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## Effects of fluoropolymer addition to an epoxy on scratch depth and recovery

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**Abstract** Samples were prepared by addition of a fluorinated poly(aryl ether ketone) (12F-PEK) to a commercial epoxy resin and curing at either 24 °C or 70 °C. The concentrations of fluoropolymer in the samples were 0, 5, 10, 20, 30, 40, and 50%. Phase inversion facilitates the formation of more and more smooth surfaces for scratch testing with increasing fluoropolymer concentration. A progressively increasing load from 0.03 N to 12 N was administered with a diamond tip to the surfaces of the samples; depths were determined within  $\pm 7.5$  nm. The original scratch depth is a function of the fluoropolymer concentration. Scratch recovery (healing) reaches values up to 95%. Plots of the residual depth versus concentration of the fluoropolymer at 4, 6, 8, and 10 N reveal minima for all forces and both temperatures. Addition of only 5% or 10% 12F-PEK improves the scratch recovery significantly. The results are explained by changes of material morphology with the fluoropolymer concentration.

**Keywords** Scratch resistance · Scratch depth polymer wear · Epoxy surfaces · Fluoropolymer

### Introduction

Scratch resistance is one of the most important service parameters. Nevertheless, scratch testing is an underappreciated area of Materials Science and Engineering (MSE). The scratch test was originally designed as a measurement

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of adhesion of thin hard films. Among the various techniques proposed for adhesion testing, the only one which led consistently to meaningful results and which could be used for quality control in large-scale production is precisely the scratch test. The test was first proposed by Heavens in 1950 [1] and implemented in the 1960s by Benjamin and Weaver [2] who were also responsible for developing the first model. However, their model failed to describe the behavior of hard coatings. The scratch test consists of deforming the surface by indentation under load of a moving diamond tip. The applied load can be held constant, increased continuously, or increased stepwise. The smallest load at which the coating is damaged is called the critical load  $L_c$  and is determined by optical or electron microscopy. In the case of very hard coatings the critical load is determined by acoustic emission. The critical load typically involves the beginning of a graph representing the beginning of a continuously applied force. In 1985, Steinmann and Hintermann [3] used a scratch test method that relied upon an acoustic emission signal to determine the critical loads for TiC deposited by chemical vapor deposition upon various substrate materials. Their scratch test method reported data as an acoustic emission (AE) versus load  $L$  graph.

Kody and Martin developed a fairly sophisticated scratch testing methodology in 1996 [4] which involved quantifying the light scattered from solid polymer and polymer composite surfaces due to surface deformation. The technique is based on deforming the material in a controlled, reproducible manner. The machine used a conical diamond stylus to induce scratches into a flat piece of material mounted on a rotating stage. The results could then be used to compare the scratch resistance of materials with different compositions and different textures.

### Scope

As noted in the preceding paper [5], this work starts from two premises. First, epoxies have a large number of applications [6, 7] and interesting properties [8] while

better epoxies – that is with lower friction and lower wear – are needed. Second, fluoropolymers (FPs) exhibit low friction but high wear. Hence the idea of epoxy + FP systems in which we hope to achieve simultaneously low friction and low wear. In [5] we have reported results for a series of such systems. Indeed, addition of a low concentration of a FP has lowered significantly both static and dynamic friction of the epoxy [5]. We now report results of an investigation of scratch resistance and wear in the same series of systems. Several parameters are obtained; in the last Section of this paper we discuss which of those parameters are important as a measure of wear.

We use a scratch test method that involves scratching the surface of various compositions of epoxy + fluoropolymer systems and measuring the depth of the scratch while the scratch is being made. The scratch depth is typically measured in microns. Typically, a viscoelastic material should recover or heal after the scratch. The *penetration depth* is the measure of the original scratch depth. The *residual depth* is determined after the surface scratch has been completed. Comparison of the two provides the amount of *recovery* or *healing* the surface has experienced after the scratch. In materials that heal well, the residual depth will typically be much less than the initial penetration depth. One expects that the amount of healing that takes place can be manipulated by the addition of a second component – as we have done in this work.

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## Materials

Epoxy resin + fluorinated poly(aryl ether ketone) (12F-PEK) was synthesized in the Department of Chemistry of the Southwest Texas State University according to a procedure already reported [9, 10]. The epoxy used was a diglycidyl ether of bisphenol A resin (Shell Chemicals – EPON 828) cured with an aliphatic amine (triethylene-tetramine TETA – Shell Chemicals – EPI-CURE 3234).

The fluoropolymer was dissolved in acetone (20 ml acetone/1 g 12F-PEK) and then the epoxy resin was added. The mixture was completely miscible. Samples containing 5 to 50% 12F-PEK by weight in the final systems were studied. The final samples thus contained the epoxy + 12F-PEK + curing agent. A pure epoxy or 0% 12F-PEK sample was also prepared and studied for comparison. No acetone was left; its normal boiling point is 56.10 °C [11]. The vapor pressure of acetone at 24 °C calculated from the Antoine equation [11] is 29.44 kPa = 221 Torr. The ratio of the curing agent to the epoxy was 13 g/100 g. According to the producer specifications, one half was cured at 24 °C in order to simulate room temperature curing applications and the other half was cured at 70 °C for 3 hours. The samples were stored at 24 °C.

The glass transition temperatures in our system have been reported in the previous paper [5]. We have  $T_g = 92$  °C for the pure epoxy and  $T_g = 186$  °C for 12F-PEK. Addition of the fluoropolymer to the epoxy initially in-

creases the  $T_g$  value, and at 20% 12F-PEK we see two glass transitions.

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## Scratch and recovery determination

Scratch resistance was measured with a Swiss micro-scratch tester (MST) from CSEM Instruments utilizing the CSEM Scratch Software Version 2.3. A minimum of 8 scratches were performed for each sample by progressively increasing the load from 0.03 N to 12 N; 25–40 runs per given kind of a sample were made and all numbers reported below are averages. The scratch speed was 5.3 mm/min and the scan length was 5 mm.

The indenter (scratcher) was of the Rockwell type made of diamond with the point radius of 200  $\mu\text{m}$ . Each run included a pre-scan, the scratch, and a post-scan. The pre-scan was necessary to characterize the topology of the sample before the scratch was made. The post-scan was performed to measure the response of the material after the scratch was made. As noted in the Scope Section, in viscoelastic materials we expect healing to occur. Therefore, the post-scan serves for the determination of the amount of recovery after a scratch. The pre-scan and the post-scan operate on a principle similar to atomic force microscopy (AFM). The topology of the surface is obtained before the scratch and after the scratch by applying the tip with a very small constant force (0.03 N) to obtain a “map” of the surface.

The penetration depth of the scratch was plotted versus the force in Newtons. The same plot was performed for the residual depth. The accuracy of the depth determination is  $\pm 7.5$  nm, far more than sufficient for our purposes since we report below effects of the order of microns or hundreds of microns.

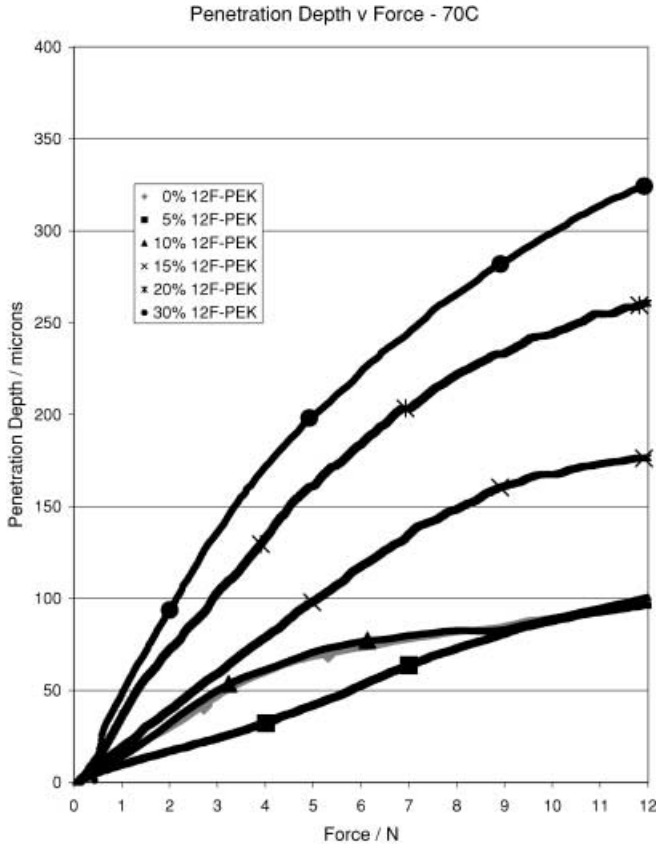
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## Penetration depths

We have results for samples cured at two temperatures; hence we display direct experimental results for one of them. In Fig. 1 we show curves of the penetration depth as a function of the force applied in the progressive mode for several fluoropolymer concentrations for samples cured at 70 °C. The curves for the samples cured at 24 °C are similar.

We see in Figure 1 that the addition of the fluoropolymer to the epoxy causes first a decrease and then an increase in the penetration depth. To understand the phenomenon involved, we have created plots of the penetration depth versus concentration of 12F-PEK for several forces; see Figure 2. The curves in Figure 2 as well as in all later Figures of depth versus concentration of 12F-PEK represent 4th degree polynomials with the parameters determined by a least squares procedure.

We see in Figure 2 that the initial addition of the fluoropolymer to the epoxy causes first a certain but not very significant lowering of the penetration depth. We know from the scanning electron micrographs (SEM) [5]

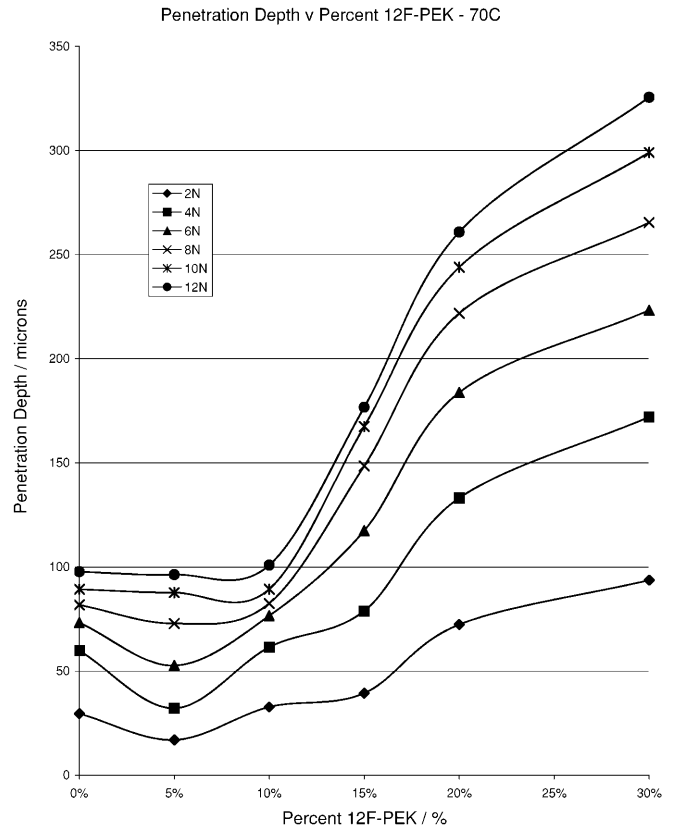


**Fig. 1** Penetration depth as a function of applied force for several concentrations of 12F-PEK in the epoxy cured at 70 °C

that the fluoropolymer comes preferentially to the surface and attempts to produce the phase inversion even at low concentrations. Before the phase inversion occurs, the diamond indenter tip encounters more or less alternating regions of both phases. This makes the penetration more difficult and the depth decreases along with increasing fluoropolymer concentration. The effect is not large, since – as also noted in [5] – the curing reaction interferes with the travel of the FP towards the surface.

Later on, when more 12F-PEK is added, the phase inversion begins. We know that Teflon has low scratch resistance and high wear. Our 12F-PEK + epoxy at the surface apparently provide a softer surface; the penetration depth begins to increase starting at 10% FP or so, tending towards a maximum or a plateau.

Consider in turn the penetration depths for samples cured at 24 °C. For brevity we do not include the depth vs. force curves. In Fig. 3 we show a plot corresponding to that in Fig. 2. There is a significant drop of the penetration depth upon addition of 5% FP only for all forces except the lowest one. That lowest force necessarily affects the surface the least. We reported in [5] that the phase inversion occurs earlier at 24 °C – and this fact is reflected by increases of the curves for various forces towards maxima at lower FP concentrations than for samples cured at 70 °C. At still higher FP concentrations the surface layer has more cohesion the penetration depth decreases.



**Fig. 2** Penetration depth as a function of 12F-PEK concentration at several applied forces. The epoxy curing was performed at 70 °C

The significant lowering of the penetration depth at 5% can be explained by the fact that at 24 °C the migration of fluoropolymer towards the surface is *not* hindered by simultaneous fast curing. It is due to this phenomenon that we achieve the desired result.

### Residual (recovery) depths

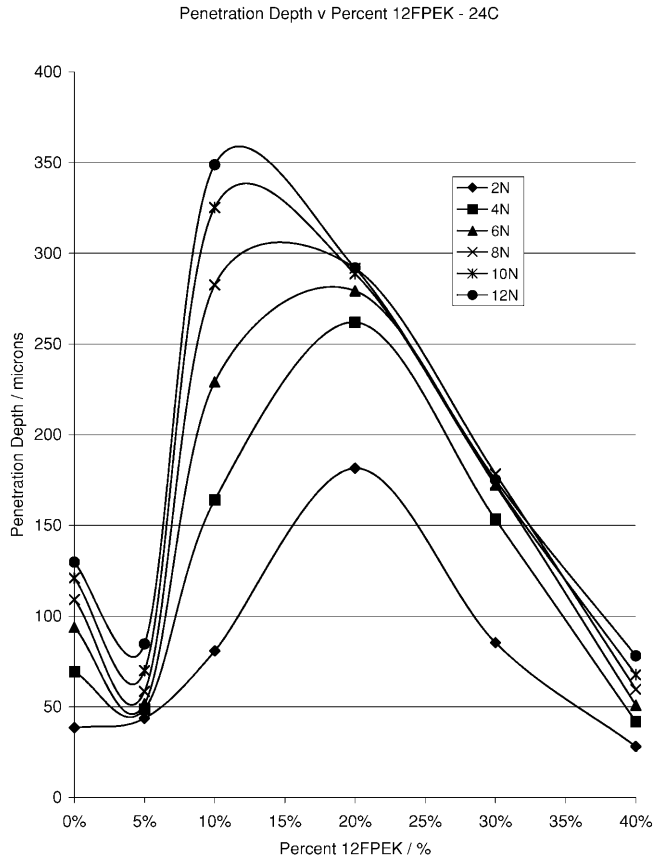
As noted in the Scope Section, our materials are viscoelastic; the penetration depth is also a function of *time*. The recovery is actually quite quick and takes more than 5 minutes.

In Fig. 4 we show the curves of the residual depth as a function of the FP concentration for a number of values of the applied force for samples cured at 70 °C. Starting from the pure epoxy, the curves show first minima then maxima. Thus, the results are similar to the original penetration depths – for analogous reasons.

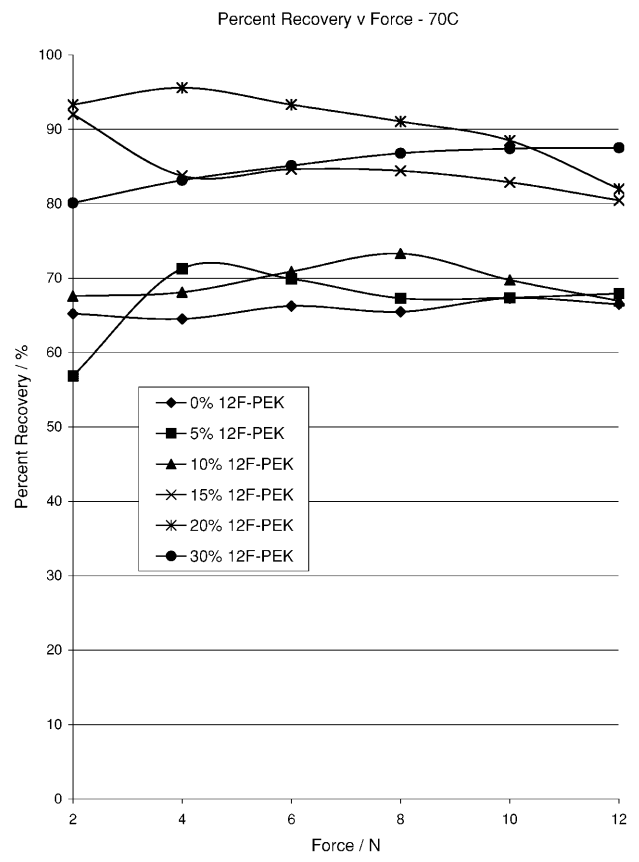
However, when we compare Figs. 2 and 4 quantitatively rather than qualitatively, we see that the strong recovery occurs in all cases. To have a measure of the healing that took place, we define the percentage recovery as

$$f = (1 - R_h/R_p) \cdot 100\% \quad (1)$$

where  $f$  is the fractional recovery in percent,  $R_p$  is the original penetration depth while  $R_h$  is the depth after

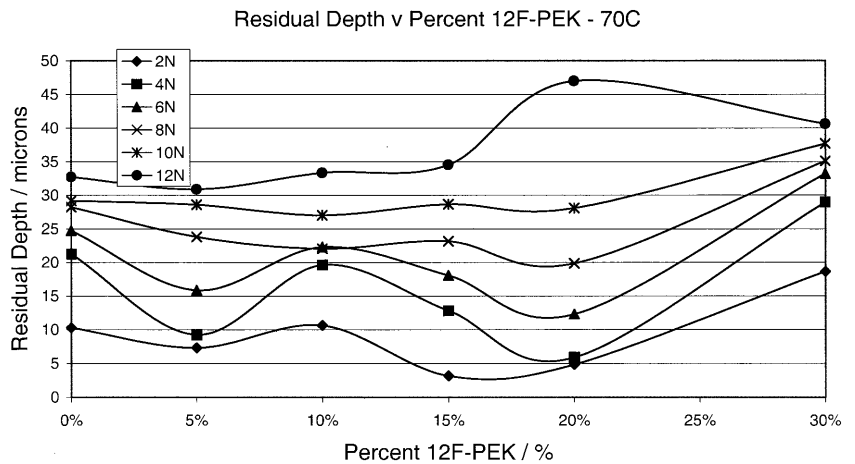


**Fig. 3** Penetration depth as a function of 12F-PEK concentration at several applied forces. The epoxy curing was performed at 24 °C



**Fig. 5** Percentage recovery of the scratch depth (healing) as a function of the applied force for samples cured at 70 °C

**Fig. 4** Residual (recovery) depth as a function of the 12F-PEK concentration for several applied forces in the epoxy cured at 70 °C

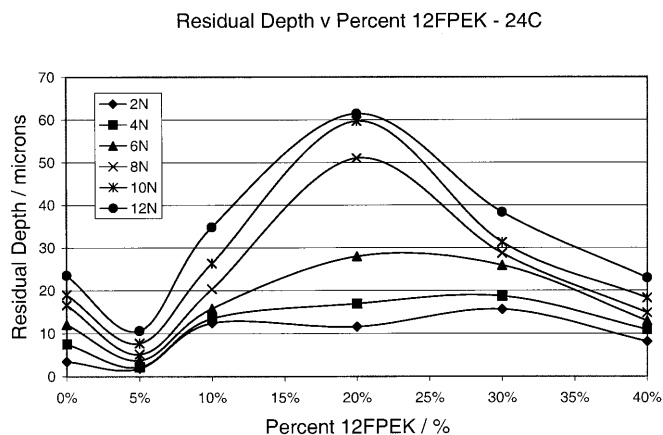


healing. The curves were calculated simply by using the above equation at each applied force – resulting in some 650 points on each curve that appear as a continuous line.

In Figure 5 we show the  $f$  values calculated from Eq. (1) for a number of concentrations of 12F-PEK. In most cases the dependence on the applied force is only weak. The 5% FP concentration is an exception: higher applied forces provide first an *increase* in the recovery, a desirable result; later on a plateau is reached. We recall

the minima in the penetration depth also around 5% FP in Fig. 2.

Figure 6 is an analog of Fig. 4 but for samples cured at 24 °C. We observe strong minima first for low fluoropolymer concentrations, followed by maxima. The minima occur at lower FP concentrations than in Fig. 4. The explanation is again the earlier and unhindered phase inversion at the lower temperature. The higher the applied force, the deeper the minimum at 5% 12F-PEK – another desired result.



**Fig. 6** Residual (recovery) depth as a function of 12F-PEK concentration for several applied forces. The curing was performed at 24 °C

### Relation to mechanical properties

Let us now connect the present values to mechanical testing results reported in the previous paper [5]. A plot of the flexural modulus versus the concentration of 12F-PEK [5] shows a minimum at about 1.1 GPa ( $1.1 \times 10^9 \text{ N/m}^2$ ) in the flexural modulus slightly above 5% 12F-PEK. The area  $A$  of the spherical diamond tip in contact with the sample can be represented by the standard equation for a partial area of the outer surface of a sphere,  $A = 2\pi \cdot r \cdot h$ ; substituting the height  $h$  by  $R_h$ , we obtain

$$A = 2\pi \cdot r \cdot R_h \quad (2)$$

where  $r$  is the radius of the indenter and  $R_h$  as before is the *recovery depth after healing*. Using the results obtained from scratch testing at the concentration of 5% 12F-PEK, the applied force of 2 N, and the residual depth of 4.30 microns, the area becomes  $5.40 \times 10^{-9} \text{ m}^2$  and the stress becomes 0.37 GPa. However, at this level of force less than half of the indenter seems to be causing the stress (we recall that we also apply stresses twice as large). To get a numerical value, assume that 40% of the indenter creates the stress. Our estimate gives us now 0.93 GPa. This result is comparable to the flexural modulus of 1.1 GPa [5], an altogether satisfactory agreement given the assumptions made and the different techniques used.

### Concluding Remarks

This work is a part of a larger program on epoxy modification [12–14, 5]. In the present paper we have shown that the addition of only 5% of 12F-PEK to the epoxy cured at 24 °C results in better healing after scratching. The residual depth is shallower than for the pure epoxy, the presence of the fluoropolymer enhances the recovery process.

Apart from the fluoropolymer concentration, clearly the second essential parameter is the temperature. As discussed above, at high temperatures the formation of the fluoropolymer-rich phase competes kinetically with the velocity of the epoxy crosslinking process. Comparison of the two recovery depth curves for the 70 °C and 24 °C, Figs. 4 and 6 respectively, is instructive. As already concluded when investigating static and dynamic friction, morphology and flexural behavior [5], changing the temperature gives us the capability to manipulate the properties.

The fact also noted above that fluoropolymers alone exhibit low friction and high wear, is an opportunity from the point of view of improving epoxy materials, including epoxy coatings. Our results show that a judicious choice of the fluoropolymer concentration and curing temperature for an epoxy is possible, resulting in materials with low friction and high scratch recovery *simultaneously*.

Friction and wear are still much better understood for metals than they are for polymers [15, 16]. We know much about polymer fracture surfaces [17] and also for instance about polymer coatings made from powders [18]. However, an 840 page book on polymer testing does not even have the word “wear” in its subject index [19] although surface wear is important in industry [20] as well as in medical applications of polymers [21].

Our Swiss micro-scratch tester allows the determination of wear by multiple indenter passes. The present results seem to show that the residual (recovered) depth is a parameter of at least comparable importance for the characterization of scratch, mar and wear resistance of materials.

We are also pursuing other aspects that can provide understanding of the tribology of polymer surfaces. Among others, results of liquid + polymer contact angle determinations and resulting surface tensions will be reported in a later paper.

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