Interphases in the Adhesive Bonding of Fluoropolymers*

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Strong and durable adhesive bonds may be made between polytetrafluoroethylene (PTFE) and either cyanoacrylate (CA) or epoxy adhesives, if the PTFE surface is modified by the use of a "primer" such as triphenylphosphine (TPP) or diaminodiphenylmethane (DDM). The primer mixes with the PTFE surface, and the modified surface is then capable of forming an interphase, tens to hundreds of nanometers thick, where interpenetration of the adhesive and adherend occurs. Using CA adhesives, PTFE/CA/PTFE block compression shear bond strength (ASTM D4501-85) of over 10 MPa can be achieved, with failure occurring cohesively. Initial work with epoxy adhesives indicates that the use of DDM primer gives adhesive bonds comparable in strength with those produced by modification of the fluoropolymer surface by sodium naphthalenide.

KEY WORDS Teflon®; fluoropolymer; adhesive; adhesion; interphase; primer; cyanoacrylate adhesive; epoxy adhesive; surface penetration.

INTRODUCTION

The importance of the interphase in adhesive bonding is now well established.[1–4] The thickness of this region of varying composition is highly dependent on the nature of the adhesive bond. When silane coupling agents are used, the interphase may be only a few monomolecular layers thick, while the occurrence of transcrystallinity at the boundary between some semicrystalline polymers and high energy surfaces can lead to an interphase several micrometers thick. We describe here the occurrence of a relatively thick interphase (tens to hundreds of nanometers) and its relevance to the adhesive bonding of fluoropolymers.

The adhesive bonding of fluoropolymers is the subject of continuing research, since no current method is entirely satisfactory. The most widely-used method for improving the bondability of fluoropolymers is treatment with a reducing etchant such as sodium naphthalenide,[5–7] which defluorinates the surface, typically to a

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depth of about 100 nanometers. While this is effective, it is expensive, inconvenient, and subject to environmental concerns. Other methods include plasma treatment,[8] metallization[9] and electron bombardment.[10]

We have described previously[11,12] the use of "primers" for the modification of low surface energy substrates such as polyethylene and polypropylene. These primers are soluble in the polymer surface, and produce a modified layer into which the adhesive can penetrate. The primers also raise the surface energy of the substrate and catalyze the cure of the monomeric adhesive. As an example of such a primer, triphenylphosphine (TPP) can be applied to polypropylene from a wide range of solvents, and the modified surface can be bonded with cyanoacrylate adhesives to give shear strengths of 12 MPa, with failure occurring cohesively in the polypropylene. Such adhesive bonds also showed superior water resistance, compared with conventional treatments such as the use of an air plasma.

EXPERIMENTAL

Blocks of PTFE (Industrial Safety) of dimensions $2.5 \times 2.5 \times 0.64$ cm were Soxhlet extracted with acetone to remove surface contaminants, then assembled into block compression shear joints with an ethyl cyanoacrylate (CA) adhesive (Loctite Corporation) or an epoxy adhesive comprising an epoxy resin (Epon 828, Shell, 100 parts by weight) and a diaminodiphenylmethane curative (DDM, Aldrich, 26 parts by weight). When desired, the PTFE surfaces were modified by immersion in molten TPP (Aldrich) or diaminodiphenylmethane (Aldrich). On removal from the primer bath, excess primer (as beads on the PTFE surface) were removed by shaking and wiping. Unlike the polyolefin case,[11,12] the primed surface appeared to be stable for several days, but adhesive bonds were generally formed within a few hours of priming the PTFE. Block compression shear adhesive bonds were made by applying one drop of the adhesive to each primed PTFE surface, then joining the overlapped region with the application of finger pressure. In the case of the CA adhesive, the cure was overnight at room temperature, while for the epoxy adhesive the cure cycle was one hour at 150°C and two hour at 250°C. The joints were tested in a block compression shear fixture according to ASTM D4501-85. The strengths reported here are the average of at least three specimens.

For comparison, some PTFE blocks were treated with commercial sodium naphthalenide etchant (Tetra-Etch) for sixty seconds, according to the manufacturer's instructions. This resulted in considerable darkening of the fluoropolymer surface.

The amount of primer which had penetrated the PTFE as a function of treatment conditions was determined by treatment of a small block of PTFE with accurately known surface area. After treatment with the primer, the PTFE block was placed in the sampling chamber of a dynamic headspace gas chromatography/mass spectrometer (GC/MS). The primer volatilized from the PTFE block at 275°C for TPP and 325°C for DDM, under flowing helium, and was then quantified in the GC/MS.[13] The amount of primer is quantified on a weight/surface area basis (ng/mm^2) since it is a surface-adsorbed species rather than a bulk additive.

The extent of penetration of CA adhesive into PTFE surface was determined by

preparation of a model adhesive bond, using PTFE films. In the example shown here, one film was primed by immersion in molten TPP at 120°C for 10 minutes, while the other was unprimed. The adhesive bond was prepared in the usual fashion. After cure, the unprimed film could be readily peeled off and the CA layer was removed by washing with nitromethane solvent (nitromethane solvent is a good solvent for CA, but is unable to swell PTFE). Any CA remaining must, therefore, have penetrated the PTFE, and so be inaccessible to the nitromethane solvent. The concentration profile of the CA in the PTFE surface was then estimated by examination with four surface analysis techniques with different sampling depths. X-ray photoelectron spectroscopy (XPS), with a 62-degree take-off angle, has a sampling depth of about 10 nm. Internal reflection infrared spectroscopy (IR-IRS), using a germanium element and 60-degree incidence, has a sampling depth of about 300 nm at mid-IR wavelength.[14] IR-IRS using a 45-degree incidence and a germanium element has a sampling depth of about 600 nm. IR-IRS using a 45-degree KRS-5 element has a sampling depth of about 1 micrometer.

Electron microscopy of the primed surfaces and of the fracture surfaces from adhesive joints was performed in the conventional manner.[12] Water contact angles were measured using an NRL 200-00 goniometer.

RESULTS

(a) PTFE/CA Adhesive Bonds

Figure 1 shows the extent of absorption of the primer by the PTFE, as a function of immersion time in molten TPP at 120°C. The concentration term is expressed as ng/mm^2 because it describes the extent of penetration into the surface rather than the extent of dissolution of TPP in the bulk of PTFE. For ease of visualization, $100 ng/mm^2$ is equivalent to a layer of pure TPP about 80 nm thick although, as we shall show later, the TPP dissolves in the PTFE rather than remaining as a discrete layer on the surface. Note, also, that the primer concentration absorbed into the surface region of PTFE is appreciably lower than the amount absorbed in polyolefins treated in the same manner,[12] consistent with the anticipated difficulty of dissolving additives in PTFE.

Figure 2 shows that the strength of PTFE/CA/PTFE block compression shear joints is relatively insensitive to the primer concentration (and hence treatment time) provided the primed concentration is greater than $300 ng/mm^2$ (5-minute treatment time). In the absence of primer, interfacial failure occurs at very low stresses. The mode of failure, determined by electron microscopy, appears to be mixed (Fig. 3), with different areas of the joint showing cohesive failure in the CA and in the PTFE. Cohesive failure in the PTFE is easily recognized (Fig. 3b) by the fibrillar nature of the fracture surface.

We have shown previously how TPP-primed polyolefin surfaces lose their bondability when aged at room temperature for many hours.[12] We attributed this phenomenon to the diffusion of TPP away from the polyolefin surface and into the interior of the polymer. TPP-primed PTFE appears to be much more stable to aging at room temperature, consistent with the anticipated slow rate of diffusion of
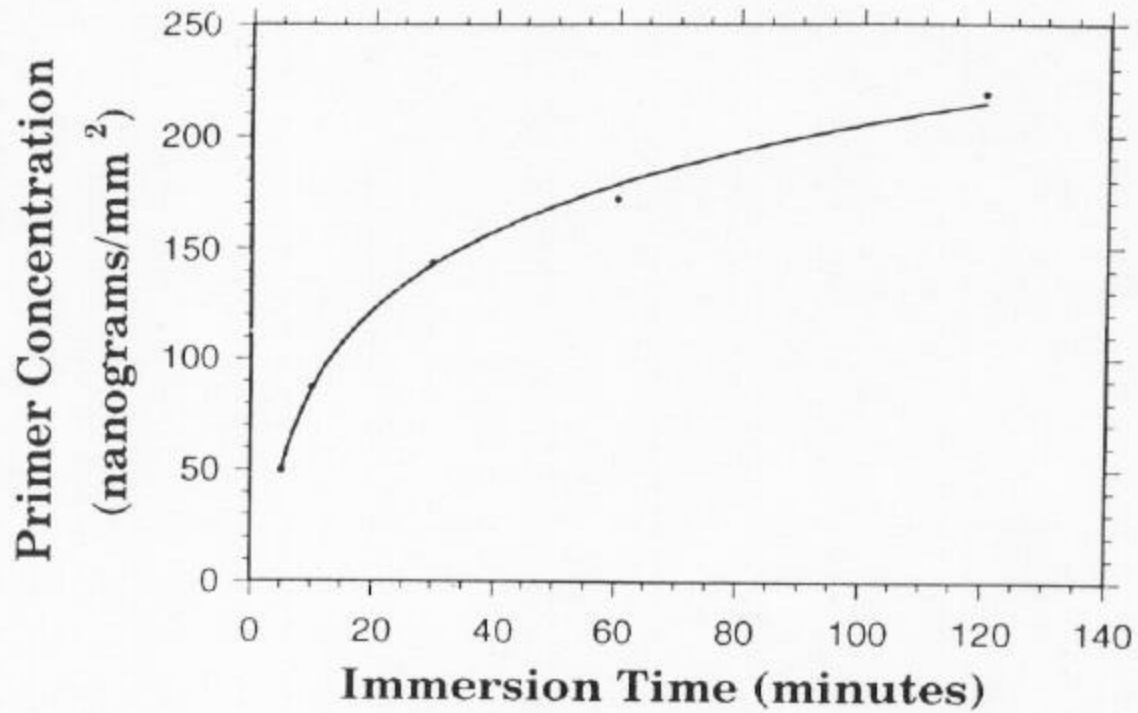
FIGURE 1   TPP surface concentration as a function of immersion time in molten primer at 120°C.
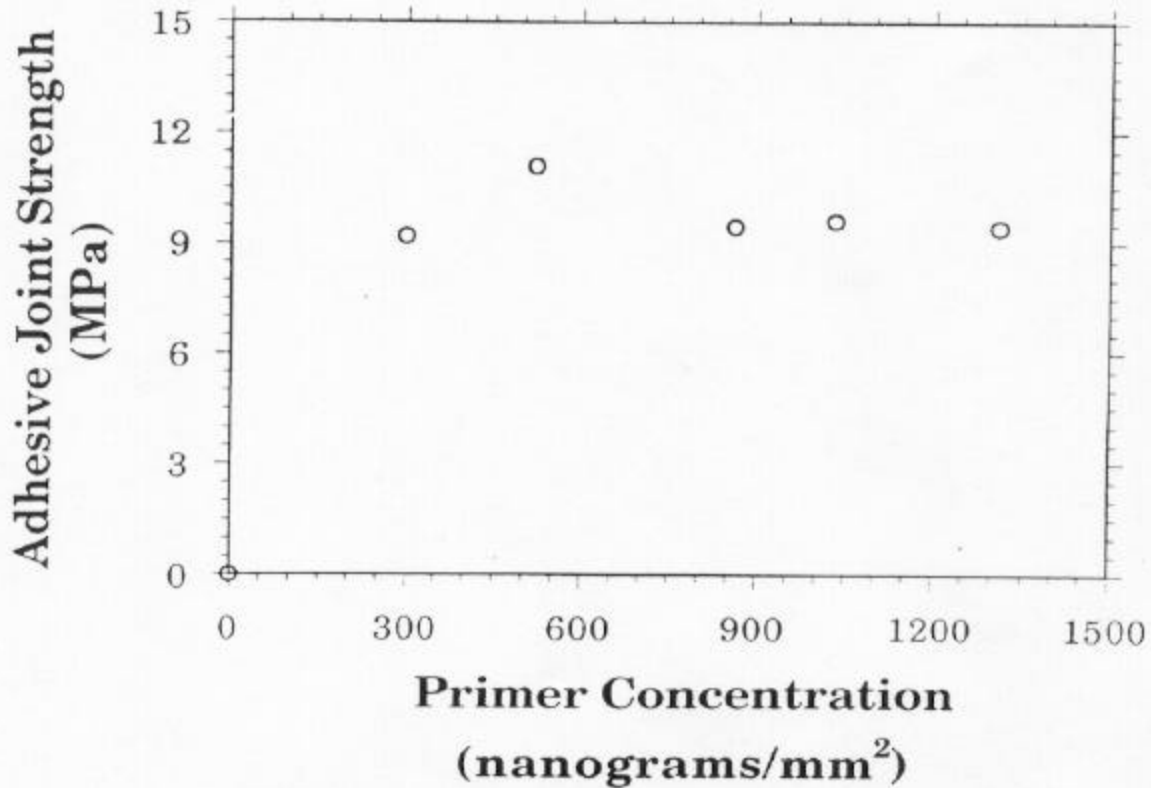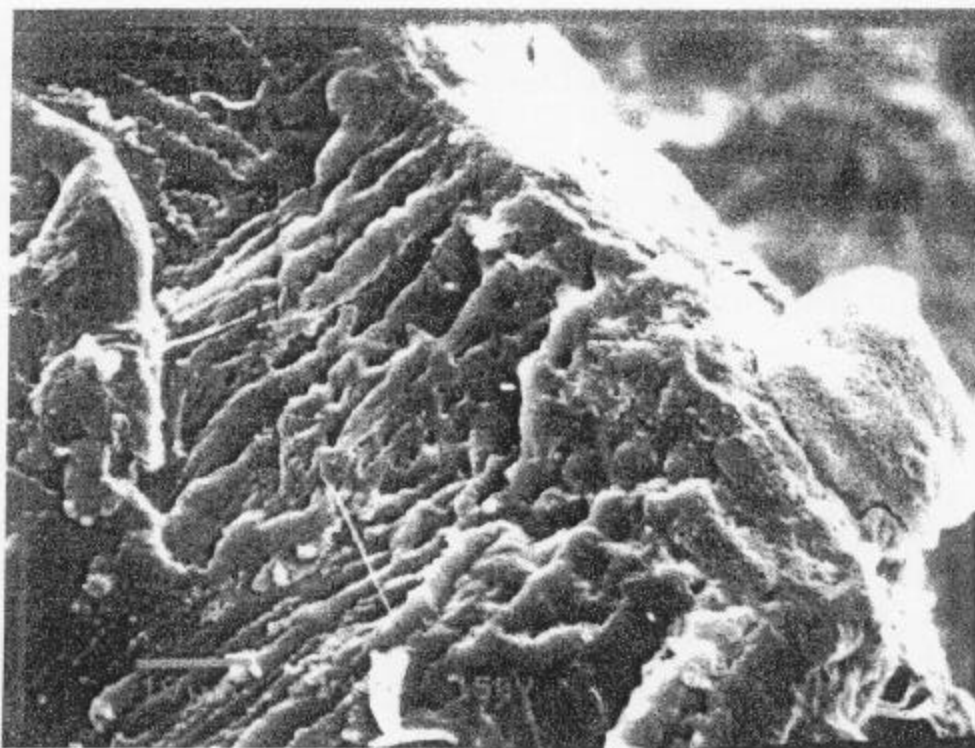

FIGURE 2   Adhesive bond strength as a function of TPP primer surface concentration.
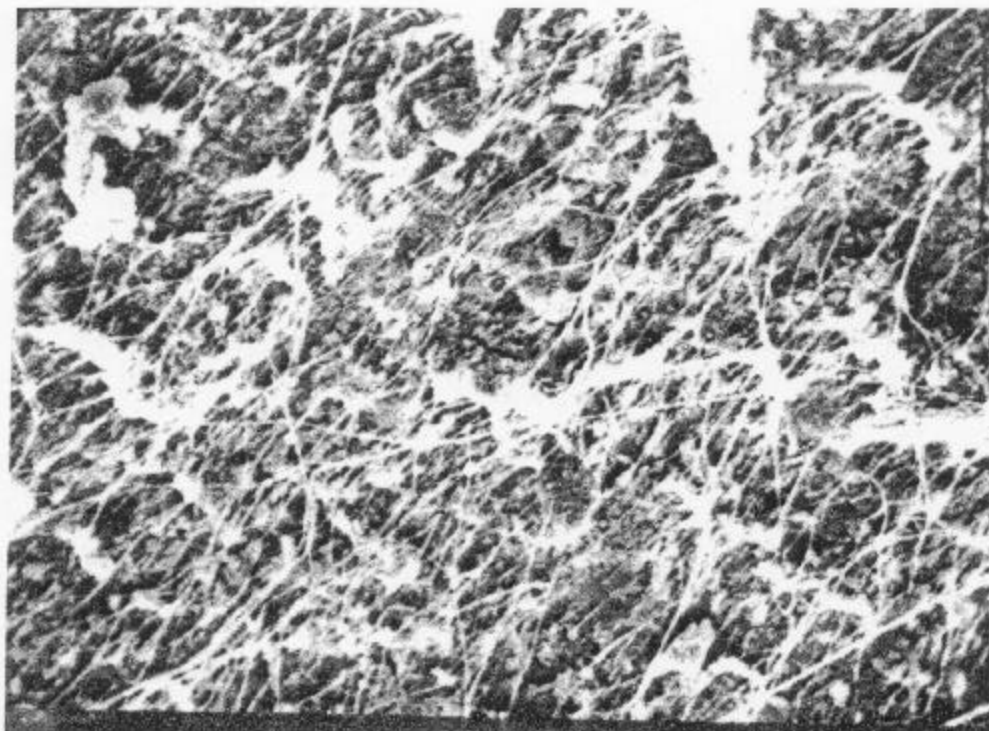
FIGURE 3 SEM of fracture surface of PTFE/CA adhesive bond showing (a) cohesive failure in CA (b) cohesive failure in PTFE.
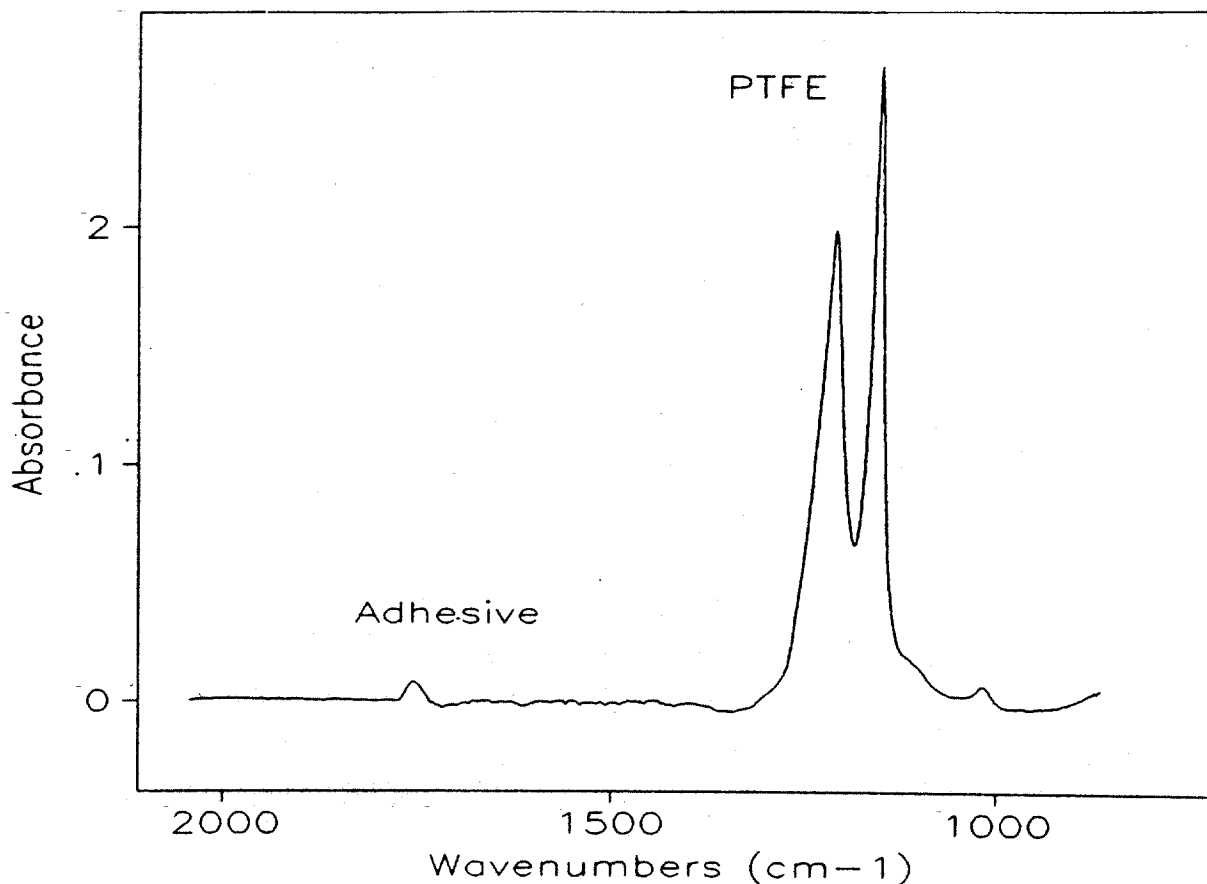
FIGURE 4   IR-IRS spectrum (germanium element, 60-degree incidence) or nitromethane-washed model adhesive bond.

additives in PTFE. After 24 hours in ambient air, the shear strength was only slightly lower (about 10%) than the control. Treatment of PTFE with TPP also results in a reduction in water contact angle from 120 degrees to about 100 degrees.

Figure 4 shows a typical IR-IRS spectrum of the nitromethane-washed model adhesive joints. The amount of adhesive which had penetrated the PTFE surface, and resisted extraction by nitromethane, was determined from the ratio of the area of the carbonyl stretch absorption of the adhesive, at about 1750 cm^{-1}, to the area of the C–F stretching mode at about 1149 cm^{-1}. This ratio was corrected for the wavelength dependence of the effective thickness in the IR-IRS technique,[14] and compared with a calibration curve obtained from transmission spectra of model compounds in heptane solution.

The XPS spectrum of the washed surface (Fig. 5) shows quantification of the residual adhesive concentration from the relative intensities of the F1s and N1s peaks, after correction for instrumental sensitivity effects. It was established separately that the nitrogen peak at 400 eV was associated with the nitrile group of the adhesive rather than with residual nitromethane solvent.

Table I summarizes the concentration profile information. A complete analysis of the profile requires either knowledge of, or assumption of, the shape of the pro-
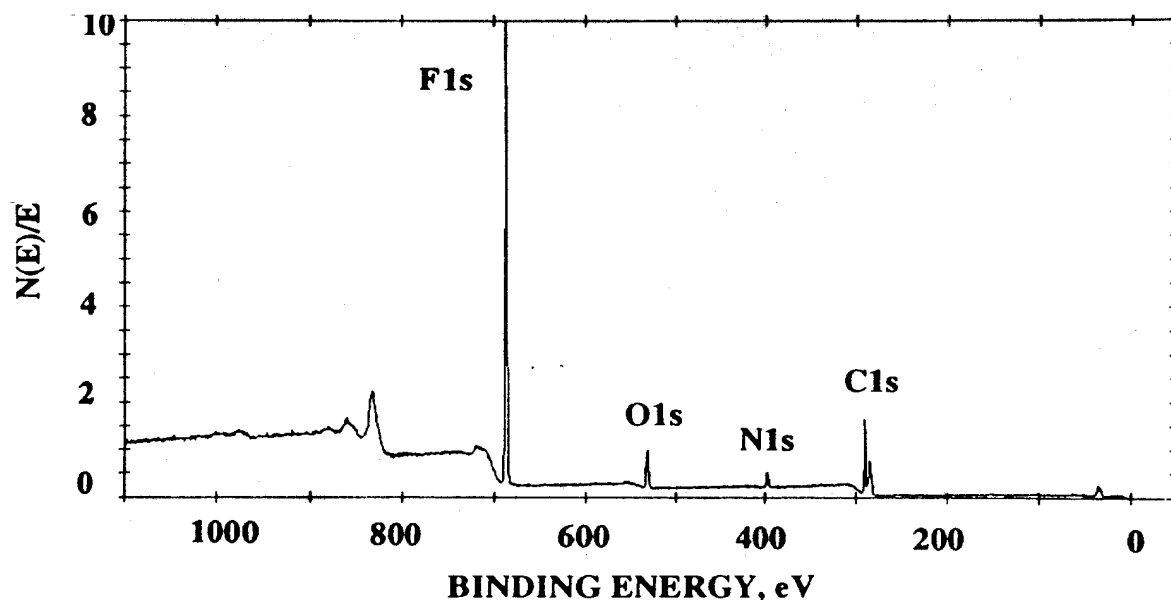
FIGURE 5 XPS spectrum of nitromethane-washed model adhesive bond.

TABLE I
Concentration profile of penetrating CA adhesive in PTFE

Analysis method	Sampling depth	Conc. of CA
XPS, 62 degree	ca. 10 nm	0.42 M
IRS, Ge 60 degree	ca. 200–300 nm	0.21 M
IRS, Ge 45 degree	ca. 500–600 nm	0.20 M
IRS, KRS-5 45 degree	ca. 1000 nm	0.06 M

file. We consider that the shape of the profile may be complex because of two competing diffusion-controlled effects (diffusion of CA into PTFE and extraction of polymerized CA out of PTFE). We, therefore, concluded that the thickness of the interphase is "a few hundreds of nanometers." Unfortunately, such a dimension is inaccessible to most microscopy techniques, although we are exploring the use of transmission electron microscopy and staining techniques.

(b) PTFE/Epoxy Adhesive Bonds

The data presented here represent an initial exploration of the potential of the primer technique for this system. No attempt has been made to optimize the choice of primer, the type of epoxy resin, or the cure cycle. It is reasonable to expect that considerable improvement on these adhesive strengths can be achieved.

Table II shows the effect of priming conditions on the DDM surface concentration and the resultant bond strengths. As with the TPP primer, the DDM surface concentration increases with priming temperature and immersion time although, where

TABLE II
PTFE/Epoxy/PTFE single lap shear joints

Specimen	Primer conc.	Strength
control, unprimed	0	
DDM-primed 15 min at 120°C	—	
DDM-primed 60 min at 120°C	580 ng/mm^2	
DDM-primed 60 min at 150°C	683 ng/mm^2	
DDM-primed 60 min at 175°C	1311 ng/mm^2	
Sodium naphthalenide treated PTFE	0	

comparable data are available, the absolute concentration of DDM primer is less than that of TPP primer.

Unlike the PTFE/TPP/CA case, the adhesive bond strength increases with increasing primer surface concentration. This is consistent with lower bond strength for epoxy/PTFE joints and their mode of failure (see above), and implies that further improvement is possible with optimization of priming conditions.

Electron microscopy of the failed joints (Fig. 6) shows that failure was largely interfacial with primed joints (Fig. 6a), but that there were small areas where cohesive failure occurred in the PTFE (Fig. 6b). This should be compared with the PTFE/CA case where the failure mode was either cohesive in the PTFE or cohesive in the CA. Clearly, the epoxy adhesive system did not respond as favorably to the priming as the CA adhesive. Possible explanations are discussed below.

Finally, since surface roughness and morphology play such a large role in adhesion, one must question whether priming affects the surface texture of the PTFE substrate. Figure 7 shows that priming with DDM at 175°C has no discernable effect on the surface texture of the skived PTFE.

DISCUSSION

The major consequence of the present work is to demonstrate that the principles of primer action elucidated for the CA/polyolefin system[12] are also applicable to fluoropolymers and other adhesives. For the primer to be effective, it must:

(a) dissolve in the surface of the PTFE substrate
(b) facilitate penetration of the adhesive into the substrate and catalyze its cure
(c) have the ability to be retained in the substrate surface rather than being either dissolved in the interior of the polymer or into the bulk of the adhesive. The migration process will be controlled by permeability and diffusion rate of the primers in the polymer
(d) increase surface wettability of the substrate although, in this case, the wettability concerns are minor because of the small magnitude of the change in water contact angle by primers.

A range of primer structures may, therefore, be proposed, with the relevant molecular characteristics being solubility parameter, diffusion coefficient, polarity, and chemical functionality (catalytic effect).
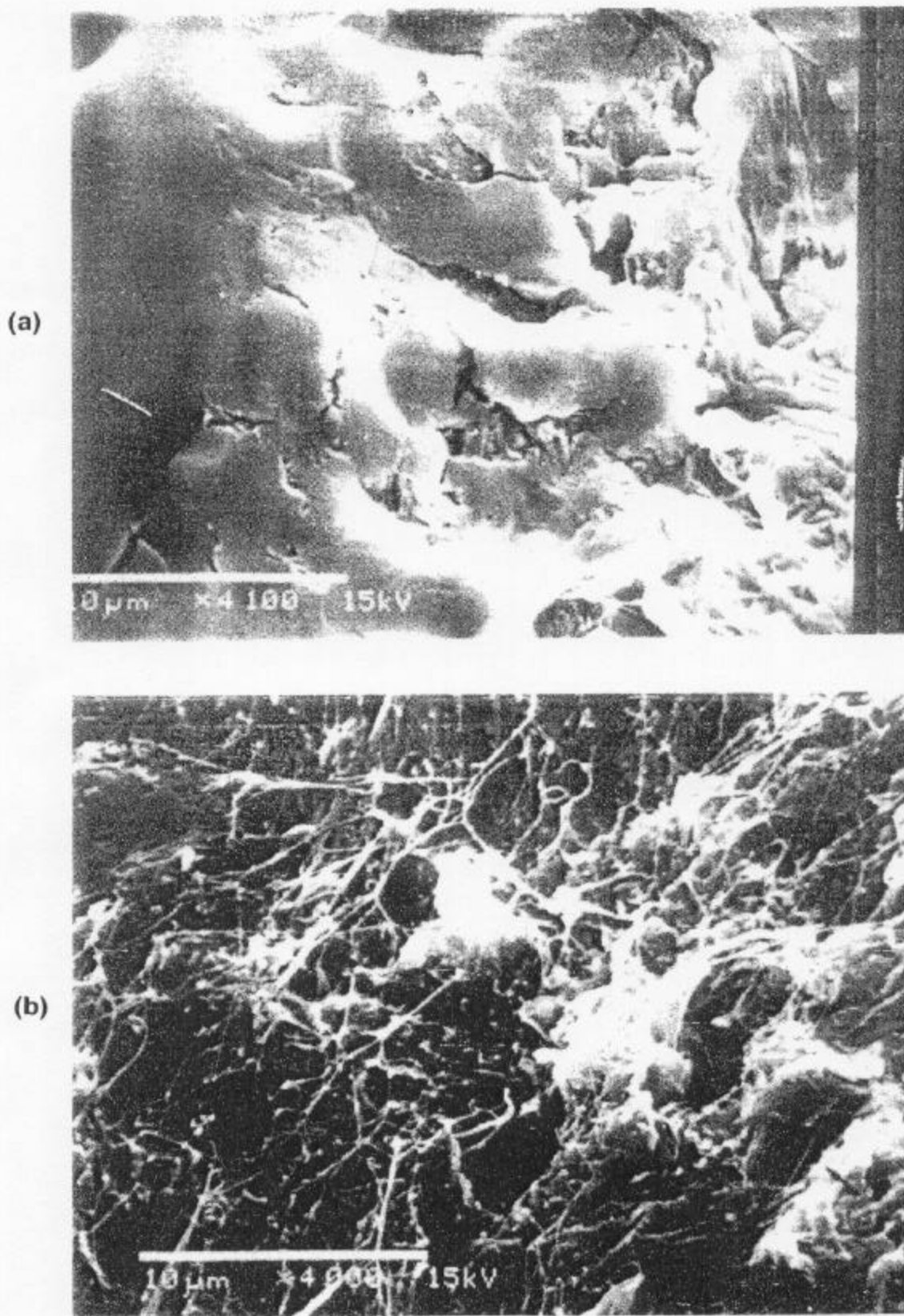
FIGURE 6 SEM of fracture surface of PTFE/Epoxy adhesive bond showing (a) interfacial (b) cohesive failure in the PTFE.

(a)

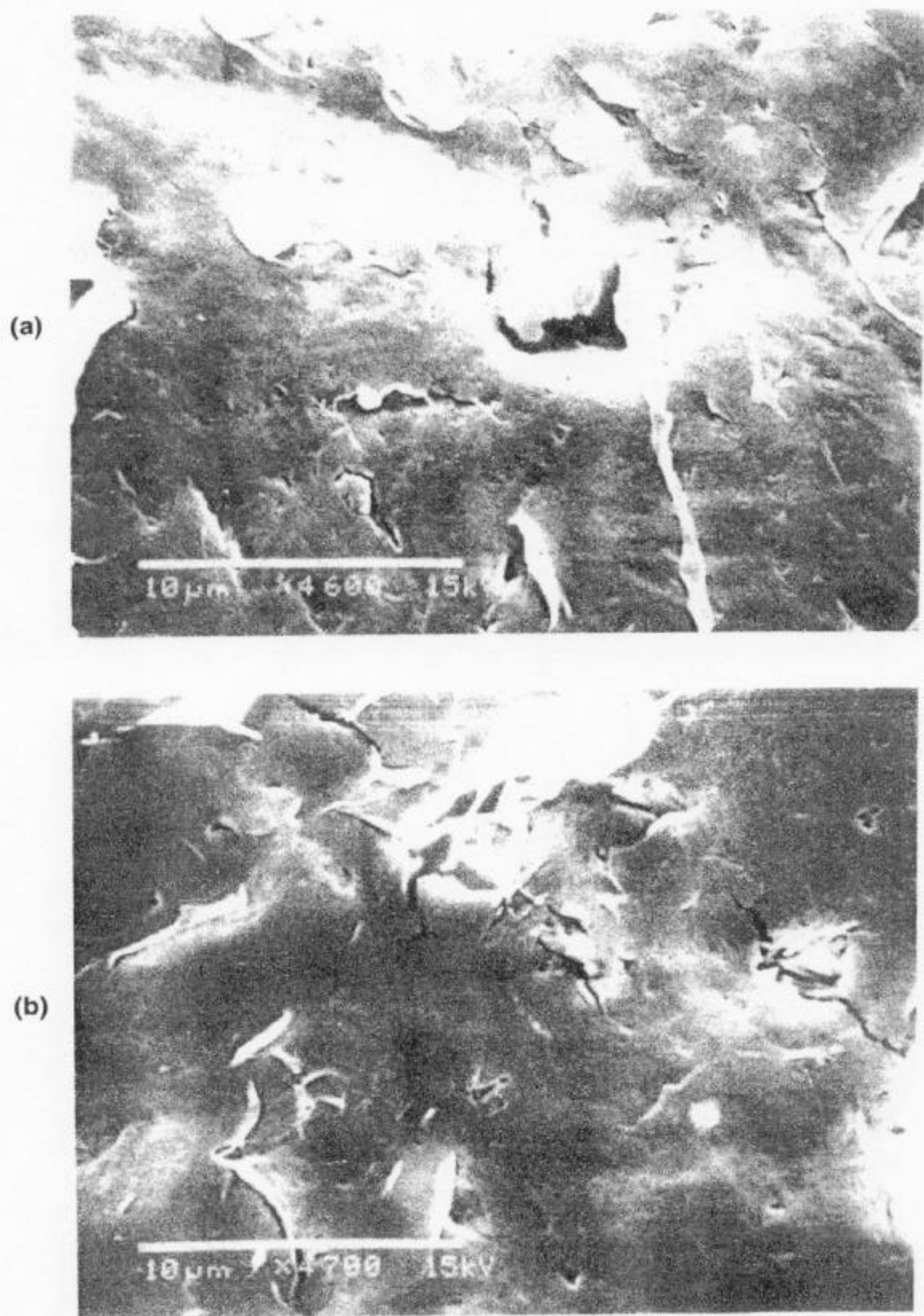10 μm   X4600   15k

(b)

10 μm   X4700   15kV

FIGURE 7   SEM of (a) original skived PTFE surface (b) DDM-primed PTFE surface.

The priming phenomenon is non-equilibrium in nature since surface energetics will eventually drive the relatively high surface energy primer away from the low energy polymer surface. The solubility and rate of diffusion of the monomeric adhesive will also play a large role in the effectiveness of the primer. One factor possibly responsible for the lower effectiveness of epoxy adhesives shown here, compared with CA, is the relative bulkiness of the monomeric epoxy resin, which hinders formation of an interpenetrating layer. Unfortunately, an independent measure of the thickness of the interpenetrating layer was not possible with the epoxy adhesive because of its insolubility in the crosslinked state. Once the monomeric adhesive has penetrated the substrate it is then necessary for the cure to occur sufficiently rapidly that trapping of the cured adhesive occurs, again a non-equilibrium phenomenon. The chemical functionality of both the primer and the adhesive are important in this regard. Other practical features will also influence the utility of primers, such as the existence of suitable application solvents,[12] toxicity, cost, vapor pressure, thermal stability, etc.

The area of surface modification by solvent-based treatment is also the subject of active research elsewhere, although there seems to be no direct overlap with the primers described here. Both Gao and Mackley[15] and Chen and Ruckenstein[16] have recently described procedures for improving adhesion involving treatment with solvents which can swell the surface of the substrates. Gao and Mackley[15] describe the swelling of ultra high molecular weight polyethylene (UHMWPE) with hot organic solvents, and cooling in the presence of the same solvent. Chen and Ruckenstein[16] describe treatment with a swelling solvent, followed by immersion in a non-solvent which is miscible with the swelling solvent. A porous surface is produced into which a second incompatible monomer (adhesive) can be polymerized so as to improve adhesion. The SEM evidence reported here (Fig. 7) indicates that our treatments involve no change in the macroscopic porosity of the surface, and we believe that interdiffusion of the adhesive and modified substrate is at a molecular level. It should be also noted that, in our earlier study of solvent-based primers for polyolefins,[12] treatment with the solvent alone had no effect on adhesive bond strength. A related use of the concept of interpenetration at a surface was described by Lewis and Katsamberis[17] for the production of an abrasion-resistant coating. A mixture of silane-treated colloidal silica, acrylic monomers, photoinitiators, and photostabilizers was applied to an acrylic polymer surface, and it was demonstrated by transmission electron microscopy that optimum coating performance was achieved when an interpenetrating layer was formed between the coating and the substrate.

It is clear from the above that there is an unavoidable degree of empiricism in the selection of an appropriate primer and application procedure for a specific adhesive/adherend pair. Our current work is directed towards an understanding of the molecular characteristics of the polymer substrate, primer molecule and adhesive, which control the thickness and composition of the interpenetrating layer.

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