

# Relationship Between Dynamic Response of Surface to Environmental Changes and Adhesive Property of Polyacrylate

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## SYNOPSIS

Acrylate copolymer composed of octadecyl acrylate (OA), 2-ethyl hexyl acrylate (2-EHA), hydroxyethyl acrylate (HEA), and vinyl acetate (VA) was synthesized. The copolymer was used to adhere polyethylene (PE) with *T*-type peel, strength 4.4 N/cm. The interfacial characteristics of copolymer and PE were investigated via ATR-FTIR, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and dynamic contact angle (DCA). Results show that apolar moieties of the adhesive enrich on the interface. Moreover, the time dependence of peel strength coincides with that of enrichment in nonpolar moieties on the interface. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

It is well known that the performance of adhesives is strongly dependent on the surface characteristic of their ingredients. Recently a number of analytical methods have been applied to polymer surfaces that can provide compositional or structural information as a function of depth from a surface.<sup>1</sup> A study on surface characteristics of segmented siloxane urethane soft block copolymer films has revealed that siloxane soft blocks are enhanced on the air-exposed surface.<sup>2</sup> One of the most sensitive methods that provide information on the outermost polymer surfaces of a few angstroms is contact angle measurement. From static and dynamic contact angle measurements we can get a deep insight into the characteristic properties of a polymer surface, e.g., the time-dependent surface reorientation of hydrophilic and hydrophobic groups occurring upon immersion of the polymer sample in water.<sup>3</sup>

In the previous paper<sup>4</sup> we correlated dynamic response of surface to environmental change with adhesive properties for both polar and nonpolar substrates. The purpose of the present work is to further elucidate the relationship between super-

ficial response to environmental changes and adhesive properties. X-ray photoelectron spectroscopy (XPS), contact angle and ATR-FTIR measurements, and transmission electron microscopy (TEM) were employed to provide information on the adhesive surface with polyethylene PE film.

## EXPERIMENTAL

### Materials

Reagent grade 2-ethyl hexyl acrylate (2-EHA), vinyl acetate (VA), octadecyl acrylate (OA), and hydroxyethyl acrylate (HEA) were obtained from Dongfang Chemical Plant. Ethyl acetate (analytical grade) was commercially available. Analytical grade azobisisobutyronitrile (AIBN) was used after recrystallizing. Polyethylene (LDPE) and poly(vinyl chloride) (PVC) were all commercial products.

### Synthesis

2-EHA, VA, OA, and AIBN were mixed with ethyl acetate in a container. The mixture was maintained at 70°C under agitation and N<sub>2</sub> for more than 6 h. The feeding compositions of the comonomer mixture applied for synthesis are listed in Table 1.

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**Table I** Detail of Synthesis of Acrylate Copolymer

Samples	OA (g)	2-EHA (g)	VA (g)	HEA (g)	AIBN (g)
1	0	60	37	3	0.2
2	2.5	60	34.5	3	0.2
3	5.0	60	32.0	3	0.2
4	7.5	60	29.5	3	0.2
5	10	60	27.0	3	0.2

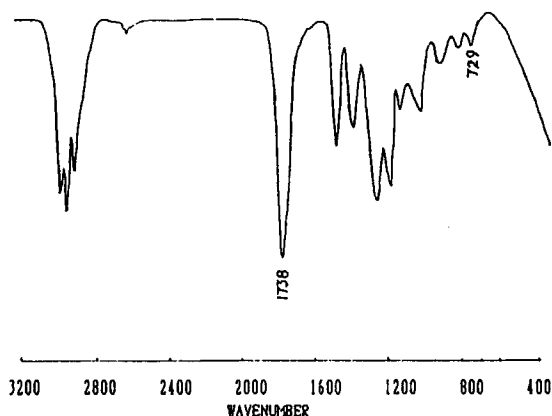
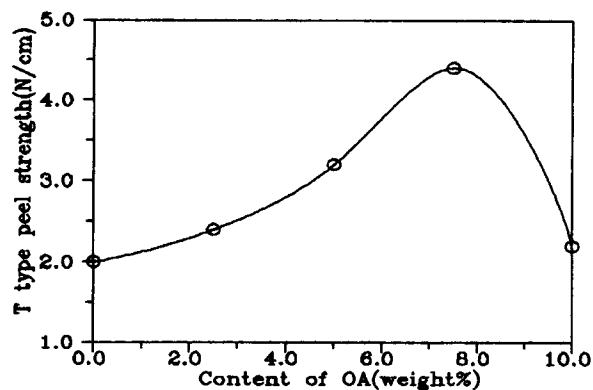
### Peel Strength

Polyethylene (PE) film (25 mm in width) pairs were adhered over 100 mm length with the adhesive, and the *T* type peel strength was determined at different time intervals on a Fiber Tensile Tester ZLL-30 at 100 mm/min at 20°C.

### Contact Angle

The static contact angles of the adhesive against water were measured at 25°C by the sessile drop method in a CA-D telescopic goniometer. After a 3  $\mu$ L water droplet had been formed on the adhesive surface for 3 min the angles were estimated.

The dynamic contact angles were evaluated on the coated slide specimens with the acrylate copolymer. Advancing and receding contact angles were obtained based on the Wilhelmy technique using a Cahn instruments dynamic contact angle analyser, DCA-302. The surface tension of distilled water was determined to be 72.6 dyn/cm. This value was used in contact angle calculation. For the purpose of comparison the dried specimens and ones immersed in water for 24 h were utilized, respectively.

**Figure 1** Infrared spectrum of adhesive 4.**Figure 2** *T* type peel strength vs. content of OA.

### XPS

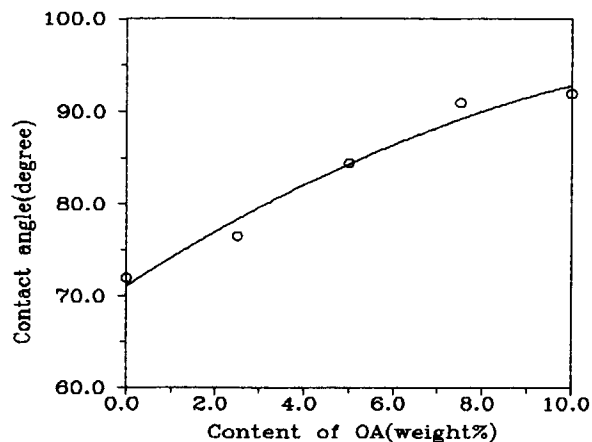
Gradient composition of adhesive layer on a PE film specimen was determined directly with a PHI-1600 X-ray photoelectron spectrometer by using the variable emission angle method.

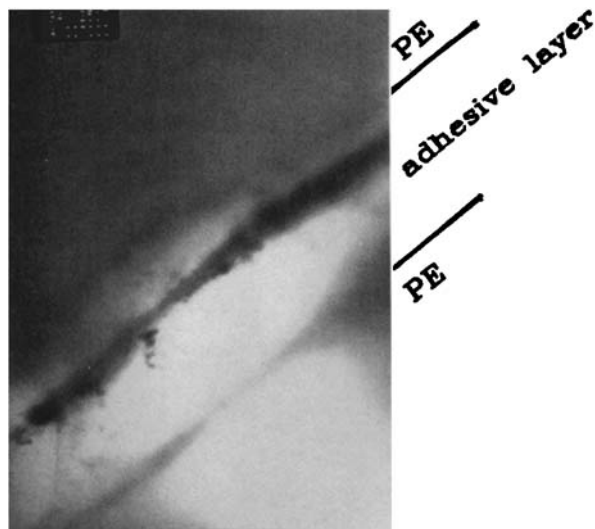
### Transmission Electron Microscopy

The adhered PE sample was cut with a microtome and dyed with OsO<sub>4</sub>. A Philips EM-400ST electron microscope was utilized to investigate the interface of the adhesive joint.

### ATR-FTIR

A Nicolet-5DX FTIR spectrophotometer was used for studying ATR spectra of adhered PE film at different time intervals. The information of the adhesive layer on the surface with PE film was obtained by subtracting the spectrum of PE film from that of the adhesive on the surface of PE film.

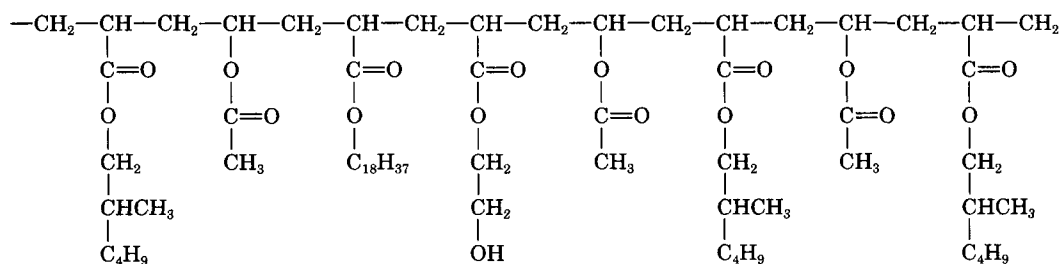
**Figure 3** Static contact angle vs. content of OA.



**Figure 4** Micrograph of adhesive sample section ( $\times 7000$ ).

## RESULTS AND DISCUSSION

The structure of the copolymer is as follows:



The infrared spectrum of adhesive 4 is shown in Figure 1 in which  $1738$  and  $729\text{ cm}^{-1}$  are characteristic peaks of carbonyl and  $\text{CH}_2$  groups, respectively.<sup>5</sup>

### Peel Strength

Figure 2 shows the  $T$  type peel strength versus OA content in weight. There is a peak at OA content being 7.5 mol % while the static contact angle data of the adhesive reach the maximum at 7.5 mol % as well (cf. Fig. 3). The data imply that the strength increases with enhancing in nonpolarity of the adhesive until 7.5 mol % OA content and then the strength decline with the transition from adherent fracture to cohesive one partially.

### Gradient Distribution of Adhesive Component

Figure 4 is the sectional micrograph of dyed joint of PE films. The dark part in the adhesive layer corresponds to more polar moieties (carbonyl groups) of the bulk of the sample in comparison with that in the interfacial layer between adhesive and PE film. In other words, the hydrocarbon moiety that is similar to PE in polarity enriches in the interfacial layer. The graph also shows that the interfacial layer is wider than the bulk one.

### XPS

Changes in interfacial composition with the depth is studied by using angle-dependent X-ray photoelectron spectroscopy. The peak of the XPS may lap together. Nonlinear least-squares fitting was used to resolve the overlapped peaks. Figure 5 is a typical result of the resolved peaks of XPS.

Wagner et al.<sup>6</sup> has pointed out the ratio  $R$  of two atomic contents as

$$R = N_1/N_2 = (I_1/S_1)/(I_2/S_2)$$

where  $I$  is the spectra intensity and  $S$  represents the atomic sensitive factor.  $S$  is the same either for carbon in carboxyl or in hydrocarbon while  $I$  is indicated by the peak area  $A$ :

$$R = N_1/N_2 = A_1/A_2$$

The detect depth  $d$  of XPS relates to the electron emission angle  $\theta$ :

**Table II** XPS Data

$\theta$ (degree)	15	60	90
$d$ (Å)	12.5	43.3	50
$R$	6.19	11.74	14.34

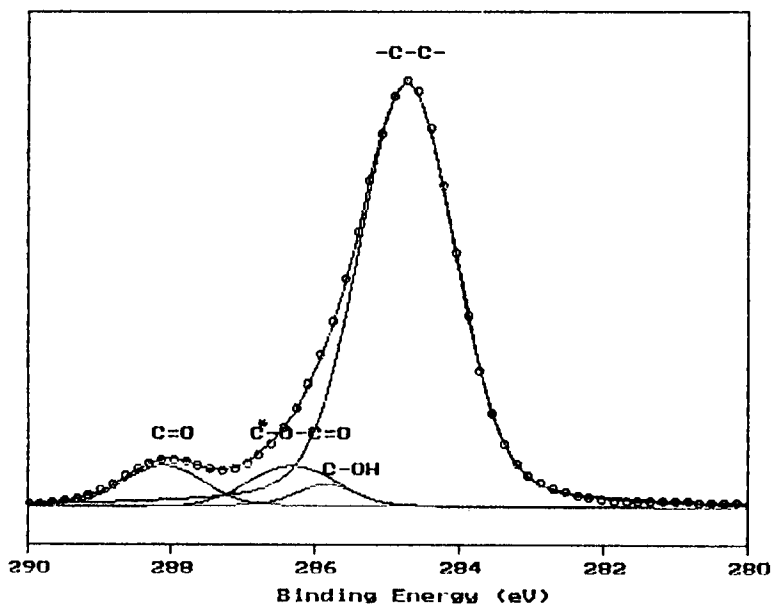


Figure 5 Typical result of dislapped peaks of XPS.

$$d = \lambda \sin \theta$$

where  $\lambda$  is the mean electron free path, which is approximately 50 Å for a polymer. Different depth information was obtained from the change of  $\theta$ . The final results of XPS of adhesion 4 are summarized in Table II.

The ratio  $R$  of carbon in hydrocarbon C—C to that in carbonyl is enhanced with increase in depth  $d$ . The data reveal that more hydrocarbon moieties of the adhesive enrich on the interface layer with PE film obviously.

#### Interfacial Response of Adhesive

Figure 6 shows the dynamic contact angle loops of

polyacrylate adhesive. Cycle 1 corresponds to the original adhesive-coated specimen; while cycle 2 represents the second turn of the DCA determination process. The advancing line changed more than the receding one. It is worth noting that the variation in the advancing contact angle ( $60^\circ$ ) is larger than that in the receding angle ( $24^\circ$ ) for the copolymer-coated specimens immersed in water for 24 h comparing the original specimen. The advancing angle is dependent mainly on the contribution from non-polar groups.<sup>7</sup> Therefore the change in dynamic contact angle implies that the nonpolar moieties of the adhesive respond more readily to a changed environment in our case.

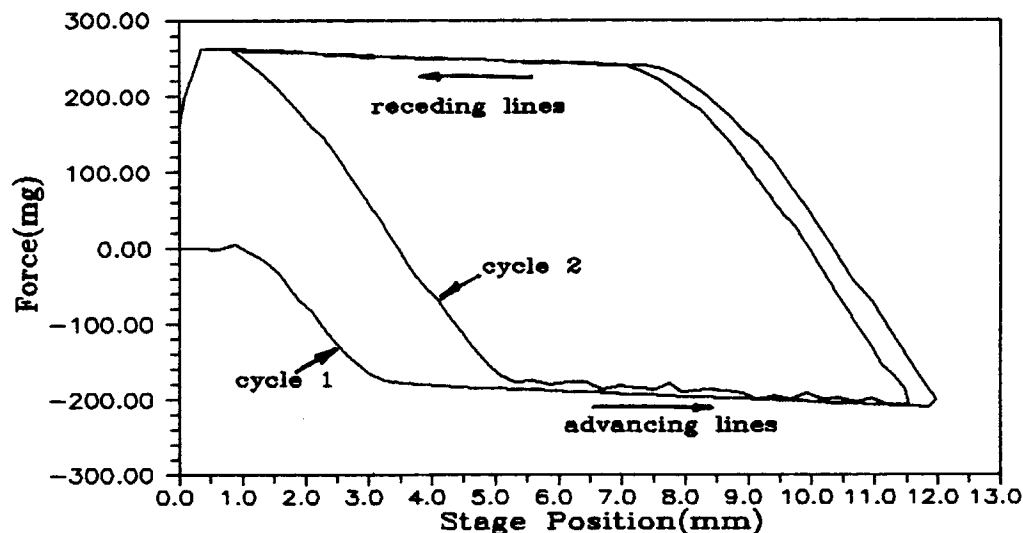


Figure 6 Dynamic contact angle loops for the adhesive.

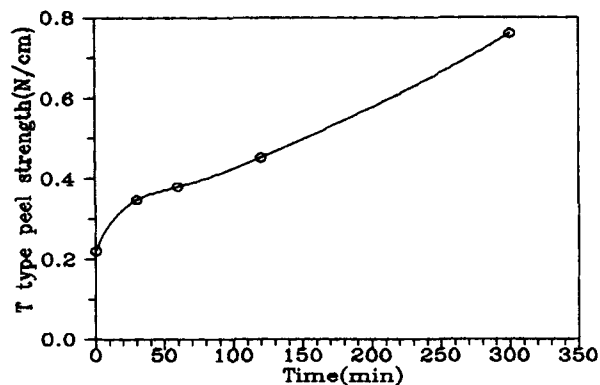


Figure 7 T type peel strength of PE pairs vs. time.

### Peel Strength of the Adhesive versus Time

Peel strength of polyacrylate adhesive 4 against the time interval is plotted in Figure 7. Results show that adhesive strength grows with time. In this process, there was neither chemical reaction nor hydrogen bond between PE and adhesive because of the inertness of the PE film. So the adhesive strength mainly comes from van der Waals forces between PE and adhesive molecules. The rise in adhesive strength with an increase in time means that the van der Waals force enlarges with elapsing time.

### Increase in Nonpolar CH<sub>2</sub> Enrichment Degree with Time

The ATR-FTIR subtracting spectrum of adhesive on polyethylene is displayed in Figure 8 where 1736 and 729 cm<sup>-1</sup> are assigned to carbonyl and CH<sub>2</sub> groups, respectively. The variation in absorbance ratio ( $A_{\text{CH}_2}/A_{\text{C=O}}$ ) are listed in Table III. The data indicate that the nonpolar moiety enriches with extended adhesive time. It may be attributed to the relaxation characteristic of the segmental movement of the apolar section of the adhesive.

In considering increase of adhesive strength with absorbance ratio of CH<sub>2</sub> to C=O, we can say that enrichment of nonpolar groups of the adhesive has

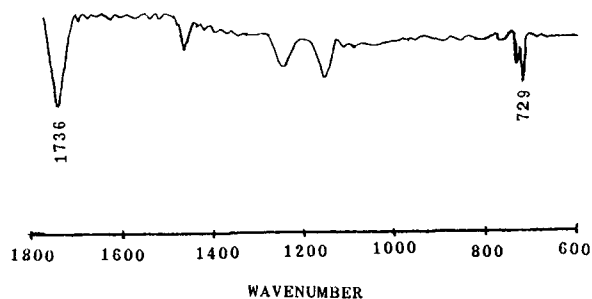


Figure 8 ATR-FTIR spectrum of adhesive on interfacial layer between PE and adhesive.

Table III ATR-FTIR Data

Time (s)	Absorbance ratio ( $A_{\text{CH}_2}/A_{\text{C=O}}$ )
342	0.1728
1028	0.1799
1495	0.1894
2014	0.2269
2941	0.1801
4341	0.2527

enhanced the van der Waals force between PE and adhesive.

### CONCLUSIONS

Acrylate and vinyl acetate copolymer containing octadecyl acrylate can be used to adhere polyethylene (PE) films. The nonpolar moieties of the adhesive enrich on the interface of PE. The peel strength of the PE joint with the adhesive is time dependent, that coincides with an increase in nonpolar hydrocarbon moieties enrichment degree with time. Results reveal that there is a correlation between dynamic response performance of the surface of the adhesive to environment (substrate) and T type peel strength of the PE joint with the adhesive.

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