CORRELATION BETWEEN MECHANICAL AND VISCOELASTIC PROPERTIES OF SOME PEROXIDE-CATALYZED SILICONE PRESSURE SENSITIVE ADHESIVES

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Introduction :

Silicone Pressure Sensitive Adhesives (PSAs) are widely used in applications where common organic PSAs are not fully adapted. Typical applications are for masking, plating and splicing tapes, electrical insulation wraps, protective films for touch screens and medical devices. Their main advantages are high temperature, chemical and environmental resistance, low surface energy adhesion, low toxicity and high gas permeability. Today, several grades of silicone PSAs with complementary performances are available on the market. Nevertheless, up to now, they are generally proposed at 50-60% solids in an organic solvent and alternative delivery systems (emulsion, solventless, etc.) are still quite rare.[1,2]

Typically, silicones PSA compositions consist of two main components : a silicate resin (MQ) and a high molecular weight polydimethylsiloxane gum (PDMS). Although silicone PSAs exhibit pressure sensitive behavior just after solvent removal, further crosslinking may be performed to enhance the cohesive strength. There are two basic cure systems commercially available for silicone PSAs : peroxide-catalyzed free-radical cure and platinum-catalyzed silicon hydride to vinyl addition cure.

The mechanical properties of PSAs are usually described by tack, peel strength and shear resistance, which are strongly dependent on the bulk viscoelastic properties of the adhesive system. Rheology is a fast way to detect adhesion properties and is frequently used in adhesive studies. Several years ago, a viscoelastic windows (VW) concept has been proposed to identify different types of PSAs.[3,4] The VW is constructed by only using the viscoelastic properties measured at one low frequency which corresponds to bonding and one high frequency that corresponds to debonding. The purpose of this paper is to highlight the correlation between the mechanical and viscoelastic properties of several peroxide catalyzed silicone PSAs with the help of the rheological profiles and the VW concept.

Experimental methods :

Cold-blend and bodied PSAs :

Three grades of silicone PSAs with different raw materials and resin-to-gum ratios were prepared for the study : **PSA A** has to be considered as the reference. **PSA B** contains an MQ resin with a lower viscosity for the same solid content as used for PSA A. The resin-to-gum ratio is the same. **PSA C** contains the same MQ resin as in PSA B. The resin-to-gum ratio is higher in comparison with PSA A and B. For each, we evaluated a “cold blend” and a “bodied” version. The cold blend version was based on a simple mixture of MQ resin and PDMS gum. For the bodied version, an additional base-catalyzed condensation reaction (i.e the bodying process) was carried out through the OH groups contained in the two components. The role of co-reacting the MQ resin with the PDMS gum is to reduce the large scale mobility of the gum thus permitting the MQ resin to be trapped in the silicone matrix during the network formation.[5] In other words, this step is to achieve improved crosslinking density and cohesive strength.

Adhesive coating preparation :

Each cold blend and bodied product was used to prepare some silicone PSA tapes having 50 microns dry adhesive on 36 microns polyethylene terephthalate (PET) substrate. To prepare the peroxide-cured silicone PSA tapes, the adhesive mixtures were catalyzed with 3% (based on silicone solids) of a stiff paste consisting of 50% di-(2,4-dichlorobenzoyl)peroxide desensitized with silicone oil. The coated adhesives were first left to dry at room temperature for 15 minutes, then cured for 2 minutes at 170°C.

Testing :

The PEEL adhesion of the cured adhesive tapes was measured by performing a 180° PEEL test against a polished stainless steel plate (Instron). The measurement was carried out according to the FTM 1 (or ASTM D3330) method at a speed of 300 mm/min.

The Probe TACK adhesion was measured according to the ASTM D2979 method using a Polyken Probe TACK tester (ChemInstruments) at a contact pressure of 9.79 +/- 0.10 kPa, a probe movement rate of 1 cm/sec, and a dwell time of 1 sec.

The Loop TACK test measures the strength of bonding, after a contact time of about 5 sec, between the adhesive and a 2.54cm wide polished stainless steel plate. The test was carried out using a Loop Tack tester (Chelsinruments) according to the FTM 9 method at a rate of 300 mm/min.

The SHEAR resistance was measured according to the ASTM D3654 method using a room temperature 30 bank SHEAR tester (ChemInstruments). A strip of adhesive tape (1.25 cm x 7 cm) is applied to a polished stainless steel panel under controlled roll down. The contact surface area is 12.5mm^2. The panel is tilted backwards at an angle of 2°. A standard mass of 1 kg is attached to the free end of the tape and the time to failure is determined.

A Thermo Scientific HAAKE Rheostress 78 was used to characterize the PSAs viscoelastic properties. After removing of solvent, dried bulk adhesive samples were used in the form of a disk of 25 mm diameter with a thickness of 1-2 mm. Some parallel plates with a diameter of 20 mm, a gap width of 1.5 mm and a strain of 600 Pa were chosen in order to run the trials. Viscoelastic data were generated at room temperature, over a wide frequency range (between 0.01 and 100 Hz).

Results and discussion :

Tapes properties :

All the peel, tack and shear results for the different cured adhesive tapes prepared from the three silicone PSAs compositions are summarized in the following table (Table 1) :

Table 1.

	PSA A		**PSA B**		**PSA C**	
	bodied	**cold blend**	**bodied**	**cold blend**	**bodied**	**cold blend**
Peel (g/cm)	**450**	**402**	**449**	**429**	**504**	**482**
Probe Tack (g/cm²)	**1863**	**1143**	**2817**	**2374**	**2393**	**2097**
Loop Tack (g/cm)	**850**	**940**	**748**	**1303**	**872**	**1212**
Shear (h)	**OK**	**OK**	**NOK***	**NOK****	**OK**	**OK**

*** : adhesive failure**

**** : cohesive failure**

Firstly, a positive impact of the bodying process on the peel, probe tack and shear performances is observed for the three PSAs. However, the loop tack results are better for the cured adhesive tapes based on the cold blend approach. The comparison of PSA A and PSA B results highlights also the positive impact of the low viscosity MQ resin on the probe tack performance with a same level of peel adhesion due to an identical resin-to-gum ratio. Nevertheless, the consequence is a loss of shear resistance for PSA B even if the bodying process is applied. For PSA C, as more resin is added in comparison with PSA B, a more tightly cross-linked network is achieved to provide the cohesive strength required to give substantial shear resistance under load. A higher resin level also produces a stronger bond between the substrate and the adhesive, resulting in higher adhesive strength. The increase in adhesion and cohesive strength are accompanied, however, by a lower probe tack.

Rheological properties :

Bonding of adhesion has been found to be correlated to the elastic modulus at low frequency - G’ (0.015 Hz) - and debonding has been shown to be correlated to a ratio of the elastic modulus at both high and low frequency – G’ (15 Hz)/G’ (0.015 Hz). More precisely, PSA with 20000 Pa < G’ (0.015 Hz) < 40000 Pa and 5 < G’ (15 Hz)/G’ (0.015 Hz) < 300 would have an optimum combination of tack, peel and shear properties.[6,7] Table 2 shows a summary of viscoelastic properties related to PSA characteristics[8] :

Table 2. (cited from reference 8)

Mechanical test	Rheological behavior	Performances
TACK	Low Tan δ peak and low G' Low cross-links (G" > G') at approx. 1 Hz	HIGH TACK
SHEAR resitance	High G' at low frequencies (< 0.1 Hz) High viscosity at low shear rates	HIGH SHEAR
PEEL strength	High G" at high frequencies (100 Hz)	HIGH PEEL
Cohesive strength	High G' and low Tan δ	HIGH cohesive strength (Bulk properties)
Adhesive strength	High G" and high Tan δ	HIGH adhesion strength with surface

Dynamic mechanical analysis – bodied PSAs :

The frequency curves are sensitive to structural differences (i.e. crosslink density) and formulation changes (i.e. resin-to-gum ratio). As shown in Figure 1, elastic modulus values for the three PSAs increase relatively quickly as the frequency increased. At low frequency rates (between 0.01 and 0.1 Hz), the lowest G’ values are measured for PSA B and the highest G’ values are measured for PSA A. This is in agreement with the good tack performances for PSA B and the good shear performance for PSA A. Moreover, for PSA C, a higher slope exists for G’ and G” as the frequency is increased. With relatively low G’ values for low frequencies, low crosslink (G” > G’) at 1 Hz and the highest G” value at 100 Hz, PSA C can be considered as a PSA with a good tack and peel compromise.

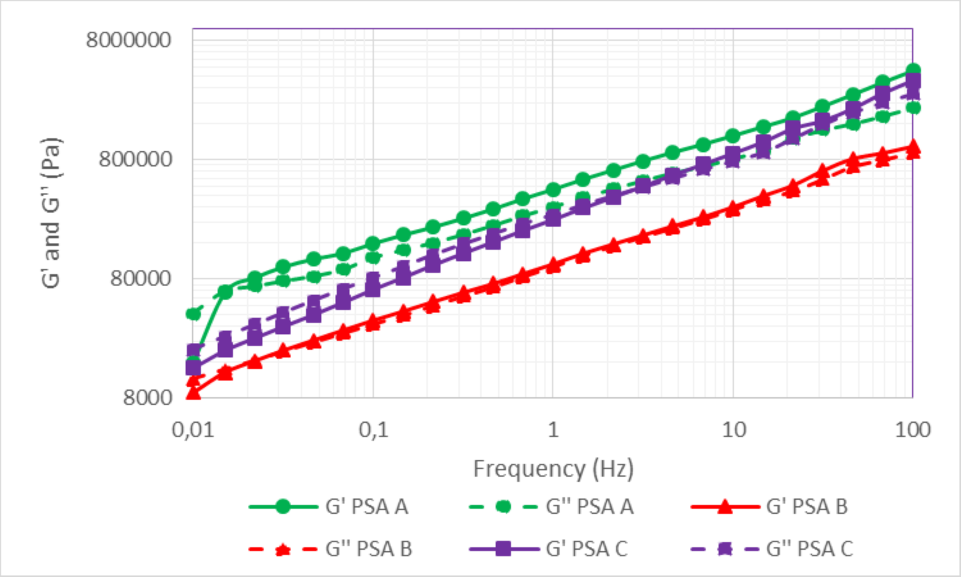

Figure 1

The range in tan δ (G”/G’) values over the frequency range evaluated gives complementary information on the viscoelastic behavior of the three PSAs (Figure 2). For PSA A, the frequency at which tan δ = 1 is low and for higher frequencies, tan δ is lower than for PSA B and C. High G’ and low tan δ are the signature of a good cohesive strength for PSA A. On the contrary, for a wide range of frequencies, tan δ > 1 for PSA C. High G” at high frequencies and tan δ > 1 are the signature of a good adhesive strength for PSA C.

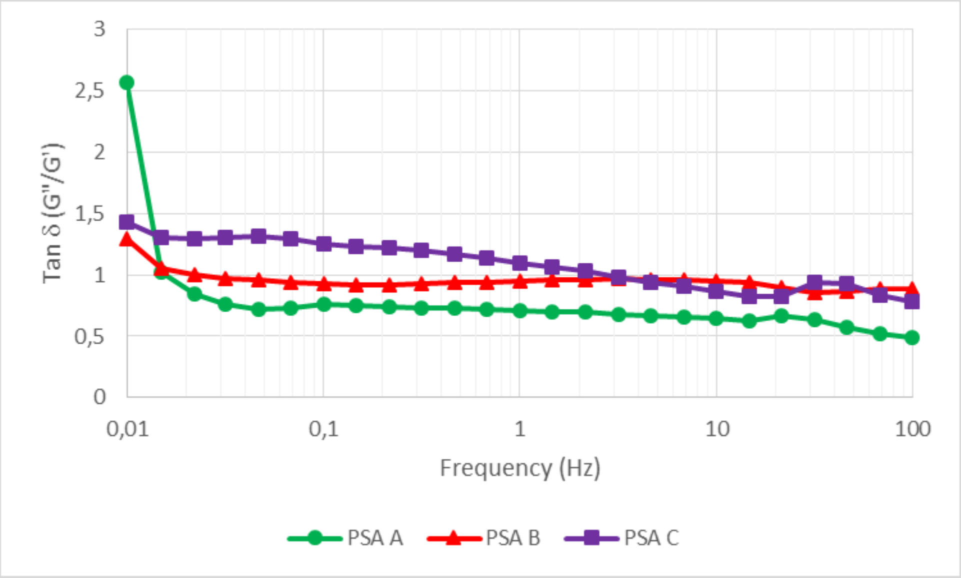

Figure 2

The highest complex viscosity η* values at low frequencies are measured for PSA A (Figure 3). This is in agreement with the better shear performances of PSA A in comparison with PSA B and C. When the resin component increases between PSA B and PSA C, the viscosity of the adhesive increases. This is observed in the frequency curves by an increase in η*, G’ and G” at low frequencies and a different change as frequency increases.

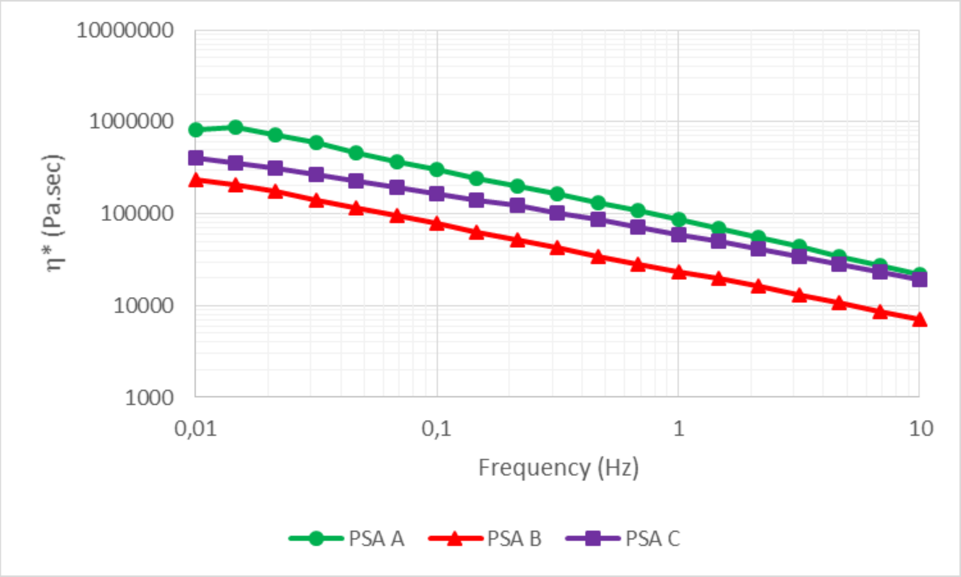

Figure 3

In the following table, the main significant data was collected to highlight the correlation between tack, peel and shear performances and G’, G”, tan δ and η* values at different frequencies (Table 3) :

Table 3.

			PSA A	PSA B	PSA C
	TACK (g/cm2)		1863	2817	2393
	PEEL (g/cm)		450	449	504
	SHEAR		OK	NOK	OK
TACK	G'(0.01 Hz)	LOW	16037	8973	14384
	G'(0.1 Hz)	LOW	158982	36071	65455
	Tan δ (0.01 Hz)	LOW	2,57	1,3	1,43
	G" > G' (1Hz)	YES	NO	NO	YES
SHEAR	η* (0.01 Hz)	HIGH	815623	233701	398685
	η* (0.1 Hz)	HIGH	305591	78149	166916
	G' (0.01 Hz)	HIGH	16037	8973	14384
	G' (0.1 Hz)	HIGH	158982	36071	65455
PEEL	G" (100 Hz)	HIGH	2181725	921510	2864838
Cohesive strenght	G'	HIGH	***	*	**
	Tan δ	LOW	***	**	*
Adhesive strenght	G"	HIGH	**	*	***
	Tan δ	HIGH	*	**	***
TACK, PEEL, SHEAR Compromise	20K < G'(0.015 Hz) < 40K		61517	13236	20172
	5 < G' (15 Hz)/G'(0.015 Hz) < 300		24,6	30,1	55,8

In this table, the best tack performances are confirmed for PSA B due to low G’ modulus values and low Tan delta for low frequencies following by PSA C. The best shear performances are observed for PSA A due to high η* and G’ at low frequencies. This is also consistent with the PSA A first rank for the cohesive strength. The best peel performances are observed for PSA C due to high G” at high frequencies. This is also consistent with the PSA C first rank for the adhesive strength. Moreover, the comparison of the G’ (0.015 Hz) values and the G’ (15 Hz)/G’ (0.015 Hz) ratio show that the best tack, peel and shear compromise is obtained for PSA C.

Dynamic mechanical analysis – differences between cold blend and bodied PSAs :

The following two graphs highlight the differences of storage modulus and loss modulus evolution over the frequency range for the cold blend and bodied versions of PSA A and C (Figure 4 and 5) :

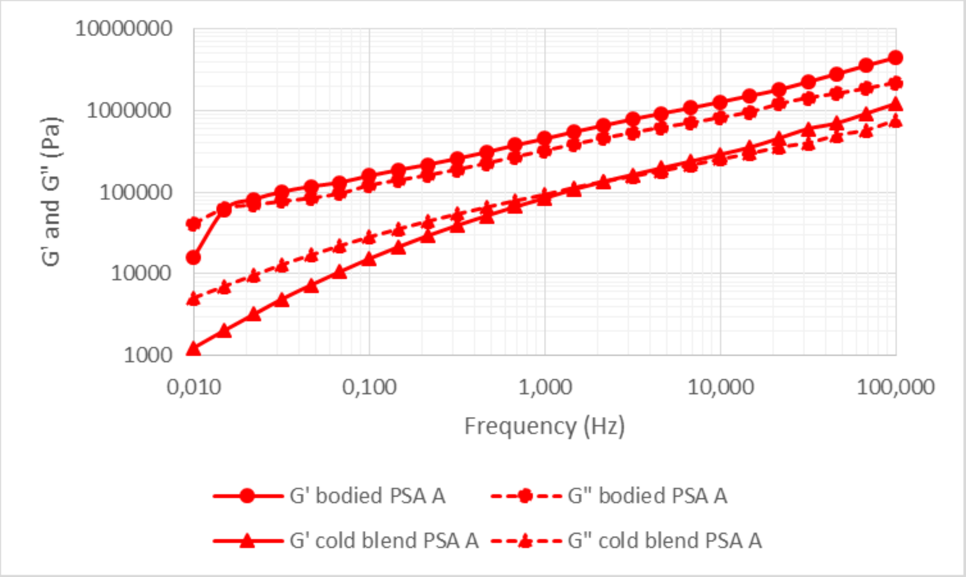

Figure 4

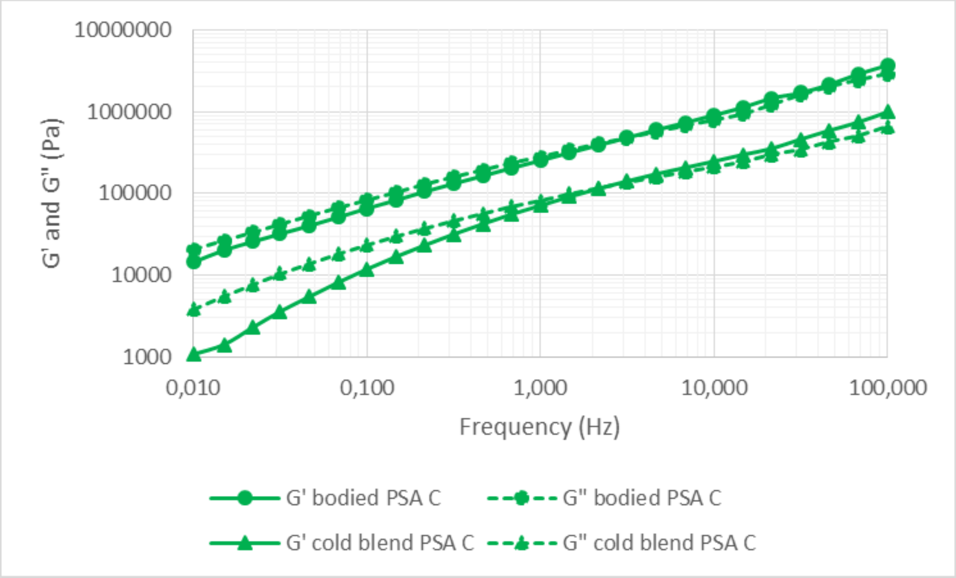

Figure 5

The global profiles tend to confirm the lack of cohesive strength with lower G' values for the cold blend PSAs than for the bodied PSAs. Moreover, tan δ is high for the low frequencies (Figure 6) :

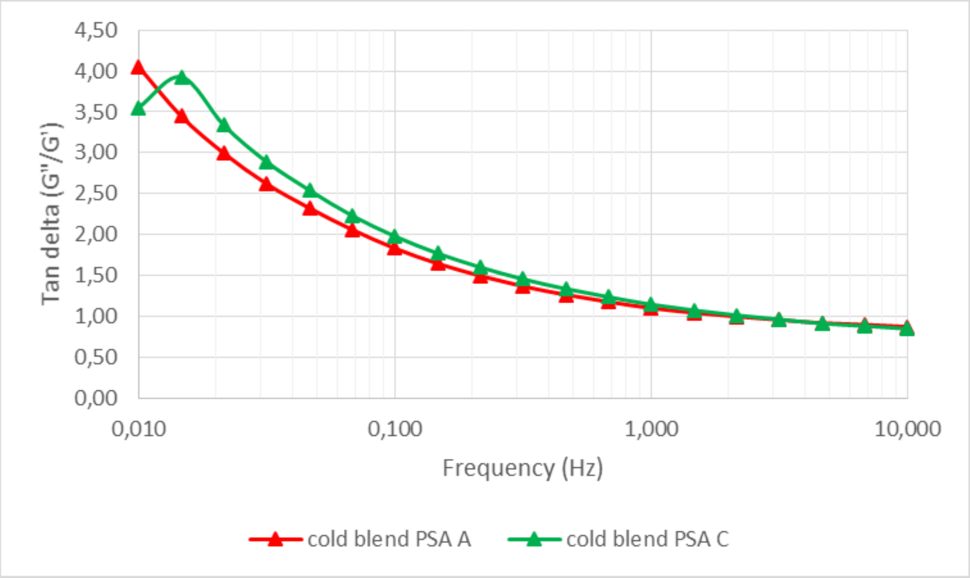

Figure 6

For the low frequencies, the G' values are generally very low for the cold blend PSAs in comparison with the bodied PSAs. Moreover, G" is slightly higher than G' at 1 Hz. The consequence should be some higher tack performances for the cold blend PSAs. This is not the case for the probe tack but this is the global tendency for the loop tack. These results demonstrate the complexity of tack measurements and highlight the need to have complementary measurements to fully characterize a silicone PSA.

Viscoelastic window concept :

Definition :

The viscoelastic windows (VW) are constructed from the values of dynamic storage modulus G' and dynamic loss modulus G" at two different frequencies : for example at 0.015 and 15 Hz. A four quadrant concept is proposed to categorize different types of PSAs based on the location of their VW's on the log-log cross plot of G' and G". The proposed four-quadrants correspond respectively to : Quadrant 1 : non-PSA or release coatings - Quadrant 2 : high SHEAR PSAs - Quadrant 3 : removable PSAs and medical PSAs - Quadrant 4 : quick and cold stick PSAs. The VWs of general purpose permanent PSAs occupy the central region (Figure 7) :

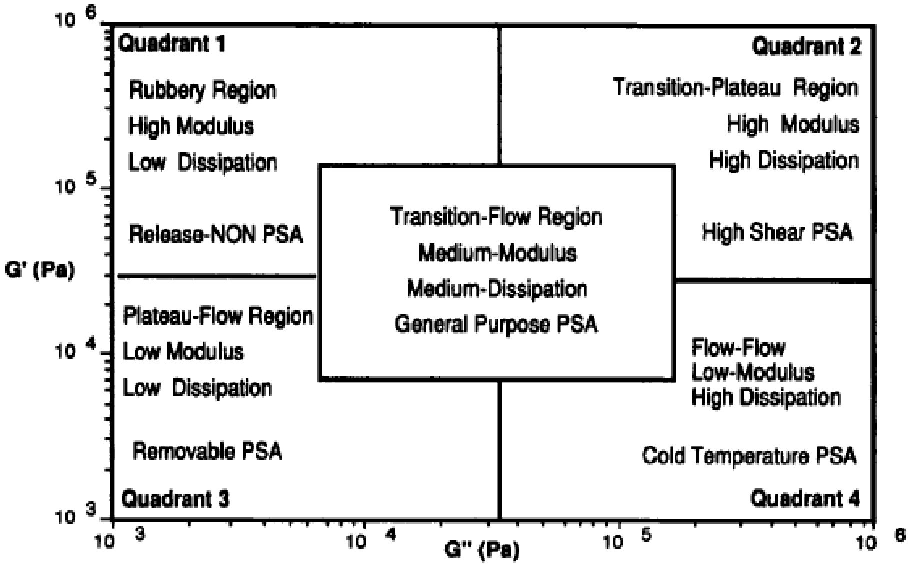

Figure 7 (cited from reference 3).

Each VW of different PSAs samples is constructed by plotting the four coordinates : G’ and G” at 0.015 Hz – G’ at 15 Hz and G” at 0.015 Hz – G’ at 0.015 Hz and G” at 15 Hz – G’ and G” at 15 Hz.

Application for the three bodied PSAs :

The VWs for the three bodied PSAs are illustrated in the following graph (Figure 8) :

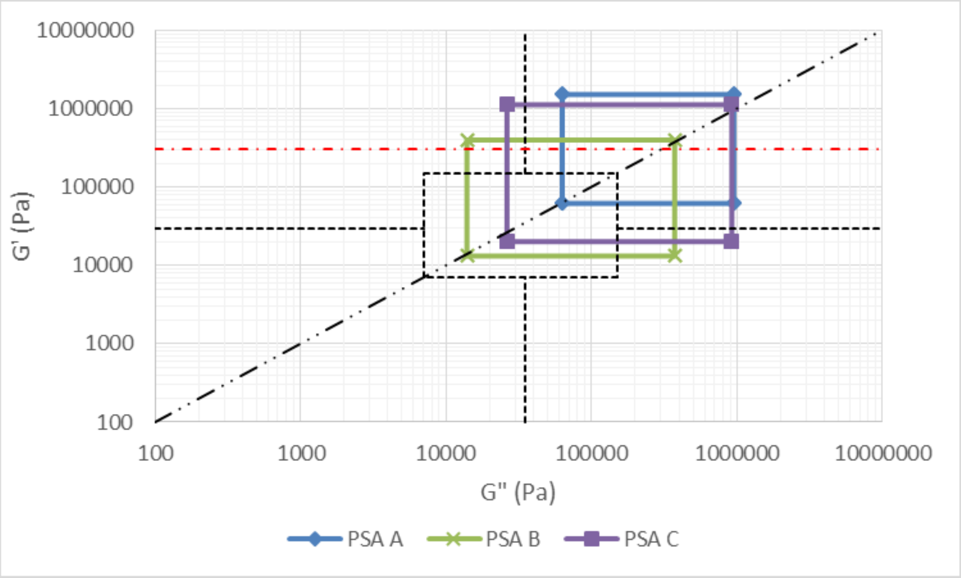

Figure 8

First, the three PSAs have the base of their window much below the Dahlquist’s contact criterion line (G’ = 300000 Pa)[9]. This indicates a good contact efficiency of the three PSAs. Then, the diagonal line (Tan delta = 1) separates regions where the storage modulus G’ is greater or smaller than the loss modulus G”. The portion of the window to the left of the line indicates the more elastic region. The portion of the window to the right of the line indicates the more viscous region. All the three PSAs have the top-left and lower-right hand corners of their window centered on the diagonal line. Thus, they behave as well balanced viscoelastic materials with good removability and no cohesive failure tendency. At least, the three PSAs occupy more or less the quadrant 2 and the central region indicating a high shear and general purpose PSA behavior due to high crosslink density.

To go deeper in the interpretation of the VW, the bonding efficiency can be correlated with the G' value at low frequency (0.015 Hz). The lower is the base of the window, the more favorable is the bonding. This is in agreement with the tack performances found for the three PSAs. We confirm higher tack performances for PSA B and C than for PSA A. On the contrary, the higher the base of the window, the better the shear. Here again, the shear performances of the three PSAs fit with their VW's respective position on the four quadrants' graph. We confirm higher shear performances for PSA A and C than for PSA B.

To finish, energy of dissipation and cohesive strength participate to the debonding strength. These two contributing terms are respectively related to the storage and loss modulus measured at high frequency. The higher the top right-hand corner of the window, the higher the debonding strength. In this case, even if the G' and G" values at 15 Hz can be considered high for the three PSAs, this is not possible to highlight the highest peel adhesion level for PSA C with the VW. In fact, for PSA C, G" values become significantly higher than for PSA A between 15 Hz and 100 Hz. This allows to mention the potential limitations of the VW concept due to the focus on only two selected frequencies. Moreover, the VWs of PSA A and B indicate significant differences for their G' or G" values at high frequencies. This is not in agreement with the peel performances for these two PSAs which are quite similar.

Summary :

Tack, peel strength and shear resistance are directly related to a PSA's response to the application of stress and may be measured using rheology. The profiles of G', G", tan δ and η* for a wide range of frequencies are the signature of the viscoelastic properties of the PSAs. The viscoelastic window concept allows to simplify the dynamic mechanical analysis with only two selected frequencies. The interpretation of the three selected silicone PSAs' viscoelastic windows gives a maximum of information that are relevant to correlate the mechanical performances and the viscoelastic properties. Nevertheless, in some cases, the VW concept may have some limitations and a deeper analysis of the rheological master curves is required.

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