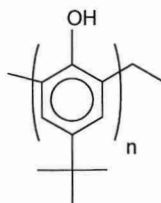


The MQ resin structure, where M is monofunctional trimethylsilane and Q is hydrolyzed quadrafunctional silane



Tertiary butyl phenolic resin

Figure 9.5 Chemistry of the MQ resin and the t-butyl phenolic resin

9.2.3 Testing of Pressure-Sensitive Adhesives

It is necessary to discuss mechanical tests for PSAs before we discuss the relationship among chemistry, mechanical properties, and performance. In Section 9.2.4, use is made of the knowledge gained from previous chapters in understanding PSA performance. Many of the test methods and specifications for PSAs are provided by the ASTM, but the Pressure-sensitive Tape Council (PSTC) also publishes test methods and specifications for these products.

9.2.3.1 Measurements of Tack

One of the primary features of PSAs in contrast to other adhesives is their ability to bond with little applied pressure. Known as “tack”, this capability is defined by the PSTC as “the condition of the adhesive when it feels sticky or highly adhesive. Sometimes used to express the idea of pressure sensitivity.” [3] The ASTM provides another definition: “the property of an adhesive that enables it to form a bond of measurable strength immediately after the adherend and adhesive are brought into contact under low pressure.” This definition includes some important features of tack, including “measurable bond strength” and “low pressure.” A simple definition is that an adhesive is said to display “tack” when the application of light finger pressure enables one to deflect or lift the backing on which the adhesive is coated.

The next section shows that tack is a viscoelastic property of the adhesive. Therefore, the rate and temperature of the test must be controlled variables in tack testing. In particular, it is important that all PSA tests are done under conditions of controlled temperature and humidity and that the test samples are conditioned at the test temperature for a minimum of 24 hours prior to the test.

A number of methods can be used to measure tack. The PSTC describes two methods for tack measurement [1], "quick stick" (PSTC-5) and the rolling ball tack test (PSTC-6). The quick-stick method involves the application of tape under no load conditions. The tape specimen is held taut over a pre-cleaned substrate and then allowed to drape smoothly over the substrate with no applied load. The adhered tape is then loaded into a tensile testing machine and tested using the 90° peel fixture described shortly. The tape is removed at a crosshead speed of 30.5 cm/min (12"/min) and the force to remove the tape is recorded. The recorded force is the "quick stick" value. This test, although functionally measuring the level of tack, does not provide the information necessary to understand tack, since the pressure and the rate of application of the tape are not controlled. The backing stiffness also has a marked effect, since stiffer backings do not allow easy intimate contact of the adhesive to a surface.

In the rolling ball tack test (PSTC-6) a ramp is constructed having a specified angle of 21°30' with respect to the horizontal. The ramp is grooved so that a steel ball having a diameter of 1.11 cm (7/16") rolls on the edges of the groove. The top of the ramp is 6.51 cm (2.562") from the bottom. A piece of tape is placed at the bottom of the ramp and held there securely. The ball is placed on a catch mechanism which releases the ball at the desired time. The tack is recorded as the distance the ball travels down the length of tape. High tack tapes stop the ball as it comes off the ramp while low tack tapes stop the ball at longer distances of travel. This test, although functionally testing tack, also does not provide the level of control needed to understand tack, since the rate of application of force varies somewhat as the ball travels the length of the tape. This test does eliminate the backing as a variable, however. ASTM D3121 also describes a related tack test [3].

A tack test not published by either of these standards agencies is the loop tack test. In this test, a loop of PSA tape is attached to the jaws of a tensile testing machine. The loop is brought into contact with the pre-cleaned substrate by lowering the loop at a specified rate so that it touches a certain area of the panel. The tensile testing machine is then reversed and the force to remove the tape is recorded. The virtue of this test is that the rate of contact and withdrawal are controlled. However, the backing stiffness once again has a dramatic effect on the wetting contact of the adhesive with the substrate.

The test which best controls all parameters having an effect on tack is known as the probe tack test, described in ASTM D2979. A schematic of the test apparatus is shown in Fig. 9.6. In this apparatus, the effect of the tape backing is eliminated because the tape is either rigidly affixed to a steel plate or mounted on an annular ring of known weight. The probe is usually made of stainless steel which must be cleaned before the test. Any surface roughness at the tip of the probe should be known as well as its cross sectional area. Usually, the tip is highly polished. The key features of the probe tack apparatus are the controlled rate of approach as well as

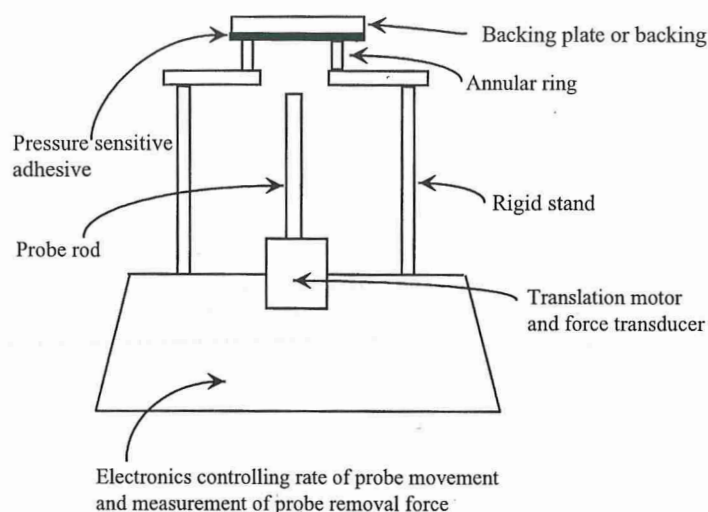


Figure 9.6 Diagram of probe tack tester. This test is described in ASTM D2979

the rate of detachment. The results of probe tack are reported as force per area of probe tip at a specific rate of attachment and detachment and at a specified temperature. Once again, since PSA performance is determined by viscoelasticity, these parameters must be scrupulously controlled to obtain meaningful data.

9.2.3.2 Measurement of Peel

Before peel tests are discussed, it is necessary to look at "roll down", a testing parameter important for PSAs when determining peel or shear. Since the performance of a PSA depends highly upon the degree of contact under the application of a light pressure, the parameters surrounding the application of the tape are exceedingly important. It is important to have a "roll down" methodology used before the testing of tape. The roll down methodology usually requires the tape to be laid down on a substrate with little or no applied pressure (such as that described above for the quick stick test). A roller of known weight and dimensions is rolled over the tape at a specified rate and number of times up and down the tape. The roll down conditions control the degree the PSA "wets out" the substrate.

Peel, in addition to tack, is one of the parameters by which PSA performance is easily recognized. We have all removed a box sealing tape from a package and either exclaimed or complained about how hard it was to remove. In general, that removal was accomplished by peeling back the tape. Peel is tested most commonly by the 180° and 90° peel tests. The first peel test is easier to describe and is shown schematically in Fig. 9.7.

The PSA tape is applied and rolled down onto the stiff, usually stainless steel or glass adherend. The tape is then folded back over itself, forming a long tab. The top of the stiff adherend is clamped into a tensile testing machine, as is the end of the

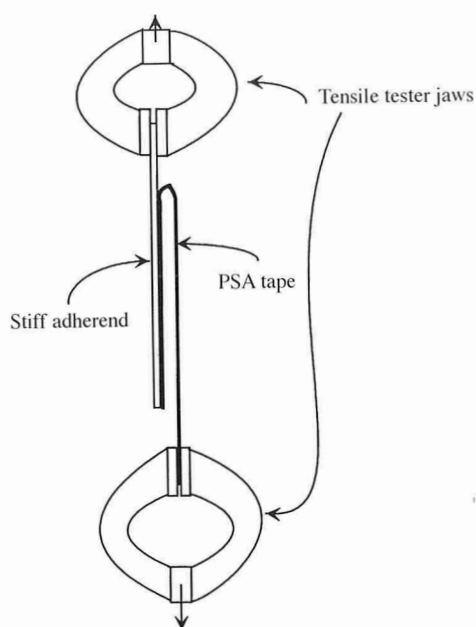


Figure 9.7 Diagram of a 180° peel test, showing the specimen configuration in the jaws of the tensile testing machine

long tab. The 180° is formed by the tape backing against tape backing. The angle of peel is not truly 180°, since the backing interferes with the actual attainment of a 180° angle. The actual angle depends upon the backing stiffness and the backing thickness. The measurement is usually conducted at a constant crosshead speed and at a few temperatures although better data is obtained if the experiment is carried out at several temperatures and as many rates of peel as possible.

The 90° peel experiment is slightly more complicated than the 180° peel measurement. The key difference between the two is how the peel angle is kept constant. Figure 9.8 provides a schematic of an apparatus for measuring 90° peel.

The adherend in the 90° peel test is cleaned and the adhesive is properly rolled down on it. The adherend is then clamped firmly into a trolley. The entire trolley mechanism is clamped into the bottom clamp of a tensile testing machine. The trolley is designed as to roll freely in the direction perpendicular to the movement of the jaws of the tensile testing machine. The trolley is connected through a pulley and rod to the upper, moving jaw of the tensile testing machine. The pulley arrangement is set so that an upward movement of the upper clamp provides a corresponding lateral movement of the trolley. In this way, the peel angle is kept at 90°.

9.2.3.3 Measurement of Shear

In Chapter 3, various measurements of the shear strength of adhesive bonds were discussed. If the shear strength of a PSA were measured using methods described in

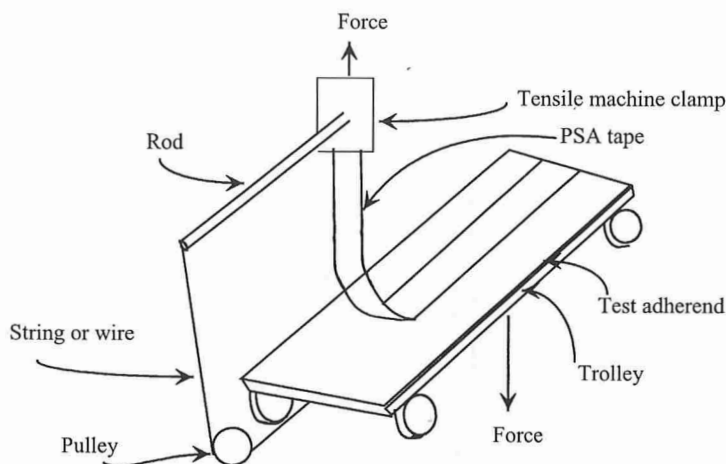


Figure 9.8 Diagram of a test fixture for 90° peel of a PSAT. Note that the test adherend is attached to a moveable trolley which traverses horizontally, while the tensile testing machine clamp moves vertically

Chapter 3, a low value, on the order of only a few psi would be obtained. In general, PSAs are not judged by their shear strength. Rather, PSAs are expected to sustain a low load for the time period of use. Thus, if masking tape is used, one would expect the tape would hold its own backing or perhaps a backing and some covering material on that substrate for the time period of the paint job. If the application were to hold a picture up on a wall, the tape would be expected to hold a few psi load for an indefinite period of time. So, the factor of interest is not shear strength, but rather the resistance of the material to a constant small shear stress for a period of time. The PSA industry has applied the term "shear holding power" to this PSAT performance parameter. This term is definitely a misnomer since there is no aspect of power (as defined in physics) in the test. Rather the test is a constant load creep test. Nonetheless, the term is pervasive in the industry and it is used interchangeably with "constant load creep test" in this book. A schematic of the shear holding power test is shown in Fig. 9.9.

The rigid adherend is appropriately prepared. The adhesive tape is applied to the edge of the specimen as shown in Fig. 9.9. The adhesive is rolled down and excess is removed to provide a known and specified area of contact. The other end of the tape is looped around a rod attached to a hook to which a weight can be added. The rigid adherend is placed in a fixture and held firmly during the measurement. It is very important that the temperature and humidity be carefully controlled. The elapsed time between the attachment of the weight and the point when it drops is recorded. The measurement can, of course, be mechanized so that a timer is switched off when the weight falls. Thus "shear holding power" is recorded as the time to failure at a specified load. Typical loads are 0.5 to 1 kg.

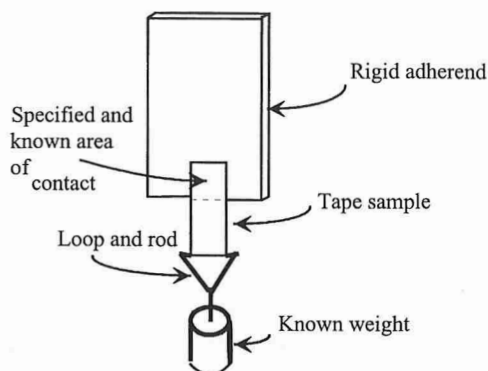


Figure 9.9 Diagram of a "shear holding power" test of a PSAT. The important test parameters are the applied weight, the contact area, and the conditions of the test (temperature and humidity)

9.2.4 Balance of Properties

The properties of a pressure-sensitive tape seem to be at odds with one another. The tapes are expected to wet quickly, have enough resistance to peel, and also have shear holding power. Attainment of this balance of performance is the main objective of the formulator. For PSA tapes, formulation tools are the rubber to resin ratio and the degree of crosslinking placed in the system. Figure 9.10 shows the usual balance of performance obtained for a single elastomer and a tackifier resin when the ratio of the rubber to the resin is varied.

As the resin to rubber ratio increases, the shear strength usually goes through a shallow maximum (this assumes that the crosslinking is constant for the formulations in this figure). The peel strength usually rises as the resin to rubber ratio increases while the tack goes through a maximum. It is the job of the PSA formulator to maximize all three of these performance parameters to meet the specifications of the customer. The following sections describe the physico-chemical phenomena controlling the performance parameters shown in Fig. 9.10.

9.2.5 PSA Performance Viewed as a Timescale in Viscoelastic Response

When a pressure-sensitive tape is applied to a substrate, the adhesive is expected to spontaneously spread on the surface with little or no applied pressure. That is, the PSA is expected to act as a liquid. However, when the adhesive is peeled or a weight is hung from it, we expect the adhesive to resist the force. That is, it should act as a solid. This contradictory behavior is available from viscoelastic materials. Consider the timescale of the two processes discussed above. A PSA tape is not applied to a substrate rapidly. In fact, the tape is often allowed to sit on the substrate for a while after application. Thus, the timescale of application is long, usually on the order of a

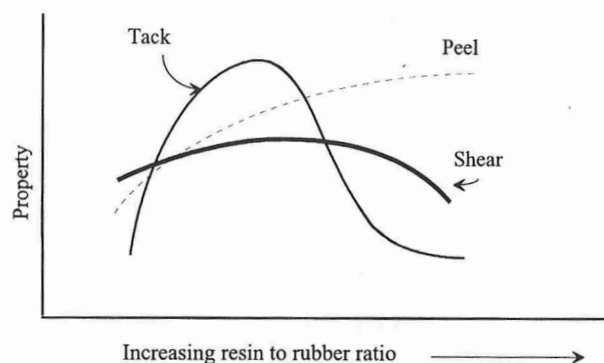


Figure 9.10 Diagram of the relationship of performance properties to the rubber-to-resin ratio in a natural rubber-based PSA. Note that the highest value of each performance property is not obtained at the same rubber-to-resin ratio. Optimum performance of a PSAT is obtained with the best balance of properties which meet the customer's expectations (redrawn from Satas)

second or more. When a PSA is removed, the timescale is much shorter. Typical peel measurements are usually done on the order of inches per minute which, when looked at from the point of view of the adhesive, is on the order of tenths of a second. Therefore, a PSA is expected to behave as a liquid for timescales of seconds or longer and to behave as a solid for timescales of tenths of seconds or less. At any particular temperature, these are properties which a viscoelastic material can achieve. The formulation of PSAs is the attainment of viscoelastic properties which allow wetting (liquid-like properties) at long timescales and peel (solid-like properties) at short timescales at the temperature of use.

9.2.6 PSA Viscoelasticity and Tack

Tack is the instantaneous wetting of a substrate under little or no applied pressure to rapidly develop a measurable strength. Since tack requires the adhesive to act as a liquid, it might be expected that if the adhesive becomes too stiff (too high a modulus), then the adhesive does not display tack. This phenomenon was studied in detail for rubber-resin adhesives. It is that work which forms the basis for this discussion.

The variation of probe tack with temperature is one key to understanding which property of materials leads to the phenomenon of tack. The discussion above indicates that the timescale of the probe tack test is important. Figure 9.11 represents the measurement of probe tack as a function of temperature when the measurement is taken at a withdrawal rate of a few centimeters per second and a contact time on the order of a second.

There are several important features in Fig. 9.11. First, probe tack goes rapidly to zero as the temperature falls even slightly below room temperature. Second, tack

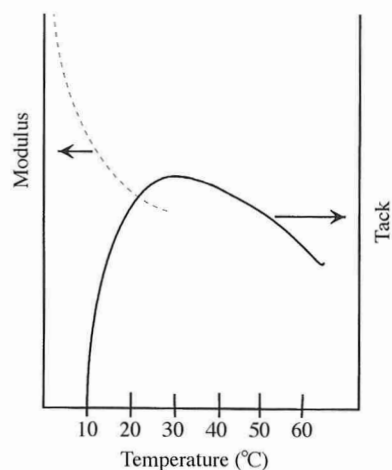


Figure 9.11 Plot of the tack and modulus measured at a rate of 1 Hz for a rubber-resin adhesive. Note that the tack reaches a maximum when the modulus drops below a certain level. The modulus value which corresponds to the onset of a high tack is known as the Dahlquist criterion

is maximized near room temperature (this is done by formulation). Third, tack falls slowly as the temperature is increased.

Examine the modulus (dashed line) of the adhesive as a function of temperature using a rate of application of stress similar to the rate of the probe tack experiment in Fig. 9.11. The modulus of this rubber resin adhesive decreases rather dramatically as a function of temperature. In fact, as the temperature nears room temperature (the point at which the probe tack increases to a maximum), the modulus decreases to less than 3×10^6 dynes/cm². (Figure 9.11, which is only for demonstration, does not have units other than temperature.) In fact, it is found that the room temperature modulus of any tacky adhesive is less than 3×10^6 dynes/cm² when measured at a frequency of about 1 Hz. This finding is a criterion for tack and has been given the name "Dahlquist criterion for tack" after the scientist who studied this phenomenon [4].

Figure 9.10 showed that the way in which tack is obtained in a PSA is through the addition of a tackifying resin to an elastomer. As the resin concentration in the elastomer is increased, various practical adhesion properties change. Figure 9.12 shows a schematic of the modulus of a natural rubber/resin PSA as a function of the frequency of measurement and of the resin content. The dotted line shows the variation in modulus with frequency. The modulus curve is flat and is also above the Dahlquist criterion. As tackifier is added, the modulus decreases and at the frequencies in the graph, the second curve goes below the Dahlquist tack criterion. If the peel resistance of this PSA were measured, it would be relatively low. If we increase to another level of tackifier, we would find that now the modulus at low frequency was much below the tack criterion and the modulus at high frequency was now increased measurably. If the peel strength of this PSA is measured, it would be

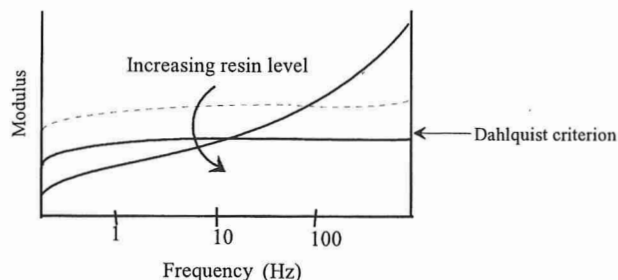


Figure 9.12 Plot of modulus of a pressure sensitive formulation as a function of frequency at three different resin levels in the adhesive

found that it had now increased to a substantial value. Understanding this phenomenon is key to understanding the tack and peel performance.

Another way of examining this phenomenon is to plot of the shear modulus of a PSA base elastomer as a function of temperature measured at about 1 Hz as well as that of the tackified base elastomer, as shown in Fig. 9.13. This type of data is similar to the dynamic mechanical data presented in Chapter 5. The base elastomer is shown as the dashed line. The glass transition temperature, when measured at 1 Hz is somewhat below room temperature. The dynamic mechanical determination of the shear storage modulus of the tackified adhesive is shown as the solid line in Fig. 9.13. The very interesting effect of having the tackifier act as an anti-plasticizer, that is, increasing the T_g of the tackified adhesive is seen. Above the T_g , however, the plateau modulus is decreased. It is indicated that the storage modulus has decreased below that required by the Dahlquist criterion.

The time-temperature superposition principle states that the effects of time and temperature on a viscoelastic material are inversely related. Therefore, when the same physical properties as shown in Fig. 9.13 are measured at a higher frequency, one might expect to obtain the plot shown in Fig. 9.14. When measured at 100 Hz, it is

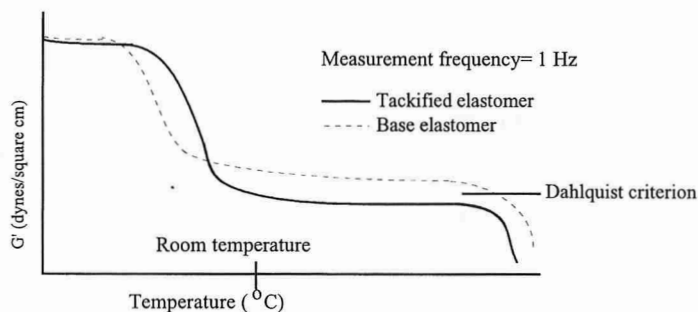


Figure 9.13 Dynamic mechanical spectrum of a PSA-based elastomer in the tackified and non-tackified state. The measurement is done at a single frequency but as a function of temperature. Note that the tackified elastomer has a plateau modulus below that of the Dahlquist criterion

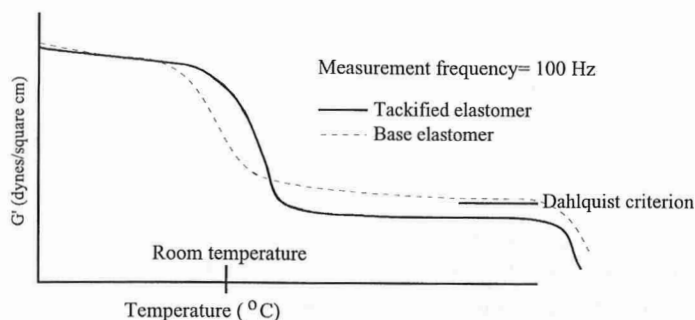


Figure 9.14 Plot of the shear modulus of a PSA elastomer with and without tackification measured as a function of temperature but at a frequency of 100 Hz. Note that the curves have shifted towards higher temperatures as the frequency was increased

seen that the entire dynamic mechanical spectrum of the shear storage modulus of the adhesive has shifted to higher temperatures. The T_g of the tackified adhesive is now above room temperature. This adhesive would be expected to exhibit greater stiffness and thus provide some physical strength when the tape is tested.

The above discussion implies that the resin must be completely miscible with the base elastomer. Indeed, if the resin were not soluble, one would not expect a change in the physical properties of the base elastomer. Instead, two glass transition temperatures, with no change in the T_g of the base elastomer, would be expected. In systems where two materials of substantially differing T_g s are mixed and these materials are soluble in one another, the overall glass transition temperature of the solid solution can often be predicted by the Fox equation [5]:

$$\frac{1}{T_g} = \sum_i \phi_i \frac{1}{T_{g,i}}$$

where the ϕ_i is the weight fraction of the i th soluble component in the mixture and $T_{g,i}$ is the glass transition temperature of the i th soluble component. The Fox equation can often be used to predict the T_g of elastomer/resin solid solutions and in fact, can show that components are not soluble in one another.

If the elastomer and the tackifier are not soluble in one another, what sort of physical situation might be expected? In the case of normal polymer solutions, several results could occur. One possibility is gross separation of the two phases, particularly when the interfacial tension between the components is large. When the incompatibility and the interfacial tension are not that large, microscopic phase separation occurs similar to that discussed in Chapter 8 on toughening epoxy resins. In this situation two T_g s are exhibited. In a particularly sinister situation, the resin could phase separate into microscopic phases, and by surface tension effects, phase separate into a solid layer at the surface of the PSA. Since the resin is glassy, it would not exhibit tack and the PSA would not perform as expected. Therefore, care must be taken to choose tackifiers that are completely soluble in the elastomer to be tackified.

Tack depends upon more than the resin to rubber ratio and the rate of the tack test, however. Tack also depends upon the probe material (or the material to which the tape is adhered). The general dependence of tack on the constitution of the substrate is almost exactly what would be expected if the guidelines for good adhesion presented in Chapter 6 were followed. That is, for any particular PSA, the tack level increases with increasing critical wetting tension of the solid surface. The tack force usually plateaus when the critical wetting tension of the substrate exceeds that of the adhesive. So, in the regime of low rates that is associated with the attachment of PSAs, the liquid-like nature of PSAs exhibit the same wetting behavior as liquids of equivalent surface energy.

9.2.7 PSA Peel and Viscoelasticity

Figure 9.10 indicates that peel performance normally improves as resin concentration increases, primarily because the increase in tackifier increases the stiffness of the PSA at higher rates. The more tackifier, the stiffer the PSA. Obviously, a point is reached when the adhesive is too stiff and PSA character disappears. PSA viscoelasticity also plays a role in PSA performance when it is tested at various rates of peel and temperature. In fact, a master curve much like the ones we described in Chapter 5 can be constructed for PSA peel on any given substrate. An example of such a master curve is shown in Fig. 9.15.

The curve in Fig. 9.15 is similar to one published by Kaelble [6] for the peel adhesion of a PSA to polystyrene. The data is presented in a manner analogous to the WLF concepts discussed in Chapter 5 and Chapter 6. The peel force, F , becomes a reduced variable when it is multiplied by the ratio of the measurement temperature, T , and a reference temperature T_0 . The peel rate is reduced by a shift factor

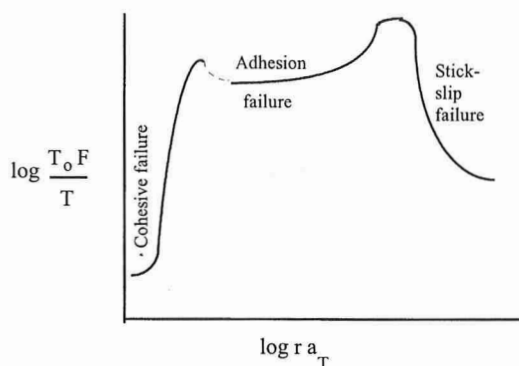


Figure 9.15 Reduced peel force as a function of reduced peel rate for a rubber-resin PSA drawn according to the data of Kaelble [6]. Note that not only is there a substantial dependence of peel force on peel rate but the mode of failure changes as a function of peel rate

that was calculated from the following relationship:

$$\log a_T = 9.8 - \frac{17.44(T - T_g)}{51.6 + T - T_g}$$

As in Chapter 5, a_T is the shift factor; T is the absolute temperature; and T_g is the glass transition temperature.

The primary interesting feature associated with the curve in Fig. 9.15 is that the peel data can be condensed into a single peel curve with multiple segments. This definitively demonstrates that the peel performance of a PSA is dependent upon its viscoelastic properties. The next interesting feature is that the peel force–peel rate curve can be divided into three segments. The first segment occurs at very low peel rates and the failure mode is cohesive within the adhesive. That is, some of the adhesive remains on the substrate. At some peel rate-temperature combination, the peel failure mode changes from cohesive failure within the adhesive to adhesion failure. This abrupt change occurs with an initial decrease in peel force, but this peel force increases with increase in rate. In both cases, increase in peel force is a consequence of the stiffening of the adhesive at either increasing rates or decreasing temperatures. The third segment of the curve, however, seems to show decreasing peel force with increasing peel rate. This region of “stick-slip” behavior is one that is marked by various degrees of oscillation in the peel force. That is, steady peel force is not achieved but rather a “shocky” peel occurs. This region of the peel force–peel rate curve is associated with a glassy response of the adhesive.

Since tack depends upon the wetting behavior of the PSA, peel force exhibited by a PSA is expected to depend upon the surface to which the PSA was adhered. Zosel [7] has investigated this behavior with results shown schematically in Fig. 9.16.

The effects of the liquid-like wetting behavior of a PSA are shown in this figure. First, the peel force after short contact time is heavily dependent upon the critical wetting tension of the substrate. If the wetting tension of the substrate is substantially lower than the surface energy of the adhesive, there is a lower peel force. The

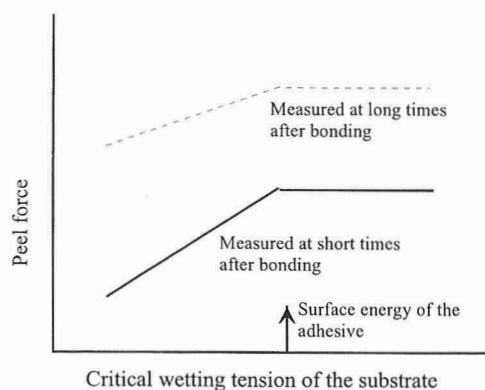


Figure 9.16 Peel force of a polyisobutylene-based PSA as a function of the critical wetting tension of the substrate to which is applied. The plot is drawn according to the data presented by Zosel [7]

bigger the mismatch, the lower the peel force because incomplete wetting means interfacial flaws which mean lower forces to failure. Once the critical wetting tension of the substrate exceeds that of the adhesive, wetting is complete and the peel force no longer increases. The dashed lines in Fig. 9.16 show what happens when the wetting of a surface by a PSA is not complete immediately after the PSA has been attached. If tack is a low rate phenomenon, then conditions in which the PSA is allowed to flow with little or no load is a very slow rate process and the adhesive behaves like a liquid. Indeed, the data in Fig. 9.16 shows that wetting does occur in this regime and the strong dependence of peel force on critical wetting tension of the substrate is somewhat decreased when the adhesive is allowed to remain in contact with the substrate for an extended time.

The dependence of peel force on substrate is also demonstrated by showing how peel force affects peel rate. However, these results are not necessarily as expected. If the peel force-peel rate curve of the same adhesive used in Fig. 9.14 is measured on a substrate which is low in critical wetting tension (such as polytetrafluoroethylene), a curve is obtained like that in Fig. 9.17. Not only is the level of the peel force decreased with respect to the higher energy surface, but also the positions of the transitions from cohesive to adhesion and adhesion to stick slip failure have changed. This indicates that the activation of the stiffening behavior of a PSA depends upon the substrate to which the adhesive is bonded. The change in the position of the first transition is not hard to explain. The transition of cohesion failure in the adhesive to adhesion failure of the adhesive to the substrate occurs at a lower reduced rate because the adhesive does not need to have as high a cohesive strength to exceed the forces of adhesion to the lower energy surface. The change in the higher peel rate transition is more difficult to explain and the appropriate criteria for explaining this change are still under study.

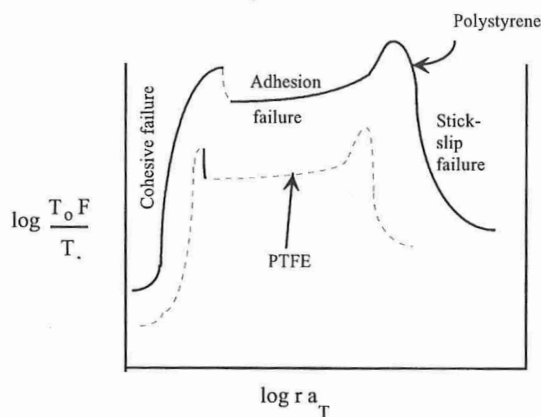


Figure 9.17 Reduced peel force versus peel rate master curves for a single PSA on two surfaces drawn according to the data of Kaelble [6]. Note that, with a change in substrate, the peel force changes and the position of the failure mode transitions changes