Theory and a test method for the assessment of tackiness of structural film adhesives.

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Abstract

This paper discusses the development of a theory and a test method to quantify the tackiness of structural film adhesives (SFA) commonly used in Aerospace industry. Industry end users are usually sophisticated enough to know whether the tack level of qualified or screened products is adequate for their application. Initial tack and repositionability are often critical handling parameters for many applications. Although the importance of the tack parameter is well understood and appreciated, it is almost never a part of specification requirements, nor a consideration in the early stages of the qualification process. This parameter is usually evaluated in the “Shop Handling Evaluations” in the later stages of evaluation and qualification.

The methodology and test procedure described in this paper are primarily intended for research and development and screening purposes. The methodology is based on Dahlquist criterion for adhesion and tack.

Carl A. Dahlquist was the first to discover a rheological criterion for tack: tack did not occur when the adhesive storage modulus was greater than $3x10^5$ Pa. Since its discovery, the Dahlquist criterion was used extensively to utilize rheology to study tack for Pressure Sensitive Adhesives (PSAs). Structural film adhesives are often considered a class of their own, but fundamentally can be evaluated using the Dahlquist criterion, and characterized through dynamic mechanical testing.

Some limitations of the approach and method are identified and future work to address them is proposed.

Key Words

Dahlquist criterion, tack, tackiness, rheology, SFA, structural film adhesive, aerospace

Introduction

Structural film adhesives (SFAs) are the workhorse of today’s Aerospace industry. The first “structural” adhesive was used on the DeHavilland “Hornet” fighter in 1944, to bond aluminum and wood parts. By 1958, Boeing Co. rolled out the first large-volume production of the Boeing 707 jetliner using a nitrile-rubber phenolic film adhesive (AF-10, a product of 3M, was widely used in this application). [1] Ever since that time, SFAs have become a major technology element enabling the modern aircraft production process today. There are many different types of SFAs, differentiated by types of chemistry used to formulate them (epoxy, nitrile-phenolic, bismaleimide (BMI), benzoxazine), types of latent curatives/initiators employed, cure and service temperatures, types of carriers, etc. Still, the most widely used SFAs are thermally-curable epoxy film adhesives. It is important to recognize that epoxy SFAs (as well as a great majority of all SFAs) are essentially one-part thermally-curable adhesives formulated and produced to maintain film form. As such, those adhesive films must be transported and stored at freezing conditions (typically at -18°C) in order to preserve shelf life and out-time and maintain performance characteristics expected from the product. A great majority of epoxy SFAs are mildly tacky (with very few exceptions) if storage and handling conditions/requirements are met, and handling experts in the industry are very well versed in determining whether the tack level is adequate for the application/specification requirements. The evaluations are commonly based on subjective expert opinion. It is relatively easy to define tack/tackiness from an application point of view, e.g. if the SFA does or does not stick to the intended substrate. The question remains whether the adhesion is due to surface energy issues or something else inherent to a film adhesive. Surprisingly, there are few aerospace industry specifications with explicit requirements for tack, and even fewer (actually none to my knowledge) with quantitative specification targets and defined test methods for tackiness evaluations/assessments. An adequate tack level of an SFA for a particular application is typically defined during a qualification process in the shop handling evaluation phase, and locked into a specification by requiring the manufacturer/supplier to not make any changes to the product, and/or through obligatory notifications to the OEM/spec custodian if changes are not avoidable. This is an anomaly in the typically-conservative aerospace industry which requires adhesive products to be qualified to a detailed industry or OEM material specification. It should also be noted that tack is usually a first indicator of structural film adhesive aging. SFAs, as a quasi-stable systems, do age at room temperature, and the perceived tack gradually diminishes and eventually disappears. The aerospace industry personnel have expertise to subjectively correlate perceived tack decrease with SFA out-time, but an industry-accepted test method would be a huge benefit.

“We all can recognize when a material is tacky or sticky. Normally, we determine how sticky a material is by touching between our thumb and forefinger, and how difficult it is to remove it from our fingers. Tacky and sticky can be used in the same sense. Tack, by definition [2], is the ability of a material to adhere instantaneously to a solid surface when brought into contact by a very light pressure. The formation of the adhesive bond is not directly measured, but assessed by breaking bonds. In addition to having the proper rheology, the liquid or an adhesive must have a low enough surface tension to wet the substrate.

There are several tests for measuring tack (adhesives' bond strength), such as the probe tack test, peel test, rolling ball, rotating wheels, etc. It is noteworthy that none of these tests can be compared with one another. It is paradoxical that all these tests are measuring bond strength; the breaking of bonds and not their formation the way tack is defined. However, this is an accepted practice” [3]. Those two opening paragraphs of Charles L. Rohn’s paper published in 1999 (determined to the best of my abilities), are the best descriptions of tack characterization and measurement published at that time. Tack, by necessity, is defined by the test used to quantify its value. It is not a basic property of the adhesive, but a composite response of the adhesive’s bulk and the adherend’s surface preparation. [4]

The quantification of tack using the Dahlquist criterion is a significant advancement for adhesion science, to remove subjectivity and adhered surface preparation components out of the tack evaluation process, and instead focus only on adhesive bulk properties.

Dahlquist was the first to discover a rheological criterion for tack: tack did not occur when the adhesive storage modulus (G') was greater than $3x10^5$ Pa ($3x10^6$ dyne/cm^2). This is known as the Dahlquist criterion and has since been confirmed (Kraus et al 1979, Foley and Chu 1986, Dale et al 1989, Han et al 1989) as applicable to a wide variety of elastomer resin systems from which PSAs are formed. The Dahlquist criterion has thus formed the foundation for study of the rheological control mechanism of pressure-sensitive tack for PSAs. On the basis of this discovery, adhesion scientists have begun to utilize dynamic mechanical testing in conjunction with empirical testing to predict or evaluate how manipulation of PSA rheological behavior influences adhesive behavior. [5]

In my opinion there is a need in the industry to develop, demonstrate, and adapt an easy-to-implement tackiness characterization method for SFAs.

Experimental

Significant research has been conducted to study the relationship between the rheological behavior of PSAs and their tackiness/stickiness. Shear rheology of viscoelastic materials is a relatively simple, fast and efficient way to access the viscoelastic response as a function of frequencies, shear rate or temperature. It is clear that the same scientific principles will apply to SFAs. SFA's, in their uncured state, have characteristics and behaviors similar to PSAs. Strict adherence to the methodology of testing PSAs would dictate shear rheology testing at 25°C, at low shear rate and 1 Hz frequency. Those measurements would determine the PSA's visco-elastic response in the linear region and are very fast and simple to conduct using a shear rheometer instrument.

Compared to almost any "typical" PSA tack level that of the SFAs would be considered non-existent or borderline at best. To one with "calibrated" fingers in the aerospace industry there is a detectable tack. Although modest, the tack of SFAs exists, and those subtle variations make significant differences when it comes to the application of SFAs. A lot of factors affect the variability of perceived tack: lot to lot variability of input raw materials, residual volatile organic content, manufacturing process and storage and aging conditions.

The Dahlquist criterion modulus is actually a storage modulus (G'), therefore we have to be very mindful of the timescale in a particular application. For any typical PSA, the application timescale is approximately 1 sec., which would dictate rheological characterization at 25°C and 1 Hz. It will become apparent why replicating this approach may not work well for assessing tack characteristics of SFAs. SFAs are inherently stiffer systems when compared to PSAs, and the application time scale useful for the characterization of PSAs may not be appropriate for SFAs. This point will be addressed further in the Results and Discussions section.

The shear rheology of SFAs was measured using TA Ares G2 rheometer using 25 mm parallel plate geometry, 1 gram applied force with (auto-adjusted with 0.2 gram sensitivity), 2% strain rate and 0.01, 0.1 and 1.0 Hz frequencies. Sample thickness ranged from 0.4 to 0.5 mm, and was created by laminating multiple layers of individual SFAs together to minimize differences in coating weight of the various adhesives studied in this paper. Shear rheology results are correlated to subjective tack evaluation by touching between our thumb and forefinger using two different time scales: 1 and 5 seconds.

For the purpose of this discussion we will identify structural film adhesives used in this study as “Structural Film Adhesive A” or “SFA A” and “Structural Film Adhesive B” or “SFA B”.

“Structural Film Adhesive A” was selected from the family of 3M™ Scotch-Weld™ Structural Adhesive Films curable at 250°F. 15 distinct lots were used through the whole study.

“Structural Film Adhesive B” was selected from the family of 3M™ Scotch-Weld™ Structural Adhesive Films curable at 350°F. One lot was used to study the effect of out-time on tack degradation.

Results and Discussion

To quantify the tack, both a subjective as well as a quantitative method were employed, and later a correlation of the two was determined. Table 1 contains the subjective tack data for the 15 distinct lots of “Structural Film Adhesive A” tested in this study, and the numerical values are further described below Table 1. There were two subjective tack assessment times evaluated, using 1 second/light pressure approach (as prescribed by classical tack definition and in theory should correlate with 1 Hz frequency of application) and 5 seconds/light pressure approach to compensate for somewhat higher stiffness of SFAs compared to traditional PSAs.

It should be noted that the subjective tack value compares the experienced evaluator’s *perceived* tack to that which the experienced evaluator *expected* the tack value to be for this SFA. It should also be noted that the studies were conducted in a blind manner, meaning the experienced evaluator did not know the quantitative tack values when conducting the subjective evaluation. All the subjective evaluations were conducted on a single SFA in a single session, on the samples pre-conditioned/equilibrated in CTH room (constant temperature/humidity) set at 25°C/50% RH (77°F/50%RH) so the samples were able to be most accurately compared to each other.

Table 1. Tack Assessment time and the resulting subjective perceived tack levels for 15 distinct lots of “Structural Film Adhesive A”.

Lot Number	Tack assessment time [sec]	perceived tack between fingers [1 sec](subjective)	Tack assessment time [sec]	perceived tack between fingers [5 sec] (subjective)
1	1	2	5	3
2	1	2	5	4
3	1	3	5	4
4	1	2	5	4
5	1	3	5	4
6	1	2	5	4
7	1	2	5	4
8	1	3	5	4
9	1	2	5	4
10	1	2	5	4

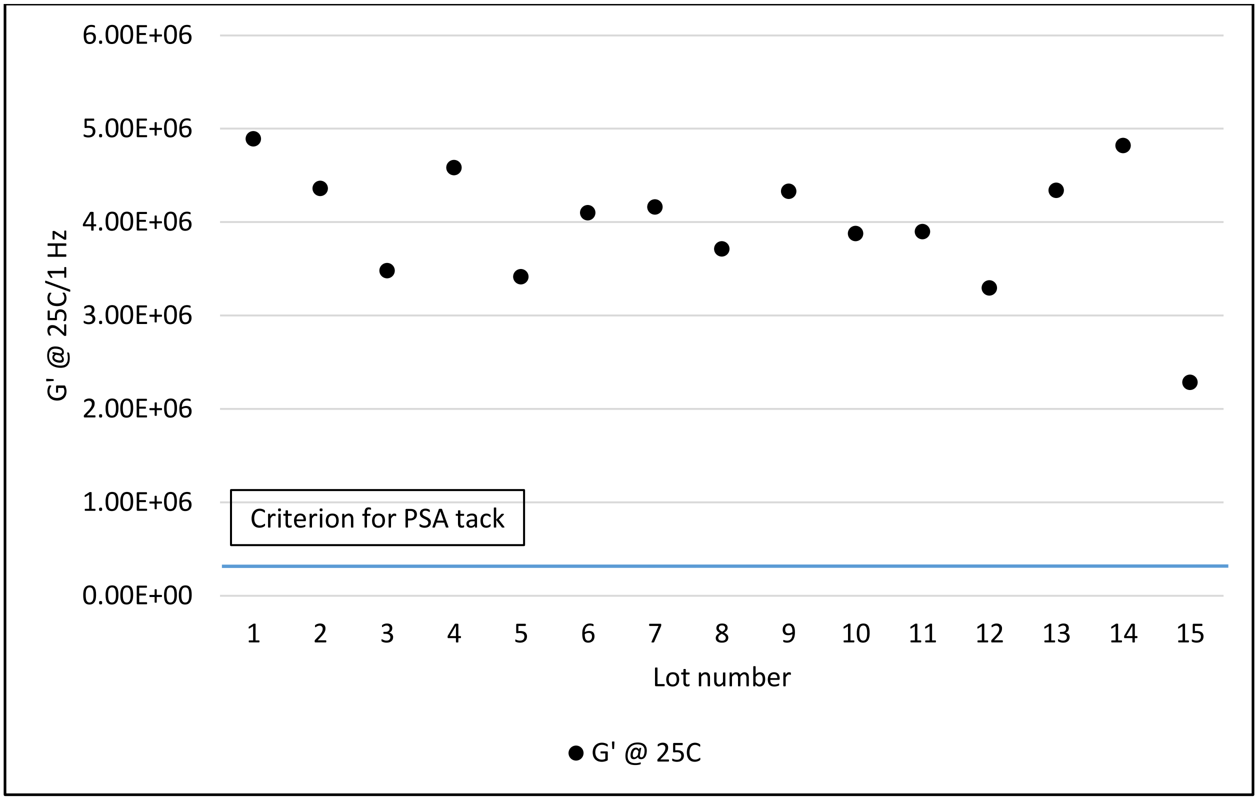
11	1	2	5	4
12	1	3	5	4
13	1	2	5	4
14	1	2	5	3
15	1	4	5	5

Descriptions correlating to the subjective numeric tack values reported in Tables 1:

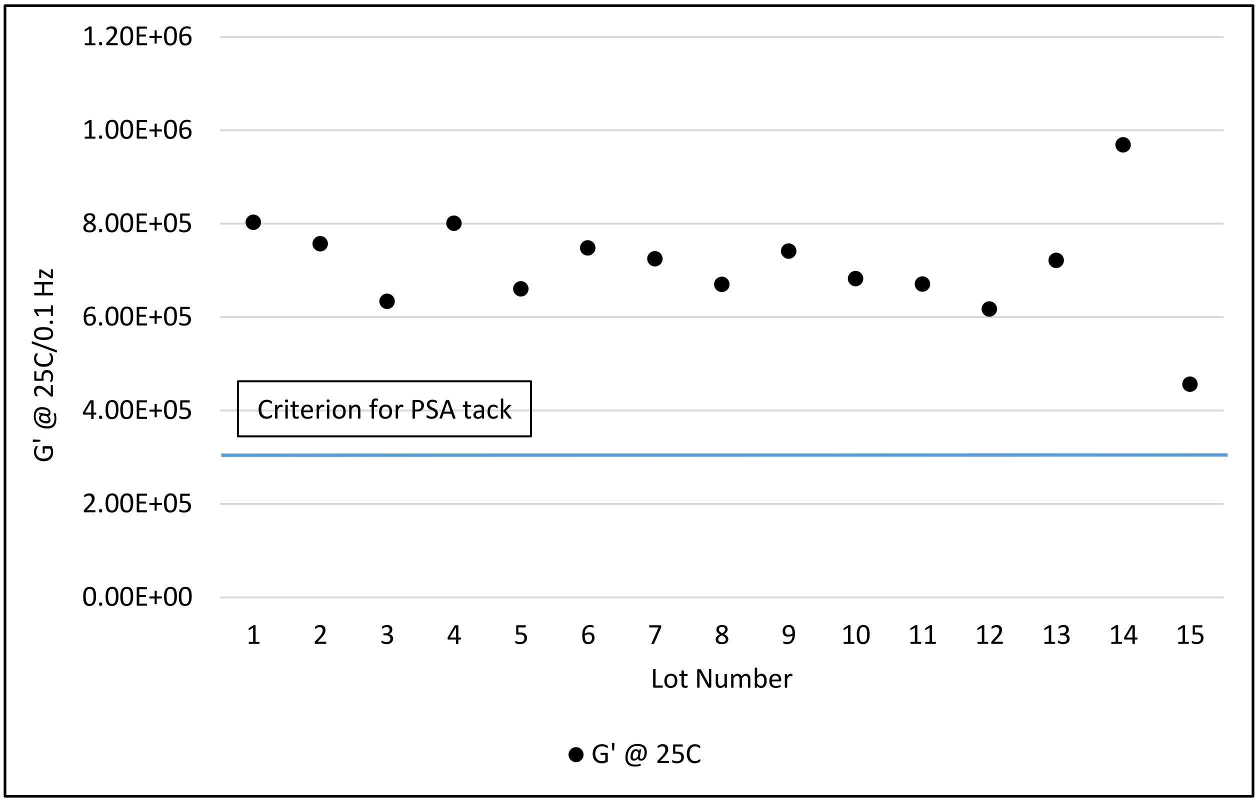
1 = no tack, 2 = very low tack (from what is expected for this particular product), 3 = low tack, 4 = tack as expected, and 5 = tack is higher than expected.

Following the subjective evaluation, the quantitative tack measurement was completed using the Ares G2 rheometer in shear mode on the same 15 individual lots of “Structural Film Adhesive A” at three frequencies: 0.01, 0.1 and 1 Hz. The “Structural Film Adhesive A” was evaluated by this method, and the results are plotted graphically as the Storage Modulus (G’) vs. the lot number of the SFA in Graphs 1, 2 and 3. The same SFA lot numbers correspond to the subjective tabled tack data and the quantitative graphs. The line on each graph represents the approximate level of Dahlquist criterion modulus for PSA tack using the classical definition and methodology of low force, and short application time (1s = 1Hz).

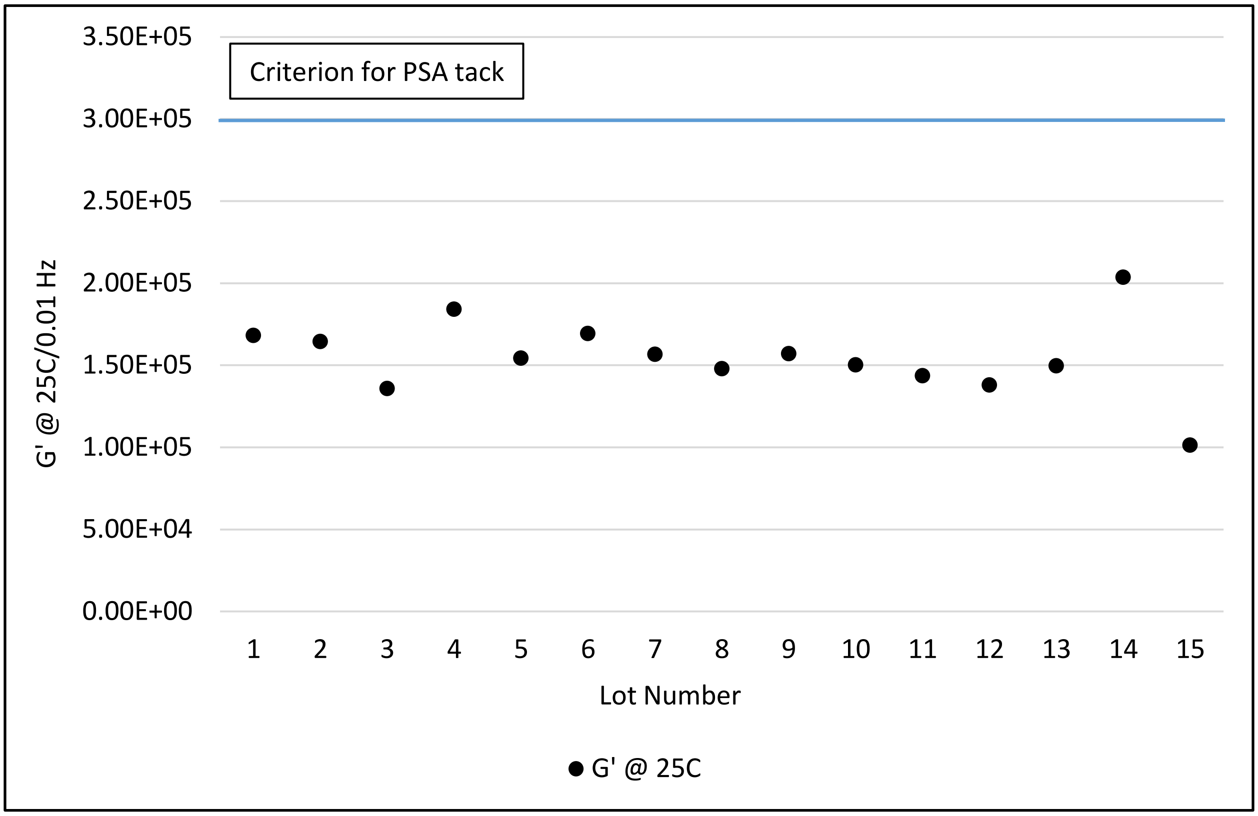
Graph 1: Plot of G’ [Pa] vs. Lot Number for “Structural Film Adhesive A” at 25°C/1Hz



Graph 2: Plot of G’ [Pa] vs. Lot Number for “Structural Film Adhesive A” at 25°C/0.1Hz



Graph 3: Plot of G’ [Pa] vs. Lot Number for “Structural Film Adhesive A” at 25°C/0.01Hz



Only in the final case where the frequency was reduced to 0.01 Hz did the measured storage modulus fall under the traditional Dahlquist Criterion for PSA tack (evident in Graph 3). This result substantiates the need to re-think and modify the testing conditions for SFAs in order to utilize the definition of tack presented in the Dahlquist Criterion. For the case in which the subjective tack was evaluated for 5 seconds (Table 1), and the storage modulus measurements were conducted at 0.01 Hz on a shear rheometer, a near perfect correlation was found to exist!. Given the fact that SFAs are stiffer systems compared to any typical PSAs, appropriate application (visco-elastic response) time needs to be increased from the classical 1 second (corresponding to 1Hz) to a somewhat more adequate longer time for SFAs of 5 sec (corresponding to 0.01Hz).

In response to elevated temperature exposure experienced in storage and transport, SFA tack is known to decrease. To illustrate this experimentally, one lot of “Structural Film Adhesive B” was exposed to 35°C shelf aging for varying periods of time, after which the storage modulus was quantified as well as evaluated subjectively. For the subjective evaluations, the methodology described above was used with some variations: 20 cm x 20 cm samples of “Structural Film Adhesive B” were aged in an air-forced oven for the necessary periods of time and subsequently pre-conditioned in a CTH (constant temperature/humidity) room set at 25°C/50% RH (77°F/50% RH) for 4 hours prior to subjective tack and shear rheology testing. Values reported in Graph 4 are averages of three measurements of fresh or aged samples after appropriate conditioning. The steady increase of values of G’ in Graph 4 can be compared to the subjective evaluation ratings in Table 2 (particularly for the 5 second time) and clearly illustrates the significant degradation of tack for “Structural Film Adhesive B” after exposure to a temperature of 35°C for up to 72 hours.

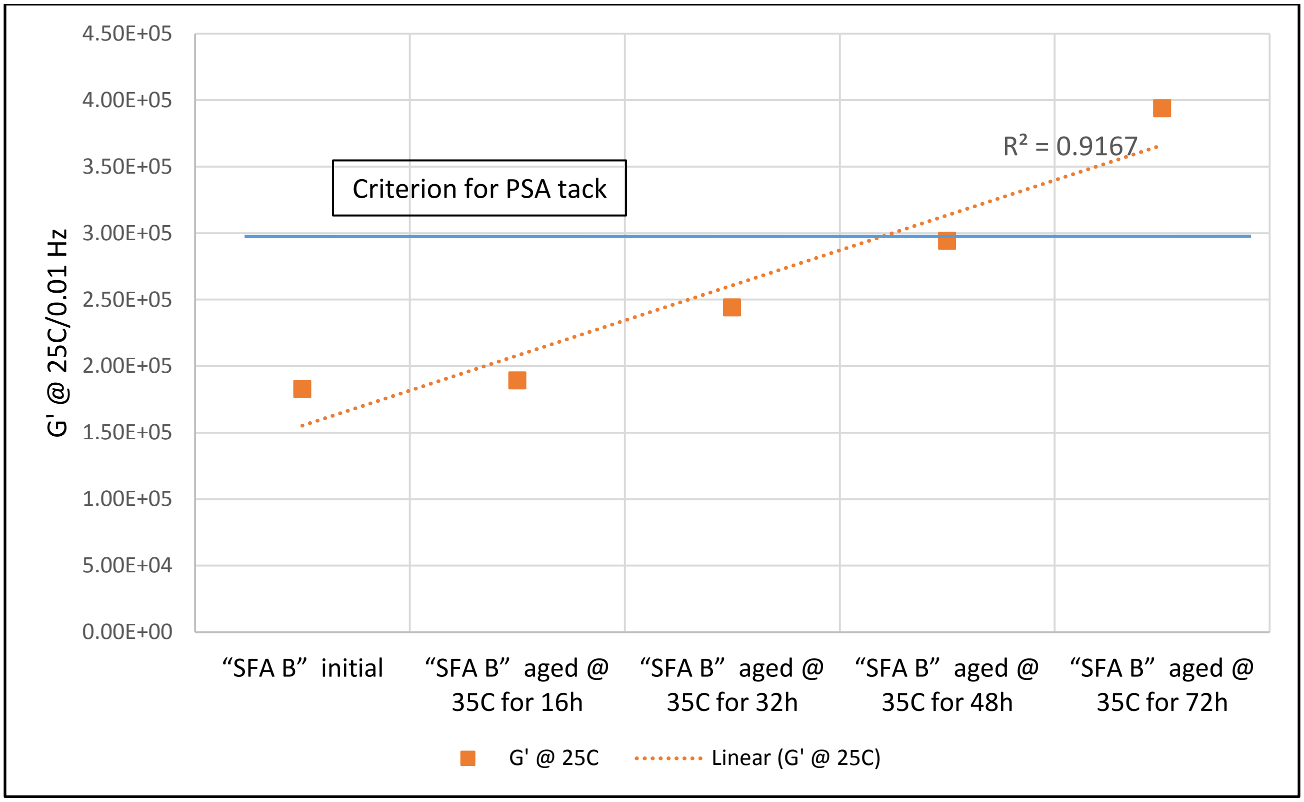
Table 2. Tack Assessment time and the resulting subjective perceived tack levels for "Structural Film Adhesive B" after exposure to a temperature of 35°C for up to 72 hours.

	Tack assessment time [s]	perceived tack between fingers[1 sec] (subjective)	Tack assessment time [s]	perceived tack between fingers [5 sec] (subjective)
"SFA B" no aging	1	2	5	4
"SFA B" @ 35C for 16h	1	2	5	3
"SFA B" @ 35C for 32h	1	1	5	3
"SFA B" @ 35C for 48h	1	1	5	2
"SFA B" @ 35C for 72h	1	1	5	1

Descriptions correlating to the subjective numeric tack values reported in Tables 1:

1 = no tack, 2 = very low tack (from what is expected for this particular product), 3 = low tack, 4 = tack as expected, and 5 = tack is higher than expected.

Graph 4: Storage Modulus measured at 25°C and 0.01 Hz frequency as a function of the aging time (out life) in hours of the "Structural Film Adhesive B" at 35°C



A more interesting correlation between the subjective tack and the quantitative shear modulus measurement was enabled by the out-life study of the "Structural Film Adhesive B". Because the tack decreased dramatically with additional out life, almost the full range of subjective tack values were able to be correlated against the shear modulus measurements. When the data in Graph 4 is compared to the subjective data in Table 2, a near perfect correlation is shown for tack changes as a function of out life between the shear modulus and the experienced evaluator's perceived tack (in the case of the 0.01 Hz frequency and the longer visco-elastic response time of 5 sec).

Conclusions

The results provide a compelling argument in favor of the Dahlquist approach for tack evaluation of SFAs. Parallel approaches of subjective expert evaluation and quantitative shear rheology (G', inherent property) have shown an exceptional level of correlation if the measurement methodologies are allowed to be adjusted for an application time more appropriate for evaluation of tack of SFAs (5 sec and 0.01 Hz). This methodology has shown promise as an effective and efficient tool for objective and quantifiable assessment of SFAs tack parameter.

For the future work, it would be interesting and beneficial to study effects of some of the variables mentioned earlier (volatile organic content, raw material variability, process history) on the tack measurements and aging dynamics of SFAs. An expanded scope of additional studies and additional SFAs would increase confidence in this methodology.

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References

1. Structural Adhesives: Chemistry and Technology, S.R. Hartshorn, Springer Science & Business Media, 2012, ISBN 1468477811, 9781468477818
2. ASTM D 1878-61 T, ASTM Bull. No. 221,64 (1957)
3. ANALYSIS OF TACK, Charles L. Rohn, Rheometric Scientific, Inc. Piscataway, NJ08854
4. Handbook of Pressure Sensitive Adhesive Technology, thurd Editio, Edited by Donatas Satas, Satas and Assosiates, Warwick, Rhode Island. Chapter 4.
5. The Dahlquist Criterion: Applicability of a Rheological Criterion to the Loss of Pressure-Sensitive Tack in Flour-Water Dough. S. S. HEDDLESON, D. D. HAMANN, and D. R. LINEBACK. Cereal Chem. 70(6):744-748
6. Characterization of Pressure Sensitive Adhesives by Rheology, Fred A. Mazzeo, Ph.D. TA Instruments, 109 Lukens Drive, New Castle DE, USA