

Role of Adhesive-Substrate Compatibility in Adhesion

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Synopsis

For substrates such as polyesters having limited capacity for hydrogen bonding or other specific interactions, thermodynamic compatibility of the substrate and adhesive is shown to be a key factor in promoting bondability to the substrate. Such compatibility occurs, as shown by Abere, when the cohesive energy densities (CED) or solubility parameters ($\delta = \sqrt{\text{CED}}$) of substrate and adhesive are matched. Investigations with polyester film-adhesive-film model systems with the use of a variety of nonpolar (hydrocarbon) and polar (chlorinated compounds, ethers, esters) adhesives illustrate how compatibility promotes bondability to poly(ethylene terephthalate). The poor adhesion of polyester fibers to resorcinol-formaldehyde-latex (RFL) adhesives is attributed to the incompatibility of resorcinol ($\delta = 16.0$) with the polyester ($\delta = 10.3$). Adhesion to RFL was improved by substituting the more compatible *n*-hexyl resorcinol ($\delta = 12.5$) for resorcinol in RFL adhesives. Currently, the best adhesive systems for polyester tire yarns are those (e.g., isocyanate-epoxy) involving formation of urethane polymers having matching δ values with poly(ethylene terephthalate).

INTRODUCTION

The excellent adhesion of polar substrates such as polyamides is believed to develop from specific interactions such as hydrogen bonding at the adhesive-substrate interface between the strongly hydrogen-bonded polyamide substrate and the adhesive.¹ Such interactions are relatively less important with substrates such as polyesters having limited functional sites in their molecular structure. Consequently, the development of adhesion for such substrates would involve mechanisms other than those arising from specific interactions between the substrate and adhesive. The main object of this paper is to examine and apply recently developed concepts to investigate the mechanism of adhesion of polar and nonpolar polymeric substrates.

ADHESIVE BOND FORMATION

Thermodynamic Compatibility

Abere² derived from the following thermodynamic considerations the concept that good bonding between a substrate and an adhesive

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is attained when their cohesive energy densities (CED) or solubility parameters ($\delta = \sqrt{\text{CED}}$) are matched.

For the development of a favorable bond, the free energy change, ΔF , for creating a new interface must be negative ($\Delta F < 0$).

$$\text{Since } \Delta F = \Delta H_m - T\Delta S \quad (1)$$

where ΔH_m is heat of mixing, T is temperature of bonding, and ΔS is entropy of mixing, eq. (1) suggests that bond formation is favorable when (1) $\Delta H_m \rightarrow 0$ (heat of mixing is low); (2) bonding temperature is high; (3) entropy change is large. The heat of mixing ΔH_m of two components 1 and 2 is given by³ eq. (2):

$$\Delta H_m = V_m \phi_1 \phi_2 (\sqrt{\Delta E_1/V_1} - \sqrt{\Delta E_2/V_2})^2 \quad (2)$$

where ΔE is the energy of vaporization, V is the molar volume, ϕ is the volume fraction, and V_m is the total volume of the mixture.

On defining the solubility parameter, δ , as the square root of cohesive energy density, $\Delta E/V$, eq. (2) becomes

$$\Delta H_m = V_m \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \quad (3)$$

If $\delta_1 = \delta_2$, then $\Delta H_m \rightarrow 0$, making ΔF in eq. (1) negative to favor bond formation between components 1 and 2.

These considerations suggest that good bonding between a substrate and adhesive is possible when their solubility parameters δ or cohesive energy densities ($\text{CED} = \delta^2$) are matched to make them mutually compatible in a thermodynamic sense. Substrate-adhesive-substrate systems were used in the present work to define the effect of adhesive-substrate thermodynamic compatibility and other specific interactions on their mutual adhesion. Such systematic investigations have not been reported previously. In viscose rayon cord-adhesive-rubber systems involving a limited number of adhesives, Basin et al.⁴ found that the adhesive-rubber bond strength was low when the cohesive energy densities of polymers in the rubber and adhesive were widely different. Buiko and Shvartz⁵ reported that dynamic bond strength of plied-up vulcanizates decreased as the components became incompatible.

Solubility Parameters δ

The solubility parameters of the polymers constituting the adhesive and substrate were determined by solubility, swelling, heat of vaporization, and surface tension methods and calculated from the structural formulas.

Solubility. The solubility of the polymer is determined in a series of solvents covering a wide spectrum of δ values. The effective solvents are arranged in increasing order of δ values. The midpoint of this range gives the δ of the polymer. Solvents used in this work and their δ values are shown in Table I.

Swelling. The swellability of the polymer is determined in solvents of known δ values. δ of the polymer is located at the maximum of the δ (solvent) versus swellability curve.

Heat of Vaporization. Since $\Delta E = \Delta H - RT$,

$$\delta = (\Delta E/V)^{1/2} = [(\Delta H - RT)/V]^{1/2} \quad (4)$$

from which δ can be calculated if heat of vaporization ΔH , molar volume V , gas constant R , and temperature T (absolute) are known. Where

TABLE I
Liquids Used for Determining Solubility Parameters

Liquid	δ , (cal./cc.) ^{1/2}
Poorly hydrogen-bonded liquids	
Pentane	7.0
Heptane	7.5
Cyclohexane	8.2
Carbon tetrachloride	8.6
Toluene	8.9
Benzene	9.2
Methylene chloride	9.7
1,2-Dichloroethane	9.8
Moderately hydrogen-bonded liquids	
Methyl isobutyl ketone	8.4
Methyl ethyl ketone	9.3
Dioxane	9.9
Acetone	10.0
Methyl Cellosolve	10.8
Strongly hydrogen-bonded liquids	
Benzyl alcohol	11.2
<i>n</i> -Butyl alcohol	11.4
<i>n</i> -Propyl alcohol	11.9
Ethyl alcohol	12.7
Ethylene glycol	14.2
Methyl alcohol	14.5
Glycerol	16.5
Water	23.4

experimental data are not available, ΔH can be estimated for nonhydrogen-bonded compounds by Hildebrand's equation relating ΔH with boiling point T_b (absolute):

$$\Delta H_{25^\circ\text{C.}} = 23.7T_b + 0.020T_b^2 - 2950 \quad (5)$$

Burrell⁶ found that good agreement between observed and calculated δ values for esters, ketones, acids, and alcohols was obtained by applying a correction factor C to the δ values calculated by eq. (4) and (5). This correction factor was used in our calculations of δ for phenols and resorcinols.

Surface Tension. Burrell⁶ points out the interesting relationship between surface tension γ and δ of liquids:

$$\delta = 4.1(\gamma/V^{1/3})^{0.43}$$

where V is the molar volume. This relationship was extended to polymeric systems by substituting Zisman's⁷ critical surface tension (γ_c) in place of γ .

Structural Formula. δ can be calculated from molecular structure by using "molar attraction constants" given by Small⁸:

$$\delta = d\Sigma G/M$$

where ΣG is the sum of molar attraction constants G for all the atoms or groups in the molecule, d is the density, and M is molecular weight. Burrell⁶ has listed the solubility parameters of several polymers. However, his δ values for polymers of interest to us, such as polyesters and polyamides, were calculated from structure and hence are not reliable, since Small's method of calculation is not valid for polar or hydrogen-bonded compounds. In view of this, the δ values of these polymers were experimentally determined.

EXPERIMENTAL

Swelling Measurements

Swelling measurements were made at room temperature (25°C.) on films of poly(ethylene terephthalate) (Mylar, Type 1000A, 10 mils) and nylons 6 and 66 (extruded, 8–15 mil) which did not contain any finish. Equilibrium swelling was expressed as cubic centimeters solvent/gram polymer calculated from the weight gain of the swollen samples after they had attained constant weight. The solvents listed in Table I were used as swelling agents. Mixtures of alcohols and water were used to cover the gap in the δ values between the alcohols and water. The δ of the mixture of two liquids is evaluated by assuming the additivity of the products of the mole fractions and the δ of the individual components.

Adhesion

A simple technique was developed to characterize bondability of film-adhesive-film model systems. The adhesives (Table II) containing the necessary curing agents were applied from a brush or film applicator (0.003–0.006 in. clearance) onto films from aqueous latices or from solutions in organic solvents. The adhesive-coated films (2 × 6 × 0.0075 in.) were dried to evaporate the vehicle or solvent, doubled up with adhesive-coated surfaces facing each other and cured in a press to give a 1 × 6 in. film-adhesive-film structure. The force required to peel the sample at 90° angle at 2 in./min. was measured, and the mode of failure was noted. The optimum peel strength of each film-adhesive-film system

TABLE II
Adhesives Used in Film-Adhesive-Film Tests
(Key to Points in Figures 3 and 4)

Point no.	Polymer	Form ^a
1	Polyethylene	A, S
2	Isoprene	A, S
3	Butadiene-styrene	A, S
4	Butadiene-styrene-2-vinylpyridine (Gen-Tac)	A
5	Chloroprene (Neoprene)	A, S
6	Chlorosulfonated polyethylene (Hypalon)	A, S
7	Acrylates, methacrylates (Hycar 4021, Rhoplex latices, methyl, ethyl, <i>n</i> -butyl and isobutyl methacrylates)	A, S
8	Ethylene-vinyl acetates (Elvax resins)	A
9	Vinyl chloride (Geon 576)	A
10	Butadiene-acrylonitrile (Hycar 1041, 1561; FR-N 501-504)	A, S
11	1,4-Oxybutylene glycol-TDI (Adiprene L-100, L-167, LD-420, C)	S
12	Vinyl acetate-dibutyl maleate (Elvacet 1454)	A
13	D-417 Adhesive ^b	A
14	Vinyl acetate (Elvacet 81-900)	A
15	Vinylidene chloride-acrylonitrile (Dow Latex 122-A-15)	A
16	Alkoxy alkylated nylon (B.C.I. nylon resin, Type 829)	S

^a A = aqueous dispersion, S = solution in toluene or other solvent.

^b Containing a phenol-blocked isocyanate (Hylene MP) and epoxide (Epon 812).

was derived from measurements on samples cured under a range of conditions of temperature, time and pressure. Optimum cures of most systems were at 285–325°F., 15–30 min., 100–300 psi. The reproducibility of peel force measurements was ± 0.5 lb. Predominantly cohesive failures inside the adhesive indicate that the strength of the adhesive-substrate bond exceeds the measured peel strength.

ADHESION AND COMPATIBILITY

Model Systems

When the swellability of polyamide was plotted against the solubility parameters of the solvents, the points showed considerable scatter (Fig. 1) so that it was not possible to draw a smooth curve. Recently, Yerrick and Beck⁹ suggested a technique for selecting solvents to minimize the scatter in swelling data attributed to dipole interactions specific to certain solvents.¹⁰ Their selected swelling agents for silicone elastomers included nonpolar aliphatic and aromatic hydrocarbons ($\delta = 6-9.2$) and strongly hydrogen-bonded alcohols ($\delta = 10.8-14.5$) but excluded chlorinated compounds, ketones, ethers, and esters. With either polar or nonpolar substrates, chlorinated solvents gave increased swelling in comparison

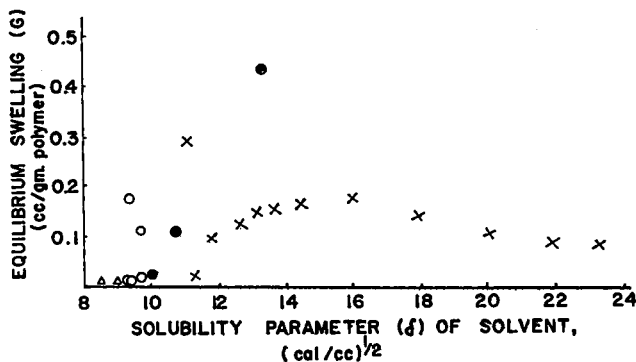


Fig. 1. Swelling vs. δ of solvent for nylon 66 films: (Δ) nonpolar solvents; (\circ) chlorinated polar solvents; (\bullet) other polar solvents; (\times) strongly hydrogen-bonded solvents.

with hydrocarbons of the same solubility parameter. The behavior of ethers and esters depended on the nature of the elastomers. In substrates of low polarity they produced less swelling than nonpolar solvents of similar δ values due to their strong solvent-solvent interactions due to permanent dipoles. The swelling was too high with polar substrates due to strong interaction of polar polymer with polar solvents. By discarding the solvents (chlorinated compounds, esters, and ethers) having dipole interactions, the scatter in our swelling data was eliminated to give smooth curves (Fig. 2) the maximum of which gave a δ value of about 16 for nylons 6 and 66. The rather broad peak for these polyamides in the region of high δ indicates the strongly hydrogen-bonding character of these substrates. The solubility parameter of poly(ethylene terephthalate) (PET) could not be determined by swelling data due to the very low level of swelling of Mylar film in the non-interacting solvents. Data on solubility and heat of vaporization of dimethyl terephthalate (DMT), was used to derive the δ for PET, since the structure of DMT is almost identical to the repeating unit in PET. The empirical relation-

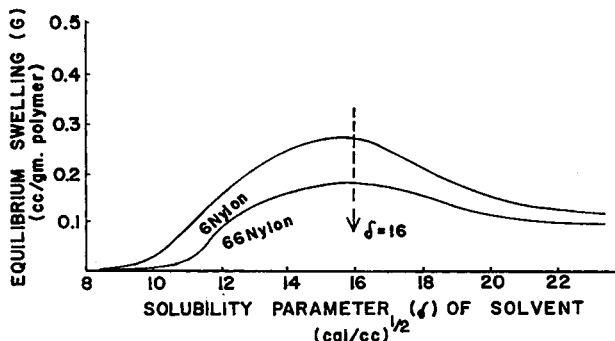
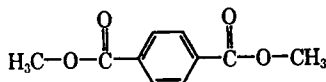


Fig. 2. δ of polymers from swelling data (nylon 6 and 66 films).

ship between surface tension and δ was also applied to calculate the δ of PET. The δ values determined by these different methods show excellent agreement among themselves (Table III), giving an average value of 10.3 for the solubility parameter of PET.

TABLE III
 δ of Dimethyl Terephthalate (DMT) and PET



Method	δ
Solubility	
Soluble in solvents of $\delta = 8.9-11.2$	10.1
Heat of vaporization (ΔH), $\delta = [(\Delta H - RT)/(M/d)]^{1/2}$	
$\Delta H = 16,400$ cal./mole (experimental data)	10.3
$\Delta H_{25^\circ\text{C.}} = 23.7T_b + 0.020 T_b^2 - 2950^a$ ($T_b =$ boiling point = 561°K.)	10.4
δ vs. surface tension γ relationship $\delta = 4.1(\gamma_c/V^{1/3})^{0.43}$	10.2
where $\gamma_c = 43$ dynes/cm. (critical surface tension of PET) and $V =$ molar volume of PET = 138 cc./mole	
Avg.	10.3

^a Hildebrand's modification of Trouton's law.

Thermodynamic compatibility of substrate and adhesive appears to be a key factor in promoting the bondability of PET. This type of compatibility is achieved when cohesive energy density (CED) or solubility parameter ($\delta = \sqrt{\text{CED}}$) of the polymeric substrate is matched with that of the adhesive. Figure 3 illustrates this effect of thermodynamic compatibility on peel strength of Mylar film-adhesive-Mylar film systems containing adhesives shown in Table II. Systems with high peel strengths and cohesive failure contain adhesives having δ values close to that of PET ($\delta = 10.3$). Adhesion is low when δ of adhesive is too low or too high but gradually increases as δ corresponding to that of PET is approached from either side. The effect of compatibility on bond strength is summarized in Table IV for adhesives with reasonably high cohesive strength.

TABLE IV

Bond strength	Failure	Compatibility
Low	Interfacial	Poor (δ adhesive \leq PET)
High	Cohesive	Good (δ adhesive \cong PET)

Note (Fig. 3) the scarcity of adhesives having δ values in the 10-11 range where thermodynamic compatibility and hence good adhesion to PET is

expected. Included in this range are vinyl acetate-dibutyl maleate copolymers, 1,4-oxbutylene glycol-TDI polymers, and D-417 adhesive, all of which showed high adhesion with cohesive failure. The δ for D-417 adhesive (Table II) was computed as the average of δ values for its main components, Epon 812 and Hylene MP. The δ values for other adhesives were obtained from the literature and also from our own solubility and swelling data.

According to Sharpe and Schonhorn,¹¹ adhesives having surface tension less than the critical surface tension⁷ γ_c of the substrate should be thermodynamically spreadable on the substrate and should show good adhesion

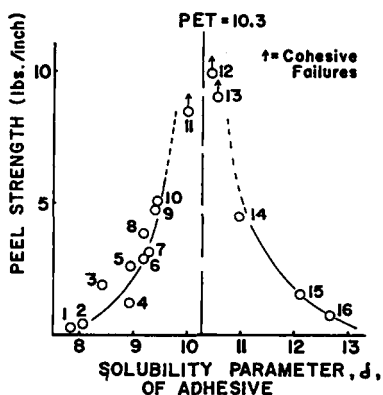


Fig. 3. Relationship of compatibility to adhesion for Mylar-adhesive-Mylar system. See Table II for key to points.

with cohesive failures inside the adhesive layer. Since many of our solvent-based adhesives (e.g., polyethylene, $\gamma = 31$ dyne/cm.) having surface tensions lower than the γ_c of PET⁷ (43 dyne/cm.) showed poor adhesion with interfacial failure, thermodynamic spreadability, as defined by Sharpe and Schonhorn, does not appear to be the sole criterion for good adhesion.

Fiber-Adhesive-Rubber Systems

The concept of bondability due to adhesive-substrate compatibility was extended to fiber-adhesive-rubber systems of importance in tires and other textile-reinforced articles. In such systems we are concerned with polymer-adhesive and adhesive-rubber bond strengths. Resorcinol-formaldehyde-latex (RFL) adhesive systems give excellent adhesion of nylon tire cord to rubber but are ineffective on polyester cords because a polyester, unlike a polyamide, is incapable of specific interaction with RF resin. The poor adhesion of RFL adhesives to polyesters may be considered in relation to the compatibility of PET polymer with the RF resin which is essentially composed of resorcinol units linked with methylene bridges. Solubility data show that the δ value of resorcinol ($\delta = 16.0$)

is very different from that of PET ($\delta = 10.3$), and hence RF resin is incompatible with PET.

A practical approach to improve the adhesion was tried by replacing resorcinol in RFL with components compatible with PET. The basic RFL system was maintained because of its excellent cure to unsaturated rubber. Solubility parameter data (Table V) on resorcinol derivatives indicate that even the substitution of long-chain alkyl groups on resorcinol does not lower the δ sufficiently to match that of PET. Apparently, the predominant influence of two strongly hydrogen-bonding OH groups in resorcinol is responsible for the high δ value of the derivatives. The interesting ester-substituted resorcinols are not available.

TABLE V
Solubility Parameter of Resorcinols

	Soluble (S) or insoluble (I) in solvents ^a				Solubility parameter δ , (cal./cc.) ^{1/2}	
	A	B	C	D	Solubility other methods	
Resorcinol (R)	S	S	S	I	15.9	15.0 ^b
2-Methyl-R	S	S	S	I	15.9	—
4-Hexyl-R	I	S	S	S	12.5	11.6 ^c
Octyl-R	I	S	S	S	11.5	11.7 ^c
$\text{R}-\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{CH}_3 \end{array}$	I	S	S	I	11.5	—
$\text{R}-\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{C}_2\text{H}_5 \end{array}$	I	S	S	I	11.5	—

^a A = water; B = strongly hydrogen-bonded solvents; C = moderately hydrogen-bonded solvents; D = poorly hydrogen-bonded solvents. List of solvents used is given in Table I.

^b Calculated from boiling point T_b by using Hildebrand's relation between latent heat of vaporization, ΔH , and T_b ($^{\circ}\text{K}.$): $\Delta H = 23.77T_b + 0.020 T_b^2 - 2950$ ($T_b = 553$), $\delta = [(\Delta H - RT)/(M/d)]^{1/2} + C$, where $R =$ gas constant, $T = 298^{\circ}\text{K}.$, $M =$ molecular weight, $d =$ density at T , and $C = 1.4$ is a correction factor derived by Burrell for hydrogen-bonded compounds.

^c Average of δ values for resorcinol and hexane or octane.

Some interesting facts are revealed from data in Table V. The solubility parameter of resorcinol determined from solubility data corresponds closely to that calculated from boiling point T_b by using Hildebrand's equation relating T_b and latent heat of vaporization. For hexyl and octyl resorcinols, δ values calculated as the average of that of resorcinol and of the hydrocarbon show good agreement with the experimentally determined values. The δ for resorcinol ($\delta = 15.9$) matches that of nylon 6 or 66 ($\delta = 16$), indicating that resorcinol is compatible with these polyamides. Thus the excellent adhesion of nylon to RFL dips arises from the combined effect of entropic and specific bonding.

Since the δ of 4-hexyl and octyl resorcinols are closer to that of PET than resorcinol, these compounds were substituted for resorcinol in single-

step RFL dips to see if they improved the poor adhesion of polyester cords to rubber. Hexylresorcinol-formaldehyde-latex adhesives containing a high resin/rubber ratio showed 60% higher adhesion to polyester than an RFL adhesive (Table VI). Although this level of adhesion is only about 60–70% of that attained by using the D-417 subcoat with a conventional RFL topcoat on polyester cords, the present results are significant, in that for the first time a modest level of adhesion has been developed with a single-step RFL type adhesive not containing isocyanates, epoxy resins, or any other additives. RFL dips containing octyl resorcinol could not be compounded, since a solid polymer separated following coagulation when octyl resorcinol was added to formaldehyde solutions.

TABLE VI
RFL Adhesive for Polyester Cords
(T-68 Dacron Tire Cord Treated with Adhesive)

R in RFL ^a	Dacron/rubber adhesion, lb./in. ^b
Resorcinol	21
<i>n</i> -Hexyl resorcinol	34
(Isocyanate + epoxy)-RFL	46

^a RFL = resorcinol-formaldehyde-latex adhesives containing butadiene-styrene-vinylpyridine latex; R/F (mole) = 1.4 and rubber/resin = 1.2.

^b Cord/adhesive/rubber (2-ply, 840/1/2 cord, 44 ends/in.).

Solubility parameters of alkyl-substituted phenols (Table VII) indicate that these monohydroxy compounds are more compatible with PET than resorcinol derivatives. However, the phenol derivatives formed weak polymers with formaldehyde and rubber latex and hence were ineffective as adhesive compounds. Investigation of the curing characteristics of 1–2 mil thin films deposited from resin solutions and resin-latex mixtures indicated that phenol or *m*-cresol-formaldehyde-latex systems are not capable of forming polymers of high cohesive strength characteristic of resorcinol-formaldehyde-latex systems although phenol or *m*-cresol can form strong polymers with formaldehyde alone. Work reported in the literature¹³ also shows that phenol or *m*-cresol-formaldehyde resins do not vulcanize unsaturated rubber, even under prolonged curing conditions (390°F./2 hr.). Apparently some aspect of resorcinol structure, probably related to the strong activation of the two mutually *meta* OH groups, promotes its balanced reaction with formaldehyde and unsaturated elastomer. The poor cohesive strength of phenol-formaldehyde-latex systems could not be improved either by catalyst¹⁴ or by resin pre-reactions.

Investigations of polymers of substituted and unsubstituted dihydroxybenzenes with formaldehyde and unsaturated rubber clearly indicated that strongly crosslinked structures are formed only when the hydroxy groups are in 1,3 (*meta*) position, and the 2, 4, and 6 positions remain

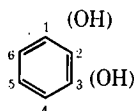
TABLE VII
Solubility Parameters of Phenols

	δ , (cal./cc.) ^{1/2}	
	Solubility	Boiling point ^a
Phenol	11.8	12.8
<i>m</i> -Cresol	11.8	12.2
	11.9 ^b	
<i>tert</i> -Butyl phenol	11.5	—
<i>sec</i> -Amyl phenol	10.8	—
Octyl phenol	10.8	—
Nonyl phenol	10.8	—

^a Calculated as described in footnote of Table V; $T_b = 455$ (phenol), $T_b = 476$ (*m*-cresol).

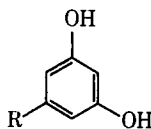
^b Data of Moore and Sheldon.¹²

unsubstituted. Film strengths of resin/latex combinations follow the sequence, 5R = R > 4R > 2R > phenol or its derivatives, where the numbers stand for substituted positions and R is the resorcinol unit (I),



I

indicating that RFL systems containing 5-substituted resorcinols compatible with PET would form strong adhesives for bonding Dacron to rubber. Examples of such compounds are the series II,



II

where R may be $\text{—C} \begin{matrix} \text{O} \\ \parallel \\ \text{O—R}' \end{matrix}$ (R' is a compatible ester group such as methyl,

vinyl, or terephthalate), $\text{—CH}_2\text{—C} \begin{matrix} \text{O} \\ \parallel \\ \text{O—R}' \end{matrix}$ (double-bond conjugation near

benzene nucleus avoided by including a —CH_2 group), or $\text{—(CH}_2)_n\text{—CH}_3$ (nonpolar hydrocarbon to introduce compatibility; $n > 4$).

These compounds are not commercially available and were therefore not evaluated in this program.

SPECIFIC INTERACTIONS AND ADHESION

Figure 4 illustrates the importance of specific interactions in adhesion of nylon 66. Although the peel adhesion of model systems initially increases with δ , specific interactions are evident in the high adhesion imparted by strongly polar or hydrogen bonding compounds such as chlorosulfonated polyethylene (Hypalon) and alkoxy alkyl substituted nylon (Belding Corticellis, B.C.I., Series 800 nylons). Specific interaction of 66 nylon with B.C.I. nylon resin may involve (a) hydrogen bonding

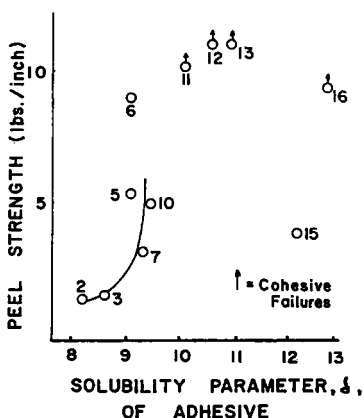
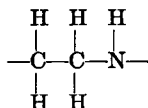


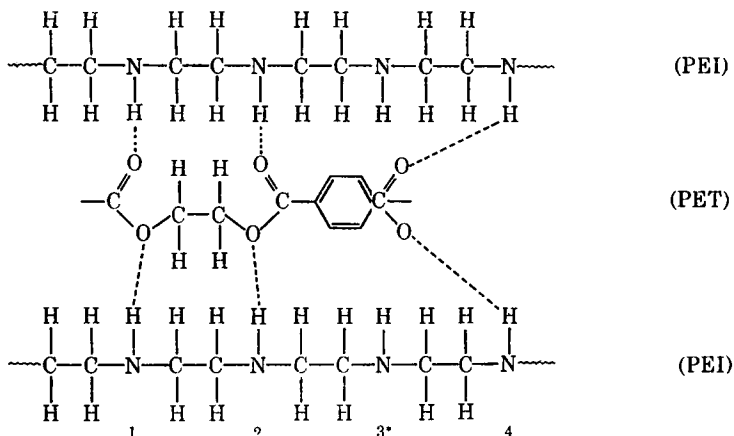
Fig. 4. Relationship of compatibility to adhesion for nylon 66 film-adhesive-nylon 66 film system. See Table II for key to points.

between —NHCO groups in the substrate and adhesive, and (b) cross-linking reaction between alkoxy alkyl groups, $\text{—(CH}_2)_n\text{—O—R}$, of B.C.I. nylon and NH groups of the polyamide substrate. These mechanisms are not possible with a PET substrate. The absence of such specific interaction between PET and B.C.I. nylon and also the lack of compatibility between the two polymers result in their poor bondability (Point 16, Fig. 3).

Although thermodynamic compatibility is a key factor in adhesion to PET, other factors may also be important under certain conditions. Recent patent literature¹⁵ claims that adhesion of polyester tire cord to rubber is improved by pretreatment of cord with a dilute aqueous solution of polyethyleneimine (PEI). No explanation has been offered for this beneficial influence of PEI. Our work showed that PEI is soluble only in strongly hydrogen-bonded solvents (water, alcohols) having δ values ranging from 10.8 to 23.4. This behavior is not surprising in view of the high concentration of NH groups available for hydrogen bonding in PEI:



Molecular models indicate that the repeating unit of PEI is such that two out of three NH bonds can be hydrogen-bonded to either the ether or ester oxygen in PET:



where the asterisk (*) denotes a nonhydrogen-bonding NH available for other reactions such as crosslinking with adhesive.

A single giant molecule of PEI can "attach" itself to PET at a large number of anchor points by periodically occurring hydrogen bonds. Such specific interaction can account for the adhesion promotion of PEI.

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15. Brit. Pat. 962,174 (to AKV, Holland).

Résumé

Pour les substrats tels que les polyesters, qui ont des capacités très limitées pour former des liaisons hydrogènes et d'autres interactions spécifiques, la compatibilité thermodynamique du substrat avec l'adhésif est un facteur déterminant du pouvoir liant au substrat. Une telle compatibilité se passe tel que cela a été montré par Abere, lorsque les densités d'énergie de cohésion (C.E.D.) ou les paramètres de solubilité ($\delta = \sqrt{\text{C.E.D.}}$) du substrat et de l'adhésif sont de valeur égale. Des recherches avec des systèmes film polyester/adhésif/film modèle, utilisant une variété d'adhésifs non-polaires (hydrocarbure) et polaires (composés chlorés, éthers, esters) illustrent comment la compatibilité favorise le pouvoir liant au téréphtalate de polyéthylène. La faible adhésion des fibres polyesters à des adhésifs à base de latex résorcinol (RFL) est due à l'incompatibilité du résorcinol ($\delta = 16.0$) avec le polyester ($\delta = 10.3$). L'adhésion au RFL est améliorée en substituant le *n*-hexyl résorcinol ($\delta = 12.5$) plus compatible au lieu de résorcinol dans des adhésifs RFL. Couramment, les systèmes adhésifs les meilleurs pour les fibres de pneu en polyester sont ceux (par exemple, isocyanate/époxy) comportant la formation de polymères uréthaniques ayant des valeurs de δ égales à celles du téréphtalate de polyéthylène.

Zusammenfassung

Für Substrate mit begrenzter Kapazität für Wasserstoffbindung oder andere spezifische Wechselwirkungen, wie Polyester, erweist sich die thermodynamische Verträglichkeit von Substrat und Adhäsiv als Schlüsselfaktor für die Beförderung der Bindungsfähigkeit an das Substrat. Eine solche Verträglichkeit tritt, wie Abere gezeigt hat, auf, wenn die Kohäsionsenergie-dichten (C.E.D.) oder Löslichkeitsparameter ($\delta = \sqrt{\text{C.E.D.}}$) von Substrat und Adhäsiv sich einander angleichen. Untersuchungen an Polyester-Film/Adhäsiv/Film-Modellsystemen mit einer Vielfalt nicht-polarer (Kohlenwasserstoff) und polarer (chlorierte Verbindungen, Äther, Ester) Adhäsivs zeigen, wie die Verträglichkeit die Bindungsfähigkeit an Polyäthylenterephthalat fördert. Die schlechte Adhäsion von Polyesterfasern an Resorcin/Formaldehyd/Latex-(RFL)-adhäsiv wird der Unverträglichkeit von Resorcin ($\delta = 16,0$) mit dem Polyester ($\delta = 10,3$) zugeschrieben. Die Adhäsion an RFL wurde durch Ersatz von Resorcin durch das besser verträgliche *n*-Hexylresorcin ($\delta = 12,5$) im RFL-Adhäsiv verbessert. Gegenwärtig sind die besten Adhäsivsysteme für Polyester-Reifengarne diejenigen (z.B. Isocyanat/Epoxy), bei denen Bildung eines Urethanpolymeren mit einem dem Polyäthylenterephthalat gleichkommenden δ -Wert auftritt.

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