

The Adhesion of Viscoelastic Polymers to Wool and Polyethylene*

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Synopsis

The relative magnitude of the rate-dependent peel force for different polymers adhering to polyethylene could be qualitatively predicted from the measured hysteresis of polymer films during stress-strain testing. Calculated values of the energy dissipated at the polymer/polyethylene interface during peeling were of the same order of magnitude as hysteresis values measured at a much lower stress than the breaking stress of the weakest polymer. This was consistent with low values of polymer/polyethylene intrinsic bond strengths expected for pure van der Waals bonding across the interface. In the wool/polymer system, fiber/polymer adhesion was an important factor in determining the shrink-resist effectiveness (sre) of polymers applied to wool fabric. Correlation between polymer shrink-resist effectiveness and polymer hysteresis was observed for two series of polymers whose intrinsic wool/polymer bond strengths could be assumed constant. In both cases, cohesive failure in the polymer occurred and hysteresis had to be measured just below the breaking stress of each polymer.

INTRODUCTION

Investigations of the adhesion between viscoelastic polymers and rigid substrates¹⁻⁶ have shown that the adhesive failure energy per unit area of interface, R , can be expressed as a function of the following parameters¹:

$$R = f[\gamma_1, \gamma_2, \gamma_{12}, E(t, T), \eta(s, T), T, t] \quad (1)$$

where γ_1 and γ_2 are surface free energies of substrate and adhesive; γ_{12} is the interfacial free energy; $E(t, T)$ is the time-temperature-dependent modulus of the adhesive; and $\eta(s, T)$ is the shear rate-temperature-dependent viscosity of the adhesive. Clearly, adhesion is a function of an equilibrium component (the $\gamma_1, \gamma_2, \gamma_{12}$ terms) and a nonequilibrium component that accounts for the observed dependence of R on the rate of separation.²⁻⁴ Most workers assume that an energy criterion for adhesive failure exists and that, for viscoelastic adhesives, the rate dependence of R arises from energy dissipation near the crack tip, these energy losses mirroring the bulk losses of the adhesive.^{5,6}

The above conclusions should also apply to wool/polymer adhesion which is assumed, a priori, to be an important factor in determining the effectiveness of synthetic polymers for reducing the felting shrinkage of wool.⁷ Studies have shown that the influence of surface properties of polymer, wool, and the surface tension of the wash liquor on polymer shrink-resist effectiveness, sre, can be interpreted in terms of the equilibrium component of eq. (1).⁸ Opinions conflict

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as to the relationship between certain polymer mechanical properties and polymer sre.⁹⁻¹¹

In an attempt to rationalize the effect of polymer properties on polymer sre, this article at first investigates the relationship between the stress-strain properties of certain commercial shrink-resist polymers and their peel adhesion to polyethylene film which is an unreactive model substrate with a critical surface energy similar to that of wool.¹² The peel test results are then compared with some measured values of fiber/polymer adhesion and polymer sre.

EXPERIMENTAL

Polymers

Synthappret BAP (Bayer AG) is a water-soluble bisulfite adduct (polycarbamoyl sulfonate) of an isocyanate-terminated polyether triol stabilized with a hindered phenolic antioxidant. It is supplied as 50% solids in water at pH 3. Acramin SLN (Bayer AG) is a self-crosslinking acrylic copolymer emulsion supplied as 50% solids. Impranal DLN (Bayer AG) and Impranal DLH (Bayer AG) are both anionic polyester-urethane disperions supplied as 40% solids.

Anionic polyester-urethane disperions with well-characterized chemical compositions have been described previously.¹³

Low-density polyethylene film, thickness 0.025 cm, (ICI), was continuously extracted with acetone before use.

Wool for shrink-resist studies was a lightweight, undyed plain-weave worsted fabric (140 g/m², 12 picks and ends/cm, R60/2 tex yarn) specially designed to felt severely. The fabric was continuously extracted with perchloroethylene before use. Lincoln fibers (radius 25 ± 5 μm) that had been extracted with methylene chloride were used for polymer/fiber adhesion studies.

Preparation and Testing of Polyethylene/Polymer Composites

Polymer films (150–500 μm thick) were prepared by pouring a dilute aqueous solution (10% w/w) of the polymer into polyethylene molds which had been fixed to glass using double-sided adhesive tape. Synthappret BAP solutions were adjusted to pH 7 with NaHCO₃ to promote curing. After two to three days at ambient temperature, the composite was removed from the glass and cured in a laboratory oven for 30 min at 100°C. After having been conditioned at 21°C and 65% RH, strips (1 × 5 cm) were cut for peel testing; 180° peel forces were measured at 21°C using an Instron. Crosshead speed was varied between 0.05 and 50 cm/min.

Polymer Stress-Strain Properties

Polymer films from the peel tests were tested at 21°C at 65% RH, or in water. Stress-strain tests were done at extension rates between 50 and 1000%/min, gauge length 2 cm. The results were analyzed according to the Mooney-Rivlin equation¹⁴:

$$\frac{\sigma}{\lambda - \lambda^{-2}} = \frac{FV_2^{1/3}}{A_0(\lambda - \lambda^{-2})} = 2C_1 + 2C_2\lambda^{-1} \quad (2)$$

where $\sigma = F/A_0$ is the stress, F is the force, A_0 is the unstrained cross-sectional area, V_2 is the volume fraction of polymer in the swollen state, λ is the deformation ratio, and C_1 and C_2 are the Mooney–Rivlin constants.

Polymer hysteresis was measured by extending films at 50–250%/min to either a predetermined stress or strain and then relaxed at the same rate. The area within the hysteresis loop was measured using a planimeter.

Fibre/Polymer Adhesion Measurements

The adhesive force between single wool fibers and cured polymers was measured using a method described by Kassenbeck¹⁵ but with a modified polymer application procedure.¹⁶ The swelling behavior of polymer interfiber bonds was investigated to detect differences between polymers cured as films and polymers cured on wool. Lincoln fibers were placed parallel ca. 120 μm apart, and drops of polymer solution were placed between the fibers to form interfiber bonds. After having been cured at room temperature or for 15 min at 150°C, the fiber/polymer composite was placed on a microscope slide under a glass cover slip and a drop of water added. Swelling was estimated from changes in the dimensions of the system at 150 \times magnification.

Polymer Shrink-Resist Effectiveness

The polymers or polymer mixtures were applied to the fabrics by padding at 100% wet pickup from an aqueous solution adjusted to pH 7 with NaHCO_3 . The samples were then air dried overnight, heated 30 min at 100°C or 15 min at 150°C, and washed in a phosphate buffer mixture at pH 7.⁸ Polymer sre was recorded as the time required for greater than 10% area shrinkage of the polymer-treated fabric.

RESULTS AND DISCUSSION

Adhesion of Shrink-Resist Polymers to Polyethylene

Polymers chosen for the initial investigation comprised varying ratios of Synthapret BAP:Acramin SLN. The stress–strain properties of polymer films could be easily varied by altering the ratio of the components (Table I and Fig. 1). Because the low surface energy component of the mixture (in this case Synthapret BAP) should accumulate at the polymer/air interface,¹⁷ the surface energy of the polymer films should be almost insensitive to the component ratio except for the pure Acramin SLN. Therefore, assuming that only van der Waals interactions operate across the polyethylene/polymer interface, the thermodynamic work of adhesion (or intrinsic bond strength) should be independent of polymer composition and the influence of polymer mechanical properties on adhesion should be observable.

The dependence of peel force measured at different speeds on polymer composition is shown in Figure 2. To compare the relative order of peel forces with the polymer properties listed in Table I, equivalent rates of extension $\dot{\epsilon}$ should be used. The rate of extension during peeling is approximately $\dot{\epsilon} = S/h$, where S is the peel rate and h is the film thickness.¹⁸ Polymer stress–strain properties

TABLE I
Properties of Synthapret BAP:Acramin SLN Films^a

Property	BAP:SLN ratio		
	0:100	20:80	50:50
Appearance	clear	slightly opaque	opaque
σ_{100} , N/mm ² ^b	0.21	0.14	0.28
σ_{100} , N/mm ² ^c	0.38	0.23	0.43
$2C_1$, N/mm ² ^b	0.02	0.01	0.06
$2C_1$, N/mm ² ^c	0.04	0.02	0.11
$2C_2$, N/mm ² ^b	0.21	0.15	0.20
$2C_2$, N/mm ² ^c	0.39	0.24	0.27
T_g , °C ^d	+22	-35 and +22	-35 and +22
$\tan \delta$ at 20°C	>1.6	>1.6	0.90
Work to break, 10 ⁻³ J/mm ³ ^c	10.08	7.47	9.42
θ , degrees ^f	84.5 ± 3.1	85.8 ± 2.0	89.0 ± 1.4
$\frac{1}{hb} \frac{dU_H}{dx}$, 10 ⁻⁶ J/mm ³ ^g	115	200	80
			50 ^h
			100:0
			clear
			1.58
			1.58
			0.53
			0.53
			0.77 ^e
			0.77 ^e
			-37
			0.12
			5.57
			90.0 ± 2.6

^a Films ($h = 0.02$ cm) cured 30 min at 100°C, conditioned 14 days at 65% RH at 21°C before testing.

^{b,c} Extension rate 50 and 1000% min⁻¹, respectively.

^d Toyo-Baldwin Rheovibron DDV-II, frequency 110 Hz.

^e Mooney-Rivlin plot nonlinear for $\lambda^{-1} > 0.8$.

^f Water contact angle on polyethylene after peeling.

^g Using eq. (8).

^h Using eq. (4).

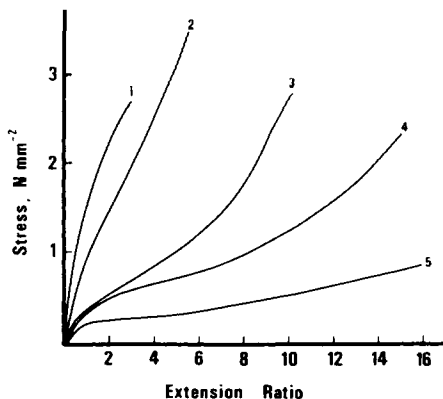


Fig. 1. Stress-strain curves for polymer films formed from mixtures containing different ratios of Synthappret BAP:Acramin SLN. Extension rate = 1000%/min; 1 = 100:0; 2 = 80:20; 3 = 50:50; 4 = 0:100; 5 = 20:80.

were measured at 50 and 1000%/min, the same approximate extension rate as peeling at 0.025 and 0.25 cm/min.

The results in Figure 2 and Table I are consistent with the observation that stiff, inflexible polymers have lower peel adhesion on polyethylene than soft, highly extensible polymers. No correlation was observed between work to break and peel force, but there was a correlation between $\tan\delta$ measured at 20°C and peel force ($r_{xy} > 0.9$ for speeds greater than or equal to 0.25 cm/min).

For all of the polymers, the adhesive force increased with speed of separation (Fig. 2), the rate of increase depending on polymer composition. At high rates of peel, films rich in Acramin SLN stretched considerably before peeling commenced. Very thin films ($<150 \mu\text{m}$) with BAP:SLN = 20:80 failed cohesively at the highest speed, whereas at low speeds failure was apparently interfacial, although the contact angle of water on polyethylene decreased from $94.6 \pm 1.6^\circ$ [95% confidence limits (c.l.)] before polymer application to slightly lower values after peeling (Table I).

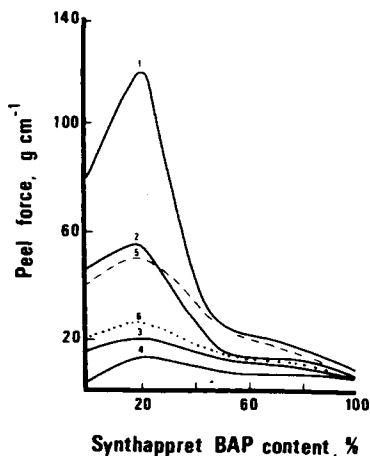


Fig. 2. 180° peel force for films containing different amounts of Synthappret BAP:Acramin SLN peeled from polyethylene at different speeds. Solid curves: 1 = 25 cm/min; 2 = 2.5 cm/min; 3 = 0.25 cm/min; 4 = 0.025 cm/min. Broken curves, polyethylene peeled from polymer: 5 = 0.25 cm/min; 6 = 0.25 cm/min with freely rotating metal roller included.

For any particular polymer, the increase in adhesive force with increasing rate of separation can be attributed to increased energy dissipation within the polymer.²⁻⁶ By analogy, for different polymers adhering to the one substrate such that the surface component of adhesion is constant, the polymer with the greatest adhesive strength at any particular rate might also be expected to have the greatest energy dissipation. Apart from $\tan\delta$ measurements, polymer hysteresis is a convenient measure of energy dissipation within the polymer. The following discussion compares measured values of polymer hysteresis during stress-strain testing with estimated values of energy dissipated in the polymer during peel testing.

One method of analyzing the peel test is based on an energy balance approach and the adhesive force is derived by equating the first derivative of the total energy to zero.⁴

For 180° peeling of an elastic film of width b , under a force F ,

$$\frac{2F}{b} = W \quad (3)$$

where W is the adhesive failure energy per unit area of interface. If van der Waals bonding only operates across the interface, W should become rate independent at very low rates of separation and identical with the thermodynamic work of adhesion W_a , provided interfacial failure occurs. If $W \gg W_a$, cohesive failure of the adhesive may be responsible²; although Gent²⁶ believes that for long, flexible molecules, an interface-strengthening effect may occur during adhesive failure similar to that suggested for the high-threshold tearing energies of elastomers.¹⁹

In the present study, only films of 100% Synthappret BAP showed peel forces approximately independent of rate below $S = 0.25$ cm/min (Fig. 2). From eq. (3), $W \sim 7$ N/m, which is two orders of magnitude greater than the estimated value of W_a (0.05–0.1 N/m).⁸ Three possible explanations for the large increase of W over W_a are: (1) true equilibrium peeling may not have been reached; (2) pure adhesive failure may not occur (as suggested by the slight decrease in water contact angle after peeling, Table I); or (3) an interface-strengthening effect as suggested by Gent may occur.

As the rate of separation increases, the peel force may increase due to energy U_H being dissipated (as heat). Equation (3) becomes

$$\frac{2F}{b} = W + \frac{1}{b} \frac{dU_H}{dx} \quad (4)$$

where x is the distance peeled. Igarashi²⁰ showed that for cohesive failure of the adhesive during peeling, $dU_H/dx = Uhb$, where h was the thickness and U was the energy dissipated per unit volume of adhesive. U was calculated from the area of the hysteresis loop of polymer films stressed nearly to the point of failure, at the same effective extension rate as during peeling. Gent and Petrich¹⁸ showed that for an uncrosslinked elastomer, energy dissipation within the adhesive accounted for almost all of the observed peel force and was given by the total area under the stress-strain curve:

$$\frac{F}{b} = h \int_0^{\sigma_a} \sigma de \quad (5)$$

where σ_a was the intrinsic bond strength of the system and was envisaged as the maximum tensile stress that the bond could withstand. In the present study, the increase in peel force with increased rate of separation for polymer films rich in Synthappret BAP can be attributed to energy dissipation near the interface, as the peel forces were not high enough to cause significant extension of the peeled section of polymer.

When significant stretching of the peeled section does occur, eq. (4) becomes

$$(1 + \lambda) \frac{F}{b} = W + \frac{1}{b} \frac{dU_H}{dx} + \frac{1}{b} \frac{dU_E}{dx} \quad (6)$$

where λ is the extension ratio of the film and U_E is the energy required to stretch the peeled section.

If the adhesive obeys the Mooney-Rivlin relationship, eq. (2), the energy expended per unit volume, U_V , in stretching the film to the extension ratio λ is²¹

$$U_V = \frac{1}{bh} \int_1^\lambda F d\lambda = C_1 \left(\lambda^2 + \frac{2}{\lambda} - 3 \right) + C_2 \left(\frac{1}{\lambda^2} + 2\lambda - 3 \right) \quad (7)$$

and eq. (6) becomes

$$\frac{W}{h} + \frac{1}{hb} \frac{dU_H}{dx} = \frac{(1 + \lambda)F}{hb} - \left[C_1 \left(\lambda^2 + \frac{2}{\lambda} - 3 \right) + C_2 \left(\frac{1}{\lambda^2} + 2\lambda - 3 \right) \right] \quad (8)$$

The left-hand side of eq (8) can be evaluated, provided C_1 and C_2 have been previously determined on films at the same rate of extension as for the peel experiment. A theoretical relation between F/hb and the left-hand side of eq. (8) is constructed by choosing values of λ and calculating the corresponding values of F/hb expected from eq. (2) (Fig. 3). From the experimentally determined peel force F , the value of the left-hand side of eq. (8) can be read directly from the theoretical curve. Using the previously estimated value of W (~ 7 N/m), the energy dissipated as heat during peeling could be calculated (Table I).

Measured values of polymer hysteresis per unit volume as a function of stress varied with the nature of the polymer (Fig. 4). Good agreement was observed

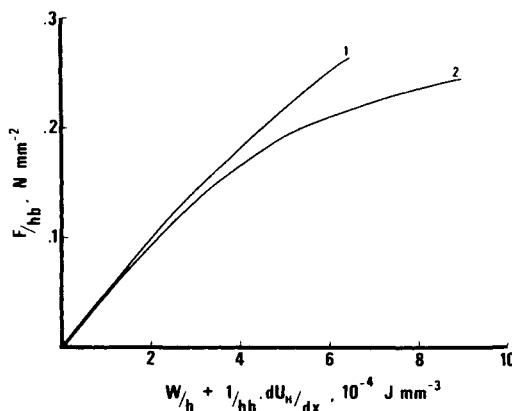


Fig. 3. Theoretical relationship for calculating the energy dissipated during peeling for films which stretch under the applied force: 1 = 0:100; 2 = 20:80.

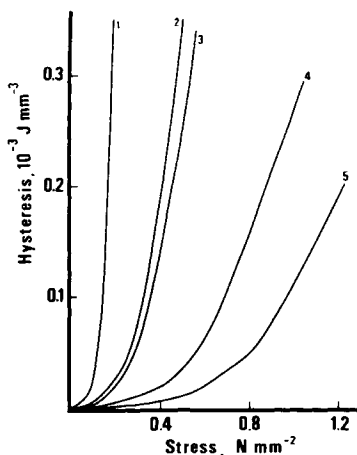


Fig. 4. Measured hysteresis of polymer films as a function of stress for polymer films containing different ratios of Synthappret BAP:Acramin SLN. Rate of extension = 250%/min: 1 = 20:80; 2 = 0:100; 3 = 50:50, 4 = 80:20; 5 = 100:0.

between the calculated values of energy dissipated per unit volume (Table I) and the measured values of polymer hysteresis (Fig. 4), provided the hysteresis was measured at stresses well below the breaking stress of the weakest polymer. This is consistent with adhesive failure at the polymer/polyethylene interface.

To eliminate the effect of polymer stretching during peeling, the polyethylene was peeled from the polymer film which had been attached to a solid support with double-sided pressure-sensitive tape (heavy broken line 5, Fig. 2). The large difference between curves 3 and 5 of Figure 2 (which were both at 0.25 cm/min) may be due to plastic yielding of the polyethylene during peeling.²² To overcome this, the polyethylene strip was bent around a freely rotating metal roller the diameter of which was large enough to prevent plastic yielding before peeling.²² The results shown by the dotted line 6 in Figure 2 are now much closer to curve 3. The residual increase is probably due to energy dissipation within the double-sided adhesive tape. At higher speeds (>2.5 cm/min), the peel force increased out of the scale of Figure 2, and plastic yielding of the polyethylene only accounted for a small part of the large increase. Gross deformation of the adhesive and double-sided tape occurred in this case.

All of the above results appear to be consistent with the suggestion that, for a series of different polymers adhering to the one substrate, such that the surface component of adhesion is small and approximately constant, the relative order of adhesive-failure energy can be predicted from the relative order of polymer hysteresis measured during stress-strain testing at rates of extension similar to that during adhesion testing. When interfacial failure occurs, polymer hysteresis must be measured at a stress much lower than the breaking stress.

Adhesion of Polymers to Wool

Fabric shrinkage during washing can be prevented by binding fibers together with small amounts of polymer,⁷ the a priori assumption being that effective polymers have good adhesion to wool.

In support of this assumption, good correlation has been found between

polymer sre and single-fiber polymer adhesion measured for three different series of polymers, viz., the polymers in Table I (Fig. 5), the polymers in Table II and a series of anionic polyester-urethane dispersions (Fig. 6 and Ref. 10). For any particular polymer/fiber system, the adhesive force increased with speed of testing; and, if it is assumed that the fiber behaves as a rigid substrate (i.e., $E_{\text{wool}} \gg E_{\text{polymer}}$), the increase in adhesive force with increasing speed can be attributed to increased energy dissipation within the polymer. From the energy criterion of adhesive failure discussed in the previous section, it follows that polymers with the greatest energy dissipation (in the wet state) should perform best in preventing felting.

For the polymers in Table I, there was no simple correlation between polymer

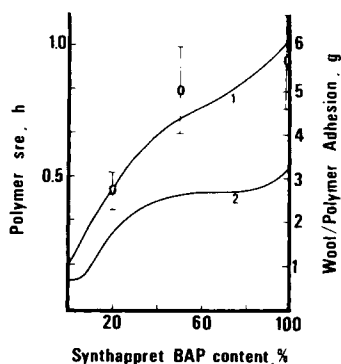


Fig. 5. Polymer sre (time to fail during washing) and single fiber/polymer adhesion as a function of Synthappret BAP:Acramin SLN ratio. Solid curves refer to polymer sre: 1 = polymer-treated fabric cured 15 min, 150°C; 2 = polymer-treated fabric cured 30 min, 100°C. Data points refer to single-fiber/polymer adhesion after curing 15 min at 150°C.

TABLE II
Properties of Films from Some Commercial Shrink-Resist Polymers^a

Property	Polymer composition, w:w		
	Synthappret BAP: Acramin SLN 50:50	Synthappret BAP: Impranil DLN 50:50	Synthappret BAP: Impranil DLH 50:50
Appearance	opaque	slightly opaque	slightly opaque
σ_{100} , N/mm ²	0.45	0.95	2.98
$\sigma_{100}^{\text{wet}}$, N/mm ²	0.38	0.85	1.87
$2C_1^{\text{wet}}$, N/mm ²	0.08	0.18	na ^d
$2C_2^{\text{wet}}$, N/mm ²	0.18	0.24	na ^d
T_g , °C	-33 and +22	-35	-38
$\tan \delta$ at 20°C	0.9	0.14	0.08
sre, h	1	2.5	>6
Wool/polymer adhesive force, wet, g	4.8 ± 1.5	6.9 ± 1.1	8.5 ± 1.5
Peel force from polyethylene, g ^c	15 ± 3	4 ± 1	6 ± 1

^a Films ($h = 0.02$ cm) cured 15 min at 150°C, conditioned 14 days at 65% RH, 21°C before testing at 250%/min.

^b Wet-state measurements were of films swollen in water.

^c Composite cured 30 min at 100°C, peeled at 2.5 cm/min.

^d Mooney-Rivlin plot nonlinear for all λ^{-1} .

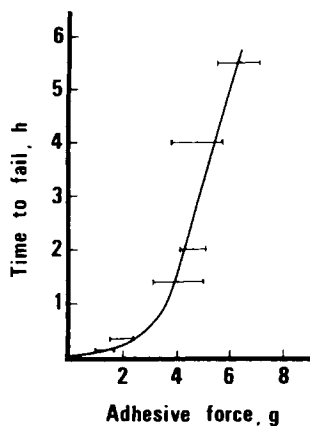


Fig. 6. Relationship between time to fail during washing (polymer sre) and wool/polymer adhesion for a series of polyester-urethane ionomers.¹⁰

hysteresis at low stresses (Fig. 4) and wool/polymer adhesion (Fig. 5); e.g., 100% Synthappret BAP films had the lowest hysteresis at a particular stress but the best sre and wool/polymer adhesion.

Several factors may complicate the wool/polymer system compared with the polyethylene/polymer system. The volume swelling behavior of interfiber bonds in water was almost identical to that of the polymer films. Therefore, polymers cured on wool should have similar mechanical properties to those cured on polyethylene. However, the surface component of wool/polymer adhesion may not be constant, in contrast to the polyethylene/polymer system. Prepolymers containing reactive end groups, e.g., isocyanate or blocked isocyanate groups, in general have better sre than unreactive prepolymers, and it has been proposed that wool/polymer adhesion is increased via covalent and/or ionic reactions between reactive groups at or near the wool surface and reactive groups in the prepolymer.^{23,24} Scanning electron microscope studies²⁵ of wool treated with certain Synthappret BAP containing polymers show evidence for cohesive failure of the polymer during washing. Cohesive failure was not evident for unreactive polymers such as Acramin SLN.

Therefore, as the polymers in Table I contain different amounts of blocked isocyanate groups, direct correlation between wool/polymer adhesion and polymer hysteresis measured at low stresses would not be expected because the surface component of wool/polymer adhesion is probably not constant. For those polymers which fail cohesively during washing, hysteresis on polymer films should be measured just before rupture; but for those polymers which fail adhesively, hysteresis should be measured at low stresses. To simplify the wool/polymer system, two series of different polymers (Tables II and III) were used such that the mechanical properties varied but the surface component of wool/polymer adhesion should remain constant. In the first series, three polymers, each containing equal proportions of Synthappret BAP, were used (Table II). Peeled from polyethylene in the dry state, the observed order of peel strengths was identical with the observed order of hysteresis of the polymer films measured at stresses below 0.5 N/mm² (Table II and Fig. 7).

The relative order of polymer sre followed the same relative order of fiber/

TABLE III
Properties of Films from Polyester-Urethane Ionomer Dispersions with Equal Isocyanate Contents

Sample ^a	$\sigma_{100}^{\text{wet}}$, N/mm ²	Polymer sre, h	Polymer hysteresis, 10 ⁻³ J/mm ³ ^b
15	0.76	2	0.20
18	1.09	4	0.30
19	0.83	2	0.22
20	1.44	6	0.38
22	1.12	2	0.23

^a Details of sample composition from Ref. 10.

^b Measured at 100% elongation at an effective rate of extension of 250%/min.

polymer adhesion in the wet state (Table II). SEM studies were consistent with the suggestion that failure at the wool/polymer interface was predominantly cohesive in the polymer, implying that polymer hysteresis should be measured just below the breaking stress of each film in the wet state. Correlation between polymer hysteresis measured just before rupture (Fig. 7, broken curves) and either polymer sre or fiber/polymer adhesion was excellent ($r_{xy} = 0.99$ and 0.89 , respectively).

The second series of polymers consisted of isocyanate-terminated polyester-urethane dispersions which formed films with different mechanical properties (Table III).^{10,13} Previous estimates of the surface component of wool/polymer adhesion were consistent with the suggestion that prepolymers containing free

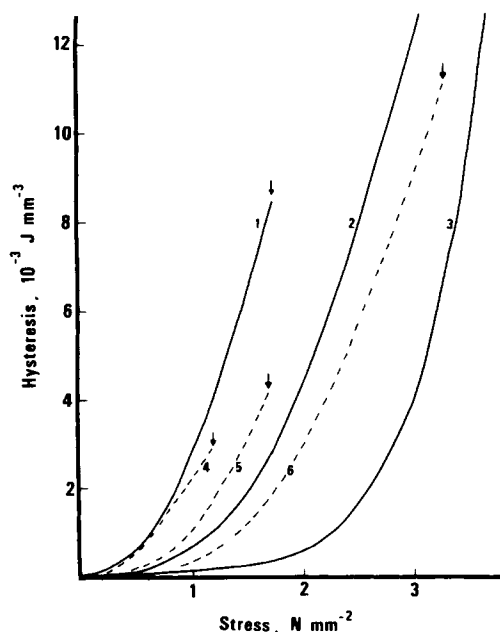


Fig. 7. Measured hysteresis as a function of stress for films from polymers listed in Table II. Rate of extension = 250%/min. Solid curves, dry state: 1 = BAP:SLN; 2 = BAP:DLN; 3 = BAP:DLH. Broken curves, wet state: 4 = BAP:SLN; 5 = BAP:DLN; 6 = BAP:DLH. Arrows signify failure stress.

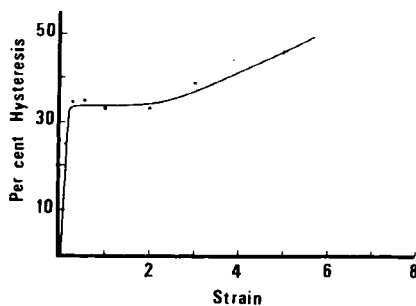


Fig. 8. Percent hysteresis of films from polyester-urethane dispersions as a function of strain. Solid-line = average for all polymers in Table III. Data points are for one polymer film (B20) only.

isocyanate groups had a higher surface component than those without.¹⁰ Evidence of some cohesive failure of the polymers was obtained from SEM studies. Therefore, polymer hysteresis should be measured just before the point of rupture of each film. However, for those films with high elongations to break (ca. 1000%), hysteresis measurements in the wet state were difficult, and an alternative procedure was adopted. The hysteresis of swollen polymer films was measured as a function of strain up to the maximum experimentally convenient strain (500–600%). The percent hysteresis H , which is the ratio of the area of the hysteresis loop to the total area under the stress-strain curve, was identical for each polymer (Fig. 8). Therefore, at any extension, absolute values of hysteresis should follow the values of stress for each polymer. For example, a good linear correlation ($r_{xy} = 0.96$) was found between $\sigma_{100}^{\text{wet}}$ and hysteresis measured at 100% elongation (Table III). Provided the relationship in Figure 8 holds up to the elongation to break, which was approximately constant for these polymers in the dry state ($660 \pm 80 \leq \epsilon_b \% \leq 830 \pm 130$), we would expect wool/polymer adhesion and polymer stress to follow stress, as was reported previously¹⁰ These results are therefore also consistent with the energy criterion for adhesive failure in the wool/polymer system.

CONCLUSIONS

The adhesion between polyethylene, a low-energy substrate, and several viscoelastic polymers has been investigated as a model for wool/polymer adhesion. Large differences in peel forces between the polymers, especially at high peel rates, could be attributed to differences in energy dissipation at the interface within each polymer.

The observed order of peel force at a particular rate could be qualitatively predicted from the order of polymer hysteresis measured during stress-strain cycling at the same effective rate. Calculated values of energy dissipated at the interface agreed with the hysteresis values measured at low stresses, as would be expected in systems with a low intrinsic bond strength.

In the wool/polymer system, the intrinsic bond strength will vary, depending on whether or not the polymer contains groups capable of reacting at or near the wool surface. A simple relationship between wool/polymer adhesion and polymer hysteresis would only be expected for a series of polymers having the same intrinsic bond strengths.

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