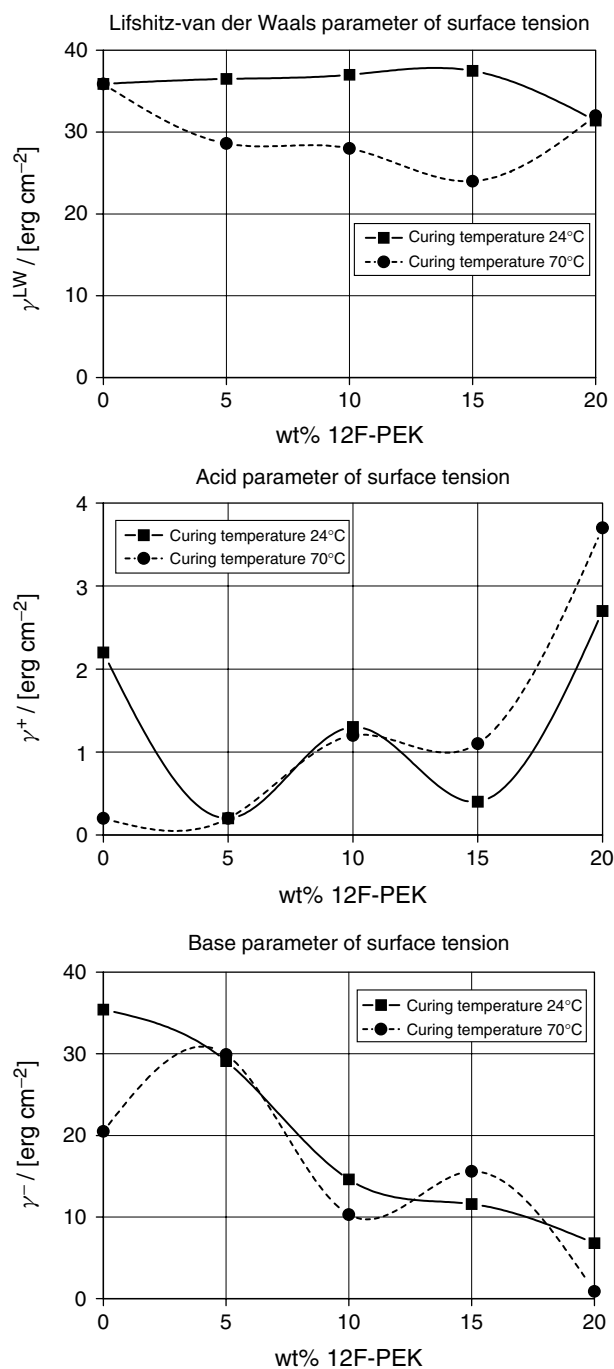
	wt% 12F-PEK	γ^{LW}	γ^+	γ^-	γ^{AB}	γ Total
Curing Temperature 24 °C	0	35.9	2.2	35.4	17.5	53.5
	5	36.5	0.2	29.1	5.0	41.5
	10	37.0	1.3	14.6	8.7	45.7
	15	37.5	0.4	11.6	4.1	41.6
	20	31.4	2.7	6.8	8.6	40.0
Curing Temperature 70 °C	0	35.9	0.2	20.5	3.7	39.6
	5	28.6	0.2	29.9	4.4	32.9
	10	28.0	1.2	10.3	7.0	35.0
	15	24.0	1.1	15.6	8.5	32.5
	20	32.0	3.7	0.9	3.6	35.6

Given this situation, let us focus on comparison of surface tension values obtained with the van Oss–Good method with other surface properties of our system examined in previous papers of this series.^{14,15}

COMPARISON OF SURFACE TENSIONS WITH TRIBOLOGICAL PROPERTIES

Comparison of Figs 6, 7 and 8 brings out an important feature: all the properties in question—surface tension, residual depth, penetration depth as well as static and dynamic friction—are lowered by the addition of the fluoropolymer to the epoxy in samples cured at 24 °C. Each of the surface properties under investigation shows a minimum at 12F-PEK concentration as low as 5 wt%. As already discussed in Reference 15, the first appearance of the fluoropolymer on the surface disrupts the epoxy structure; thus the surface tension is lowered. At higher 12F-PEK concentrations the fluoropolymer is becoming the matrix phase, so there are now sizeable surface areas of both phases and the surface tension increases somewhat. However, at still higher concentrations of the low surface tension component, the fluoropolymer, the total γ goes down again, eventually settling at a plateau when the phase conversion is completed.

It is also worth noting that surface tension *versus* concentration curves for the top and the bottom of the samples, although very similar, show vertical shifts in values: surface tension values for the bottom of the samples are higher than the respective values for the top of the samples. This might easily be explained by the already observed proclivity of the fluoropolymer to migrate to the top surface rather than to the bottom of the samples.¹⁴ Since the surface tension of the pure fluoropolymer is lower than that of the pure epoxy, it should be obvious that top surfaces of the samples, which are more affected by the fluoropolymer, will exhibit qualitatively similar but lower values of the surface tension. Thus, there are clear and strong connections between surface tension and all four tribological properties we have investigated.

**Figure 4.** Surface tension components at 25 °C calculated from the van Oss–Good method: bottom surfaces of the samples.

Given the connections seen in Figs 6–8, a question naturally arises: are the connections between the surface tension and tribological properties found in our system an exception, or should we expect them in other polymeric systems as well? To answer this question, we need to consider frictional properties separately from scratch behaviour.

For both static and dynamic friction we have expected a connection to surface tension *a priori*. High surface tension is caused by a strong tendency of surface molecules, or of surface polymer chain segments, to go towards the centre of the material, minimizing the surface area. Thus, there

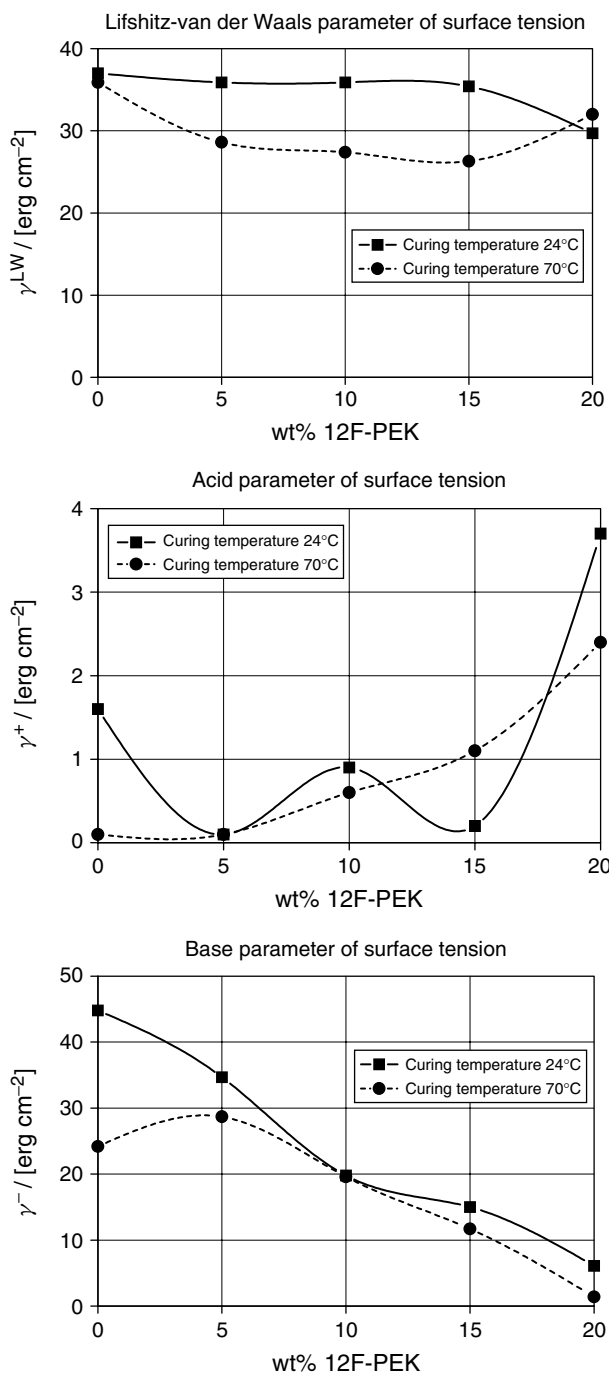


Figure 5. Surface tension components at 25 °C calculated from the van Oss–Good method: top surfaces of the samples.

are strong forces approximately normal to the surface acting downwards. During friction determination, we have an object moving along the surface. The object is in contact with the material surface and hence also subject to the downward forces.

Thus, high surface tension should be accompanied by high friction. It is on this basis that we have expected lowering of friction of the epoxy by a fluoropolymer to be accompanied by lowering of surface tension. The experiments have confirmed our reasoning, and we expect confirmations of the connection in other systems.

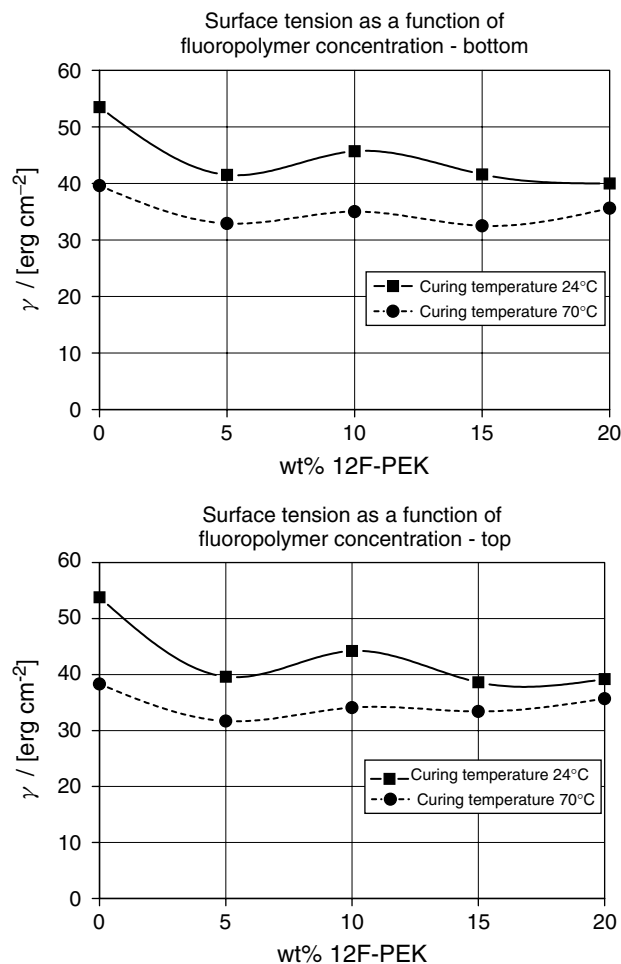


Figure 6. Surface tension total values at 25 °C calculated from the van Oss–Good method.

This approach should apply to systems in which an equilibrium is reached. As argued in Reference 14, epoxy curing at 70 °C results in a structure in which many fluoropolymer molecules did not have sufficient time to reach the surface, in spite of their low surface energy, but became trapped by crosslinks of the already cured polymer. By contrast, for samples cured at 24 °C, the fluoropolymer molecules had sufficient time to reach the surface. We see that the curves of static and dynamic friction for these samples have undulations at the same fluoropolymer concentrations as the total surface tension diagrams in Fig 6 pertaining to 25 °C.

The situation with respect to the surface tension–scratch behaviour connection is different. Teflon coatings have extensive use because of their low friction, but the scratch resistance of Teflon is poor. To quantify this situation, we have now obtained scratch penetration depth and scratch residual depth results for Teflon and some other materials.³² When, a few years ago, we started the work on polymer tribology, the conventional wisdom was that one could get either low friction or high scratch resistance but not both. Possibly this opinion resulted from a generalization of Teflon behaviour. While we have proven a case of simultaneous low friction¹⁴ and high scratch resistance,¹⁵ there is no general connection. Thus, we

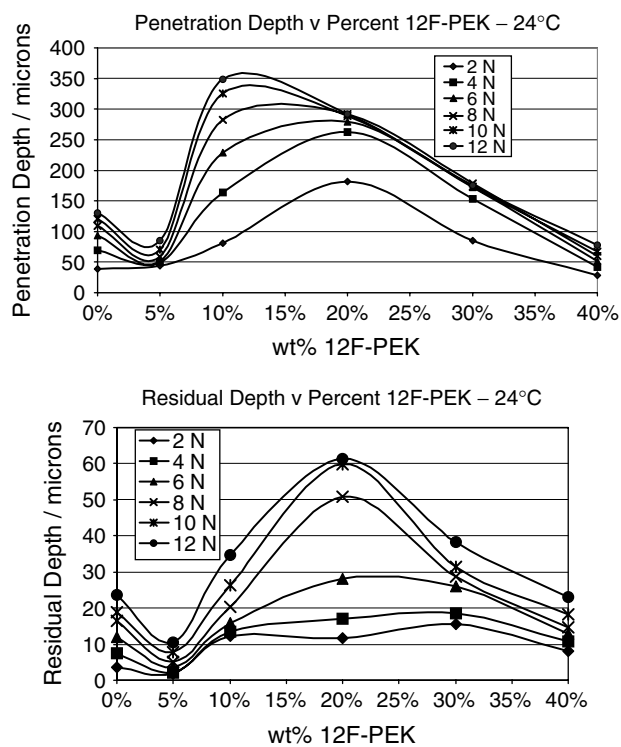


Figure 7. Penetration depth and residual depth *versus* 12F-PEK concentration for samples cured at 24 °C (after detail in Reference 15).

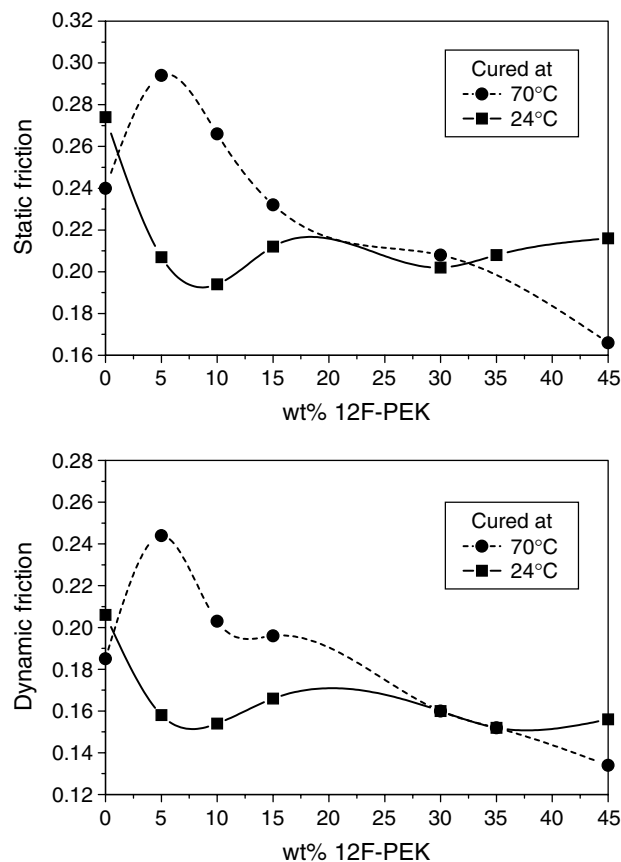


Figure 8. Static and dynamic friction for the blends as a function of 12F-PEK concentration for samples cured at 24 °C; based on data reported in Reference 14.

do not see a simple relationship between γ and the scratch test parameters R_p and R_h .

What exists is a reflection in the surface tension, and its dependence on concentration, of changes in the surface structure morphology. The morphological changes necessarily manifest themselves also in the scratching behaviour. In the system under investigation, we have found consecutive minima and maxima of γ accompanied by similar minima and maxima of both R_p and R_h . More work is needed to elucidate further the connection of the surface tension to scratch test parameters.

All these results, especially the similar appearance of the curves of several surface properties *versus* concentration, confirm our expectation regarding epoxy + fluoropolymer blends. It is particularly exciting that such significant improvements in all surface properties under investigation are reached at such low concentrations of the additive. Since our fluoropolymer is not exactly cheap, using higher concentrations would significantly raise the costs of such materials. Nevertheless, with concentrations of 5% we have reached two goals at the same time: improving surface properties while simultaneously maintaining costs at a reasonable level. A further investigation of such systems is worthwhile. Our group, encouraged by the results we have already obtained, is continuing research on other epoxy + fluoropolymer systems.

CONCLUSION

We have demonstrated for the first time that there is a connection between total surface tension of a polymer solid calculated from wetting angle experiments (three liquids for each polymer) and tribology. Static friction, dynamic friction, penetration depth and residual scratch depth have all been connected to the surface tension. We have advanced a hypothesis explaining the mechanism of the interactions at the surface affecting surface tension as well as the frictional properties. Our model is applicable to thermoplastics as well as thermosets.

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