

HOW CAN A PEEL MASTER CURVE BE USEFUL FOR PRACTICAL PRODUCT PERFORMANCE PREDICTION?

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Introduction:

It is generally known among adhesive practitioners that the peel force of any tape product is dependent on temperature and on the speed of peeling. Generally higher temperature or slower peeling results in lower peel force. However much of the work done to evaluate pressure sensitive adhesive (PSA) products focuses on measuring three main properties: peel, tack, and shear, with the peel force measured only under one rate and temperature condition, often following a PSTC or ASTM standard testing protocol, usually at a speed of about 5 mm/s. Although it is certainly important to obtain balanced values of these three properties for specific applications, a very important feature is missed by these measurements because the peel measurement is made at a relatively high peeling speed compared to important modes of tape failures, namely resistance to peeling while under small peeling loads for long times. We will show how measurement of peeling master curves can be used to provide a more comprehensive view to compare different adhesive systems and make predictions about these modes of failure. We will begin by describing the procedure for generating master curves for viscoelastic properties data and then show how this same procedure can be applied to peel properties and used for understanding performance under real application conditions.

Time-Temperature Superposition:

The concept of time-temperature superposition is well known in the field of polymer viscoelasticity and was well described by John Ferry(1). The basic idea is that for rheologically simple polymer systems, if one measures a property which is a function of time (or rate), measuring the same property at a different but nearby temperature will produce a function with the same shape but simply shifted horizontally on a log time (or log rate) axis. The explanation for this is that the viscoelastic behavior of such systems has to do with the relationship between the relaxation times of the polymer system and the testing time scale. If raising the temperature simply accelerates all the relaxation processes of the polymer by a multiplicative factor, R , then the identical mechanical response will be seen at a time scale that is shorter than the original time scale by the ratio $1/R$.

These standard methods of viscoelastic property measurement and master curve generation have been widely used in characterizing PSAs and much has been written about the general relations between these properties and adhesive performance (2, 3). Since peel of PSA tapes is heavily influenced by the deformation of the adhesive, it perhaps should not be too surprising that the peel is subject to the same relationship between temperature and rate as governs the mechanical properties of the adhesive. Before examining example data and discussing how they relate to practical performance, let us review the methods behind creating a master curve from viscoelastic properties and then look at how it is done with peel data.

A very common viscoelasticity measurement is of a material's dynamic mechanical properties as a function of frequency. In this measurement, the material is sandwiched between two parallel disks and one of the disks is oscillated through a small rotation angle in a sinusoidal manner at an angular frequency, ω , which creates an oscillating shearing strain in the sample. The torque on the other disk is

measured and from that, a shear stress is calculated. This shear stress will oscillate at the same frequency but, in general, will be out of phase with the oscillation of the strain. The ratio of the amplitude of the stress wave to that of the strain wave is called the dynamic modulus, G^* , and the offset in the phase of the two sine waves is expressed as the phase angle, δ , expressed in degrees or radians where one cycle of oscillation corresponds to a phase angle of 2π radians or 360 degrees. Although G^* and δ are the basic parameters measured, these are usually used to derive other quantities, especially the following:

$$G' = G^* \cos(\delta)$$

$$G'' = G^* \sin(\delta)$$

Furthermore, the phase angle is often plotted as the tangent of δ .

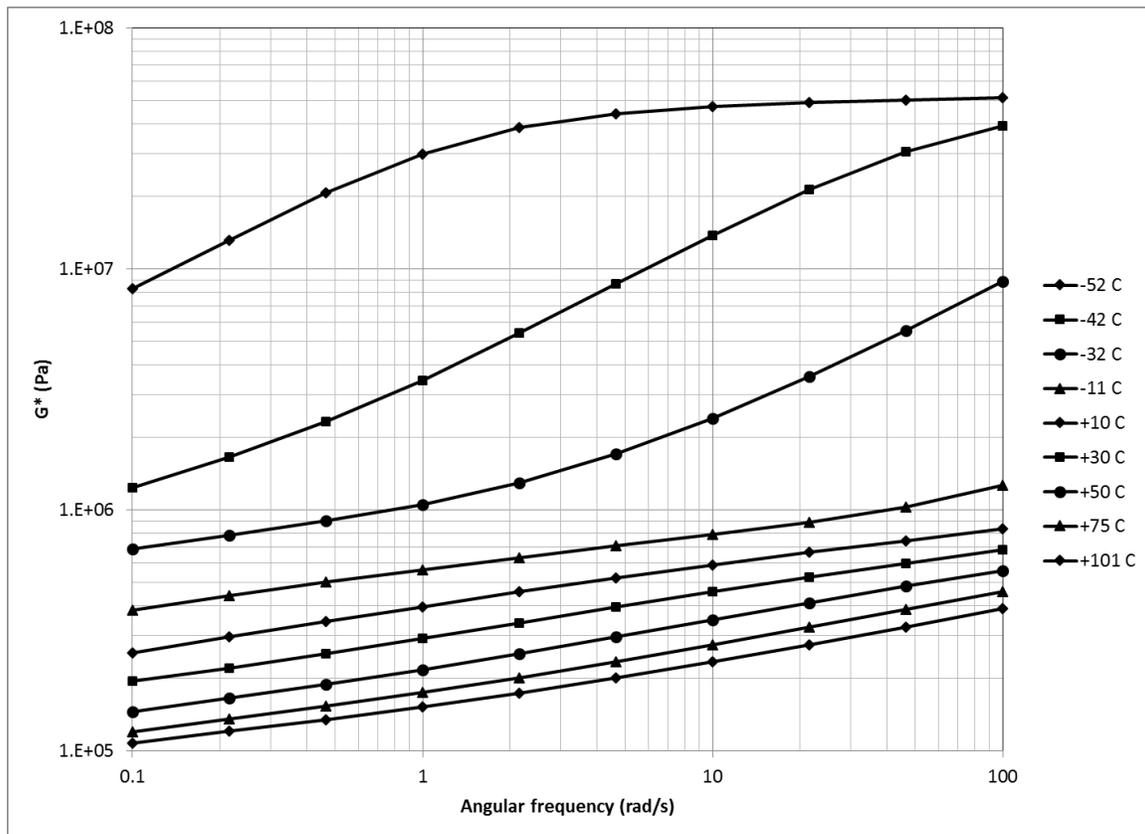


Figure 1
Dynamic Modulus vs. Frequency at Various Temperatures

These properties are plotted vs. $\log \omega$. Measurements are made at multiple temperatures over the same range of frequency with the temperatures chosen close enough together so that there is overlap between the ranges of values of G^* from the low to the high frequency at neighboring temperatures. The data in **Figure 1** show G^* vs. frequency for a lightly crosslinked rubber based pressure sensitive adhesive measured at a range of temperatures.

To construct the master curve, one first chooses one of the temperatures as a reference temperature. Then the modulus values are adjusted by the ratio of the reference temperature to the measurement temperature in absolute temperature units (K). This is a small minor vertical adjustment on the $\log G^*$

axis, the reasons for which are explained by Ferry (1) but will not be elaborated here. Starting with the next neighboring temperature (higher or lower), one moves the data horizontally on the $\log \omega$ axis until the two curves lie on top of one another as much as possible. If time-temperature superposition works, the two curves should overlay very closely. One then progresses to the next temperature and moves it until it overlays the composite curve formed from the previous data. This process continues for all temperatures higher and lower than the reference temperature until all the data lie on one composite curve. As the shifting is done, one keeps track of the amount of horizontal shift necessary to bring each curve onto the composite curve which is called the master curve. The amount of horizontal shift on a $\log \omega$ axis is the log of the shift factor, a . The separate values of a at each measurement temperature comprise samplings of the shift factor as a function of temperature, $a(T)$.

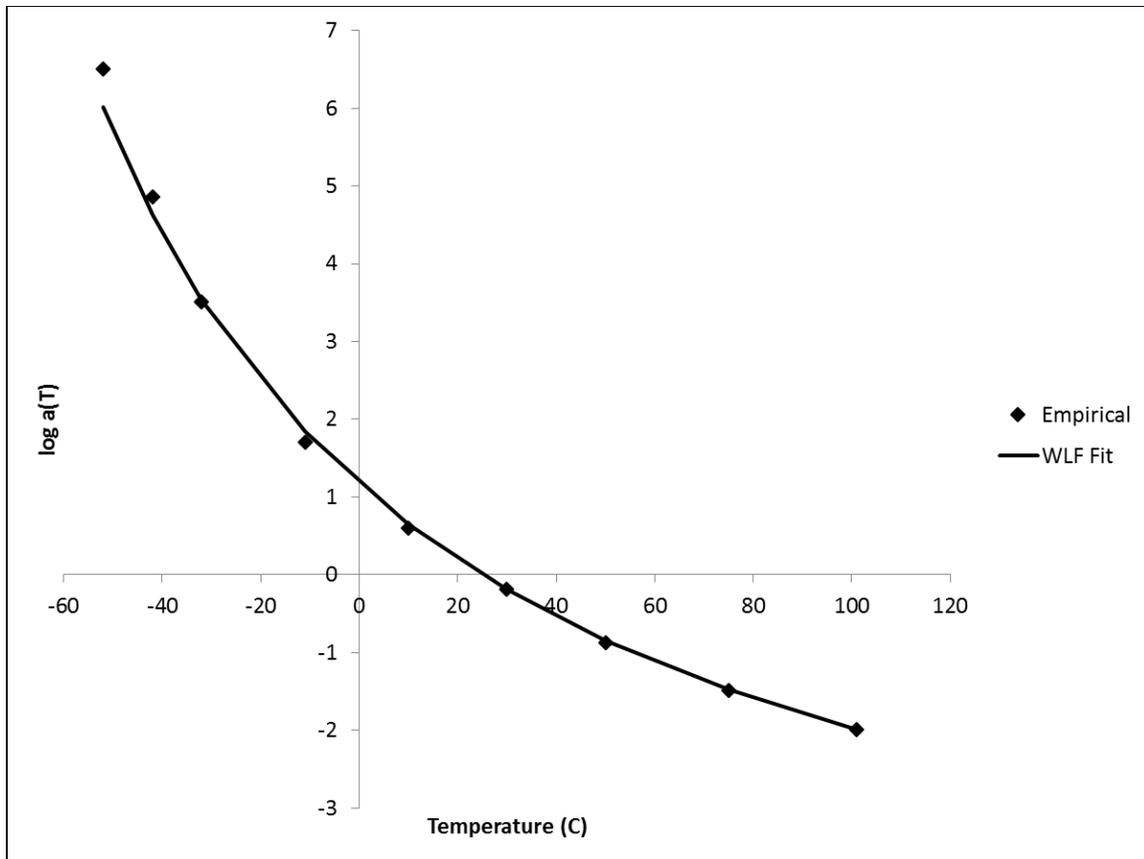


Figure 2
Shift Factors vs. Temperature

The shift factor as a function of temperature represents the ratio of the speed of the relaxation processes at the reference temperature to their speed at the measurement temperature. By this convention, $\log a(T)$ is negative for temperatures above the reference temperature and positive for temperatures below it. The shift factors needed to align the data from Figure 1 as a function of temperature are shown in **Figure 2**. These shift factors have been found to generally follow a functional form proposed by Williams, Landel, and Ferry⁴:

$$\log a(T) = \frac{-C_1(T - T_r)}{C_2(T - T_r)}$$

Where T_r is the reference temperature. The constants, C_1 and C_2 are adjusted to fit the data. The fit of this equation (called the WLF equation) is also shown as the solid line in **Figure 2**.

The x-axis of the shifted master curve can be thought of as a combination variable which includes the frequency of the measurement and the shift factor associated with the temperature of the measurement. Since each curve was shifted horizontally by $\log a(T)$, the axis is $\log \omega + \log a(T)$. Since the sum of logarithms is the logarithm of the product, this is the same as $\log \omega \cdot a(T)$. The master curve showing the adjusted modulus y-axis and combined x-axis variables is shown in **Figure 3**.

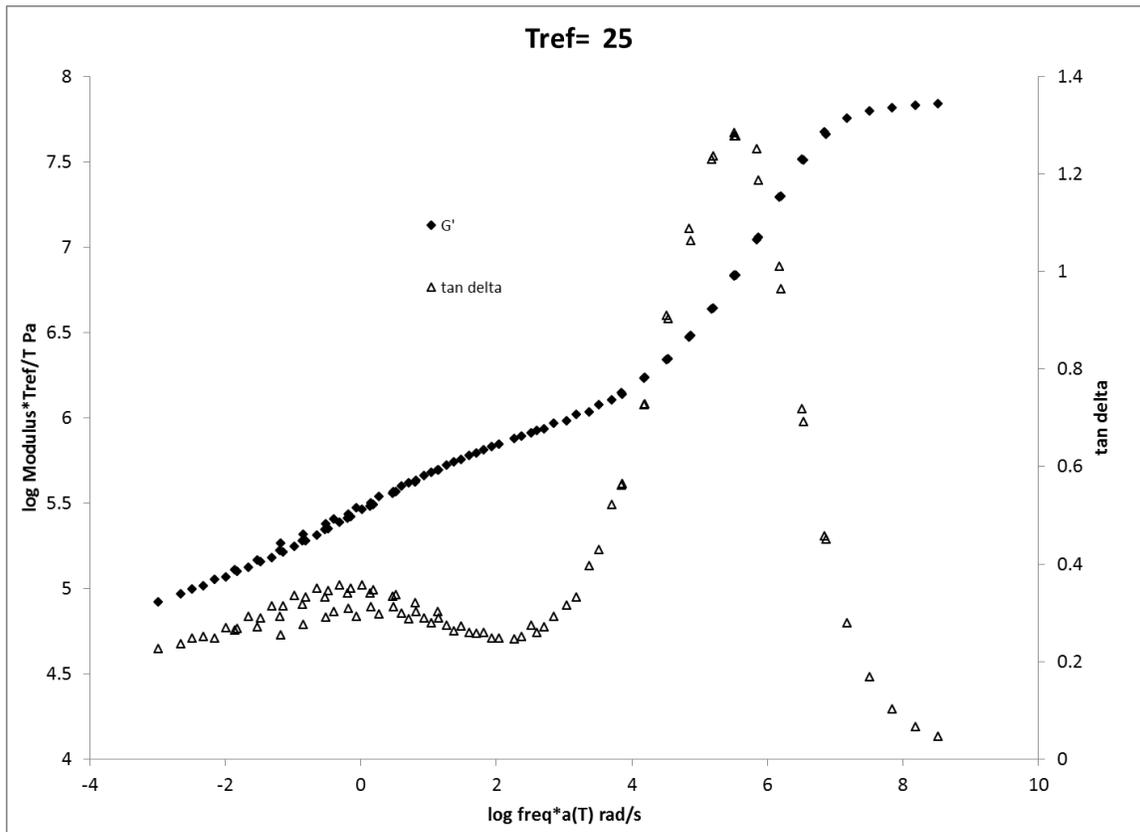


Figure 3
Master Curve of Dynamic Mechanical Properties

Although modern software on rheological test instruments can perform these operations automatically, it is helpful to understand what is going on “under the hood” for understanding and interpretation of such data.

The reason the time-temperature superposition principle and the resulting master curve are so useful is two-fold. First it allows one to make predictions about what would happen at very short and very long time scales which are beyond the ability to directly measure with ease. Essentially, one uses the acceleration and deceleration effect of temperature to obtain that information. Second, it allows estimation of behavior at a wide range of possible time scales and temperatures representing different uses of a material with a relatively small set of measurements.

To use this master curve, it is necessary to have both the master curve function of frequency and shift factor and the shift factor as a function of temperature. If one wants to know what property to expect at a

particular frequency and temperature, one first calculates the value of $\log a(T)$ at the temperature of interest and then adds that to $\log \omega$ for the frequency of interest to determine the position along the x-axis. One can then read off the property of interest on the appropriate master curve and adjust for the ratio of T/T_r as appropriate. Perhaps more intuitively, one can use the master curve and shift factor information to replot predicted property values vs. frequency at any chosen temperature. The master curve is exactly that for the reference temperature where the shift factor $a(T)$ is 1 ($\log a(T) = 0$) by definition.

Time-temperature superposition is valid for materials in which the only effect of temperature changes is to change the rates of molecular motion (relaxation) processes in the system. If temperature causes a change of thermodynamic state such as melting of crystals or a change in phase separation morphology, then such superposition attempts will fail. Luckily, most PSA systems fall into this class. They are generally amorphous polymers (lacking in crystallinity) and many of them are thermodynamically miscible single phase systems, e.g. typical acrylic and rubber PSAs not employing block copolymers. Block copolymer rubber PSAs such as those based on styrene-isoprene-styrene block polymers will obey time-temperature superposition so long as the temperature is below the softening temperature of the styrene domains so the only relevant relaxation processes are those involving the rubbery midblock and the tackifier dissolved in that mid-block. When the styrene domains approach their glass transition temperature, the temperature dependence of those relaxation processes will be very different from that of the midblock relaxations and the data will no longer superpose.

Master Curves of Peel Force Data

Kaelble(5) showed that this same procedure could be used for peel force of tapes as a function of peeling rate. Since peel force of a PSA tape depends both on the bonding process and the debonding process, each of which is sensitive to time and temperature, Kaelble chose to equilibrate the bond before testing peel to remove the bonding process dependence from the data. After laminating the tapes to the target surface, he aged them at 70°C for 60 minutes and argued from the rheological properties master curve that this was equivalent to an extended bonding time at room temperature. He then mounted the test panel in a universal testing machine (Instron™) equipped with an environmental test chamber to control the temperature. When the sample had equilibrated at the chamber temperature, the sample was peeled at a series of logarithmically spaced peeling rates. A new sample had to be used for each temperature. He conducted tests at 7 to 11 temperatures ranging from 70°C to -35°C.

He applied the same vertical correction to the force per unit width data based on the absolute temperature ratio as is used for modulus data and found that the very same shift factor function determined for viscoelastic properties of the adhesive would cause the peel data to superpose. An example plot of some of his data calculated for the reference temperature of 23°C is shown in **Figure 4**.

As Kaelble and others (6, 7, 8) have found using similar procedures, peel master curves have certain characteristic features which are shown in **Figure 5**. (On the y-axis, b represents the tape width so F/b is the force per unit width.) At low rates and/or high temperatures, one often sees cohesive splitting of the adhesive. At a critical rate/temperature point, the peel transitions to interfacial failure with the adhesive separating from the test surface. At this transition, the peel force often drops but not always. The cohesive failure regime at low rates can be suppressed if the adhesive is sufficiently crosslinked. The peel force increases with rate (or lower temperature) through a broad region where the peel is stable and smooth. At some critical rate/temperature, the peel becomes unstable or “shocky” such that the peel front moves in a series of sudden jumps, often making a loud sound in the process.

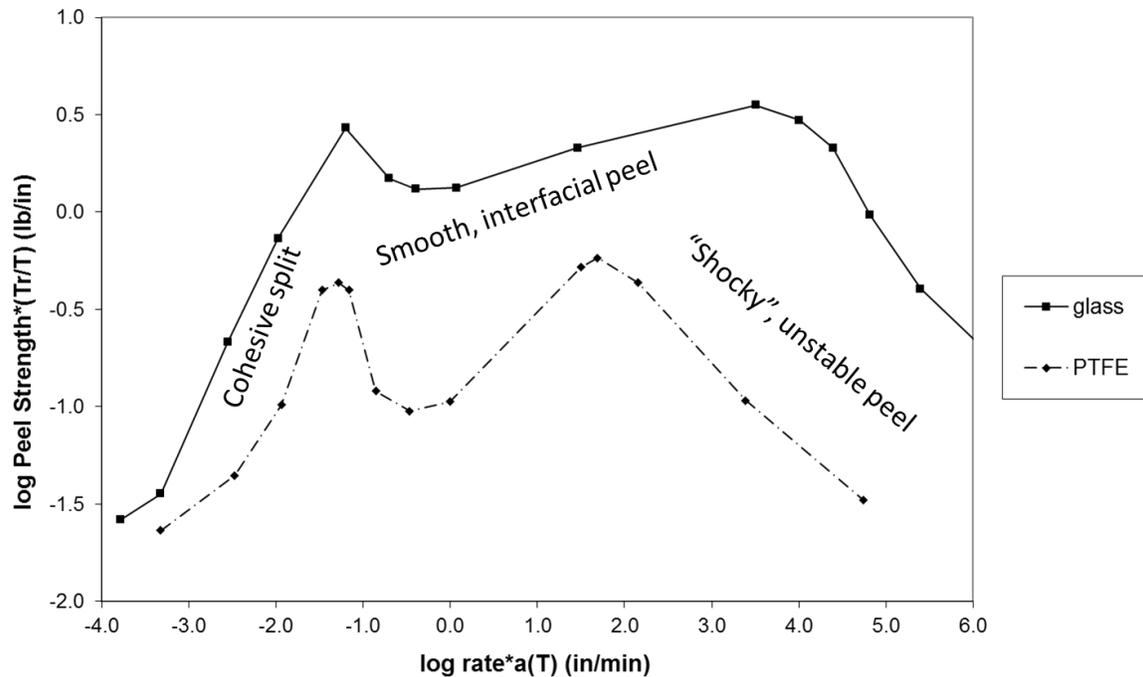


Figure 4

Kaelble master curve for acrylic adhesive peeling from glass and PTFE at $T_r = 23^\circ\text{C}$

As shown by Yarusso (9), these features can be predicted from the rheological properties of the adhesive with a suitable choice for a material model and a de-bonding criterion. The transition from cohesive to interfacial failure is strongly associated with the time scale at which the material becomes capable of viscous flow (if it does) and the transition from smooth to shocky peel is associated with the time scale at which the material makes the transition from rubbery to glassy behavior.

Relating Peel Master Curve to Tape Performance

The peel master curve contains a lot of information about how a tape will respond to different conditions. One can see what sort of peel force and behavior would be expected for removal of the tape at any peeling speed or temperature covered by the range of the master curve and shift factor functions. However, the peeling or removal force of tape is often not the relevant question. More often, one might want to know how fast a tape will peel when subjected to a constant peeling force. To do that using the master curve, find the force value of interest (and temperature of interest) on the y-axis and read across to find the rate-shift factor combination at which from the curve. Use the shift factor value at the temperature of interest to find the predicted peeling rate. Note that for a system which exhibits a transition from cohesive to interfacial failure at low rates with a maximum in the force, there are forces for which there are multiple possible peeling rates with different modes of failure. If the experiment is actually done in this way (applying a load and measuring the rate), one will normally only observe the stable peeling modes in which the force is increasing with rate and not the unstable mode at high rate. Which of the two rates and modes is observed can be dependent on how fast the weight is dropped.

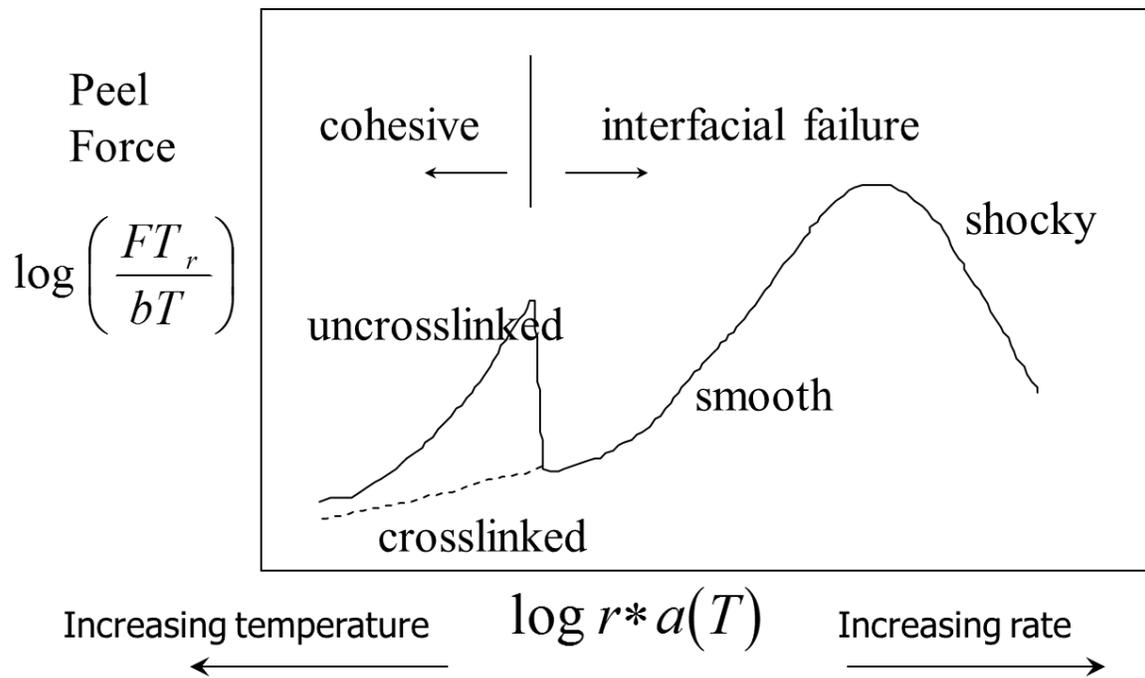


Figure 5
Typical Features of PSA Tape Peel Master Curves

Although we might not know exactly what the peeling force will be in applications, there are certainly situations where it is known that there is such a force which leads to failure in the form of tape lifting or flagging or mounted objects falling off. Let's consider some of the sources of peeling loads. When a tape is unwound from a roll or an adhesive note is peeled from a pad, the backing can be permanently deformed, taking on a curl. When that curled tape or note is then applied to a surface, the backing has a memory of that curled state and exerts a force to try to spring back to that shape. Another example is when a paint is applied on a masking tape. As the paint dries, the paint film may want to shrink relative to the tape backing, producing a stress which makes the tape want to curl away from the substrate. A backing that is stretched while wrapping tape around an object has a stress trying to return it to its unstretched state which also creates a curling force in the tape. The fact that these situations generate a peeling type of stress is probably apparent to most. However, even situations that we might think of as shear loading can create peeling stresses. When we use a PSA tape or adhesive to mount a hook on a vertical wall and a weight is applied to that hook, there are surely shear stresses applied to the adhesive. However, because the load is applied at a finite distance from the wall, there is also a rotational moment to the force which creates a peeling stress at the top of the bond. Even when there is no hook and the adhesive is mounting a film, slab, or sheet, the center of force for the weight being supported is still a finite distance away from the wall and so a peeling stress is still created. The ability of the adhesive to resist peeling under that level of peel force is critical to the performance of the tape in such an application. Even though we frequently test hanging shear of tapes, the failure is often in an interfacial de-bonding mode, suggesting that the failure process may be controlled by slow peel. These test methods are usually done with sufficient loads to make the failure times be experimentally reasonable but they may be much higher load and faster de-bonding rates than those relevant to application use. In other words, we may be getting data that are governed by a part of the master curve further to the right than is actually relevant.

If we think about what is desirable for high holding power (against peeling forces), we would like the left side of the master curve to be as high as possible so that under actual loads, the peeling rate is vanishingly low. It is possible for different adhesive formulations to have very different behavior in this portion of the master curve while having very similar or even reversed performance at rates typical of normal laboratory peel tests. Comparison of the full shape of the master curve would allow a much better assessment of the suitability of an adhesive for its various requirements which may include high holding power (slow rate) and easy removability (high rate).

In this paper we have discussed the use of time-temperature superposition to look at the de-bonding (peeling) process at various rates and temperatures. However, others have also looked at using it to understand the bonding process in the context of tack or quick stick. See for example the work of Tsukatani, Hatano, and Mizumachi (10).

In summary, the concept of time-temperature superposition can often be applied not only to rheological properties of adhesives but to tack and peel behavior as well, providing a tool for prediction of performance at a wide range of rates, times, and temperatures relevant to the use of these materials.

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1. John D. Ferry (1980), "Viscoelastic Properties of Polymers," John Wiley and Sons, 3rd edition, New York
 2. E.P. Chang (1997), "Viscoelastic Properties of Pressure Sensitive Adhesives," *J. Adhesion*, **60**, 233-248
 3. David J. Yarusso (2002), "Effect of Rheology on PSA Performance," Chapter in "The Mechanics of Adhesion," ed. By D.A. Dillard and A.V. Pocius, Elsevier, Amsterdam
 4. M.L. Williams, R.F. Landel, and J.D. Ferry, (1955), *J. Amer. Chem. Soc.*, **77**, 3701
 5. D.H. Kaelble (1969), "Peel Adhesion: Influence of Surface Energies and Adhesive Rheology," *J. Adhesion*, **1**, 102-123
 6. C. Verdier, J.-M. Piau, and L. Benyahia, (1998), "Peeling of Acrylic Pressure Sensitive Adhesives: Cross-Linked vs. Uncross-Linked Adhesives," *J. Adhesion*, **68**, 93-116
 7. C. Derail, A. Allal, G. Marin, and Ph. Tordjeman, (1997), "Relationship Between Viscoelastic and Peeling Properties of Model Adhesives. Part 1. Cohesive Fracture," *J. Adhesion*, **61**, 123-157
 8. C. Derail, A. Allal, G. Marin, and Ph. Tordjeman, (1998), "Relationship Between Viscoelastic and Peeling Properties of Model Adhesives. Part 2. The Interfacial Fracture Domains," *J. Adhesion*, **68**, 203-228
 9. D. J. Yarusso, (1999), "Quantifying the Relationship Between Peel and Rheology for Pressure Sensitive Adhesives," *J. Adhesion*, **70**, 299-320
 10. T. Tsukatani, Y. Hatano, H. Mizumachi, (1989), "Bonding and Debonding Processes in Tack of Pressure-Sensitive Adhesives," *J. Adhesion*, **31**, 59-71