

PEEL-APART DEVELOPMENT IN PHOTOPOLYMER IMAGING SYSTEMS

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ABSTRACT

DuPont pioneered the technology of dry processed, peel-apart development in photopolymer imaging films in the 1960's with the introduction of Crolux®, a black architectural drafting film. Since then, several other graphic arts and electronic products; notably, negative Cromalin® and Cromacheck®, have emerged from development using peel-apart technology, in which distinct, inherent advantages over wet processed systems have steadily gained customer interest.

Peel apart processing is simple, fast and dry requiring no wet processing chemicals, no expensive investment in processing equipment and no costs associated with spent developer disposal. A peel apart film requires a minimum of 3 layers for operation; a peelable coversheet (usually a PET film), an image forming photopolymer layer and a supportive bottom layer. The peel development, following an imagewise exposure to actinic radiation, creates positive or negative readouts, depending upon adhesional and rheological changes taking place in the photopolymer layer as a result of the photochemical reactions.

Considerable effort has been expended in understanding the peel-apart mechanism by using negative imaging films. A viscoelastic model, showing the postulated mechanism, will be presented for the peel-apart image development based upon:

- o quantitatively measuring the peel force while varying physical-mechanical factors; such as peel rate, peel angle, peel temperature and coversheet thickness,

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- o correlating the observed peel force to the effective adhesive strength using fundamental concepts in rheology and adhesion, and
- o considering other factors affecting image resolution in terms of the effective adhesive strength.

Examples, depicting both the positive and negative modes of peel separation relying upon structural and compositional changes, will be discussed.

FUNDAMENTAL

In actual polymeric systems, the mode of failure at peel separation is usually heterogeneous, i.e., mixtures of intermolecular failures (weak bonds such as van der Waals forces, hydrogen bonds, London dispersion forces) and chemical bond failures. If these energies are only important energy factors involved at the peel separation, then the required peel force (energy) would be approximately in the same order of magnitude as the sum of these energies. However, the actual measured peel force (energy) usually greatly exceeds the total energy of the failed chemical bonds often by several orders of magnitude (Gent, 1977). The failure pattern usually occurs irrespective of their chemical bond strengths. This suggests that energy factors other than the chemical bonds dominate the failure strength. The dominating factors originate from the viscoelastic nature of the polymer systems. Bending, stretching, or compression involved in the peel operation causes a rheological deformation of the adjoining members. Deformation of a non-elastic system always accompanies irreversible energy loss via heat due to viscoelastic hysteresis, whose magnitude strongly depends on the degree of deformation. Since such energy loss must be provided externally, the required peel force is expected to strongly depend upon the various physical-mechanical factors that affect the degree of deformation. Such factors are: peel rate, peel angle, temperature during peel, and the physical thicknesses of the coversheets. These factors, however, lead to the same rheological result, because they are interrelated by the time-temperature superposition principle (Ferry, 1980). The results obtained by varying one factor; for instance, peel rate, can be duplicated by varying another, for instance, peel temperature.

The most simple peel-apart film, shown in Figure 1A, has a 3-layer structure: a peelable coversheet, an image forming photopolymer layer, and a bottom support layer. Basically, three force components are involved in such a peel-apart system. They are the adhesive strength at the coversheet/photopolymer interface, the adhesive strength at the photopolymer/support interface, and the shear cohesive strength of the photopolymer layer, denoted respectively by A_1 , A_2 , and C_s . If the film is exposed to actinic radiation, A_1 , A_2 and C_s undergo changes because of the photochemical reactions that take place within the photopolymer layer. When conditions are met (as discussed later in this paper), two opposite modes of separation (shown in Figures 1B and 1C) are possible when peeled after an imagewise exposure.

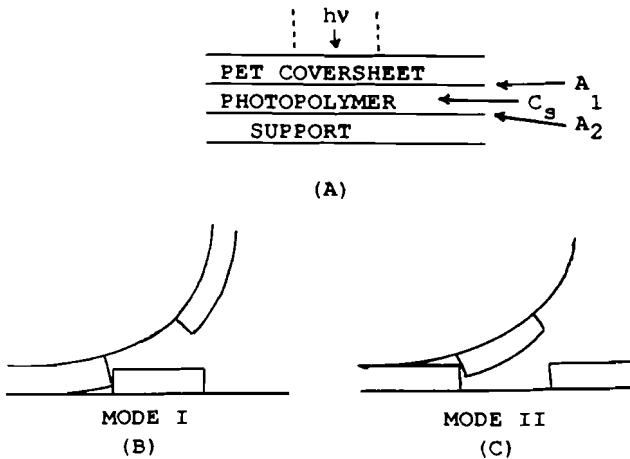


FIGURE 1. (A) Film Structure and two peel modes

In the imaging applications, the term "positive film" or "negative film" is used depending on whether the images on the substrate that is selected by the user are positive or negative with respect to the target images used for the imaging exposure. In a simple and qualitative manner, the condition for image separation can be expressed in terms of A_1 , A_2 and C_s . Since image separation requires a cohesive breakage of the photopolymer layer by the shear stress generated by peeling, the adhesion difference between A_1 and A_2 must exceed the C_s that is associated with an image area to be separated from its surroundings. If the image area is a circular shape, then C_s is the force required to break the wall area generated by the circumference of the image dot and the thickness of the photopolymer layer. Qualitative

conditions for Mode I (Figure 1B) and Mode II (Figure 1C) separations are shown in terms of A_1 , A_2 and C_s as follows:

	<u>UNEXPOSED AREA</u>	<u>EXPOSED AREA</u>
PEEL MODE I	$(A_1 - A_2) > C_s$	$(A_2 - A_1) > C_s$
PEEL MODE II	$(A_2 - A_1) > C_s$	$(A_1 - A_2) > C_s$

In half-tone imaging, the image resolution is usually judged by the smallest dot held in the highlight side of the developed image and by the smallest hole in the shadow side. The shape of the dot or hole can vary depending upon the manufacturing technique used for to make the targets. Many dot shapes are circular or cylindrical. Irrespective of the dot shape, as the dot or hole size decreases, the wall area (which determines the nature of the cohesive failure) becomes increasingly significant. In addition, the thickness of the photopolymer layer is the primary factor contributing to the cohesive strength and its magnitude is most significant compared to the image size. Therefore, as the dot or the hole size decreases, the above inequalities required for the image separation no longer hold and the resolution reaches the limit. A way of enhancing the resolution in peel-apart systems is to increase the adhesion difference between A_1 and A_2 or to reduce the cohesive strength, C_s , or by a combination of both techniques. A detail analysis can be found elsewhere (Choi, 1989).

The strength of the above force components is a strong function of the extrinsic physical-mechanical factors associated with peeling. As such, the image characteristics of the system can vary widely, depending upon these factors. The behavior of each force component can be studied as a function of the extrinsic factors and the results can be used to design a peel-apart system that works in either mode by simply controlling one factor. However, such versatility can limit the product latitude in the peel-apart process-of-use. If the peel behavior of a film is determined as a function of peel rate (the most important control factor in a peel apart system) then the effect of other factors; such as, peel angle, peel temperature, and layer thickness can be deduced because their effects are rheologically related to one another.

EFFECT OF PEEL RATE ON PEEL BEHAVIOR

EXAMPLE I - A SYMMETRICAL SYSTEM

A simple peel-apart system with a symmetrical structure illustrates how the peel adhesion can change under varying peel rate. Such a system is shown in Figure 2A where a polymeric layer is sandwiched between two identical PET films. For the convenience of discussion,

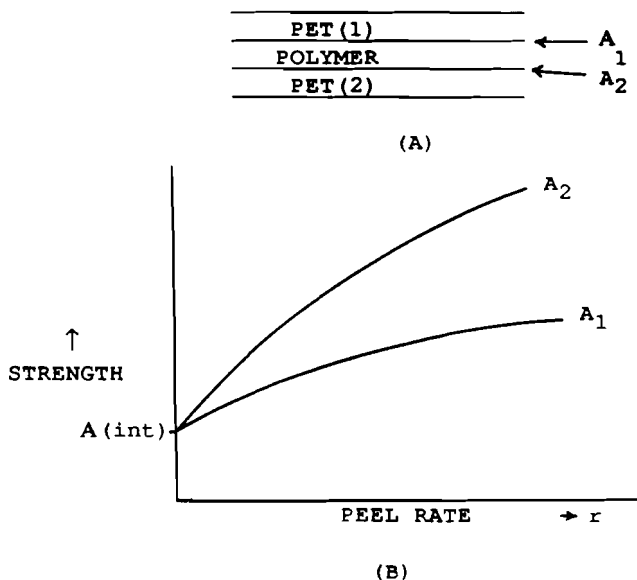


Figure 2. Structure of a symmetrical peel apart system (A) and adhesion strengths as a function of peel rate (B)

the two PET films are labelled (1) and (2); and consequently A_1 and A_2 represent the adhesion strengths at the polymer/PET(1) and polymer/PET(2) interfaces, respectively. Since both interfaces are identical, their the chemical adhesions are same, ie.,

$$A_1(\text{int}) = A_2(\text{int}) \quad (1)$$

where (int) represents the intrinsic adhesion, a term often used for the chemical energy only. If the PET(1) sheet is peeled while the PET(2) sheet is kept flat, the rheological change occurs unevenly and subsequently alters the adhesion balance. At peel rate r , each adhesive strength is the intrinsic chemical strength plus the viscoelastic rate-dependent terms (Equations (2), (3)).

$$A_1(r) = A_1(\text{int}) + P_1(r) \quad (2)$$

$$A_2(r) = A_2(\text{int}) + P_2(r) + B(r) \quad (3)$$

The $P(r)$ terms represent the rate dependent strengths arising from the stretching deformation caused by peeling. The $B(r)$ term is the rate dependent strength originating from the resisting force of the polymer layer against the bending deformation. These rate dependent terms usually increase with the strain rate rapidly at low rates and then plateau off at high rates (Figure 2B). The rate dependent terms vanish as the peel rate approaches zero. Therefore, the intercept values in Figure 2B are the intrinsic adhesion terms. Since the two interfaces are identical, $A_1(\text{int}) = A_2(\text{int})$ and $P_1(r) = P_2(r)$. Therefore,

$$A_2(r) > A_1(r) \quad (4)$$

because of the extra term, $B(r)$, in the $A_2(r)$ (Equation (3)). As a result, peel separation occurs always at the A_1 interface at any peel rate. It is assumed that the tensile cohesive strength of the polymer layer is greater than A_1 . Otherwise, the failure occurs cohesively within the polymer layer. In this example, the rate dependence of the cohesive strength is not important.

EXAMPLE II - AN UNSYMMETRICAL SYSTEM

An unsymmetrical system, where two interfaces are different, represents the most practical adhesive system. Such a system is shown in Figure 3A, which consists of a PET/polymer/support structure, where the support is different from the coversheet PET film. Using the same notations; A_1 represents the adhesion at the coversheet/polymer interface; A_2 , the adhesion at the polymer/support interface, and C_g , the shear cohesive strength of the photopolymer layer. The system was chosen so that the intrinsic adhesion of A_1 is greater than A_2 , i.e.,

$$A_1(\text{int}) > A_2(\text{int}) \quad (5)$$

At extremely slow peel rates, where the strain rate by the peel deformation is too low to have a rheological effect, the intrinsic adhesion dominates and the polymer layer separates with the coversheet. As the peel rate increases, the rheological effect becomes significant and starts to dominate in the separation process. Each force

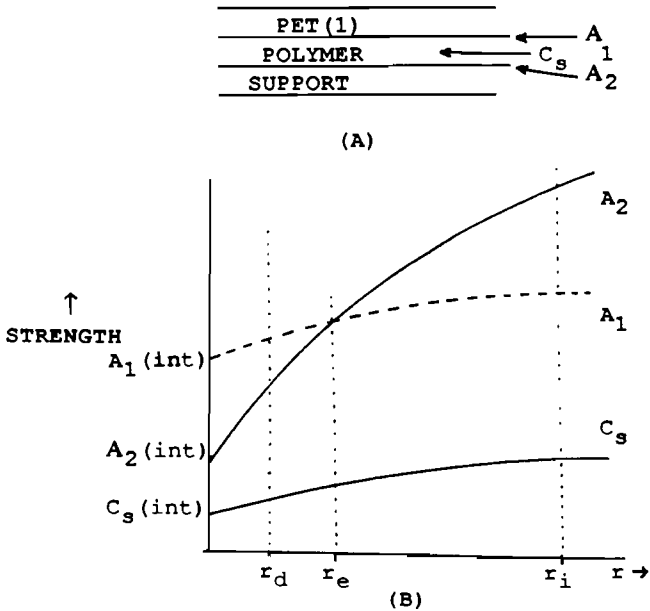


Figure 3. Structure of an unsymmetrical peel-apart system (A) and adhesion strengths as a function of peel rate (B)

component, including cohesive strength, can be written similarly as as a function of peel rate, r , (Equations (6)-(8)).

$$A_1(r) = A_1(\text{int}) + P_1(r) \quad (6)$$

$$A_2(r) = A_2(\text{int}) + P_2(r) + B(r) \quad (7)$$

$$C_s(r) = C_s(\text{int}) + P_c(r) \quad (8)$$

Since no two terms are the same, each force component has its own unique response characteristics to peel rate. Figure 3B shows one example of the strength behavior as function of peel rate. The values, r_d and r_i , are the peel rates where the adhesion difference becomes equal to the cohesive strength (Equations (9), (10)) and r_e is the value where the two adhesions become equal.

$$A_2(r_d) - A_1(r_d) = C_s(r_d) \quad (9)$$

$$A_1(r_i) - A_2(r_i) = C_s(r_i) \quad (10)$$

Considerable information about the system can be obtained by examining how the peel mode changes as the peel rate increases from 0 to a value larger than r_i and then decreases back down to 0. Referring to Figure 3B, as peeling starts, the A_2 interface begins to separate and the polymer layer adheres to the coversheet because $A_1(r) > A_2(r)$ when r is small. As the rate increases, A_2 increases faster than A_1 and exceeds A_1 at $r=r_e$. However, the peel separation remains at the A_2 interface until the rate reaches r_i . This is because the difference (A_2-A_1) does not overcome the cohesive strength, even though $A_2 > A_1$. When the peel rate increases further past r_i , the difference exceeds C_s and consequently the photopolymer breaks cohesively. In other words, the peel mode switches from the A_2 separation to A_1 separation at $r=r_i$. If the peel rate decreases from $r>r_i$, the peel mode switches not at r_i , but at r_d by the same reasons given above. This is an example where the mode is affected by both the magnitude and the history of the peel rate.

EXAMPLE III - A UNSYMMETRICAL PHOTOREACTIVE SYSTEM

If the polymer layer from Example II is photopolymerizable, then photoexposure alters not only the viscoelastic characteristics of the film but also the intrinsic adhesive and cohesive strengths. Therefore all rate dependent and independent terms in Equations (6)-(8) change under exposure. Photopolymerization usually enhances the modulus and thus the cohesive strength, $C_g(\text{int})$; but not always the adhesive strength. If interdiffusion or mechanical locking is an important factor for adhesion at the interface, then photopolymerization or crosslinking enhances the adhesion strength. Alternatively, if the polymer layer adheres to a smooth, nonpenetrable, hard film, then the interface is well separated and photopolymerization usually reduces the adhesion strength.

In a photoimaging peel-apart film, image separation results from a cohesive failure of the photopolymer at the exposed/unexposed boundary. The cohesive strength of the exposed area is greater than that of the unexposed area over most of the peel rate range. As a result, the failure occurs in the weaker (unexposed) side at the boundary and consequently the rate characteristics of the cohesive strength of the unexposed photopolymer are important in studying the peel behavior.

If a photoreactive peel-apart film, before photoexposure, behaves exactly like Example II; but, after exposure, $A_1(r)$ and $A_2(r)$ reverse themselves, i.e., $A_1^*(r) = A_2(r)$ and $A_2^*(r) = A_1(r)$, where * denotes exposed property, then the film becomes a dual response photoimaging film (positive and negative) depending on the peel rate. At a low peel rate ($r < r_d$), the unexposed image of the photopolymer is peeled with the coversheet, whereas at a high peel rate ($r > r_i$) the exposed image adheres to the coversheet.

EFFECT OF PEEL ANGLE, COVERSHEET THICKNESS AND TEMPERATURE IN RELATION TO PEEL RATE

Peel angle is usually defined by the angle formed between the flat portion of the coversheet being peeled and the peeled support. For example, in Figure 4, the peel angle formed in a common peel back mode is 180 degrees. When a PET coversheet is peeled, a curvature is formed by the at the peel front and the radius of the curvature differs depending upon the peel angle. At a large peel angle; for example, at 180 degree peel back, the bending is sharp and consequently the radius of curvature (R_{180}) is small. As the peel angle decreases from the 180 degree peel back to a 90 degree peel, for example, the curvature increases with a larger radius (R_{90}). From Figure 4, it

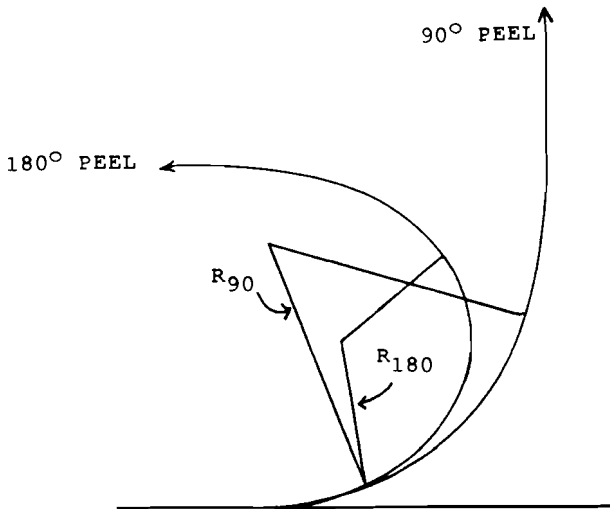


Figure 4. Geometry at peel front for two different peel angles (180 and 90 degrees)

is clear that $R_{180} < R_{90}$. As a result, the bending deformation rate applied to the imaging polymer layer varies depending on the peel angle. The bending deformation rate, which can be equated to the angular velocity ($d\alpha/dt$) along the curvature, is simply related to the radius of curvature (R) by Equation (11).

$$d\alpha/dt = (1/R)dl/dt \quad (11)$$

where dl/dt is linear peel rate, as depicted in Figure 4. Since the radius of curvature decreases as peel angle increases, the bending deformation rate increases with peel rate (ie., increasing the peel angle at a fixed peel rate has the same effect as increasing the peel rate keeping the peel angle fixed). Quantitative estimates of the radius of curvature can be obtained if the stiffness of the coversheet and the applied peel force are known.

The effect of the coversheet thickness leads to the same net effect as the peel angle, because both factors result from the effect of the radius of curvature at the peel front. A thicker (or stiffer) coversheet creates a larger radius of curvature and consequently a smaller bending deformation rate than a thinner (or softer) coversheet. From the elementary theory of elasticity, the radius of curvature, R , under a constant load, depends upon the coversheet thickness, T , by the relationship

$$R = K \cdot T^{3/2} \quad (12)$$

where K is the proportionality constant related to Young's modulus, the sample width, and the applied load. Since the deformation rate is inversely proportional to the radius of curvature (Equation (11)), it can be shown that (from Equation (11) and (12)), increasing the coversheet thickness has the effect of decreasing the peel rate to $(-3/2)$ power of its value. For example, increasing the coversheet thickness by a factor of 2 at a fixed peel rate is the same as peeling at a rate reduced to about 35% of the initial value.

Temperature can also change the intrinsic strengths as well as the rheological characteristics of all three force components. Unless changes in the intrinsic values are unusually large, the force behavior is mainly influenced by the rheological changes. In polymer rheology, temperature and peel rate are interrelated by the well-known time-temperature superposition phenomenon. Qualitatively, increasing the temperature has the same effect as reducing

the peel rate, and vice versa. Their relationships can be determined by experimentally measuring stress-strain behaviors as a function of temperature.

MEASUREMENT OF ADHESIVE OR COHESIVE STRENGTH

Experimental determinations of the above adhesive or cohesive strengths are difficult. The measured value varies widely depending on the measurement method employed. Each method creates a unique stress pattern to the system and consequently requires a different energy. For example, the adhesive strength of an interfacial joint, tested and determined to be strong under one method, may easily display weak strength under a different method. Therefore, the term "adhesion or cohesion strength" without specifying the test method used, has little practical meaning. The best experimental method is the one that most closely resembles the actual product use. Therefore, peel force measurements best reflect "peel adhesion" (adhesion strength under peeling) of a peel-apart film.

However, peel force is not a direct measure of the adhesive or cohesive strength because energy is expended not only by the adhesive or cohesive interface but also by the coversheet. For example, the peel force measured for separating at the interface A_1 of Example I above at peel rate r includes A_1 (int) and $F_1(r)$ plus the energy expended in the bending deformation of the coversheet (Gent, 1977). If the energy expended in the coversheet is kept to a negligible level, then the measured peel force can represent the adhesion strength $A_1(r)$. This is the case when a thick or stiff coversheet is used because under a fixed load the bending deformation decreases with increasing stiffness. Such energy factors contributed by the coversheet can be very large if the coversheet is very thin or soft leading to a high peel force.

A number of commercial instruments are available for measuring the peel force. Typically, at peel angles of 180 and 90 degrees, the Instron can be reliably used for peel force measurements for low peel rates (<100 inch/min). However, for this work, a peel machine was built to handle peel rates over a wide range from a few hundred inch/min to a few thousand ft/min and then combined with a load cell and computer hardware to acquire the peel force signals at a rate up to 10 KHz. Details on the experimental set-ups are available elsewhere (Choi, 1989).

SAMPLE PRODUCTS AND THEIR PEEL-APART CHARACTERISTICS

DuPont has two commercial peel-apart products in the color proofing area. They are Negative Cromalin® (a surprint toning film) and Cromacheck® (a negative-working precolored overlay film). Since both of these films are similar in structure and in peel characteristics, only Cromacheck® will be discussed here. Figure 5 illustrates the structure of Cromacheck® and its normal peel behavior with the correct process-of-use. Cromacheck® has a four-layer structure with two inner viscoelastic layers. Since both inner layers undergo plastic deformation during peeling, the energy relationship must include the energy dissipation not only in the photopolymer layer but also in the adhesive layer. Using the notations used earlier, A_1 and A_2 in Cromacheck® represent the Mylar®/photopolymer

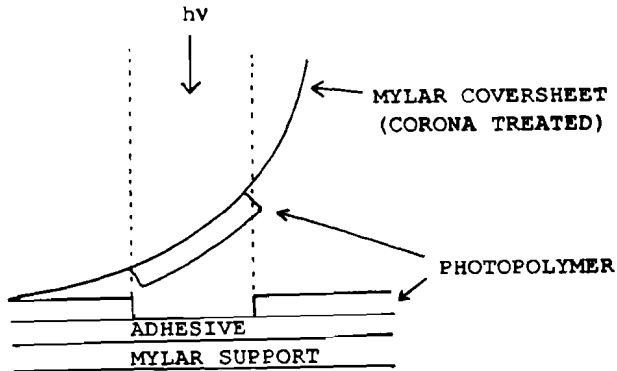


Figure 5. Structure and peel-apart behavior of Cromacheck® (DuPont negative overlay film)

and photopolymer/adhesive interface, respectively, and C_s , the cohesive strength of the photopolymer. (Mylar® is trade mark for Du Pont PET films.) The peel force has been experimentally measured for a given interface separation as a function of peel rate. The results are given in Figure 6. The curve for A_1 is the measured peel force for unexposed Cromacheck®, where the peel separation occurs at the Mylar®/photopolymer interface as shown in Figure 5. The curve for A_2^* is measured using an exposed Cromacheck®, where the peel separation occurs at the photopolymer/adhesive interface. The curves for A_1^* and A_2 have been measured with specific sample geometries that limit the separation to the specified interfaces,

respectively. (Details of experimental procedures can be found in the cited literature (Choi, 1989).

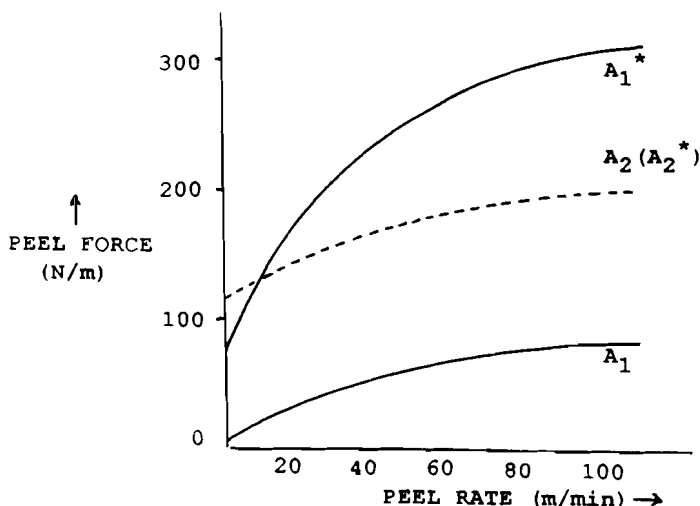


Figure 6. Peel force as a function of peel rate for exposed and unexposed adhesive interfaces

The coversheet of Cromacheck® is a 2 mil thick Mylar®, which undergoes little permanent deformation under the peel force involved in the film. Therefore, the measured peel force very closely represents the adhesion strength. Comparing the curves for A_1 and A_1^* in Figure 5 indicates that the photoexposure greatly enhances both the intrinsic adhesion strength (intercept values) and the rate-dependent terms (curvatures). On the other hand, for the A_2 interface, photoexposure marginally affects the adhesion strength. This result suggests that for the A_2 interface separation, the energy dissipated within the photopolymer layer is insignificant compared to the energy dissipated within the adhesive layer, which is non-photoreactive. This is reasonable because the adhesive layer is highly viscoelastic and its thickness is about 3 times that of the photopolymer layer (Taylor, Jr., 1984). (Note that the total dissipated energy depends on the degree of deformation and also on the deformation volume (Gent, 1977).)

The drastic increase of the A_1 adhesion caused by photoexposure is called the "photoadhesion" effect. This effect is the operational cornerstone of Du Pont peel-apart

products. Such photoadhesion only occurs when the Mylar® PET surface is specially treated by corona discharge. The characteristics of the adhesion increase suggest that photoadhesion may be involved with chemical bond formation between the photopolymer layer and the PET surface. Several published analytical results have shown that a considerable population of pendant peroxide groups are found to be present at the corona-treated PET surface (Bradley, 1970). The peroxide groups can be attacked by radicals to form chemical bonds with polymerizing monomer radicals or undergo cleavage reactions to form radicals to interact with monomers.

Table I summarizes the product characteristics of Cromacheck®.

Table I. Cromacheck® Product Characteristics

Peel Rate : Fast manual peel (>100 m/min)
Peel Force of Exposed Film : 100 - 200 g wt/cm
Peel Temperature : Room Temperature (25C)
Resolution : 3-97% on a 150 line/inch screen
Film Colors : 13 (4 process, 5 commercial, 4 special)

Positive working analogs to Cromacheck® could be developed using similar technologies described in this paper. This requires a total reversal of the adhesion balance and thus the peel-apart separation. For example, referring to earlier diagrams in this discussion, A_1 (the initial photopolymer adhesion to the PET coversheet) is higher than A_2 (photopolymer adhesion to the support) in the unexposed state. However, after exposure to actinic radiation, A_1^* is preferentially lower than A_2^* ($\sim A_2$). This effect is called the "photorelease" effect and give rise to image reversal in peel-apart systems.

A simple approach to reverse the adhesion balance is to modify the surface properties of the PET film. Various surface treatments can be used to change the adhesion characteristics of the PET. Such treatments include various chemical subbing technologies as well as numerous other mechanical photolytic treatments; such as, uv, corona, flame, electron-beam, rf plasma methods etc.

SUMMARY

The peel-apart product examples discussed have been studied by simple surface modification of one of the two interfaces involved in the structures. The adhesional changes can also be produced by altering the physical properties of the photopolymer imaging layer to give the desired rheological response of the system. Chemically inert components; such as binders and fillers, when they constitute the major component in the photopolymer, can determine the rheological response characteristics and thus the peel-apart behavior of the system.

The exact relationships between chemical structure and rheological behavior in peel-apart systems await further definition. However, the proposed models for peel-apart behavior presented in this paper agree well with classical viscoelastic theories and modern peel dynamics. The systems described form the foundation for more exciting work in this very challenging area of technology used for chemical proofing in the Graphic Arts arena.

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