

Peel Adhesion. I. Some Phenomenological Aspects of the Test*

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In the peel test the results strongly depend on some variables related to the test method such as the thickness of the substrate and of the adhesive, rate of testing, geometrical arrangement in the test, testing temperature, composition of the surrounding medium, and method of sample preparation. Generally, these variables will change the effective rheological properties of the substrate or the adhesive and may also influence the effective interfacial bond strength. The present study concentrates on the rate of testing and the thickness of the adhesive layer. The chosen testing arrangement is that where two flexible substrate films are peeled apart so that the plane of the unperturbed portion of the laminate is at a right angle to the plane in which the peeling force is applied. Some observations will also be presented concerning the effect of sample preparation. The effects of substrate thickness, testing temperature and the composition of the surrounding medium are not investigated experimentally and these variables are held constant.

The substrate film used is cellophane and the binders are acrylic polymers which are applied to the cellophane from aqueous dispersions. These materials were chosen for study because it was desired to learn more about the specific interaction between cellulose and polymers which are used in finishing or bonding of textiles.

In the present first part of this study it is shown how the peeling force varies with the peeling rate and the adhesive layer thickness. The nature of the variability of the steady-state force when all testing variables are held constant is also discussed. The following paper, referred to hereafter as Part II, contains a theoretical analysis of the dependence of the peeling force upon the thickness of the adhesive layer for the case where the force is rate independent. Suitable results of the present report will be discussed in terms of this theory in Part II.

EXPERIMENTAL

Materials

DuPont 600 P.T. uncoated cellophane of 40.5μ thickness was used as substrate. This film contains glycerol as a plasticizer but a few hours

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extraction with water did not cause measurable losses in bulk weight. At an elongation rate of 12.5%/min. this film has an initial modulus of about 10^{10} dyne/cm², its ultimate strength is about 4×10^8 dyne/cm², and it breaks at about 50% extension.

The binders were dispersions of acrylate copolymers prepared by emulsion polymerization. Rhoplex* HA-8 is an aqueous latex of pH 3. The main constituent of this polymer is a relatively nonpolar acrylic ester. It also contains a small percentage of polar monomers which have groups on them that are capable of crosslinking the polymer when subjected to heat under dry acidic conditions. It is assumed that at room temperature this crosslinking reaction does not take place to a significant extent; i.e., when the latex is dried at room temperature, the polymer film obtained is essentially not crosslinked. Crosslinking only takes place during high temperature annealing. Annealed unsupported Rhoplex HA-8 films have a glass transition temperature below 0°C. At 40 to 4000%/min. testing rate their initial modulus varies between 1.85 and 5.5×10^6 dyne/cm², their ultimate strength is 5 to 19×10^6 dyne/cm², and they break at 550 to 680% extension.

Rhoplex B-60 is an acrylic polymer containing a small amount of carboxyl groups. When a dispersion of this polymer is dried at a temperature above 9°C., a continuous film is formed. Free films prepared from this latex have an initial modulus of 1 to 1.7×10^7 dyne/cm², ultimate stress of 3.2 to 8.6×10^7 dyne/cm², and a breaking elongation of 780 to 1060% at 40 to 4000%/min. straining rates.

Polymer 305-A is a soapless copolymer emulsion of 99% ethyl acrylate and 1% acrylic acid. The glass transition temperature of the free films is below 0°C. and their initial modulus ranges from 6 to 8×10^6 dyne/cm². At 4000% extension rate the films break at 1880% elongation and at 10^7 dyne/cm² stress. At lower testing rates the films exhibit cold flow without rupturing.

Peel Adhesion Tests

Cellophane strips about 6 in. wide and 8 in. long were used. Each end of the strips was clamped between a pair of glass rods by rubber bands. The purpose of the glass rods was to inhibit excessive wrinkling in the cellophane. The strips were dipped in the polymer dispersion and then hung to dry at room temperature. As long as the emulsion concentration did not exceed 30%, the thickness of the coating near the bottom of the strip was the same as that near the top. The thickness of the coating was varied by changing the emulsion concentration. To give a few examples, some emulsion concentrations and corresponding adhesive layer thicknesses are: 1% 0.2 μ , 7%, 2 μ ; 20%, 10 μ ; 25%, 30 μ ; 30%, 60 μ ; and 46%, 260 μ .

Two dried coated sheets were pressed together by hand between two 1-mil thick Teflon films in a way that wrinkle formation was kept to mini-

* Rhoplex is a trade mark of the Rohm and Haas Co.

mum. The sandwich with the Teflon was placed between two smooth 5×5 in. aluminum plates of $\frac{1}{16}$ in. thickness, and the whole assembly was placed into a steam-heated Carver press at 140°C . The load was adjusted to 2000 lb. and maintained for 3 min. while the temperature rose to about 150°C . Subsequently water was allowed to circulate in the press to cool it to about 50°C . in 1.5 to 2 min., and then the sample was removed. The Teflon films were stripped off and the sample was cut into 1 in. wide strips and conditioned at 65% R.H. and 21°C . for at least 24 hr. prior to testing. It should be noted that this procedure led to complete annealing with Rhoplex HA-8 and Polymer 305-A since a control experiment showed that increasing the annealing pressure to 8000 lb., the annealing temperature to 160°C ., and the annealing time to 20 min. did not change the peeling force.

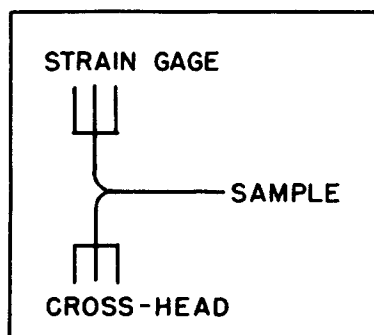


Fig. 1. Testing arrangement in determining peel adhesion.

The conditioned samples were clamped in the jaws of the Instron tester, as shown in Figure 1, and peeled apart at cross-head speeds ranging from 0.02 to 20 in./min. When the steady state force was reached, as indicated by a lack in long-range upward or downward trend in the peeling force, the recording chart and the integrator were started. When possible, the mean peeling force was established from the integrator reading. The number of replicate runs depended on the variability of the results. At very low adhesive thicknesses, in the 0.2 to 2μ range, as many as eight 4-in. strips were peeled apart at a given rate. At higher adhesive interlayer thicknesses four 1-min. integrator readings were taken on at least two different samples and at different positions on each sample.

At this point it may be mentioned that Bikerman¹ observed significant variation in the ratio between peeling force and sample width as the width was increased, and he attributed it to edge effects. To check this, some experiments were run with samples having 0.5 to 1 in. width but the force/width ratio was found to be constant.

Differentiation Between Cohesive and Adhesive Failure

Following McLaren's² procedure, the peeled samples were immersed in an aqueous 2% Rhodamine B solution for about 1 min., rinsed with cold water, and then inspected. This basic red dye affects only the cellophane and not the acrylate polymer.

When the failure was adhesive, i.e., between the binder and the cellophane, the cellophane surface was bared and the sample picked up dye with the result that an interlocking pattern of dyed and undyed areas was obtained along any given width of the two halves of the sandwich. After cohesive failure, when the sample failed within the binder layer, the sample could not be dyed. This distinction between cohesive and adhesive failure was normally unequivocal. In some instances only small portions of the samples could be dyed and no completely interlocking pattern of dyed and undyed areas were obtained. When this happened, adhesive and cohesive failure occurred simultaneously, and this is designated as mixed failure.

Determination of the Thickness of the Adhesive Layer

This thickness was determined from the g./cm.² surface coverage on some dried but not annealed cellophane sheets which were coated in the same manner as the films for adhesion tests. The most convenient method was to cut out a sample of known area from the center of the sheet and immerse it for 1 hr. in an aqueous 1% dispersion of Celathrene Red 3 BN, a dyestuff which dyes the polyacrylate but not the cellophane. The sample was transferred into distilled water and the colored polyacrylate was rubbed off with fingers, collected, dried, and weighed. The purpose of dyeing the polyacrylate was to make it visible so that no film particles were lost in the processing. From the color of dyed films it was estimated that the dye was absorbed by the film to an extent not higher than 4% based on film weight. The wet polyacrylate films had very poor adhesion to the cellophane and could be easily rubbed off. From the g./cm.² surface coverage the thickness was determined by assuming that the polyacrylates had a density of 1.3. Actually, their density is probably in the 1.2 range, but 1.3 density gave the best agreement between the thickness values obtained by this method and by the method of determining the thickness of relatively thick films directly by micrometer caliper.

Stress-Strain Properties of Unsupported Acrylate Films

These properties were cited above. For determining them the polymers were cast on mercury and dried at room temperature. The film was removed from the mercury, placed between Teflon sheets and annealed in the Carver press in the same way as the adhesion test samples. The films were about 20 μ thick after the Teflon was stripped off. One inch wide samples of these films were tested in the Instron tester at 0.5 in. gage length.

VARIABILITY OF THE PEELING FORCE IN A SINGLE TEST

Randomly Oscillating Force

Figure 2 gives a typical variation in the steady-state force as a sample with Rhoplex HA-8 binder is peeled. To determine the variability of this force, the Instron chart was divided into intervals corresponding to 5 g. increments in force and the sum of length fractions which gave force values lying within each interval was divided by the total length tested, to find the % length which gave the force assigned to the center of the chosen interval.

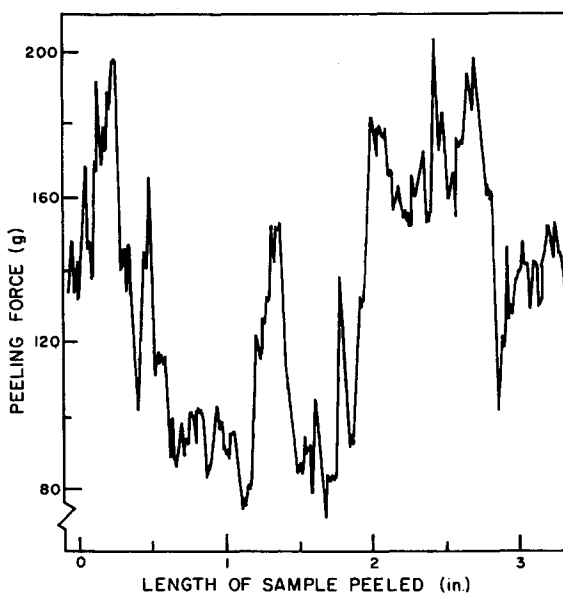


Fig. 2. Copy of an Instron chart segment obtained when a 1-in. wide sample with 0.45μ Rhoplex HA-8 layer thickness was peeled at a cross-head speed of 5 in./min. The variability of the peeling force was much less when the adhesive layer thickness was increased.

The data were plotted on probability paper and could be represented by a straight line as shown in Figure 3. This indicates that the force values recorded on the Instron chart were randomly distributed. The standard deviation of any point on the Instron chart was calculated as being half of the difference between the force values corresponding to 16 and 84% in the cumulative distribution. This standard deviation is of course higher than the standard deviation that would be associated with the mean force value. The mean force value, as determined from the integrator reading, was within 3% of the median force value determined from the probability plot. Such determinations were carried out at a number of adhesive layer thicknesses. It was found that at low adhesive layer thicknesses standard deviation was 30 to 50% of the mean force value while at very high thick-

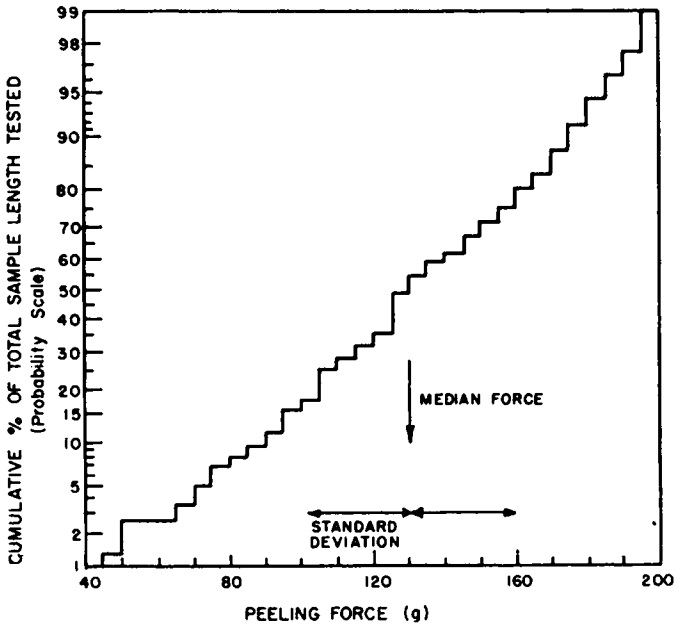


Fig. 3. Probability plot of force distribution for 1 in. wide samples with 0.45μ Rhoplex HA-8 layer thickness. Eight samples 3 to 4 in. long were tested and the data were pooled. The cross-head speed was 5 in./min.

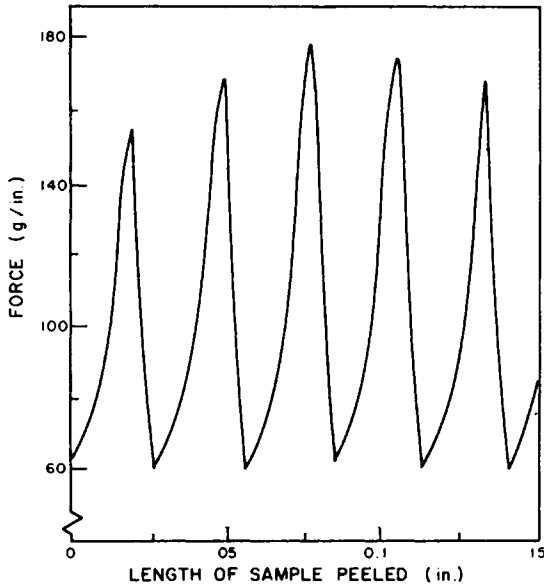


Fig. 4. Copy of an Instron chart showing typical nonrandomly oscillating steady-state force. Cross-head speed: 1 in./min. Binder: Rhoplex B-60. Thickness: 24μ . After the samples were impregnated with the emulsion, they were entered wet into a 150°C . oven and dried for 5 min. Subsequently they were laminated in the Carver Press at 270 psi and $150\text{--}160^{\circ}\text{C}$. for 20 min.

nesses it was only 7 to 10%. The reason for the lower variability of the force when the adhesive layer is thick will be given in Part II. At present it should suffice to say that this type of variability is probably due to the nonuniformity of the samples. It is noteworthy that the results obtained with Polymer 305-A gave the same type of randomly oscillating pattern.

It follows from this analysis that in this type of variation the steady-state peeling force follows Gaussian statistics and its mean value, determined with the integrator, is a well-defined quantity.

Nonrandomly Oscillating Force

Another type of variability in the force value is shown in Figure 4 and is characteristic of the Rhoplex B-60 binder. In this type of failure the oscillation in the force is nonrandom, the minima and maxima are well defined and are subject to only very little variation for a given sample at a given testing rate. The distance between two adjacent maxima or minima, the wavelength of the oscillation, is a well-defined quantity which, surprisingly, does not change with the rate of testing although the values of the maxima and minima generally decrease with increasing rate. This type of behavior is quite different from the randomly oscillating force and is in most instances clearly distinguishable from it.

Visual observations indicated that the force increased as the radius of curvature of the cellophane at the peeling edge decreased until a point was reached where failure in the glue line is initiated. The failure apparently propagated spontaneously faster than the rate of peeling. In this interval the radius of curvature of the cellophane increased and the force decreased. When a certain minimum in the force value was reached, the failure ceased to propagate and the cycle was started anew. In this case the oscillations appear to be inherent in the binder-substrate system and are not due to the nonuniformity of the sample.

DEPENDENCE OF THE MEAN PEELING FORCE UPON RATE OF TESTING AND UPON THE ADHESIVE INTERLAYER THICKNESS AT CONTINUOUS FAILURE INITIATION

Figure 5 shows that when samples of the same Rhoplex HA-8 interlayer thickness are tested, the force increases roughly linearly with the log of the testing rate at low rates and the failure is cohesive. At high rates of testing, the force is independent of the rate and the failure is adhesive. It can be seen that at any given rate of testing the force increases with the Rhoplex HA-8 interlayer thickness. The critical rate, where cohesive failure is replaced by adhesive failure, increases with the thickness of the Rhoplex HA-8 interlayer, and at very high thicknesses it was not possible to observe adhesive failure within the experimental range of testing rates. Polymer 305-A gave a similar pattern of results with lower force values at a given rate and thickness.

The fact that the peeling force increases with the rate of testing has been

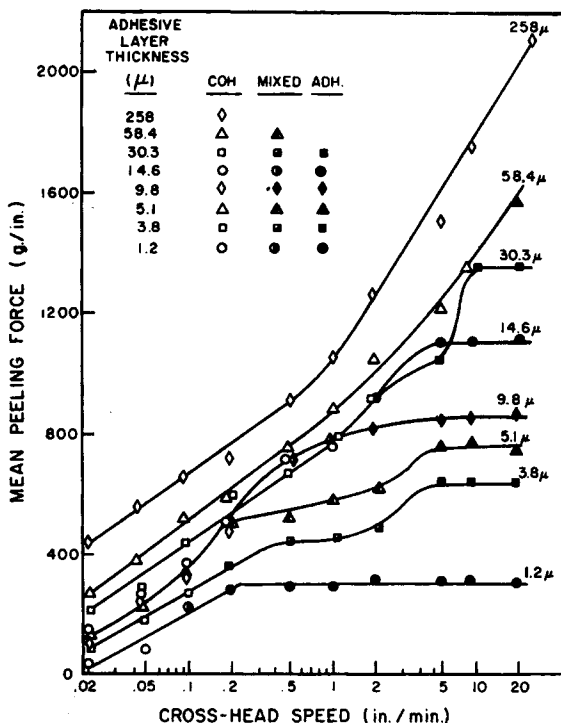


Fig. 5. Dependence of peeling force upon rate of testing at different Rhoplex HA-8 layer thicknesses. The force values are mean values obtained from integrator readings. Cellophane thickness is 40.5μ .

noted by other authors.³⁻¹² Levelling off of the force at high rates of peeling was observed by Rivlin,¹³ and according to Deryagin's results¹⁴ the force was rate independent at very high and very low rates, while at intermediate rates it increased with the testing rate. No indication could be found in the literature concerning the change in failure pattern from cohesive to adhesive as the testing rate was increased.

The rate dependence of the results can be intuitively explained as follows. The rate of strain in the deformation of the adhesive interlayer is necessarily increased as the rate of peeling is increased. The ultimate strength of polymers above their glass transition temperature is known to increase with the rate of testing¹⁵⁻¹⁷ and, in fact, the results of Part II show that this happens in the case of Rhoplex HA-8 and Polymer 305-A. For cohesive failure we can equate the maximum stress at the point where failure occurs in the peel test with the ultimate tensile strength of the binder and predict that the peeling force will increase with this maximum stress. With increasing rate of peeling, i.e., with increasing rate of deformation in the binder layer, the ultimate cohesive strength, the maximum stress, and the peeling force must increase until a point is reached where the cohesive strength of the binder surpasses the adhesive bond strength between the

binder and the substrate. If the adhesive bond strength is independent of the rate of testing, the peeling force should also be independent of the testing rate after this point is reached.

It may be noted that Deryagin^{14,18} has an alternate explanation for the rate dependence of the peeling force. This author believes that the electrical double layer at the binder-substrate interface is mostly responsible for the bond strength at high rates of peeling. This is not so at low rates of peeling because there is enough time available for the charges to dissipate without offering resistance to stripping. This theory does not explain why there is a change-over from cohesive to adhesive failure in the case of some polymeric binders.

Published experimental data concerning the dependence of the force on the adhesive layer thickness are scant^{1,4,19} and are in agreement with the present results in that the force was shown to increase with the interlayer thickness. The theory presented in Part II predicts that the peeling force should increase with the thickness of the binder even if the modulus of the binder and the maximum stress developed in the binder layer are independent of the straining rate. The main reason for this is that the peeling force must be equal to the sum of all stresses developed in the binder layer which are parallel and opposed to it. The maximum stress is only a fraction of all stresses and the sum of the stresses depends on the size of the area in the strip which is under stress. This area can be expected to increase with the thickness of the binder layer.

In this context it is of interest that, as pointed out for example by Deryagin¹⁸ and Rivlin,¹³ the peeling force F , measured as force/width, is proportional to the work needed for separation of a unit area in the test sample. To show this it may be convenient to define R , the rate of peeling in cm./min., as the length of sample peeled apart in unit time. In the present experimental set-up R is equal to half of the cross-head speed. The work done by the testing machine in unit time per unit sample width is $F \times 2R$ and the work per unit sample area is $(F \times 2R)/R = 2F$, i.e., twice the peeling force per unit width. It may be noted that this result is dimensionally correct since the unit dyne/cm. is equivalent to erg/cm.².

The work in peeling is expended not only on overcoming the bond energies and causing failure but also on deforming the substrate and the adhesive layer prior to failure. If the substrate is completely elastic, the work expended in deforming it is recovered and can be neglected. The work expended to deform the adhesive is irrecoverable and will increase with the volume of the binder per unit area, i.e., with the thickness of the binder layer. This picture again shows that the peeling force must increase with the thickness of the adhesive interlayer.

One would also expect that the peeling work per unit area should have about the same order of magnitude as the surface free energy of the binder when the failure is cohesive. The presently found cohesive failure forces are in the range of 0.2 to 5×10^5 dyne/cm., being several orders of magnitude higher than the surface free energy values that one would expect to

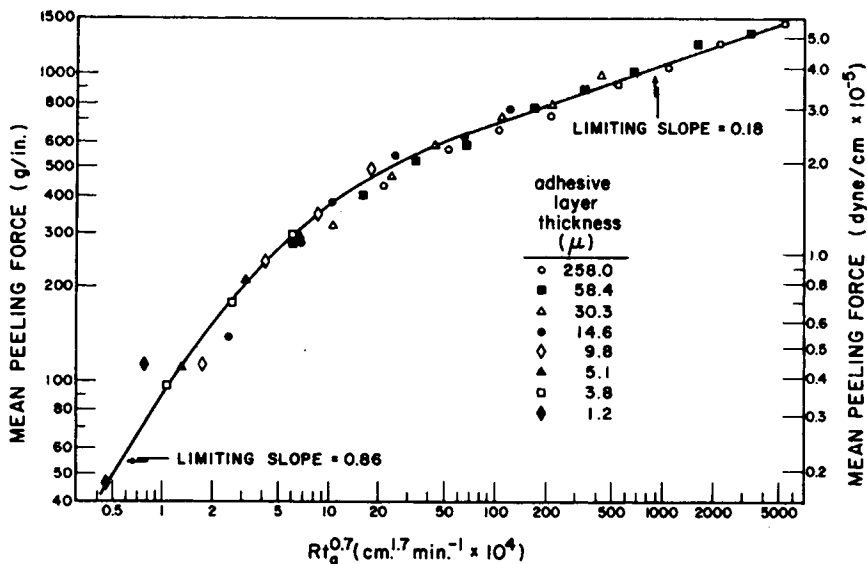


Fig. 6. Variation of the peeling force with $Rt_a^{0.7}$ when the failure is cohesive and the binder is Rhoplex HA-8. In the abscissa R is rate of peeling equal to half of the cross-head speed in cm/min. and t_a is the adhesive layer thickness in cm. The data are taken from Fig. 5.

obtain based on the chemical composition of these materials alone. However, Berry²⁰ points out that part of the work needed to create a new surface in polymers is expended on orienting the polymer molecules at the new surface when the new surface is created by a fracture process. He finds that poly(methyl methacrylate) has about 3×10^5 dyne/cm. surface energy which is of the same order of magnitude as the presently found values.

Quite obviously, theoretical analysis of the cohesive failure would be very complicated because of the rate dependent effects. Just to see whether the cohesive failure results obtained at different thicknesses were internally consistent, attempts were made to find a single empirical function which would fit all cohesive failure data obtained with Rhoplex HA-8 or Polymer 305-A. When the log of peeling rate (R) is plotted against the log of interlayer thickness (t_a) for the values which gave the same cohesive failure peeling force, straight lines were obtained, the slope being -0.7 for Rhoplex HA-8 and -0.5 for Polymer 305-A. It was concluded that the cohesive failure portions of curves like those presented in Figure 5 can be superimposed on a single master curve when F is plotted against Rt_a^n , where n is 0.7 for Rhoplex HA-8 and 0.5 for Polymer 305-A. Such plots are shown in Figure 6 and 7. The theoretical significance of these master curves and the reason for the difference in the power coefficients of Rhoplex HA-8 and Polymers 305-A is not known.

Since the results in adhesive failure are rate independent, their theoretical interpretation should be easier than that of the cohesive failure data. The log-log plots of adhesive failure force against interlayer thickness give

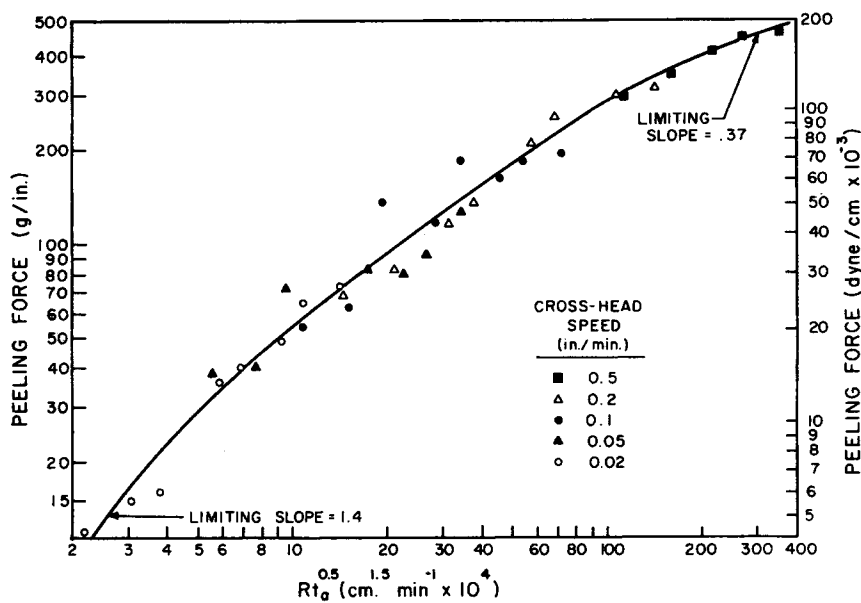


Fig. 7. Variation of the peeling force with $Rt_a^{0.5}$ when the failure is cohesive and the binder is Polymer 305-A. R is the length of sample peeled per minute, being half of the cross-head speed and t_a is the thickness of the adhesive layer.

curves concave towards the thickness axis with slope values varying between 0.90 and 0.25. Such curves obtained with Rhoplex HA-8 and Polymer 305-A will be presented and discussed in Part II.

The case was discussed above where the peeling force increased with the rate at low rates and the failure was cohesive, while at high rates the failure was adhesive and the force was rate independent. It should be pointed out that this is not the only type of observed rate dependence. For example, if the Rhoplex HA-8 latex was neutralized before applying it to cellophane, the crosslinking reaction during annealing was inhibited and a binder of characteristics different from those of acidic Rhoplex HA-8 was obtained. The peeling force at adhesive failure was rate dependent with this binder. Such behavior was also found with a number of experimental polymers. Another type of response to rate was found with an experimental polymer mixture which gave rate independent adhesive failure force at high and low rates and a minimum in the peeling force at intermediate rates. At the minimum the failure was mixed adhesive-cohesive. In all these instances the steady-state force in a single experiment was of the randomly oscillating type, and the force at a given rate increased with the adhesive layer thickness.

The presently available data are unsuited and insufficient to be able to draw a generally valid conclusion as to the required structural characteristics of the binder for giving a certain type of peel test pattern. In Part II it will be shown that the sufficient and necessary requirement for rate

independent failure is that the effective modulus of the binder and of the substrate and the maximum stress in the laminate, which is the adhesive bond strength at adhesive failure, should be independent of the effective rate of strain at the range of peeling rates where the peeling force is rate independent. If relatively short range secondary valence forces are responsible for the adhesive bond, rupturing would not be a viscous process and it is reasonable to expect the adhesive bond strength to be relatively insensitive to testing rates. However, the effective moduli, which in Part II are defined in terms of a Hookean model, are very sensitive to rate effects in viscoelastic bodies. Study of the relaxation time distributions of binder and substrate could possibly provide some clue as to pattern of peel failure.

Before closing the discussion of the randomly oscillating steady state peeling force, it may be of interest to mention the following experiment. A Polymer 305-A film was cast on mercury. The dry film was placed between two cellophane sheets and this assembly was cured in the Carver press. The laminate obtained had no measurable peel resistance. This result indicates that the method of film deposition has an important effect on adhesion. There is a good possibility that good bonding properties are furthered by forming films *in situ* on swollen cellophane, as was done in all other experiments.

EFFECT OF TESTING RATE AND METHOD OF SAMPLE PREPARATION UPON THE NONRANDOMLY OSCILLATING STEADY STATE FORCE

Rhoplex B-60 did not adhere at all to cellophane when the laminates were annealed at 67 p.s.i., 140–150°C., and 3 min., like the other two binders. However, annealing at 270 p.s.i. at 150–160°C. for 20 min. gave measurable peel resistance. In Figure 8 three laminates are compared which were annealed at this schedule. When the cellophane was coated and dried at room temperature prior to annealing, the force values were relatively low and randomly oscillating, and the values of maxima and minima decreased with increasing peeling rate. In the second experiment the cellophane was impregnated at room temperature, hung vertically to allow the excess emulsion to drip off, and then entered into the oven to be dried so that the continuous polymer film and the cellophane/polymer interface was formed at an elevated temperature. The thus coated films were subsequently laminated and gave considerably higher peel resistance than the first experiment. At low peeling rates the force increased with rate and was randomly oscillating. At high rates it was nonrandomly oscillating, and the maxima and minima decreased with increasing rate. In the third experiment the cellophane surface was roughened with sandpaper prior to coating it with polymer. The method of coating was the same as in the first experiment. The peeling force was, however, relatively high, randomly oscillating and relatively insensitive to peeling rate.

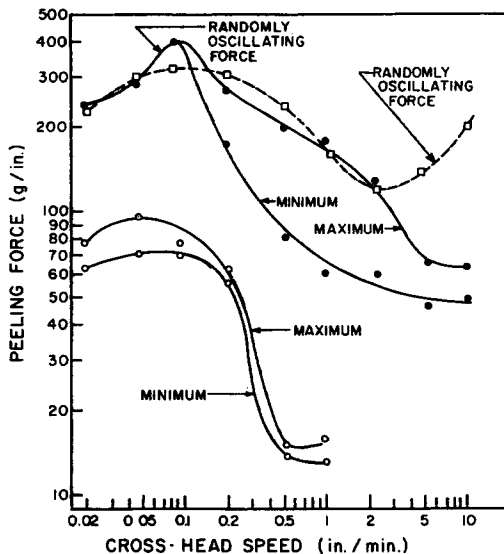


Fig. 8. Results obtained with Rhoplex B-60. (O) After impregnation the cellophane was dried at room temperature and laminated at 270 psi at 150–160°C. for 20 min. The force was nonrandomly oscillating and the failure was adhesive. Adhesive layer thickness: 24 μ . (●) After impregnation the wet cellophane was entered into a 100°C. oven for 5 min. to be dried. Subsequently lamination was carried out as above. The force was nonrandomly oscillating only at 0.2 in./min. or higher cross-head speeds. The failure was cohesive. Adhesive layer thickness: 24 μ . (□) Instead of 600 P.T. cellophane, denitrated nitrocellulose was used with its surface roughened with sandpaper prior to impregnation. Impregnation, drying, and lamination as with the first sample. Adhesive layer thickness: about 16 μ . The force was randomly oscillating at every cross-head speed and the nature of failure was uncertain.

In connection with the results obtained on sandpapered cellophane it should be mentioned that Voyutskii²¹ carried out similar experiments with cellophane and polyisobutylene. It is possible that in these experiments similar phenomena took place as in the Rhoplex B-60/cellophane system because the average peel force was higher and the variability of the results was lower when the polymer was applied to sandpapered cellophane. It is also of interest that Dannenberg²² occasionally observed smooth and other times jerky detachment of polymeric coatings from metals when adhesion was measured by the blister method. Similarly, Bailey²³ found that the cleavage of mica occasionally proceeded in a jerky fashion. The jerky detachment observed by these authors may be related to the phenomenon discussed here.

The present results are tentatively explained below. Although the minimum film formation temperature of Rhoplex B-60 is below room temperature, it is conceivable that the films formed at room temperature contain mechanical imperfections and are imperfectly bonded to cellophane. The imperfections or cracks are not completely eliminated by annealing during lamination although the results indicate that increasing the lami-

nating pressure, temperature, and time are beneficial in this respect. The results also indicate that when the coatings on the cellophane are prepared at an elevated temperature, the imperfections are less serious. When the laminated films are peeled apart, failure propagates along these imperfections, giving rise to the observed regular oscillation in the peeling force. No such oscillation is observed with sandpapered cellophane for two possible reasons. First, the elevations in the surface may provide barriers to failure propagation. Second, the effective area of the interface is greatly increased by sandpapering the cellophane with the result that better interfacial bonding is obtained and the relative importance of the imperfections is reduced. The shortcoming of this explanation is that it does not take into account the observed constancy of the wavelength of the oscillation.

An alternative explanation is not based on imperfections but on the difference of the shear and tensile strength. At the maximum of the oscillations the cellophane radius of curvature is so low that the maximum stress in the glue line runs parallel to the cellophane stressed between the jaws of the tester. This shear stress can be distributed over a relatively wide area along the cellophane surface before failure starts and for this reason the peeling force is relatively high. As the failure propagates, the shear stresses at the edge are replaced by tensile stresses. At the minimum only tensile stresses oppose the peeling force. From here on there is no failure in the glue line and the work of the tester is used to reduce the radius of curvature of cellophane and to change the stress pattern in the glue line, till at the maximum of the peeling force the cycle starts anew. Thus the constant wavelength observed is characteristic of the cellophane and corresponds to the path difference between maximum and minimum curvature. By roughening the cellophane surface this effect is eliminated because the shear stress distribution is narrowed and thus the order of magnitude of the shear force approaches that of the tensile force. This explanation, however, does not explain how we can sometimes get cohesive and under somewhat different conditions adhesive failure, as shown in Figure 8, since it is unlikely that there should be the same type of difference between cohesive and adhesive shear and tensile strength.

It may be mentioned that the effect of adhesive layer thickness on the nonrandomly oscillating force has not yet been investigated and that there are no clues yet available as to type of binder properties that are required to obtain periodic instead of continuous failure initiation in the glue line.

CONCLUSIONS

In evaluating peel test data the variability of the force in a single test and the dependence of the force upon testing rate and adhesive layer thickness are important factors to be considered. The behavior where the failure in the glue line is periodically initiated giving a nonrandomly oscillating force is not well understood at present. The case where the steady-state peeling force is randomly oscillating and increases with interlayer thickness and

with rate can be qualitatively explained. A quantitative theoretical relationship, presented in Part II of this study, can be fitted to the data where the steady-state force is randomly oscillating, and its mean value is rate independent and increases with the thickness of the adhesive layer.

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Synopsis

Cellophane sheets were coated with acrylic latex polymers, pressed together in pairs at elevated temperature, and peeled apart at constant relative humidity and temperature. The effect of the rate of peeling and the adhesive layer thickness upon the peeling force was investigated. When a laminate is peeled, the steady-state peeling force is generally not constant, but the frequency distribution of the instantaneously measured steady state force values is Gaussian. The mean value of the force is well defined and is equal to the median force. This type of variability is probably due to sample nonuniformity. The second type of variability in the steady-state peeling force is inherent in the binder/substrate system. Here failure in the glue line is not initiated continuously but periodically, and the failure propagates faster than the rate of peeling. Consequently the steady-state peeling force passes through well-defined maxima and minima. It was also observed that the distance between two adjacent maxima or minima was constant and insensitive to the testing rate. When the force is randomly oscillating, the mean force generally either increases with the rate of testing or is insensitive to it. It always increases with the thickness of the adhesive layer. A special case was extensively investi-

gated where at low rates there was cohesive failure and the peeling force increased with the testing rate, while at high rates the force was rate independent and produced adhesive failure. The cohesive failure force could be represented by a single master curve when the force was plotted against Rt_a^n , where R is the peeling rate, t_a is the thickness of the adhesive layer, and the exponent n is a constant characteristic of the system. When the binder/substrate system gives a steady-state force with well-defined periodicity, the maxima and minima in the force generally decrease with increasing testing rate. The periodicity of the steady-state force can be eliminated by having a rough instead of smooth binder/substrate interface.

Résumé

Des feuilles de cellophane sont enduites de latex acryliques, pressées par paires à température élevée, et séparées à nouveau à température et humidité relative constantes. L'effet de la vitesse de détachement et de l'épaisseur de la couche d'adhésif sur la force de détachement est étudié. Quand un produit laminé est détaché, la force stationnaire de détachement n'est généralement pas constante, mais la fréquence de distribution de la force stationnaire mesurée instantanément est gaussienne. La valeur moyenne de la force est bien définie et est égale à la force médiane. Ce type de variabilité est probablement dû au manque d'uniformité de l'échantillon. La seconde variable dans la force stationnaire de détachement est inhérente au système colle/substrat. Ici la faille dans la ligne d'encollage n'est pas initiée d'une manière continue mais périodique et la faille se propage plus rapidement que la vitesse de détachement. Par conséquent la force stationnaire de détachement passe par des maxima et minima bien définis. On a observé également que la distance entre deux maxima ou minima adjacents était constante et insensible à la vitesse de l'essai. Quand la force oscille au hasard, la force moyenne s'accroît généralement avec la vitesse de l'essai ou est insensible à celle-ci. Elle s'accroît toujours avec l'épaisseur de la couche d'adhésif. Un cas spécial a été étudié en détail; quand à faibles vitesses il y avait une lacune de cohésion, la force de détachement croissait avec la vitesse de l'essai, tandis qu'à grandes vitesses la force était indépendante de la vitesse et produisait une lacune de l'adhésif. La force de cohésion d'une fêlure peut être représentée par une seule courbe maîtresse, où la force est portée en diagramme en fonction de RT_a^n , où R est la vitesse de détachement, t_a l'épaisseur de la couche de l'adhésif et l'exposant n une constante caractéristique du système. Quand le système liant/substrat donne une force stationnaire à périodicité bien définie, les maxima et les minima de la force décroissent généralement avec l'accroissement de la vitesse de l'essai. La périodicité de la force stationnaire peut être éliminée en utilisant une interface rugueuse et non lisse dans le système liant/substrat.

Zusammenfassung

Cellophanblätter wurden mit Acrylpolymer-Latex überzogen, bei erhöhter Temperatur paarweise zusammengedrückt und bei konstanter relativer Feuchtigkeit und Temperatur von einander abgezogen. Der Einfluss der Abziehgeschwindigkeit und der Dicke der Klebeschichte auf die Abziehkraft wurde untersucht. Beim Abziehen einer Verleimung ist die Abziehkraft im stationären Zustand im allgemeinen nicht konstant, sondern es besteht eine Gauss-Verteilung der Häufigkeit der Momentanwerte der Kraft im stationären Zustand. Der Mittelwert der Kraft ist gut definiert und ist der in der Mitte vorhandenen Kraft gleich. Diese Form der Abhängigkeit ist wahrscheinlich durch die Uneinheitlichkeit der Probe bedingt. Die zweite Art der Abhängigkeit der Abziehkraft im stationären Zustand ist für das Binder-Substratsystem typisch. Hier wird der Bruch in der Verleimungslinie nicht kontinuierlich sondern periodisch erzeugt und der Bruch pflanzt sich rascher fort als der Abziehgeschwindigkeit entspricht. Infolgedessen geht die stationäre Abziehkraft durch gut definierte Maxima und Minima. Weiters wurde gefunden, dass der Abstand zwischen zwei benachbarten Maxima oder Minima konstant und von der Testgeschwindigkeit unabhängig war. Bei statistischem Oszillieren der

Kraft nimmt die mittlere Kraft im allgemeinen entweder mit der Testgeschwindigkeit zu oder bleibt unabhängig davon. Sie nimmt mit der Dicke der Klebeschichte immer zu. Ein spezieller Fall, bei dem bei niedriger Geschwindigkeit Kohäsionsbruch eintrat und die Abziehkraft mit der Testgeschwindigkeit zunahm, während bei hoher Geschwindigkeit die Kraft geschwindigkeitsunabhängig war und Adhäsionsbruch erzeugt, wurde eingehend untersucht. Bei Auftragen der Kraft gegen Rt_a^n , wo R die Abziehgeschwindigkeit, t_a die Dicke der Klebeschichte und der Exponent n eine für das System charakteristische Konstante ist, konnte die Kohäsionsbruchkraft durch eine einzige, gemeinsame Kurve dargestellt werden. Wenn das Binder-Substratsystem eine stationäre Kraft mit gut definierter Periodizität liefert, nehmen die Maxima und Minima der Kraft im allgemeinen mit steigender Testgeschwindigkeit ab. Die Periodizität der stationären Kraft kann durch Anwendung einer rauhen Binder-Substratgrenzfläche an Stelle einer glatten beseitigt werden.

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