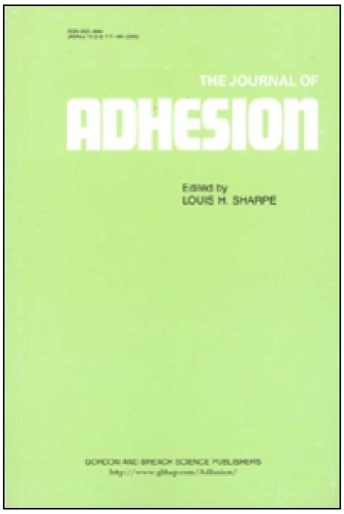

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Use of X-Ray Photoelectron Spectroscopy to Study the Failure of an Adhesive Joint Between Two Polymers

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The interface of the Kynar®–Nylon adhesive joint was examined by X-ray photoelectron spectroscopy. It was found that the failure was neither adhesive nor cohesive. XPS results indicated that the fracture path occurred through a weak boundary layer which migrated to the interface possibly during the bonding process. The weak boundary layer consists of molecules which have $\text{-}(\text{-CH}_2\text{-})\text{-}_n$ and $\text{-}(\text{-CF}_2\text{-})\text{-}_n$ structural units which are probably present as low molecular weight impurities formed during the polymerization of vinylidene fluoride or subsurface contaminants in the samples. This work presents the first conclusive evidence that confirms the existence of a weak boundary layer in an adhesive joint.

INTRODUCTION

The mode of failure of adhesive joints is very important in the understanding of the phenomenon of adhesion. Frequently, it is difficult to determine whether the failure is cohesive, adhesive or a mixture of both by just visual examination. Particularly, the failure of an adhesive joint due to the presence of a weak boundary layer has been the subject of considerably controversy in the study of the phenomenon of adhesion.[1–4] Bikerman initiated the idea of a weak boundary layer to explain the failure of adhesive joints.[1] The weak boundary layer is a discrete surface layer of material, such as low molecular weight fragments of a material, with mechanical properties inferior to the bulk material from which it originated. This theory is based on the assumption that adhesive failure cannot occur at the interface. Sharpe[3] has concluded that the existence of the weak boundary layer in polyethylene may be virtual rather than real. Several studies have also pointed out that Bikerman's theory does not hold for most practical systems.[5,6] Furthermore, much experimental evidence[5,7,8,9] has been published indicating that interfacial failure can and does occur frequently.

To date, there are a variety of surface analysis techniques that are extremely useful in the study of phenomenon of adhesion. In particular, X-ray photoelectron spectroscopy (XPS),[10-18] Auger electron spectroscopy,[10,11,15] and Ion scattering spectroscopy[19,20] and secondary ion mass spectroscopy[18-20] have been used successfully to study adhesive failures and surface bondings. In particular, XPS and Auger studies[11,18] have confirmed the possibility of interfacial failure. Despite all these experimental facts that point against the theory of a weak boundary layer, no definitive proof has been estabilished to refute its existence. However, on the other hand, no concrete experimental evidence has ever been found to confirm the existence of a weak boundary layer in adhesive joints. This problematic situation presents a very challenging and important problem in the field of adhesion.

The purpose of this study is to use X-ray photoelectron spectroscopy to identify the mode of failure for an adhesive joint between two polymers; Kynar® and Nylon. It is found that the failure is neither adhesive nor cohesive. The XPS results indicate that the joint fracture path occurs through a weak boundary layer which migrates to the interface, possibly during the bonding process. The work presents the first unequivocal experimental evidence to demonstrate the existence of a weak boundary layer in an adhesive joint.

EXPERIMENTAL

Adhesive joints were made by bonding two Kynar® (Pennwalt's polyvinylidene fluoride) strips with Nylon 11 adhesive (RDP-21, Rilsan Industrial Inc.) in a hot press at 200°C for five minutes. The adhesive joint failure was achieved by tapping the sample after it has been placed under liquid nitrogen for several minutes. Visual inspection indicated that fracture occurred very near to the interface between Kynar® and Nylon. The Nylon surface appeared to be covered with a very thin layer of Kynar®. The fractured Nylon and Kynar® surfaces were analyzed by a HP5950A spectrometer equipped with monochromatized Al $K\alpha_{1,2}$

radiation (*hν* = 1486.6 eV). The hydrocarbon peak at 285 eV was used as the reference. The analytic chamber was kept at a pressure less than 10^{-8} torr. The X-ray gun was operated at 800 watts. During the analysis, sample charging was minimized by using an electron flood-gun to neutralize the sample.

RESULTS AND DISCUSSION

XPS measures the binding energies of the photoelectrons ejected by a solid excited by soft X-ray. The binding energies of core electrons are sensitive to the electronic environment of an atom. The binding energy of a core electron changes as the electronic environment of the atom changes. The shift in the binding energy of a core electron can provide useful chemical and structural information of a molecule. The shifts in the binding energy of the C(1S) electron will serve as an excellent example for the illustration. Table I shows the shifts in the binding energy as the hydrogen atoms are replaced by the more electronegative fluorine atoms.[21] The C(1S) electron in a $\text{-(-}CH_2\text{—}CH_2\text{-)-}_n$ unit has a binding energy of 285.0 eV. As all the hydrogen atoms are replaced by the more electronegative fluorine atoms, the C(1S) binding energy of the carbon atoms bonded to the fluorine atoms increases to 292.2 eV which corresponds to a chemical shift, ΔC(1S), of 7.2 eV. Hence, the detailed study of the chemical shift observed in a spectrum will provide very useful chemical and structural information for a molecule.

TABLE I

Binding energies of the homopolymers of ethylene and fluorethylenes.

	C(1S), eV	ΔC(1S), eV
$\text{-(-}CH_2\text{—}\underline{C}H_2\text{-)-}$	285.0	0
$\text{-(-}CF_2\text{—}\underline{C}H_2\text{-)-}$	286.3	1.3
$\text{-(-}\underline{C}F_2\text{—}CH_2\text{-)-}$	290.8	5.8
$\text{-(-}\underline{C}F_2\text{—}CF_2\text{-)-}$	292.2	7.2

Figure 1 shows a C(1S) spectrum of a clean Kynar® surface. The peaks at 286.3 and 290.8 eV correspond to the $\text{-(-}CF_2\text{—}CH_2\text{-)-}$ and $\text{-(-}\underline{C}F_2\text{—}CH_2\text{-)-}$ carbons, respectively. The areas under these two peaks are approximately equal. This indicates that there are equal amounts of $\text{-(-}CF_2\text{—}\underline{C}H_2\text{-)-}$ and $\text{-(-}\underline{C}F_2\text{—}CH_2\text{-)-}$ carbons. These results are consistent with the chemical structure of Kynar®. Figure 2

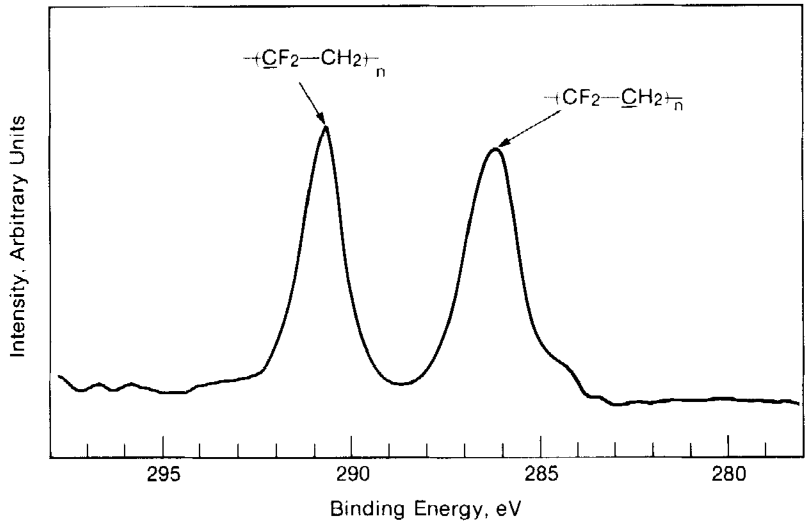

FIGURE 1 C(1S) spectrum of a clean Kynar® surface.

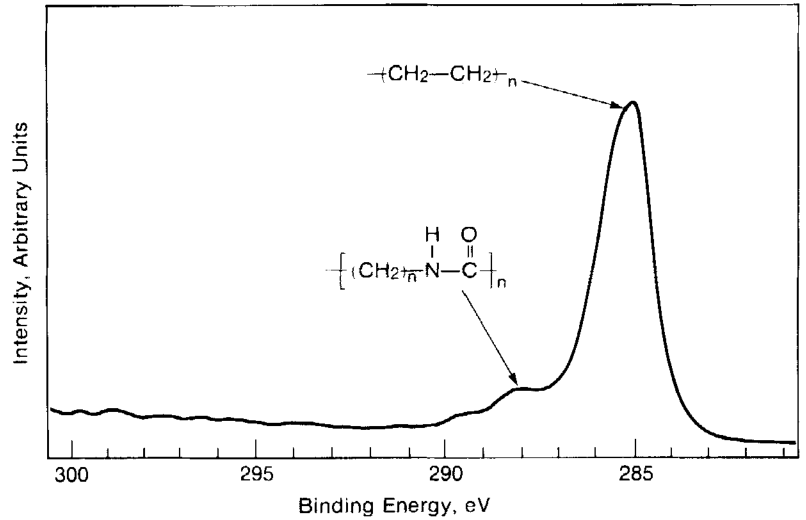

FIGURE 2 C(1S) spectrum of a clean Nylon surface.

shows a C(1S) spectrum of a clean Nylon surface. The major peak at 285.0 eV represents the $-(-\underline{C}H_2-)-$ carbons, while the small peak at the high energy side of the peak corresponds to $-NH-\underline{C}O-(-CH_2-)-_n$

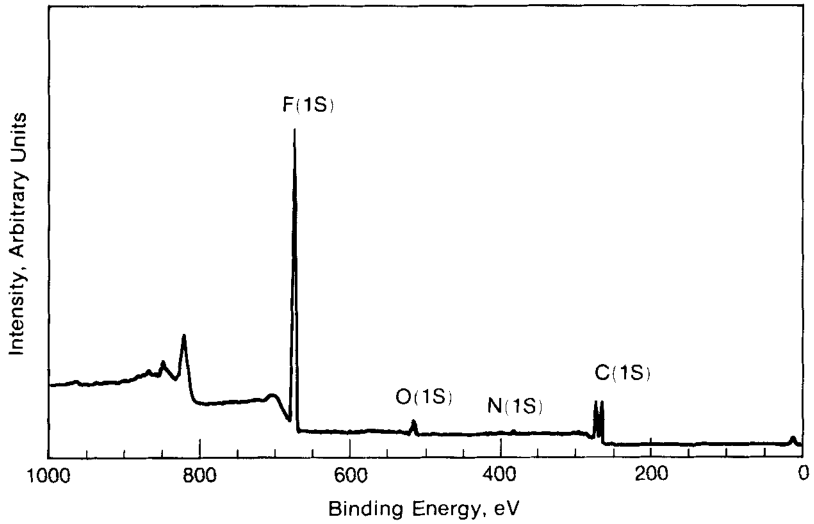

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FIGURE 3 A survey spectrum of the Nylon surface of the fractured adhesive joint.

TABLE II
Elemental Composition of the fractured Nylon surface.

Element	Atomic %
C	48.7
O	3.2
F	47.3
N	0.8

carbons. A survey scan of the fractured Nylon surface is shown in Figure 3. The elemental composition of the surface is shown in Table II. From the results shown in Table II, it seems that the Nylon surface is covered with a thin layer of Kynar®. To confirm such an idea, the C(1S) spectrum of this surface was obtained and is shown in Figure 4 (the solid line). The C(1S) spectrum appears to be similar to the one obtained for the clean Kynar® surface as shown in Figure 1, but the major low and high energy peaks are at 285.0 and 292.2 eV respectively. These results indicate that the Nylon surface is not covered by Kynar®. The major peaks at 285.0 and 292.2 eV correspond to $-(-CH_2-\underline{C}H_2-)-$ and $-(-CF_2-\underline{C}F_2-)-$ carbons, respectively. The peaks corresponding to the Kynar® carbons are much lower in intensity as indicated in Figure 4. This suggests that molecules with structural units of $-(-CF_2-CF_2-)-_n$

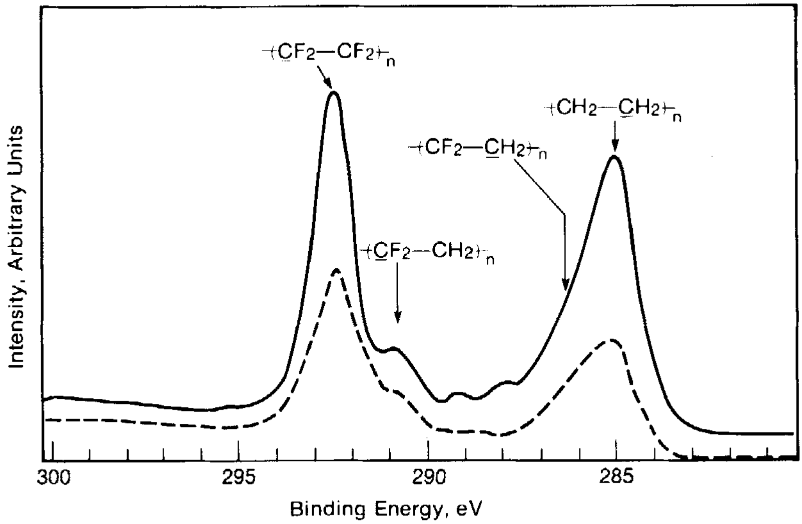

FIGURE 4 C(1S) spectra of the Nylon surface (the solid line) and the Kynar® surface (the dashed line) of the fractured adhesive joint.

and $-(-CH_2—CH_2-)-_n$ have migrated to the interface forming a weaker boundary layer during bonding at 200°C. A C(1S) spectrum of the Kynar® surface of the fractured adhesive joint was also obtained and is shown in Figure 4 (the dashed line curve). Comparisons between the spectra obtained from the Nylon and Kynar® surfaces show no observable difference. This leads to the conclusion that the fracture path occurs through a layer which forms possibly during the bonding process. The layer consists of molecules having $-(-CF_2—CF_2-)-_n$ and $-(-CH_2—CH_2-)-_n$ structural units.

To confirm the conclusion that a weak boundary layer has migrated to the interface, a thin layer of surface was mechanically removed from the Kynar® surface. This was achieved by scraping the surface with a stainless-steel knife edge. The "new" surface was re-examined by XPS. The C(1S) spectrum of this "new" surface is shown in Figure 5 (the solid line). The C(1S) spectrum of the Kynar® surface right after the fracture of the adhesive joint is represented by the dotted line in Figure 5. The comparison between the two spectra shows that the "new" surface has dominant features exhibited by a clean Kynar® surface. This confirms that the spectrum obtained from the fractured surface shown in Figure 4 is not an artifact. A clean Kynar® surface which has been heated to 200°C for several minutes was examined by XPS. A small amount of

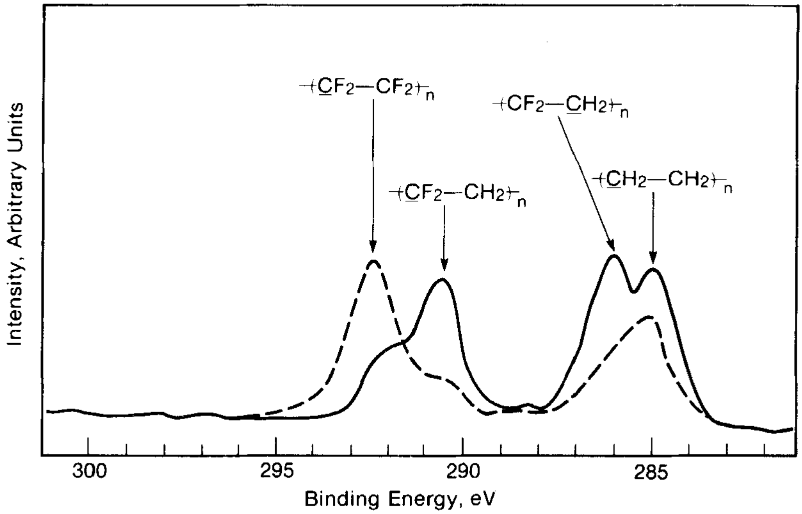

FIGURE 5 C(1S) spectra of the Kynar® surface of the fractured adhesive joint before (the dotted line) and after (the solid line) a thin layer of the surface was mechanically removed.

hydrocarbon was found to have migrated to the surface. This result seems to suggest that the migration of impurities was largely occurring during the bonding formation.

It was very probable that the weak boundary layer was caused by the subsurface contamination. Alternatively, this weak boundary layer which consists of molecules having $-(-CF_2-CF_2-)-_n$ and $-(-CH_2-CH_2-)-_n$ structural units can be due to the impurities formed during the polymerization of Kynar®. Under normal conditions, monomers polymerize in a head-to-tail arrangement to give $-(-CF_2-CH_2-)-_n$ units. However, head-to-head or tail-to-tail arrangement can occur to produce $-(-CF_2-CF_2-)-_n$ and $-(-CH_2-CH_2-)-_n$ units.

CONCLUSIONS

The fracture path of the Kynar®–Nylon adhesive joint has been determined. Fracture occurs in a weak boundary layer which migrates to the interface possibly during the bonding process at 200°C. This layer consists of molecules having $-(-CF_2-CF_2-)-_n$ and $-(-CH_2-CH_2-)-_n$ structural units. These molecules are probably present as low molecular weight impurities formed during the polymerization of vinylidene fluoride. This work presents the first conclusive evidence that confirms the existence of a weak boundary layer in an adhesive joint between two polymers (Kynar®–Nylon).

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