

DEFINING VISCOELASTIC ADHESIVE COORDINATES THAT MATTER

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Introduction

In a mixture design of experiments (DOE) analysis^[1] on a pressure sensitive adhesive (PSA) the relative concentrations of the various components constitute the selected predictor variables. These can be related to viscoelastic outcome variables and other PSA performance properties. A properly designed DOE study can deliver useful information about the individual contributions of the predictor variables and as well as interaction effects on an empirical basis in an effective way. However, such a mixture design based DOE outcome will not *per se* lead to a better scientific understanding of key factors governing PSA adhesive performance.

Dahlquist^[2] observed that materials that exhibit pressure sensitivity are those that have an elasticity modulus less than 3×10^5 Pa at room temperature. Herein, the modulus is a property which not only depends uniquely on the concentration coordinates but also on the interactions between the various components. This resulted in the well accepted empirical “Dahlquist criterion”; a necessary requirement for PSA performance. This formed the basis in further defining the pivotal role of viscoelasticity as main PSA property determinant.

Chang^[3] pursued a viscoelastic window concept as an alternative dynamic mechanical analysis (DMA) based approach to classify different types of PSA. The values of G' and G'' at two relevant frequencies (10^{-2} and 10^2 rad/sec) were determined herein. Although this concept has turned out to be useful in the rough categorization of different types of PSA in four performance quadrants its main drawback is that it cannot accurately predict more detailed PSA viscoelastic behavior. This prompted an alternative DMA based PSA characterization approach which is outlined herein.

Aogaki *et al.*^[4] described PSA as a typical viscoelastic body and the Burgers rheology model as associated to the shearing of PSA tapes. Herein, we describe an alternative and more comprehensive method.

The Burgers four component viscoelastic model shows substantial similarities with the viscoelastic profile of an PSA. The comparison provides a better understanding of the Williams-Landel-Ferry time temperature superposition principle and provides another viewpoint on the Dahlquist criterion. Our method aids in clearly defining a set of PSA key parameters from a viscoelastic profile as determined by means of DMA. It is associated in a physical scientific context to PSA performance.

Background

Viscoelastic profile of a Hot Melt PSA

Figure 1 displays a typical PSA DMA viscoelastic profile showing the viscoelastic moduli, storage modulus (G') and loss modulus (G''), and the ratio thereof (G''/G'), which is also referred to as the loss tangent ($\tan\delta$), as a function of temperature.

A modulus is an indicator of an object or substance's resistance to being deformed by an applied stress. Stress is the force causing the deformation divided by the area to which the force is applied. The elastic (G') and viscous (G'') parts of the modulus can both be determined by means of DMA.

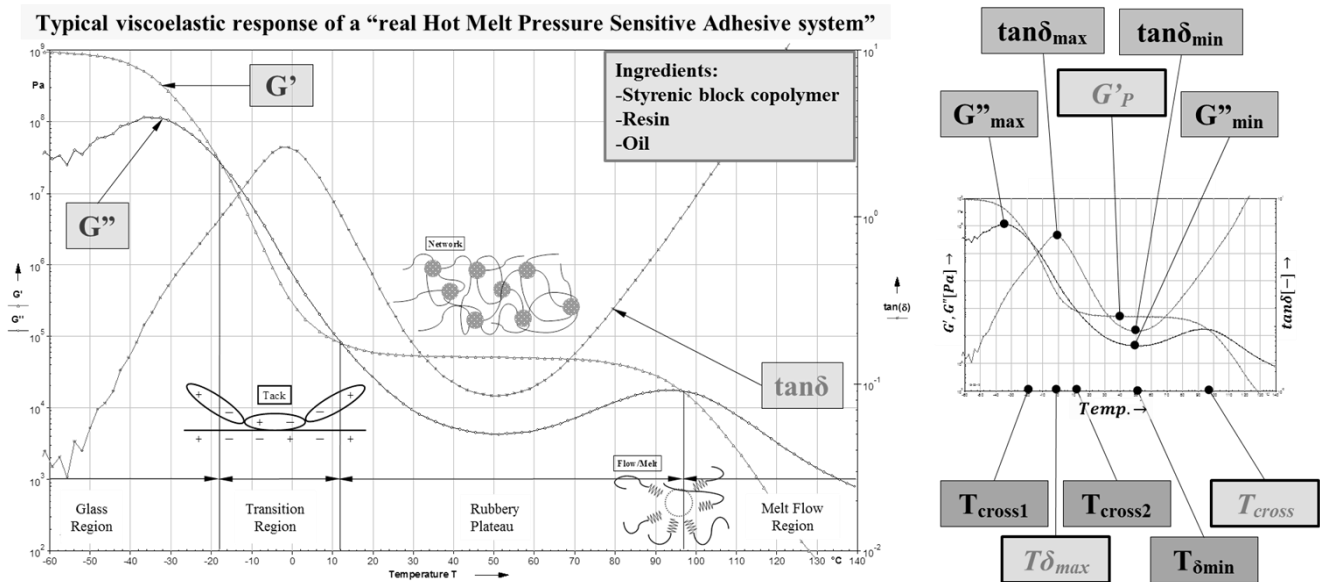


Figure 1. A typical viscoelastic profile with the legend displaying a selection of specific viscoelastic parameters.

In the viscoelastic profile (Figure 1), of a model PSA consisting of a blend of a block copolymer, resin and an oil, four different regions, separated by three cross overs of the G' and G'' curves, can be distinguished^[5]. Each region contains specific information related to the PSA performance as follows:

- Glass region: High moduli of both G' , G'' wherein G' dominates G'' resulting in a low $\tan\delta$ value. The low degree of molecular flexibility and mobility results in negligible tackiness.
- Transition region: Decreasing moduli, $\tan\delta$ reaches relative maximum value: Here the readings for the height of the rubber plateau (G'_P) and the temperature where the $\tan\delta$ peak occurs ($T\delta_{max}$) relative to the application temperature should be optimized by means of varying the PSA component ratio's towards an optimum adhesive performance.
- Rubbery Plateau: Medium moduli values, $\tan\delta$ reaches a relative minimum: This indicates the presence of a polymeric network (entanglement). The G'_P together with the $\tan\delta_{min}$ value provide information about the adhesion/cohesion balance and (modified) polymer network quality.
- Melt Flow-region: Indication of excessive loss of cohesion: Here the high temperature cross over (T_{cross}) can be used as a relative shear strength indicator.

Four viscoelastic parameters have been identified with a close relation to adhesive properties; $T\delta_{max}$, G'_P , $T\delta_{min}$ and T_{cross} . With the Burgers model it can be demonstrated that ($T\delta_{max}$, G'_P , T_{cross}) form a

complete set of relevant coordinates which represent a unique viscoelastic profile for blends consisting up to four components.

Theory

Burgers model

Figure 2 displays the viscoelastic profile based on a Burgers model calculation as a function of the frequency or temperature, compared to that of a real hotmelt PSA (HMPSA) as function of temperature.

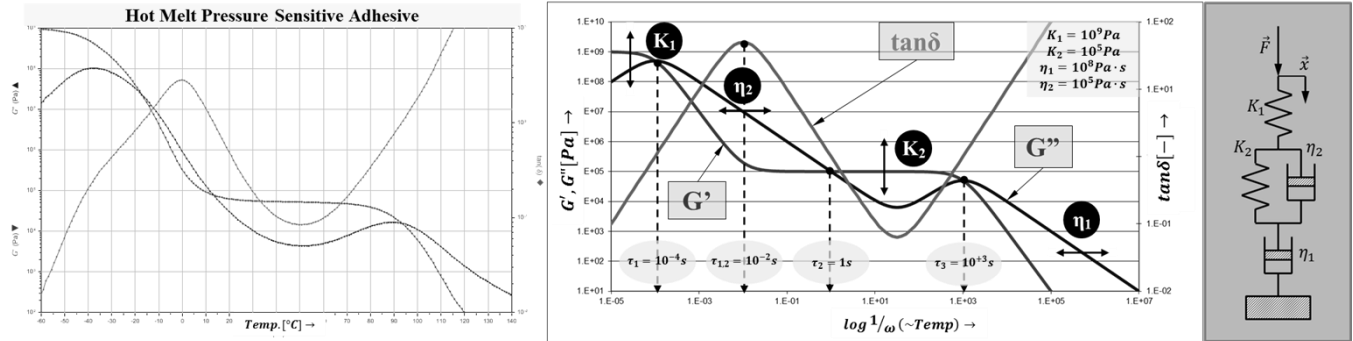


Figure 2. DMA viscoelastic HMPSA response as compared to a schematic response based on Burgers model calculations.

The displayed Burgers profile is generated by means of varying the frequency (expressed as radians per second) while keeping both the spring (K_i) and dashpot (η_i) parameter values constant. Here the whole profile is uniquely defined by the four parameters giving them the status of a “complete set of coordinates” (further referred to as “Burgers coordinates”).

By giving the dashpots an “Osborne Reynolds” temperature dependency and by varying the temperature while keeping the frequency constant the result will be a similar outcome but then as a function of temperature. Here from, the so-called William-Landel-Ferry Time Temperature Superposition relation for the Burgers model can be derived:

$$\eta_i = \eta_{0,i} e^{-B_i T} \text{ (Osborne Reynolds)}$$

$$T \leftrightarrow \log 1/\omega ; \text{ (WLFTTS relation)}$$

The “Burgers coordinates” are associated with their own specific areas in the viscoelastic profile as follows:

- K_1 : Controls the height of G' in the glass region which can be regarded as a constant ($\sim 10^9$ Pa) for most hydrocarbon materials.
- η_2 : Controls the position of the transition region; $G'' = \eta_2 \cdot \omega$.
- K_2 : Controls the height of the rubber plateau; $K_2 = G'_P$: Controls Adhesion/Cohesion balance (No WLF is required herein).
- η_1 : Controls the position of the beginning of the melt flow region; $G'' = \eta_1 \cdot \omega$ (Cox-Merz).

The cross over values in the frequency spectrum are related to so-called characteristic times τ_i which are a measure of the time processes need to happen (*Cf.* relaxation time) or, by using the WLF principle, temperatures at which processes will happen within a similar or shorter time frame as compared to the experiment time frame. (*Cf.* PSA related processes like substrate bonding, debonding, and flow/wetting). The relation with the Burgers coordinates and the WLF consequences are as follows:

- $\tau_1 = \eta_2 / K_1$
- $\tau_{1,2} = \sqrt{\tau_1 \tau_2} = \eta_2 / \sqrt{K_1 K_2} \xleftrightarrow{WLF} T \delta_{max}$
- $\tau_2 = \eta_2 / K_2$
- $\tau_3 = \eta_1 / K_2 \xleftrightarrow{WLF} T_{cross}$

By considering K_1 as a constant and replacing the two - position controlling - Burgers coordinates (η_1 and η_2) by the characteristic times (τ_3 and $\tau_{1,2}$) another complete set of coordinates is obtained which directly can be related to their countertypes which form a complete set of adhesive coordinates in the temperature spectrum:

$$\{K_1 \cong 10^9, \eta_2, K_2, \eta_1\} \leftrightarrow \{\tau_{1,2}, K_2, \tau_3\} \xleftrightarrow{WLF} \{T \delta_{max}, G'_P, T_{cross}\}$$

Herewith, physical meanings can be dedicated to the various coordinates as follows:

- $\tau_{1,2}, T \delta_{max}$: Control “fast processes”
- K_2, G'_P : Control “cohesion/ adhesion balance”
- τ_3, T_{cross} : Control “slow processes”

Experimental

Independent control of the viscoelastic adhesive coordinates.

An adhesive system with a unique independent control of all three adhesive coordinates should preferably consist of four components; a polymer, two different resins and a mineral oil. The polymer is more or less restricted to a styrenic block copolymer type, in this specific case an 18% styrene SIS having low (~0%) diblock polymer content was applied, to obtain the typical Burgers DMA rheology profile. The resins should preferably have different styrene compatibilities to enable an effective control of the T_{cross} reading by means of the Resin A/ Resin B ratio. Resin softening points may be different and the isoprene compatibility preferably is similar. The function of the oil is to control the $T\delta_{\text{max}}$ by means of varying the oil to resin ratio. The polymer content controls the G'_p plateau level.

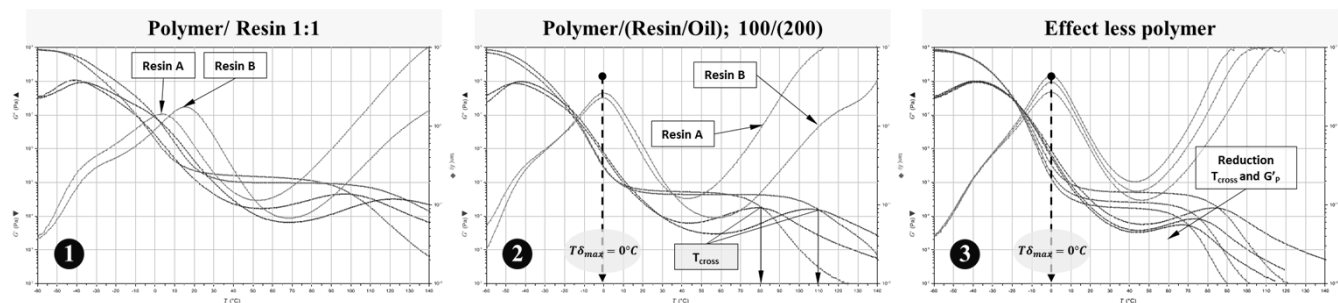


Figure 3. Resin characteristics in terms of viscoelastic profiles.

The viscoelastic profiles of the 1:1 polymer resin blends (Figure 3-1) illustrate that the resins are different. The profiles of the “Polymer/ (Resin/Oil); 100/200” blends have their $T\delta_{\text{max}}$ values adjusted to the same temperature, in this case 0°C, by means of varying the resin oil ratio (Figure 3-2). The differences in observed T_{cross} values indicate that the dependency on the Resin A/ Resin B ratio may be relatively high. The “Effect of less polymer” profiles (Figure 3-3) illustrates that lowering the rubber plateau by means of lowering the polymer concentration also requires resin/oil and Resin A/Resin B adjustments in order to keep the readings for $T\delta_{\text{max}}$ and T_{cross} constant (in this specific case the $T\delta_{\text{max}}$ readings have already been adjusted), rendering this approach slightly more challenging for the formulator than a mixture DOE.

Adhesive performance as a function of the adhesive coordinates

SAFT (shear adhesion failure temperature) was selected to represent a “slow process”. Loop tack and 180° peel adhesive application tests were selected to represent the “fast processes” in order to verify the theoretical statements made for $T\delta_{\text{max}}$ (control fast processes) and T_{cross} (control slow processes). From G'_p an increasing effect can be expected on SAFT and peel as these test procedures prescribe to apply a well-defined force, ensuring good adhesion of the bond, during the test specimen preparation. As this well-defined force is not applied as part of the loop tack procedure an increase of cohesion may affect the magnitude of the adhesion sooner. Figure 4-6 display on the left side the main changing adhesive coordinate and on the right side the impact on the selected adhesive performance tests.

The overlays of the rheograms in Figure 4 display equidistant variations in the $T\delta_{\max}$ coordinate while G'_P and T_{cross} are kept constant. The $\tan\delta$ curves change smoothly which indicates that the samples were well prepared, the changes in the moduli G' and G'' are less smooth because of unavoidable geometry errors. The adhesive performance test result display a dominant influence of the $T\delta_{\max}$ on the “fast processes” loop tack and 180° peel.

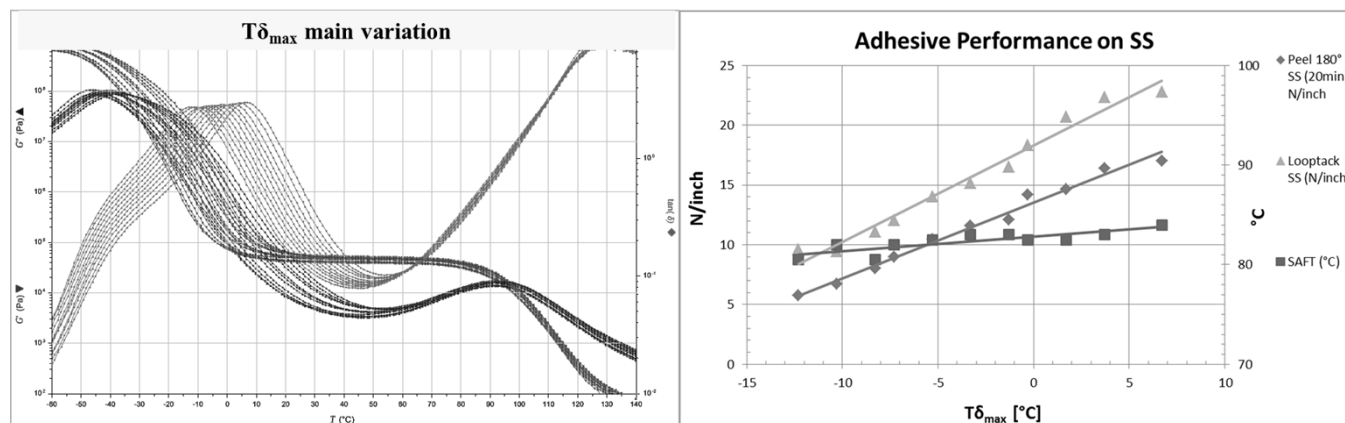


Figure 4. Variation of $T\delta_{\max}$: DMA graph overlays (left) and the impact on three adhesive test outcomes (right).

Figure 5 displays the variations in the T_{cross} coordinate while $T\delta_{\max}$ and G'_P are kept constant. The adhesive performance test result display a dominant influence of the T_{cross} on the “slow process” SAFT.

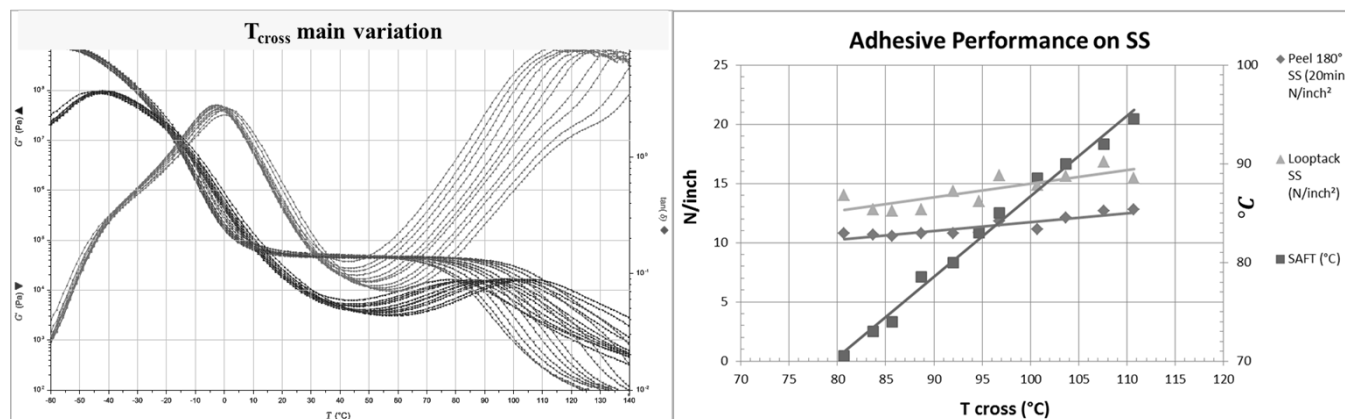


Figure 5. Variation of T_{cross} : DMA graph overlays (left) and the impact on three adhesive test outcomes (right).

Figure 6 displays the variations in the G'_P coordinate while $T\delta_{\max}$ and T_{cross} are kept constant. The rheograms display a relatively small difference in response as function of variation in polymer concentration (from ~30% to 40%, w/w). The small response together with the unavoidable geometry error, rendering the use of G'_P as a coordinate less suitable, are reasons to use the more accurate polymer concentration instead. As expected the SAFT and 180°C peel displayed an increasing trend with

increasing polymer content due to an increase of cohesion. More polymer did not increase loop tack indicating most likely a decreased molecular mobility and consequently a decrease in adhesion performance.

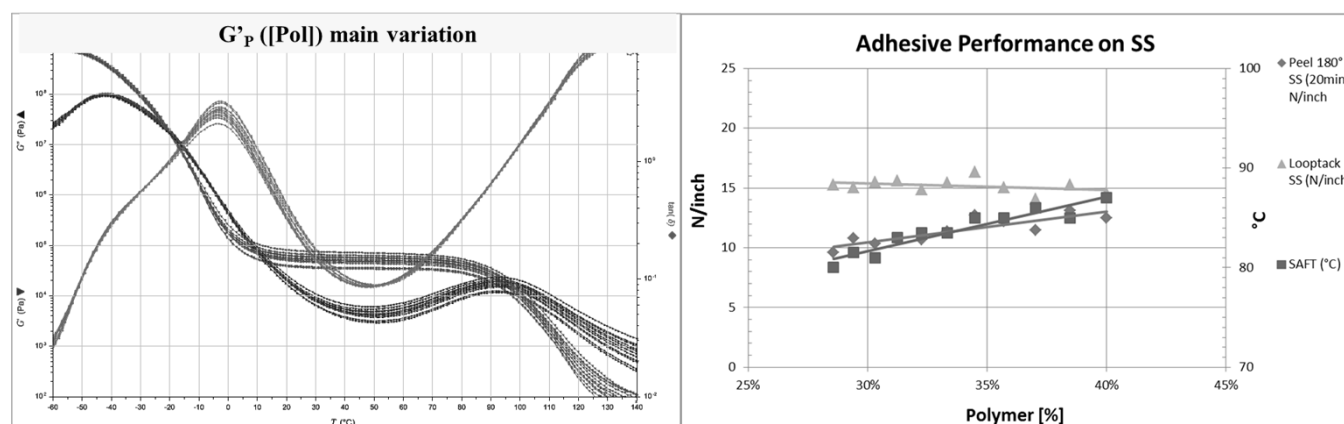


Figure 6. Varying G'_p . DMA graph overlays (left) and the impact on three adhesive test outcomes (right).

Conclusions

The Burgers model as applied herein for the DMA characterization of PSA blends defines a complete set of coordinates $\{T\delta_{max}, G'_p, T_{cross}\}$ which not only can be used to describe uniquely the viscoelastic profile of the Burgers model but also adhesive systems with similar viscoelastic profiles. This finding implies that the coordinates can also be applied to adequately describe PSA (adhesive) performance. As a consequence they can be regarded as “viscoelastic adhesive coordinates” that matter.

The physical meanings of the viscoelastic adhesive coordinates are as follows: $T\delta_{max}$ controls “fast processes”, G'_p controls “cohesion/ adhesion balance” and T_{cross} controls “slow processes”. These coordinates emerged as a consequence of the Burgers model application herein and as such will constitute a sound basis to study and predict the relation between PSA viscoelastic profiles and their adhesive performance. This can be achieved without requiring PSA chemical composition information.

References

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