The Compatibility of the Blends of PUs with PVC and the Adhesion Behavior of PU to PVC

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SYNOPSIS

Three series of polyurethane adhesives—polyethyleneadipateurethane (PEAU), polybuthyleneadipateurethane (PBAU), and polyhexyleneadipateurethane (PHAU)—with the same MW and hard/soft segment ratio, based on the three polyesters polyethyleneadipate (PEA), polybuthyleneadipate (PBA), polyhexyleneadipate (PHA), with 4,4'-diphnylmethane diisocyanate (MDI), and butendiol were synthesized by solution polymerization. The crystallinity of these polyesters and polyurethanes (PUs) and the compatibility of blends of PUs with PVC were studied by means of wide-angle x-ray diffraction (WAXD), differential scanning calorimetry (DSC), dynamic thermomechanical analysis (DMA), testing of solubility, and phase contrast microscopy. The results indicated that PBAU/PVC and PHAU/PVC were compatible systems, but PEAU/PVC was incompatible. The adhesive strengths of the three adhesives were quite different from one another, in the order of PBAU $\geq$ PHAU $\gg$ PEAU. The influences of crystallinity and compatibility on adhesion were discussed, and the Diffusion Theory for PU–PVC systems was recommended. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polyurethane adhesives are extensively employed because of their properties and versatility. A considerable quantity is used in the adhesion of PU, PE, and PVC materials, especially in the shoemaking industry.

So far, there have been several adhesion theories.[1–8] Generally speaking, the polyurethanes adhesive applies to the Absorption Theory and the Chemical Bonding Theory.[9–10] As to the Absorption Theory, there is a problem first in the compatibility between two kinds of polymers. Many studies have been done on the compatibility between polylactone–urethanes (PLCU) and polyether–urethanes (PEU)[11–14] with the conclusion of good compatibility between PLCU and PVC, and partial compatibility under a certain circumstance between PEU and PVC.[15–16] However, little is known about the compatibility between PVC and polyester-

urethanes (PESU) having been extensively applied,[17] such as polyethyleneadipateurethane (PEAU), polybuthyleneadipateurethane (PBAU), and polyhexyleneadipateurethane (PHAU). Therefore few satisfactory proofs have been obtained concerning the adhesion behavior differences of the PU series from PVC/PVC. On the other hand, the original adhesion strength of adhesive is mainly related to the crystallinity of the adhesive itself, because the crystallization can double and redouble both the cohesive force and the adhesion lamina. So the investigation of the crystallinity of segmented polyurethanes (SPUs) as well as the influence of crystallinity on adhesion behavior of SPUs were also very important.

In this article, such polyesterdiols as PEA, PBA, and PHA were synthesized, then made to react with methylene-bis-4,4'-phenylisocyanate (MDI) to obtain the corresponding PUs (PEAU, PBAU, PHAU), keeping them equal in molecular weight (MW) and the ratio of soft to hard segment (SS/HS). By means of differential scanning calorimetry (DSC), dynamic thermomechanical analysis (DMA), x-ray diffraction (WAXD), phase contrast microscopy, and testing of solubility, combining the theory

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Table I Characterization of the Polyols

Polyol Number	Acidic No. (mg KoH/g)	Hydroxylic No. (mg KoH/g)	MW by EA
PEA–1	1.4	100.6	1100
PEA–2	1.2	77.2	1430
PEA–3	1.0	55.1	2000
PEA–4	1.0	39.1	2800
PBA–1	2.0	87.0	1260
PBA–2	1.0	73.8	1500
PBA–3	1.0	60.0	1840
PBA–4	0.8	52.6	2100
PBA–5	0.8	46.0	2400
PBA–6	3.0	14.9	6200
PHA–1	0.6	61.7	1800
PHA–2	1.0	65.0	1700

of the macromolecular structure, we systematically studied the compatibility between the PU series and PVC and the crystallinity of SPU. In the meantime, a satisfactory explanation of the adhesion behaviors of PEAU, PBAU, and PHAU to PVC/PVC, which were quite different from one another, was presented.

EXPERIMENTAL

Materials

Ethylene glycol (EG), buthandiol (BDO), hexandiol (HDO), adipic acid (AA), and stannous chloride (sncl$_2 \cdot$ 2H$_2$O) are all chemical pure reagents. Methylene-bis-4,4'-phenyl diisocyanate (MDI), supplied by Yantai Synthetic Leather General Factory, was

Table II The Compatibility of the PU/PVC Blends

Blends type	Pellucidness & Stratification	Concentration (%)			
		5	10	15	20
PEAU/PVC	Pellucidness	A	B	B	C
	Stratification	D	D	E	E
PBAU/PVC	Pellucidness	A	A	A	A
	Stratification	D	D	D	D
PHAU/PVC	Pellucidness	A	A	A	A
	Stratification	D	D	D	D

Pellucidness, A: Good; B: Some opacity; C: Chaotic state
Stratification, D: No; E: Yes

Table III The Pellucidness of the PU/PVC Blends Membrane

Blends Type	PU/PVC (w/w)				
	10/90	30/70	50/50	70/30	100/0
PEAU/PVC	B	C	C	C	A
PBAU/PVC	A	A	A	A	A
PHAU/PVC	A	A	A	A	A

Notes: A: Pellucidness; B: Little opacification; C: Opacification.

99.5% pure. PVC Resin type SG–3 was supplied by Hangzhou Electro-Chemical Factory. PVC leather to a thickness of 1.2 mm was used as received. All solvents (cyclohexanon, methyl ethyl ketone, ethyl acetate, and tetrahydrofuran) were dried and distilled before use.

Polyols Synthesis and Characterization

The polyols were synthesized from (AA) and diol (EG, BDO, HDO) by melting condensation polymerization, with the sncl$_2 \cdot$ 2H$_2$O as a catalyst. The acidic number (H) of polyols was determined by neutralizing titration, and the hydroxylic number (OH) was determined by the Acid-Catalyzed Acetylation Method.[18] Therefore, the MW of polyols was calculated from the acidic number and the hydroxylic number according to:

$$MW = \frac{56.1 \times 2000}{(H) + (OH)} \quad (mg \; KoH/g)$$

The main characterization of these products is summarized in Table I.

### Polyurethanes Synthesis and Characterization

The OH-terminated segmented polyesterurethanes having 30% (wt) solid and approximately 5000 cp viscosity were prepared through one-step solution polymerization from the MDI polyol in cyclohexanone, under a continuous purge of dry N$_2$, with the Low MW diol BDO as a chain extender. The viscosity of PU solution in cyclohexanone having 30% (wt) solid was determined at 30°C by using an NDJ–79 Rotary Viscometer. The MW parameters of PU were estimated by using a Water's 150 c Gel Permation Chromatographic Sys-
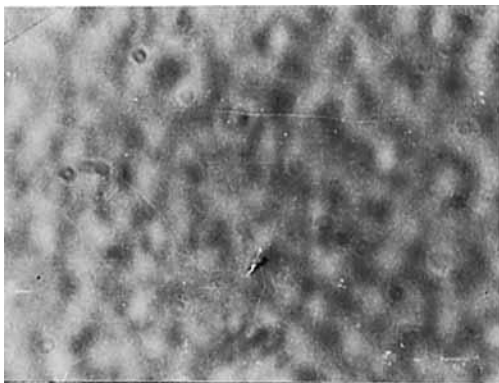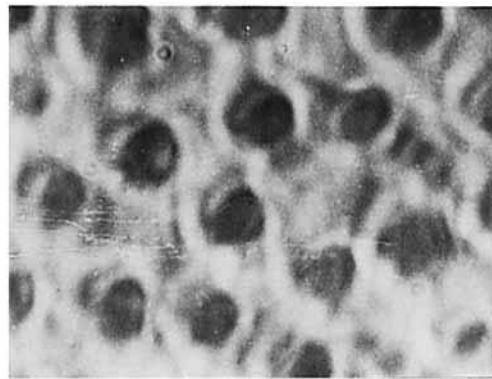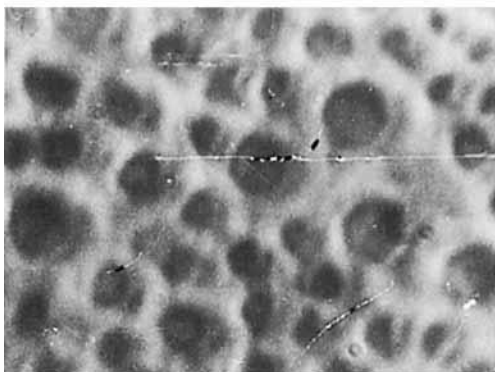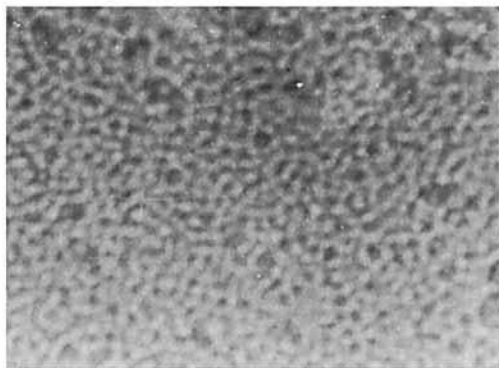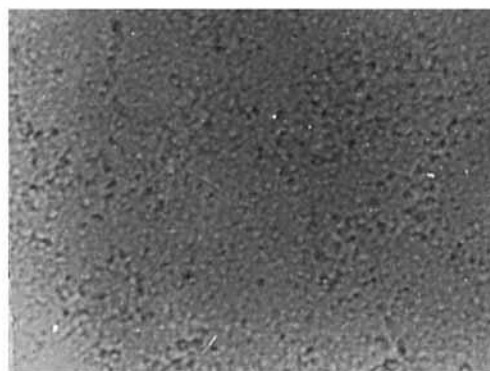
Figure 1 Photograph of phase contract microscope of the PESU/PVC blends. (×640)
(a) PEAU/PVC (10/90); (b) PEAU/PVC (30/70); (c) PEAU/PVC (50/50); (d) PEAU/PVC
(70/30); (e) PBAU/PVC (30/70); (f) PBAU/PVC (50/50).

tem. The PU samples were reprecipitated with
ethanol, then made in a solution of THF having
a concentration of 0.5% (wt). The number average
MW of products was 40,000–50,000, and the HS/
SS ratio was 17–18% (wt).

Preparation of Polymer Blends

The binary polymer blends were made by mixing
PU solution in cyclohexanone and PVC solution in
THF. The homogeneous solution was degassed at
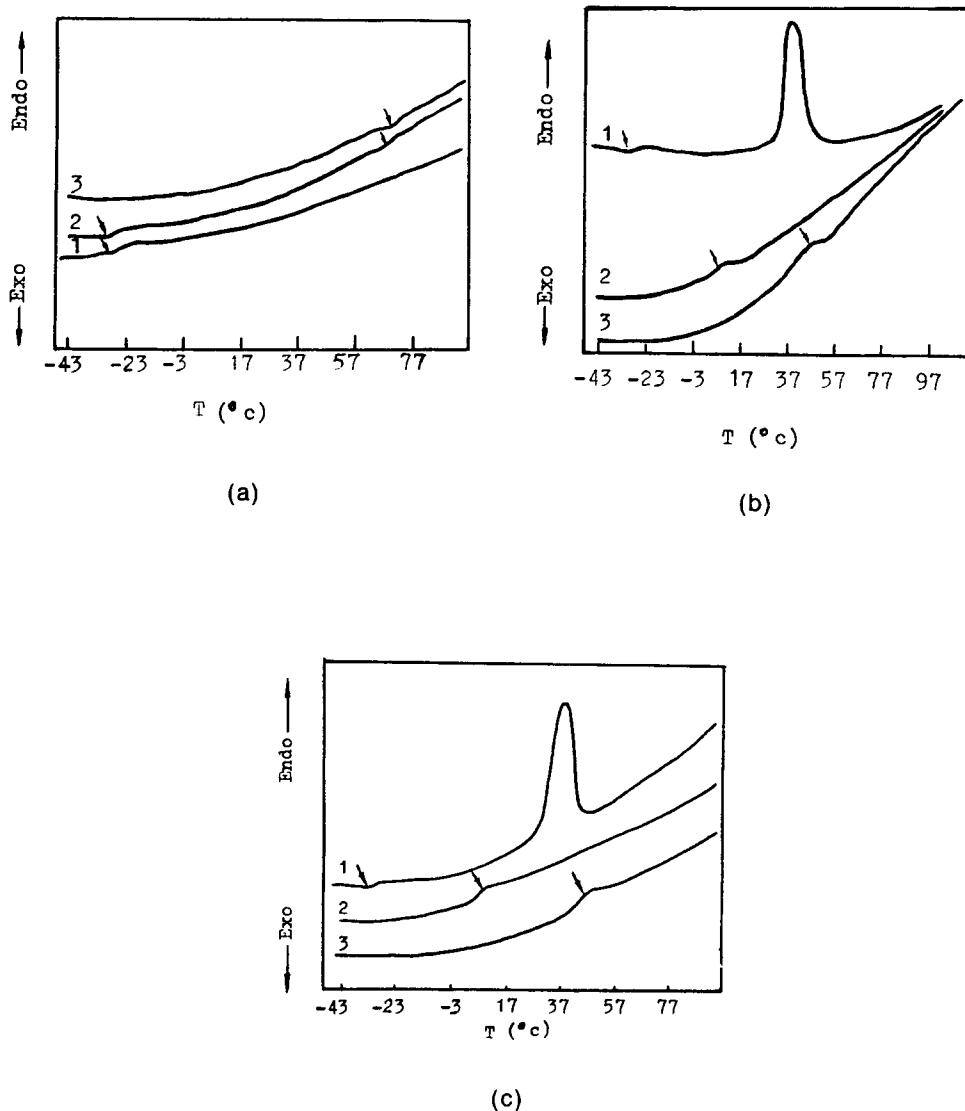
Figure 2   DSC of the PUs and the PU/PVC blends: (a) PEAU type; (b) PBAU type; (c) PHAU type. (1) PU/PVC (100/0); (2) PU/PVC (50/50); (3) PU/PVC (20/80).

room temperature. The following compositions given in terms of weight ratios of PU/PVC were studied: 100/0, 70/30, 50/50, 30/70, 0/100.

Methods of Measurement

Testing of Solubility

The series of binary polymer blends having different concentration solutions were made by mixing PU and PVC in cyclohexanone used as a solvent. The weight ratio of PU to PVC was 50/50. A week later, the changes in the faceform of these blend solutions were observed.

Optical Microscopy

Three series of PU blend films having different component ratios blended with PVC were prepared by casting the blend solution on a clear glass plant. After they had been vacuum-dried at 70°C, the pellucidness of these films to a thickness of 0.1 mm was observed. The two-phase structure of these unpellucid films was observed by means of phase contrast microscopy.

Thermal Analysis (DSC)

The samples of the three PUs, as well as their blends with PVC, were vacuum-dried at 70°C until the

Table IV **The T_g (°C) of the PUs and the PU/PVC Blends From DSC and DMA**

Blends Type	Method	PU/PVC (w/w)			
		100/0	50/50	20/80	0/100
PEAU/PVC	DSC	−27	−24, 69	73	80
	DMA	−14	−18, 69		
PBAU/PVC	DSC	−33	10	50	80
	DMA	−22	25		
PHAU/PVC	DSC	−35	6	45	80
	DMA	−28	24		

weight was a constant. After they had cooled naturally, DSC was carried out on a Perkin-Elmer DSC-II. All the analyses were run from −50°C to 100°C under a dynamic atmosphere of N_2 and with the heating rate of 10°C/min in order to determine melting peak temperature (T_{max}), glass transition temperature (T_g), and fusion heat (ΔH_m).

Dynamic Mechanical Analysis (DMA)

The storage modulus (E') and the dissipation factor (tan δ) of the specimen films of the three PUs, as well as of their blends with PVC 0.3 mm in thickness, were carried out on a Toyo Rheovibron DDV–EA at 3.5 HZ and under an N_2 purge. All the measurements were run from −100°C to 100°C under a heating rate of 3°C/min.

X-Ray Diffraction

For determining the crystallinity of the polyols and the PUs, the polyol samples were melted at 70°C, then cooled naturally; the PU solutions were cast on an F_4 plant, then dried at 80°C for 5 h and cooled naturally. All of these samples were made into a film with 1 mm thickness. A Rugaku D/MAX-B x-ray diffractometer employing Ni-filtered CuK radition, power 40 KV × 25 MA, was used for obtaining wide-angle x-ray diffraction (WAXD) patterns of the samples. The scan rate was 1°C/min and the scan range was 4° to 140°. The data obtained were calculated by using the Divide Peak Method.[19]

"T" Type Peeling Strength

The "T" type peeling strength (σ_s) was run with an XQ-2500N tensile testing apparatus at room temperature with a stretching speed of 100 mm/min. The samples were made after casting PU solution, diluted with ethyl acetate to 25% (wt),

on two PVC leathers, and making them adhere to each other 10 min later. The samples having a size of 2.5 × 15 cm were stretched as "T" type.

RESULTS AND DISCUSSION

Compatibility between PU and PVC

Generally speaking, two kinds of polymers dissolved in the same solvent are regarded as compatible if they remain uniform, transparent, and phase unseparable. Dobry and Boyer[20] proved this in their early studies. But when the film obtained after mixing the solutions of two polymers appears transparent, it means they do not have two phase ranges with different refractive indexes, i.e., they are homogeneous phase or compatible. The phase contract microscope photographs (Fig. 1) clearly indicate that the PEAU/PVC system, regardless of the PU/PVC ratio, is phase separable, and the PBAU/PVC system is homogeneous. By means of the testing of solubility and the optical transparency of blend film, we indicate that the two systems of PBAU/PVC and PHAU/PVC are compatible, but the PEAU/PVC system is not. (Tables II and III and Fig. 1)

It is learned from the DSC result of blends that the two systems of PBAU/PVC and PHAU/PVC have only one common glass transition temperature (T_g) in different composition proportions, but the PEAU/PVC system has two T_gs, with one higher and one lower. (Fig. 2 and Table IV). So generally, finding whether the blend consisting of two polymers has a common T_g is a reliable method of determining whether the polymers are compatible.

The DMA analysis result of blends also shows that the two systems of PBAU/PVC and PHAU/
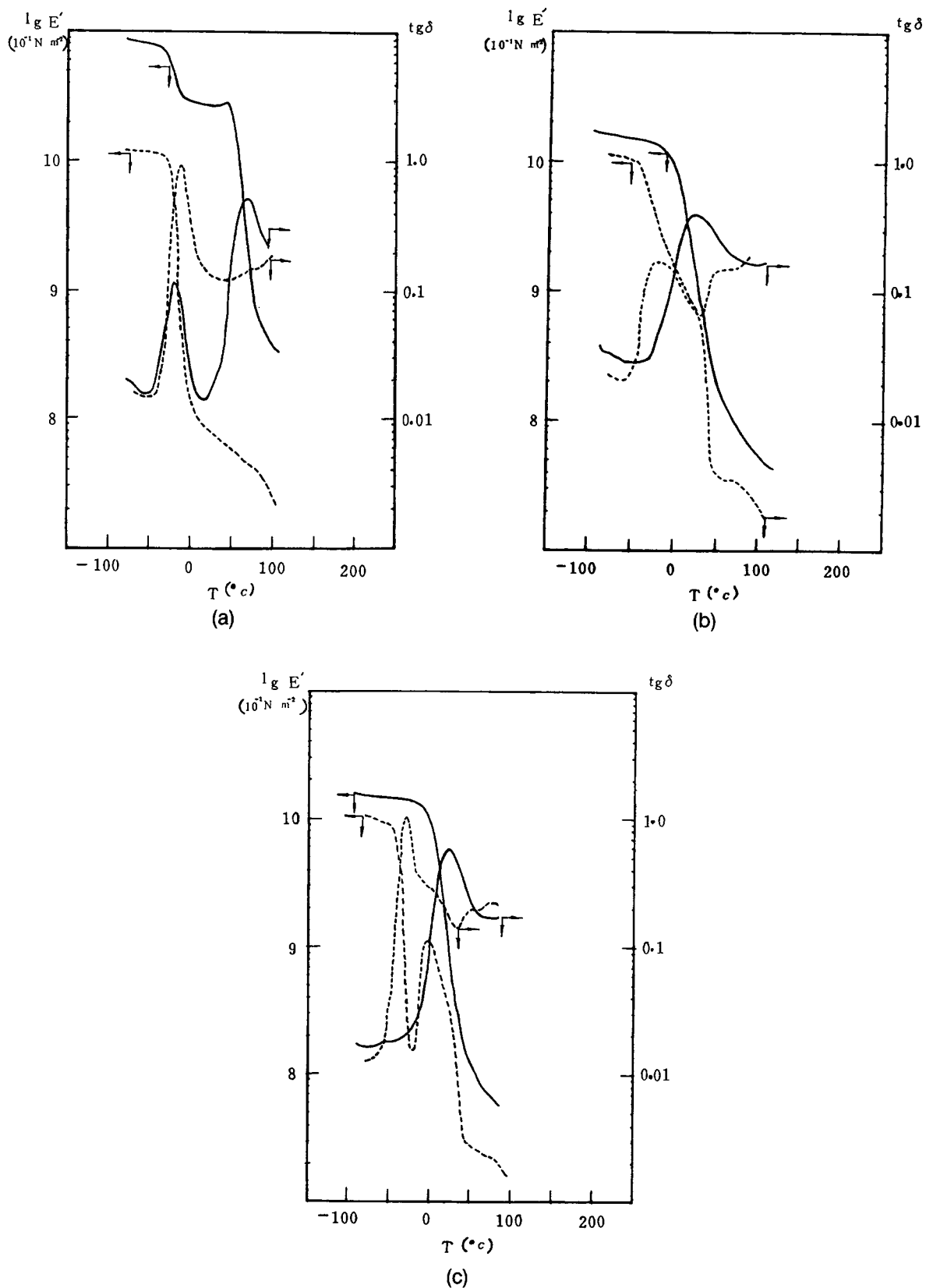
Figure 3 DMA of PUs and PU/PVC blends: ----- PU/PVC (100/0); —— PU/PVC (50/50); (a) PEAU type; (b) PBAU type; (c) PHAU type.
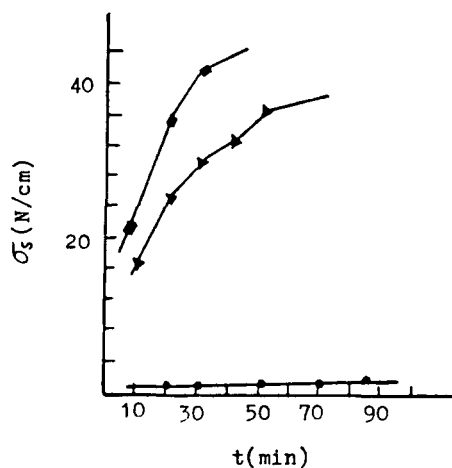
Table V   The Stripping Strength of PU to PVC/PVC

Type of PU	PEAU	PBAU	PHAU
(N/cm)	< 4	> 48	> 48
cracking type	interface	face of PVC	face of PVC

PVC each have only one mechanical loss peak, at −22°C and −28°C, respectively; but the PEAU/PVC system has two mechanical loss peaks, one at the lower temperature (−19°C) and the other at the higher temperature (69°C), corresponding respectively to the T_gs of PEAU and PVC (Fig. 3). This is more evidence demonstrating convincingly that PBAU/PVC and PHAU/PVC are compatible, but PEAU/PVC is not. Besides, the T_gs of different systems by DSC and DMA methods are very close to one another, which is consistent with the conclusion of the testing of solubility and optical transparency of blend, i.e., PBAU/PVC and PHAU/PVC are compatible systems, but PEAU/PVC is not.

The Adhesion Behavior of PU to PVC Leather

From the peeling strength test of the PVC leathers adhered by using PU adhesives, we find, under the same conditions, that PBAU and PHAU have great peeling strength; that the peeling damage is due to the adhered object (PVC leather); that PEAU has weak peeling strength; and that the peeling damage is due to the interface (Table V, Fig. 4). With the

common PU adhesion theories, such as the Absorption Theory and the Chemical Bonding Theory, it is impossible to explain such big differences in the adhesion behavior of the three kinds of PUs that are similar in structure and roughly the same in SS/HS ratios and MW.

According to the Absorption Theory, polar
$$-NH-\overset{\overset{\displaystyle O}{\|}}{C}-O- \quad and \quad -\overset{\overset{\displaystyle O}{\|}}{C}-O-$$
groups are on all the molecular chains of the three kinds of PUs, and the density of polar group is in the order of PEAU > PBAU > PHAU. Supposedly, the PEAU should be the strongest both in absorption capacity and adhesion strength. However, the tests reveal quite the contrary. On the other hand, according to the Chemical Bonding Theory, we may conclude they should be almost the same in their possibilities of forming chemical bonds with the adhered objects (PVC), considering their molecular structures. Therefore, it is unable for us to give an explanation for the aforementioned dif-
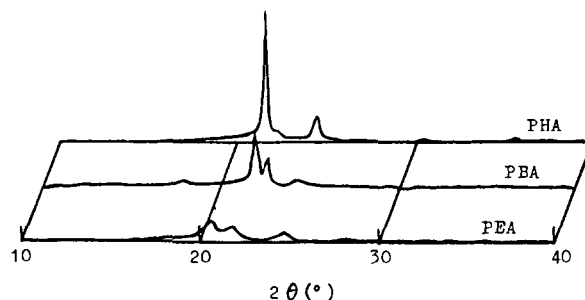
(a)
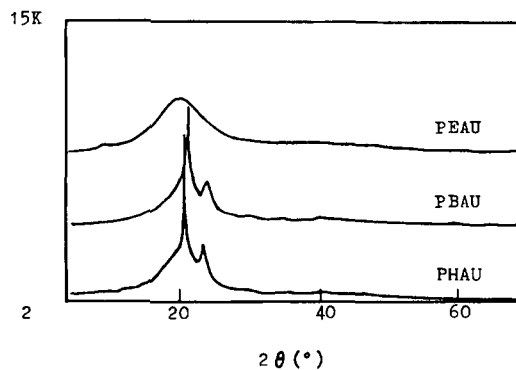
(b)

Figure 5   WAXD graphs of (a) the polyesters and (b) the polyurethanes.

Figure 4   Dependency of σ_s vs. t of PUs. (●) PEAU; (▲) PBAU; (■) PHAU.

Table VI   The WAXD and DSC Data of the Polyesters and Polyurethanes

Properties	Pes			PU		
	PEA	PBA	PHA	PEAU	PBAU	PHAU
Crysty. (%)	16.7	24.5	31.5	0	9.2	12.3
T_{max} (°C)	42	54	56		44	48
ΔH_m (j/g)	43	68	87			

Notes: MW of Pes 2000, Crysty. by WAXD, T_{max} and ΔH_m by DSC.

ference in the adhesion strength. As far as the adhesion of PU to PVC is concerned, we can safely say that the obvious difference in their adhesion behavior is first related to the compatibility between the three kinds of PUs (PEAU, PBAU, and PHAU) and PVC.

In addition, when all other conditions (MW, SS/ HS ratio, etc.) are very similar, the original adhesion strength should be mainly related to the crystallinity of the adhesive itself. The crystallinity of the three polyols and the corresponding PUs by WAXD (Fig. 5) are illustrated in Table VI. Figure 5(b) indicates that unlike PHAU and PBAU, each of which has an obvious crystalline peak, PEAU has only one continuous dispersion cycle. The calculated crystallinity indicates that the crystallizing capacity of the three types of PUs is in the order of PHAU > PBAU ≫ PEAU, which is consistent with both the order of the crystallizing capacity of the corresponding three polyols in Figure 5(a) (PHA > PBA ≫ PEA), and the order of their original adhesive and peeling strength.

So far, there have been many adhesion theories. The PU adhesion mechanism generally trends to the Absorption Theory and the Chemical Bonding Theory in the literature. Starting from the interaction among moleculars, we may see there is reason in it. But the test result indicates it is the compatibility between the PU series and PVC that plays the key role in their adhesion. The better compatibility they have, the easier it is to interdiffuse on the interface between them. Because of the interdiffusion and interpenetration of this kind of molecular chain and individual segment on the interface, the PVC/PVC interface disappears and a transition area (diffusion lamina) is formed to make a fixed adhesion. Because of the poor compatibility between PEAU and PVC, the above-mentioned interdiffusion is hard to generate or the diffusion lamina is very thin, so their combined power is poor and their adhesion strength is weak. When their

compatibility fixes, the adhesion behavior of PU adhesives is directly related to their crystallinity and their abilities to form chemical bonding, i.e., the better the crystallinity, the greater the adhesion strength. Therefore, the adhesion procedure of PU to PVC should be: compatibility–interdiffusion–crosslinking with chemical bonding or/and physical force. The adhesion behavior is a complex physical and chemical process taking place on the interface, so we should not apply to one certain kind of theory to give explanations; many factors play a part in any adhesion system. We find it is more suitable to provide explanations for the adhesion system (PU to PVC) previously mentioned in this article by using the Diffusion Theory, the compatibility, the crystallinity, and the molecular structure.[21]

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