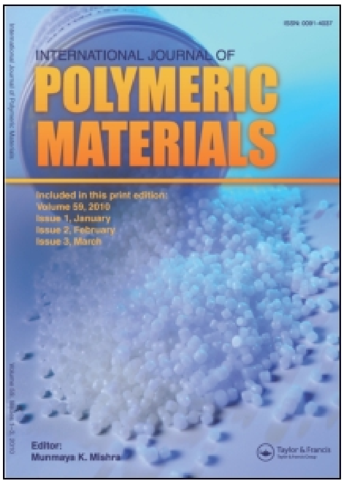

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

EPOXY + FLUOROPOLYMER SYSTEMS: NANOSCALE SURFACE ORGANIZATION AND SCRATCH RESISTANCE

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To cite this Article Brostow, Witold , Bujard, Bernard , Cassidy, Patrick E. and Venumbaka, Sreenu(2004) 'EPOXY + FLUOROPOLYMER SYSTEMS: NANOSCALE SURFACE ORGANIZATION AND SCRATCH RESISTANCE', International Journal of Polymeric Materials, 53: 12, 1045 — 1060

To link to this Article: DOI: 10.1080/00914030390214941

URL: http://dx.doi.org/10.1080/00914030390214941

International Journal of Polymeric Materials, 53:1045–1060, 2004
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ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030390214941

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EPOXY+FLUOROPOLYMER SYSTEMS: NANOSCALE SURFACE ORGANIZATION AND SCRATCH RESISTANCE

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Samples of fluoropolymers were blended with a commercial epoxy at 5 to 50 wt.% of fluoropolymer content and also with a so-called thermoplastic epoxy (BLOX). Pure epoxy samples were studied for comparison. Scratch depths and viscoelastic recoveries were determined within ±7.5 nm with a Swiss Micro-Scratch Tester; scanning electron microscopy (SEM) was also performed. Significant improvements in the original scratch penetration depth and in the scratch healing as compared to the pure epoxies are demonstrated. The extent of the improvement depends on the chemical structures of the fluoropolymers, nanoscale structure of the surface, the presence and concentration of electronegative atoms, and the presence and concentration of carbonyl and phenylene groups. A structural description of the fluoropolymers is provided on atomistic modeling.

Keywords: Epoxy modification, Scratch resistance, Scratch healing, Fluoropolymer, Epoxy, Surface structure

Received 1 April 2003; in final form 9 April 2003.

Partial financial support for this work was provided by the State of Texas Higher Education Coordinating Board, Austin (Project # 003594-0075-1999) and by the Robert A. Welch Foundation, Houston (Grant # B-1203). Dr. Javier Macossay, now at the Universidad Autonoma de Nuevo Leon, San Nicolas de la Garza, N.L., Mexico, has participated in the synthesis. Discussions with Prof. Jürgen Springer, Technical University of Berlin, are appreciated.

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INTRODUCTION

Tribology is an often underestimated science in spite of its evident practical importance. There is a similarity between tribology and corrosion: as with corrosion, inadequate knowledge of tribology carries heavy financial costs for industry. It has been known since the so-called Jost report in 1966 that billions of dollars per year could be saved by the industry if the correct use was made of tribological knowledge already existing [1–2]. Moreover, the gradual replacement of metal parts by polymeric ones is *not* reflected in tribology. Most of tribology—including the important book by Rabinowicz [2] and the collection of papers gathered by Zambelli and Vincent [3]—deals still with metal surfaces. On the other hand, a significant part of Polymer Science and Engineering is focused—for understandable reasons—on mechanical properties [4–8]. Clearly an effort in advancing polymer tribology is needed.

The task just defined needs to be narrowed to a specific class of polymeric materials. It is well known that *epoxies* constitute an important such class. Their use is well established in a number of industries such as marine, pipe, can, and drum coatings and also as adhesives, electric laminates for printed circuit boards, and more [9–13]. Epoxy coatings should be designed to impart favorable properties including low friction, scratch and abrasion resistance, as well as specific chemical, electrical, magnetic, and optical properties on various substrates. A high scratch resistance is needed to avoid damages that ruin not only the appearance but above all the function of a coating.

It is known that the fluorine content significantly affects properties of polymer systems [14]. Previously the authors have added a fluoropolymer (FP) to a commercial epoxy and obtained low static and dynamic friction [15] as well as high scratch recovery and shallow remnant depth after scratch [16]. The FP was fully fluorinated poly (aryl ethyl ketone), to be called below FP-1 for short. This does *not* mean, however, that any FP can produce similar effects. Teflon (polytetrafluoroethylene, PTFE) has received much public attention because of its low friction, use in the electronics industry [17–19] and as a nonabsorbent substrate for X-ray irradiation [20]. However, scratch susceptibility of Teflon is very high—as confirmed also by the experiments reported later. Thus, is FP-1 with—which the authors have worked before [15–16]—an exception or is Teflon an exception? Therein lies an important objective of the present work. Incidentally, FP-1 is quite expensive, thus one more reason for the present task.

Using the new FPS, the authors would like to achieve shallow final depth, called the recovery or after-healing depth R_h. Preferable are fluoropolymers blended with an epoxy or a thermoplastic in concentrations of 10% or less because FPs are relatively expensive compared to epoxies or engineering thermoplastics. FP-1 goes preferentially to the surface of the epoxy [15]—exactly where friction and scratching will occur. The new FPs need to have the same property. It is assumed that the electronegativity of the fluorine atoms—and possibly also of some other atoms—will play a role. In the present context it is worthwhile to consider both the atomic and bonding radii of the atoms. Individual atoms and their interactions need to be looked at. For example, the atomic radius of the fluorine atoms is 0.057 nm; however, when fluorine interacts with another atom to form a covalent bond its radius will increase to 0.072 nm. In contrast, the atomic radius of a carbon atom will decrease from 0.091 nm to a bonding radius of 0.077 nm.

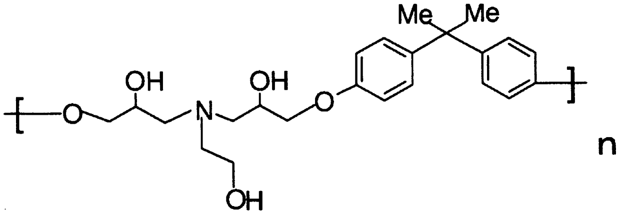
EXPERIMENTAL

The systems prepared by the authors might have commercial applications—while the science involved should be made public. Therefore, except for Teflon and already defined FP-1 the authors use simply consecutive numbers (FP-2, FP-3, etc.) but their contents in fluorine and certain functional groups will be provided when discussing the results. More importantly, they have two-phase systems. Fossey and Tripathy [21] argue convincingly that the phase structures in polymers are decisive for properties modeled at the atomic level.

FP-1, FP-2, FP-3, and FP-4 were synthesized at the Southwest Texas State University [22–24]. FP-7 was synthesized at the University of North Texas; its monomer has the lowest molecular mass among the fluoropolymers. The epoxy used was a diglycidyl ether of bisphenol A resin (Shell Chemicals EPON™828) cured with the triethylenetetramine (TETA, Shell Chemicals EPI-CURE™3234).

BLOX (received courtesy of Dow Chemical Co.) is provided as an experimental thermoplastic epoxy [25–26]. Its chemical structure is shown in Scheme 1.

The sample preparation procedure developed for FP-1 in Reference [15] was followed as far as possible also for new FPs. FP-1 was dissolved in acetone (20 ml acetone/1 g FP-1) and then the epoxy resin was added; the mixture was completely miscible. The curing agent was then added according to the producer specifications (13 g curing agent/100 g epoxy). Samples containing from 5 to 50 wt% of FP-1 in the final system (epoxy + FP-1 + curing agent) were prepared. One half of the mixture was cured at 70°C for 3 h and the other half was



SCHEME 1

cured at 24°C for one week in order to simulate room temperature curing applications. The samples were stored at 24°C.

FP-2 would not completely dissolve in pure acetone; therefore, a mixture of 30% tetrahydrofuran (THF) + 70% acetone was necessary while gently heating the mixture to 30°C. Samples were prepared containing from 5 to 50 wt% of FP-2 in the final system. 20 ml of the 30% THF + 70% acetone solution was added for each 2.4 grams of total mixture (FP-2 + epoxy + curing agent). Again the cuing was done at 24°C for one week or at 70°C for 3 h. When completely dry, the samples had a thickness of 500–600 microns with the surface area of approximately 20 cm^2—the bottom area of the aluminum sample pans. The samples were cut into approximately 1 cm^2 segments for scratch testing.

FP-3 does dissolve in pure acetone, albeit very slowly; 25 ml acetone/0.5 g of FP-3 were necessary to achieve dissolution. Otherwise the sample preparation was essentially the same as for FP-1, and the systems cured at 24°C and 70°C. The authors have used 13 g curing agent/100 g epoxy. Samples containing from 0 to 20 wt% of FP-3 were prepared.

FP-4 would not completely dissolve in 100% acetone; a mixture of 10% THF + 90% acetone was necessary—similar to the FP-2 procedure. 20 ml of the mixed solvent solution was added to each 2.4 grams of epoxy + FP-4 + curing agent.

FP-7 was blended with pulverized BLOX pellets. The pulverization involved freezing the pellets in liquid nitrogen for 10 min and then pulverizing frozen pellets for 5–10 min. The fragmented pellets were then frozen again and re-pulverized—this was repeated at least two more times until a fine powder was achieved. In each case, the pulverized BLOX was allowed to dissolve in 20 ml of THF with constant stirring for 6 h at room temperature; the beaker was covered with aluminum foil to prevent evaporation. Then the fluoropolymer was added to the solution with constant stirring until dissolved. The mixture was poured into an aluminum pan or a Teflon mold and left for the solvent to evaporate. The complexity of this sample preparation was facilitated by the Taguchi method; an L4 array [27] with possible combinations of sample preparation procedures was designed. The samples were stored at 24°C.

Scratch resistance was measured with a Swiss micro-scratch tester (MST) from CSM Instruments. The indentor (a Rockwell diamond tip with the point radius of 200 μm) is applied normal to the surface with an applied force ranging from 0.01 N to 30 N. The force F can be held constant; however, the progressively increasing mode is usually preferred in order to observe the effects of a full range of applied forces in one scratch.

The indentor passes three times over the surface for each scratch test. An initial pass or *pre-scan* is performed at the very light force of 0.03 N to determine the topography of the surface. The second pass is actual scratch, in this case made with a progressive load from 0.03 N to 15 N to determine the initial penetration depth R_p as a function of the load. The final pass of the indentor at 0.03 N, the *post-scan*, determines R_h, defined earlier. The accuracy of the depth determination is ±7.5 nm, far more than sufficient for the present purposes because this article we reports effects of the order of microns or hundreds of microns. A minimum of 10 scratches are performed at 24°C for each sample and the averages are reported.

The scratches are observed under the optical microscope in order to relate to any unusual points in the $R_p(F)$ and $R_h(F)$ diagrams. Most scratches show a characteristic teardrop-shape; the scratch begins at a point and gradually widens and deepens as the applied force increases. The authors have also studied metals such as stainless steel; the viscoelastic recovery was negligible, the original scratch depth remained several minutes later, that is $R_p \approx R_h$. By contrast, polymers demonstrate $R_p > R_h$ and we calculate the percentage recovery [16] as

$$f = (R_p - R_h)/R_p \cdot 100\% \tag{1}$$

R_h was determined 5 min after the original scratch (R_p determination) whereas the authors have verified that there are no changes in the depth after 3 min or so for these polymer systems.

Scanning electron microscopy was performed with a Jeol JSM-T300 scanning microscope equipped with a Tracor X-ray analyzer and a Polaroid camera also by Jeol-Technics Co. (Tokyo, Japan). The nonconductive polymer samples were gold plated.

SCRATCH TESTING RESULTS

In Figures 1–3 we show the residual depth R_h as function of the FP concentration respectively for FP-2, FP-3, and FP-4, all cured at 70°C.

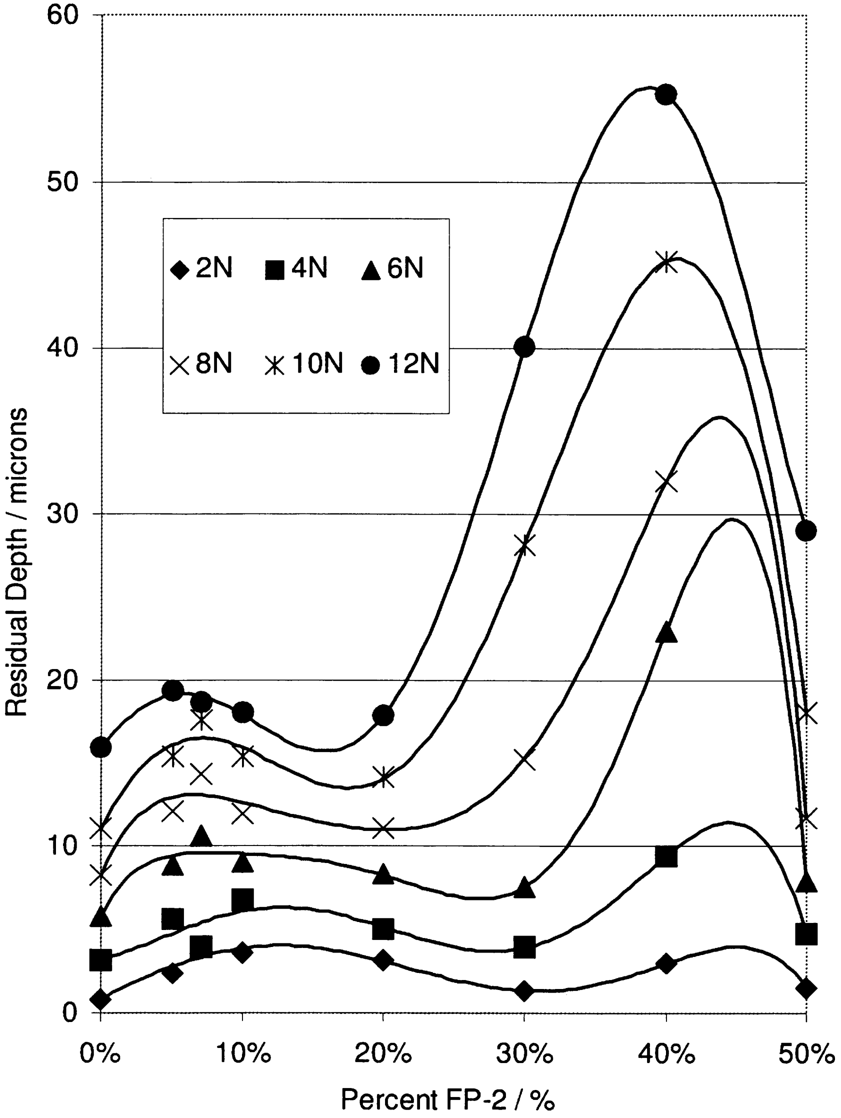


FIGURE 1 Residual depth as a function of percent FP-2 at several applied forces. The epoxy was cured at 70°C.

Continuous lines are 4th degree polynomials with the parameters determined by a least squares procedure. All diagrams show a maximum, a minimum, and then again a maximum. An explanation similar to that in Reference [16] seems applicable. First, the addition

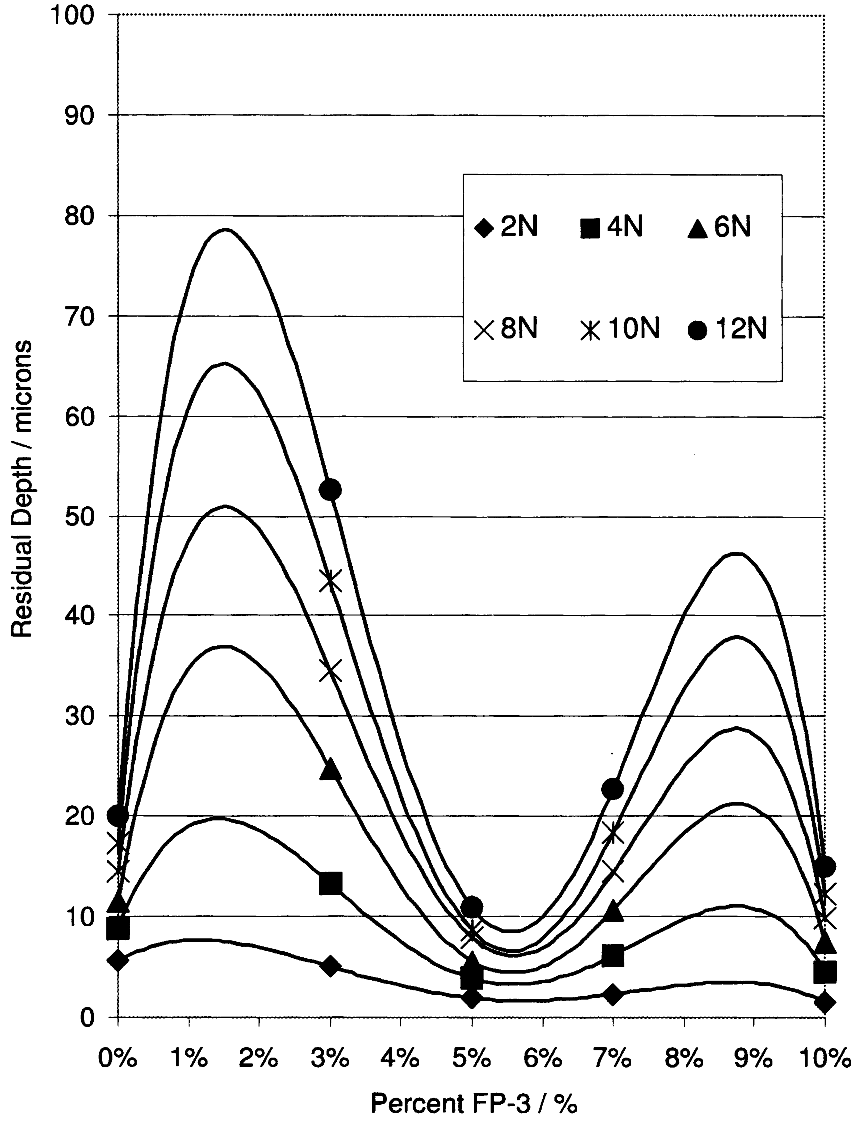


FIGURE 2 Residual depth as a function of percent FP-3 at several applied forces. The epoxy was cured at 70°C.

of a small amount of the relatively soft component (FP) decreases the scratch resistance and R_h increases. A further addition of the FP—which travels preferentially to the surface—produces somewhat larger FP "bumps" on the route of the travelling diamond, the scratch

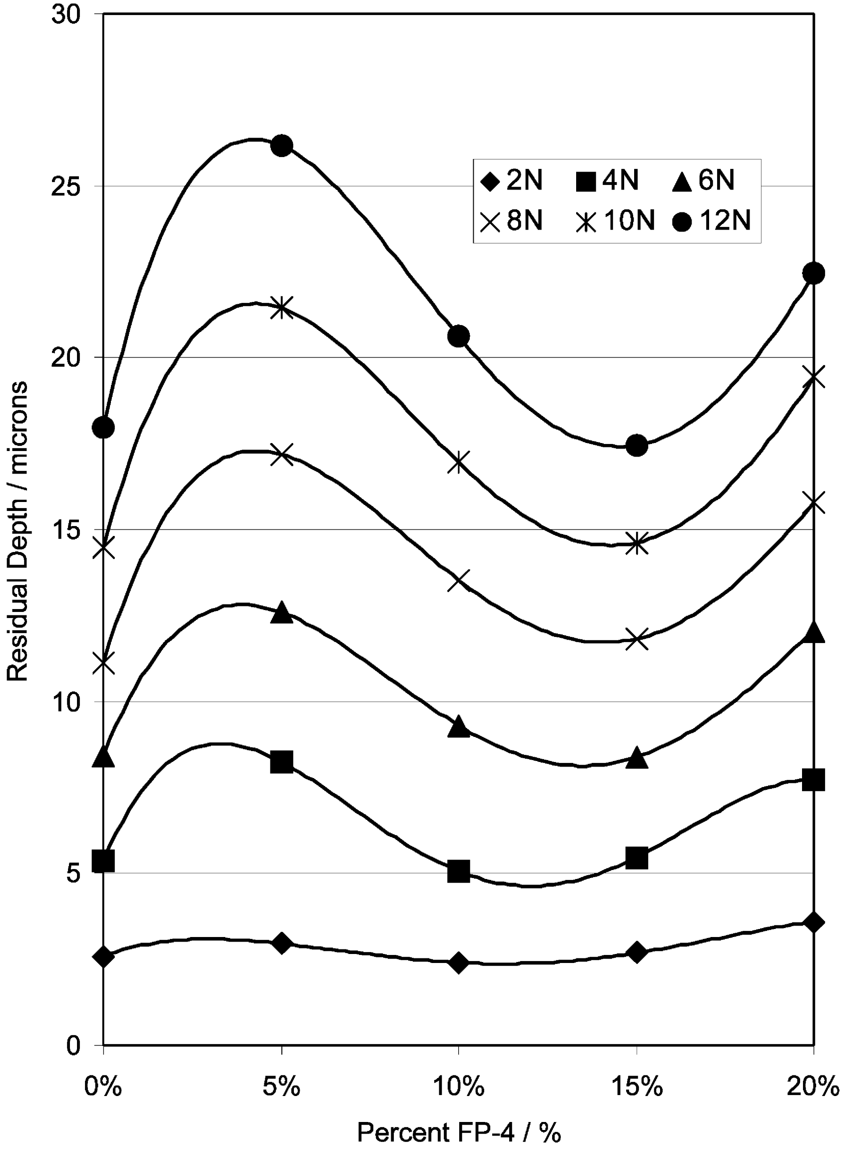


FIGURE 3 Residual depth as a function of percent FP-4 at several applied forces. The epoxy was cured at 70°C.

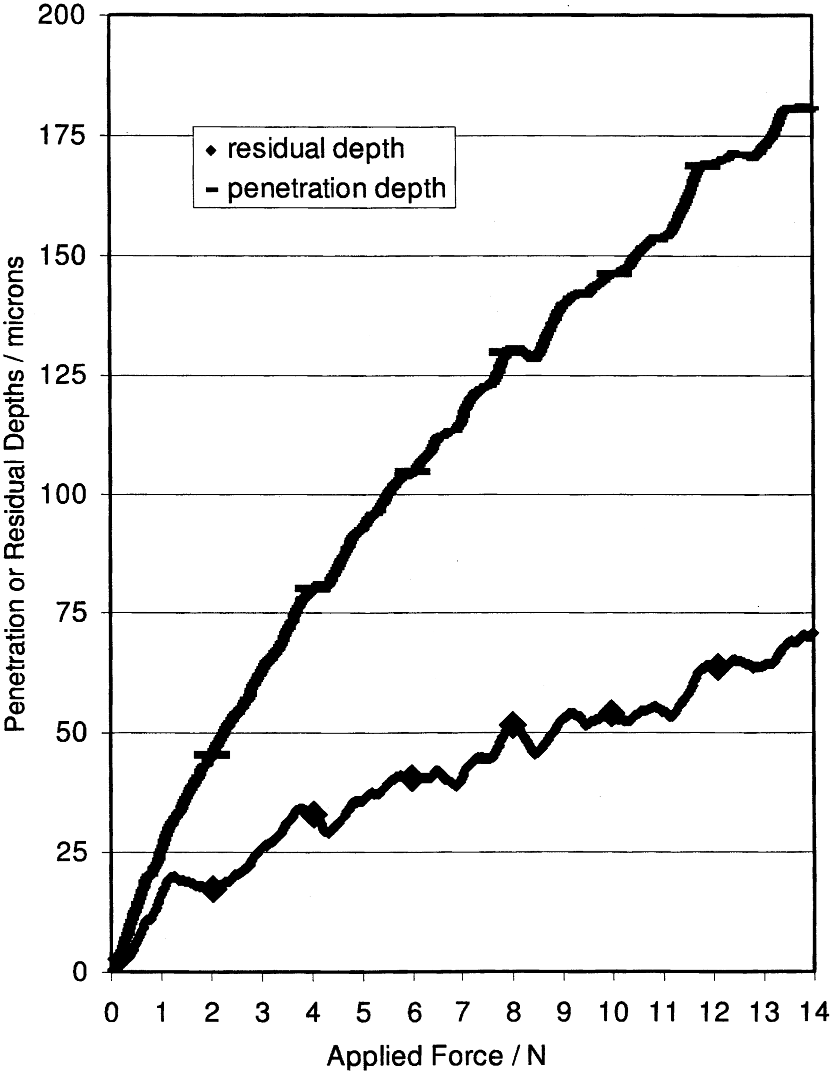


FIGURE 4 Residual depth and penetration depth for PTFE (Teflon) as a function of the applied force.

depth decreases, and improved scratch resistance is achieved. Then the phase conversion takes place (see the next section) and FP becomes the matrix. Because it is softer than the epoxy, the scratch resistance decreases. However, when the FP concentration is increased further, at the surface the epoxy becomes the minority

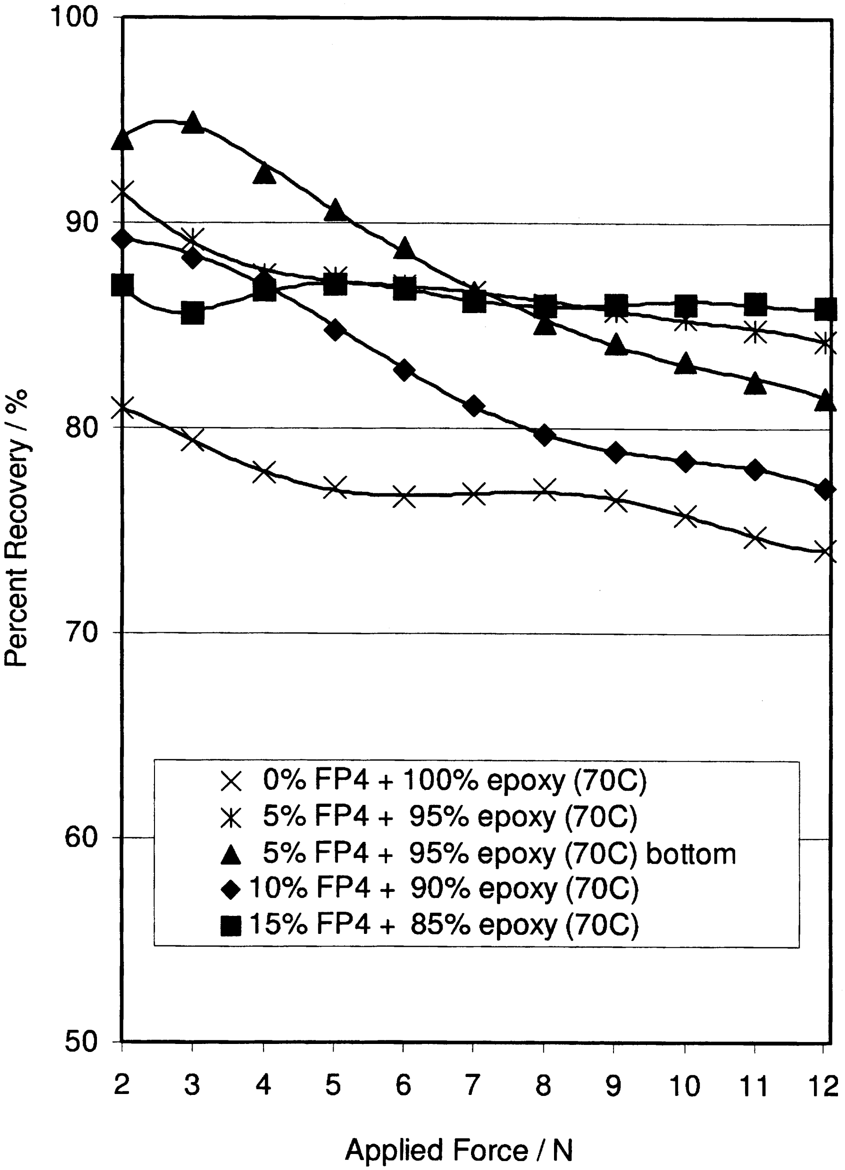


FIGURE 5 Percentage recovery of the scratch (healing) as defined by Eq. 1 as a function of the applied force for FP-4 samples cured at 70°C.

component and it now forms "bumps" that increase the scratch resistance. This seems an example par excellence how the nanoscale structure—in this case that of the surface—determines the properties. The concentrations at which the consecutive extrema occur are functions of the chemical structure of the FP (see the General Discussion Section).

Because it was noted in the beginning that PTFE owes one of its significant applications to low friction but has poor scratch resistance, the authors have quantified its scratch resistance in the same way as for other systems. The results are presented in Figure 4. While a significant healing effect is seen, the depth values are *much* larger than those for the epoxy-containing systems. Figure 4 shows that for 12 N the residual depth $R_h = 67\,\mu m$ in Teflon. By comparison, also for 12 N there is $R_h = 20\,\mu m$ in the pure epoxy and $R_h = 11\,\mu m$ in the epoxy + 5 wt% FP-3 (see again Figure 2).

Figure 5 provides some scratch recovery results calculated from the experimental data for epoxy + FP systems using Eq. 1. The beneficial effects of the presence of the fluoropolymer are clear. The pure epoxy has the lowest recovery. It can also be seen that the recovery decreases when the load applied increases. Apparently higher load produces partly irreversible structural changes.

Results of blending BLOX with several FPs are presented in Table 1-blends in which the indentor did *not* penetrate through to the

TABLE 1 BLOX + Fluoropolymer Systems

	2N			10N		
	R_p	% recovery (f)	R_h	R_p	% recovery (f)	R_h
Pure BLOX	204.16	45.40	111.40		(a)	
20% FP-1	117.28	56.44	51.09	157.18	48.20	81.41
20% FP-2	129.05	60.47	53.07	286.68	38.78	175.45
20% FP-4	68.41	66.77	27.78	135.93	44.05	76.45
5% FP-7	399.83	53.50	185.93	481.31	64.93	168.79
10% FP-7	76.31	48.76	39.10	284.17	44.19	158.59
15% FP-7	67.55	66.69	23.79	140.62	47.37	76.70
20% FP-7	69.85	53.94	32.17	222.13	45.56	120.92
30% FP-7	44.25	45.33	24.19	323.97	34.78	211.29
40% FP-7	58.84	42.81	33.65	284.95	38.02	176.62
50% FP-7	29.53	38.19	18.25	206.56	41.92	119.96
100% FP-7	30.15	83.49	4.98	88.41	49.74	43.32

(a) The indentor goes into the substrate at forces slightly above 2 N for pure BLOX prepared under similar conditions.

Scratch depths are in microns. All samples were cured at room temperature.

underlying substrate are shown; for this reason FP-3 is not included. The residual depth R_h values at 2 N for the blends are smaller than for pure BLOX, except for one case of BLOX + 5% FP-7. In addition, the percentage recovery, although a useful quantity, is not the most important one from the point of view of the user. The present results support an earlier statement [16] that the recovery depth is the most useful and practical measure of the scratch resistance. Still for 2 N, it is seen that pure BLOX has $f = 45.40$, almost identical to BLOX + 30% FP-7 with $f = 45.33$. However, the blend has almost five times better scratch resistance than the pure BLOX; the respective values are $R_h = 111.40\,\mu m$ for BLOX and $R_h = 24.19\,\mu m$ for the blend. For BLOX + 10% FP-7, $R_h = 39.10\,\mu m$. Clearly the objective has been achieved of improving the scratch resistance of both crosslinked epoxy and BLOX.

Overall, a given fluoropolymer improves the scratch resistance of the crosslinking epoxy more than of BLOX. This seems related to the vapor barrier properties of BLOX that presumably forms a “skin” over the surface trapping a certain amount of the THF solvent. The authors have not explored the use of other solvents that could render different results in this respect.

SCANNING ELECTRON MICROSCOPY (SEM) RESULTS

As reported in Reference [15], a commercial epoxy + FP-1 exhibits an early phase inversion at the surface in which the fluoropolymer becomes the matrix. The result from [16] are reproduced here for 30% FP-1 for comparison (Figure 6a). An extensive honeycomb-like structure can be observed under SEM, with the epoxy forming the honeycomb walls. Figures 6b and 6c, not reported before, show SEM surface images of pure FP-1 at large magnifications of 3,500 and 10,000, respectively. A cavernous structure is apparent in both 6b and 6c. The caverns can be explained by the low surface tension of FP-1. However, when an epoxy with a higher surface tension is the main component, there are epoxy honeycombs instead of caverns (Figure 6a). Thus, the fluoropolymer, in a way, behaves similarly in the presence and in the

FIGURE 6 (a) An SEM image of the top surface of a 30% FP-1 blended with an epoxy. A phase invers on has occurred near the surface with FP-1 becoming the matrix. The small spherical-shaped objects located within the honeycombs are epoxy globules. (b) An SEM image of pure FP-1 at a magnification of 3,500 ×. (c) An SEM image of the pure FP-1 shown in (b) at a magnification of 10,000 ×. The caverns form an extensive 3-D network throughout the interior of FP-1.

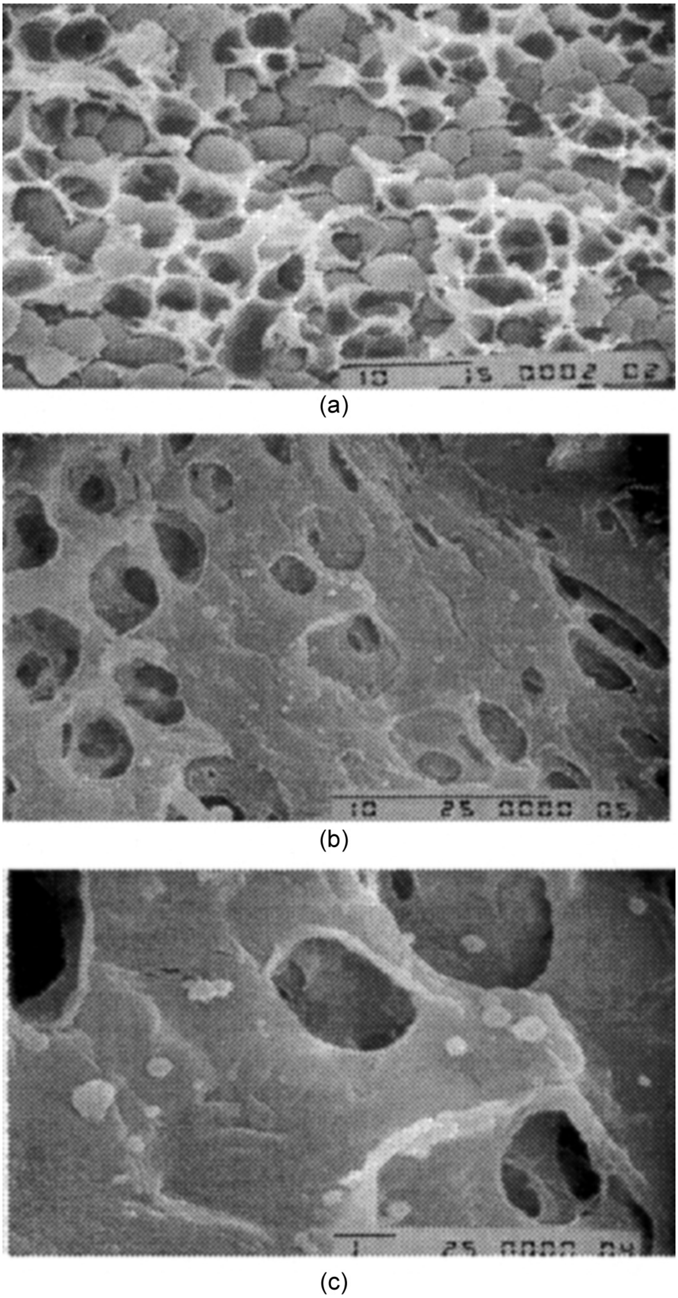


FIGURE 6

TABLE 2 Comparison of Pure Fluoropolymers

	I Free electronegative atoms	II Free electronegative atoms	III	IV
Sample	atomic %	weight %	weight % $-C{=}O$	weight % phenylenes
FP-1	**14.3**	**27.0**	**6.6**	**54.1**
FP-2	7.2	15.5	7.6	61.9
FP-3	18.8	32.9	8.1	44.0
FP-4	**9.4**	**16.5**	**9.6**	**52.1**
FP-5	4.5	11.4	11.6	45.5
FP-7	**14.3**	**28.5**	**14.0**	**38.0**
Teflon	66.7	76.0	0	0
Epoxy	5.6	12.5	6.4	52.1

absence of the epoxy. Recall that the honeycomb has the highest volume/surface ratio among regular polyhedrons.

GENERAL DISCUSSION

Fluoropolymers FP-1 through FP-4 have improved the scratch resistance of crosslinking and thermoplastic epoxies whereas FP-5 and FP-6 have not produced the desired results (the results for these blends are omitted for brevity). Unsuccessful fluoropolymers are obviously much easier to create than successful ones.

Considering the results presented in Figures 1–3 in conjunction with Table 2, it is that only FP-3 (at 5% concentration) produces a lowering of the recovery depth compared to the pure epoxy. The minima in Figures 1 and 3, for FP-2 and FP-4, are at approximately the same values as for the pure epoxy; there is no beneficial effect of the fluoropolymer addition. There is, however, a beneficial effect of the FP-1 addition reported earlier [16]. Each monomer of FP-1 or FP-3 has 12 fluorines whereas each monomer of FP-2 or FP-4 has 6 fluorines; the percentages of fluorine for these FPs are listed in Table 2, which shows a beneficial effect of fluorine. The concentration of fluorine is critical.

On the other hand, it has been known from the start that the presence of fluorine is not the only factor. Teflon—notorious for its low scratch resistance (see again Figure 4)—has 76.0 wt% of electronegative fluorines. Looking for other factors, the authors have included in Table 2 concentrations of carbonyls and phenylenes in the polymer segments (Teflon has neither). They have counted as electronegative atoms fluorines and oxygens—those not located directly between a carbonyl and a phenylene group or some combination of the two groups. An electronegative oxygen located directly between a phenylene and a carbonyl group is considered sterically hindered and is *not* counted in the atomic percentage of free electronegative atoms. When an electronegative atom is not located directly between two of these groups, then in theory that atom wil be freer to participate in other types of bonding within the epoxy—including weak bonding between the electronegative atom and another side chain for instance via hydrogen bonding. The electronegative oxygen that is a part of a carbonyl group does not appear in column I under atomic percentage of free electronegative atoms; it is counted under column II for carbonyl groups. Table 2 in conjunction with the earlier results show that the presence and an optimum concentration of carbonyl and phenylene groups play a role in improving scratch resistance. Note the model of Aharoni [28] explaining the high modulus of poly(ethylene terephthalate) in terms of resistance of terephthaloyl residues to translational and orientational motions.

CONCLUDING REMARKS

This article infers that electronegative atoms such as oxygen perform a similar role as fluorine. Clearly good scratch resistance cannot be assigned to a single factor. In the authors' systems concentrations of the electronegative atoms, of carbonyls and of phenylene groups in the macromolecules all play their roles. In general, several of the fluoropolymers have the capability to improve scratch resistance of both a crosslinking commercial epoxy and the BLOX thermoplastic epoxy. Apart from epoxy + fluoropolymer systems, chemical modification of epoxy resins alone is an alternative approach in order to fulfill particular application requirements [29–30] but so far has not provided us with sufficiently high scratch resistant materials.

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