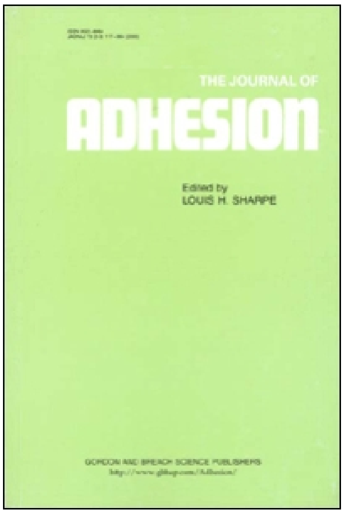

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Viscoelastic Windows of Pressure-Sensitive Adhesives

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A viscoelastic window (VW) concept has been proposed to identify different types of pressure-sensitive adhesives (PSA's). Such viscoelastic windows are constructed from the values of dynamic storage modulus: G′ and dynamic loss modulus G″ at frequencies of 10^{-2} and 10^{2} rad/sec. These frequencies are chosen because the range covers most of the time scales corresponding to the uses of PSA's at different application rates in performance tests. A four quadrant concept has also been recommended to categorize different types of PSA's based on the location of their VW's on the log-log cross plot of G′ and G″. It was found that for most PSA's, the range of G′ and G″ at room temperature within these selected frequencies falls between 10^{3} and 10^{6} Pascals. The proposed four-quadrants (top-left hand quadrant of high G′ and low G″, top-right hand quadrant of high G′ and high G″, lower left hand quadrant of low G′ and low G″, and lower right-hand quadrant of low G′ and high G″) correspond respectively to (1) non-PSA or release coatings (2) high shear PSA's, (3) removable PSA's and medical PSA's and (4) quick and cold stick PSA's. It was also observed that the VW's of general purpose permanent PSA's occupy the central region which straddles part of the four quadrants.

KEY WORDS Pressure-sensitive adhesives; dynamic mechanical analysis; viscoelastic properties; dynamic storage and loss moduli; bonding and debonding frequencies; peel, shear and tack performance.

I INTRODUCTION

It has been well established by many investigators that the performance of adhesives (*e.g.* peel, tack and shear) depends strongly on the bulk viscoelastic properties of the adhesives.[1-11] The William-Landel-Ferry (WLF) superposition procedure between rates and temperatures of the tests has been applied very successfully in adhesion tests both in peel[2,3] and in other modes of debonding.[4,7,8] The objectives of this paper are to demonstrate (1) the concept of viscoelastic windows (VW) constructed by only using the viscoelastic properties measured at one frequency which corresponds to bonding and one frequency that corresponds to debonding, (2) how different types of adhesives can be categorized by their VW based on their shape and location. The usefulness and limitations of the VW method, as compared with the master curve approach, are also discussed.

II EXPERIMENTAL

Viscoelastic Properties Measurements

The viscoelastic properties of different PSA samples were measured on the Rheometrics Mechanical Spectrometer (RMS-800) at room temperature over a frequency range of 0.01 to 100 rad/s. Samples tested were in the form of a disk of 25 mm diameter with a thickness of 1–2 mm. The strain employed was about 1%.

III CORRELATIONS OF DEFORMATION FREQUENCIES WITH TIME SCALES OF DIFFERENT PROCESSES AND ADHESION TESTS

Correlations of deformation frequencies with time scales of different processes and adhesion tests have been established[11] and are shown in Figure 1.

For example, very high frequencies (10^3 sec^{-1} or higher) would correspond to the time scale of slitting and perhaps other converting (guillotining, die-cutting, matrix stripping etc.) operations. A 10^2 sec^{-1} frequency corresponds approximately to the debonding frequency for a 50 micrometer thick adhesive at 5 mm/s in a peel or tack test. The bonding frequency of tack tests (*e.g.* thumb, Polyken or looptack) would be in the vicinity of 1 to 10^{-1} sec^{-1} frequency. Frequencies lower than 10^{-2} sec^{-1} (*i.e.* 100 seconds or longer), would correspond roughly to the onset of creep in a

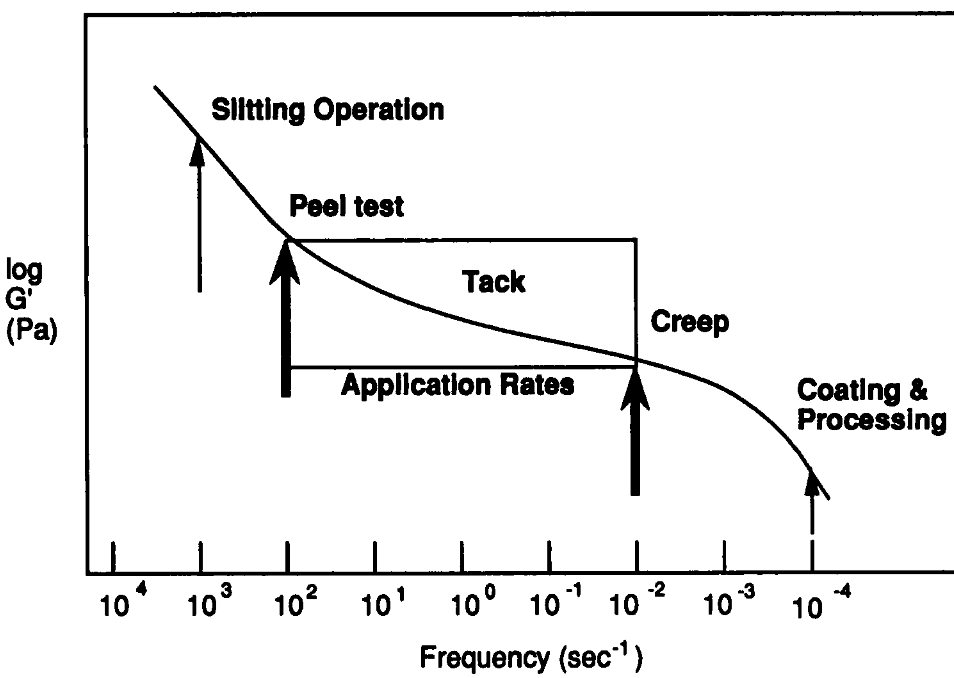

FIGURE 1 Correlations of different frequencies on the master curve *versus* the time scales of different testing and processes (Ref. 11).

shear test. Behavior at frequencies in the region of 10^{-4} rad/s (approximately equivalent to 10^4 seconds), which can be obtained by using the WLF time-temperature superposition principle, would correspond to the regime of high temperature and flow encountered in coating and processing operations.

It can be observed in Figure 1 that, excluding the converting and coating processes, the time scales for all of the adhesion tests fall between 10^{-2} to 10^2 rad/s.

IV VISCOELASTIC WINDOW CONCEPT

Using 10^{-2} and 10^2 rad/s as the frequency window for the peel, tack and shear tests, G′ and G″ values of different PSA samples at these two frequencies are measured, and the viscoelastic windows are constructed by plotting the four coordinates: (1) G′ at 10^{-2} rad/s, G″ at 10^{-2} rad/s, (2) G′ at 10^2 rad/s, G″ at 10^{-2} rad/s, (3) G′ at 10^{-2} rad/s, G″ at 10^2 rad/s, and (4) G′ at 10^2 rad/s, G″ at 10^2 rad/s on the log-log cross plot of G′ and G″. A hypothetical viscoelastic window is illustrated in Figure 2. It was found that, for most PSA's, the range of G′ and G″ at room temperature within the selected frequencies falls between 10^3 and 10^6 Pascals. In addition, there is a unique correlation between the adhesion performance of the PSA's *versus* the location of their VW's. A four quadrant concept was therefore adopted to categorize different types of PSA's.

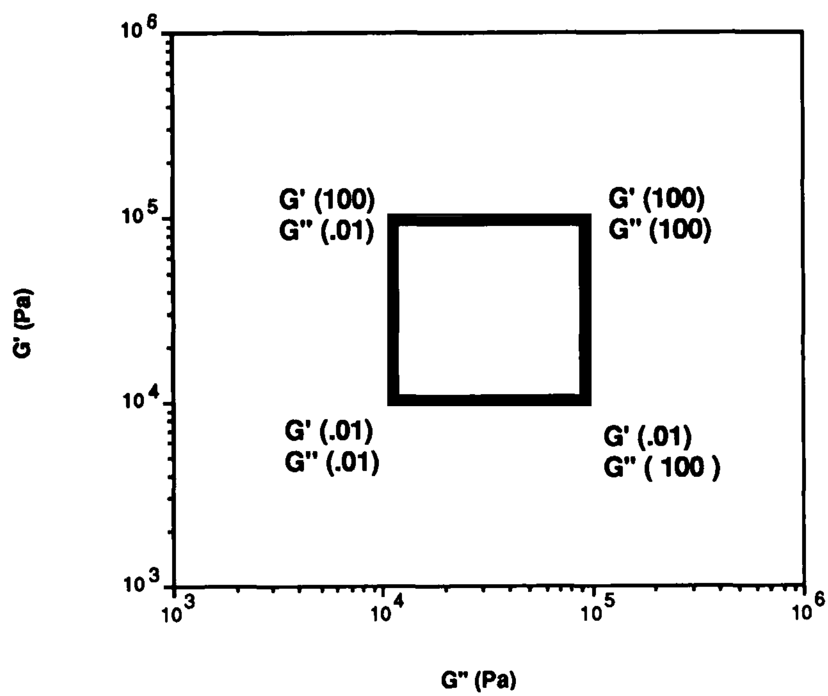

FIGURE 2 Schematics of a viscoelastic window (values within parentheses are the frequencies where G′ and G″ are measured).

IV.(a) Location of the Viscoelastic Windows: The Four Quadrants and the Central Area

The locations of different viscoelastic windows can be described by four quadrants and the central area. These are shown in Figure 3 with their corresponding operative viscoelastic regions:

Quadrant 1 (Top left hand quadrant): High G′-low G″—This quadrant corresponds to high modulus, low dissipation. The bonding and debonding frequencies both occur at the plateau region of the rheological master curve. No PSA can be found in this quadrant because of the high bonding modulus and highly elastic nature (lack of flow) of the material making the bonding step unfavorable. Some elastomer and release coatings[12] occupy this quadrant.

Quadrant 2 (Top right hand quadrant): High G′-high G″—This quadrant corresponds to high modulus and high dissipation. The bonding frequency corresponds to the plateau region, while the debonding frequency corresponds to the transition in their rheological master curves for high shear PSA's. The high bonding modulus compensated by the high dissipation or flow makes the bonding marginal. Shear is high because of the high G′ or high cohesive strength of the material.

Quadrant 3 (Bottom left hand quadrant): Low G′-low G″—This quadrant corresponds to low modulus, low dissipation. The bonding frequency corresponds to the plateau region, while the debonding frequency corresponds to the onset of the flow transition in their rheological master curves for removable PSA's. Bonding is

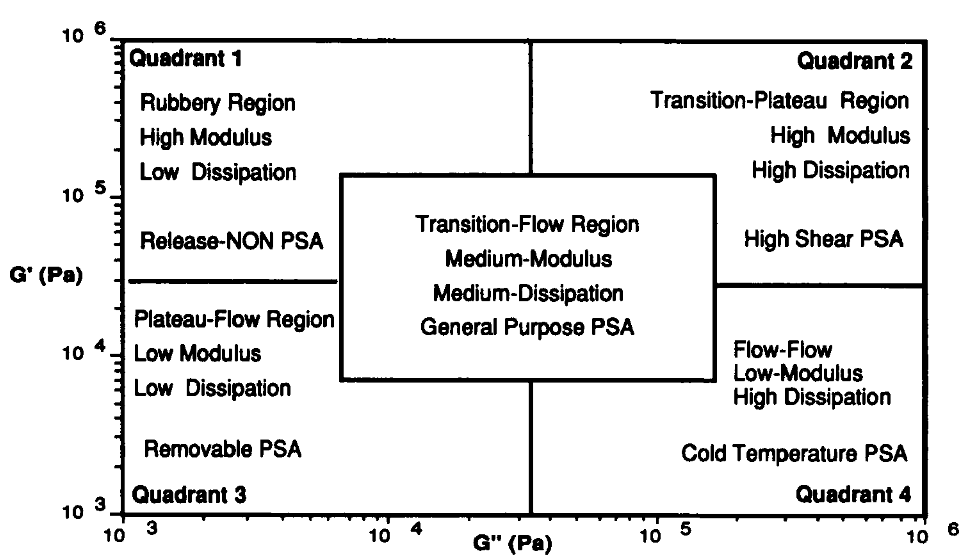

FIGURE 3 Viscoelastic windows of PSA's as related to different regions on their rheological master curves.

facilitated by the low modulus in spite of the low flow characteristics. Peel values are usually low because of the comparatively low debonding cohesive strength and low dissipation.

Quadrant 4 (Bottom right hand quadrant): Low G′-high G″—This quadrant corresponds to low modulus-high dissipation. The bonding frequency corresponds to the onset of the flow region, while the debonding frequency corresponds to the transition in their rheological master curves for very quick or very cold-stick PSA's. The low bonding modulus coupled with high flow make bonding very efficient, thus permitting the material to stick even at very low temperature or very short contact time.

Central area (Medium G′-Medium G″—This central area corresponds to medium modulus-medium dissipation. The bonding frequency corresponds to the transition region, while the debonding frequency corresponds to the flow region in the rheological master curves (usually without any distinct plateau region) of general purpose PSA's.

IV.a.1 Release Coatings (Quadrant 1)

To illustrate the consistency of the viscoelastic window concept for the different types of PSA's illustrated, several key materials in each group are shown below to ascertain their viscoelastic uniqueness. Figure 4 shows the viscoelastic windows of

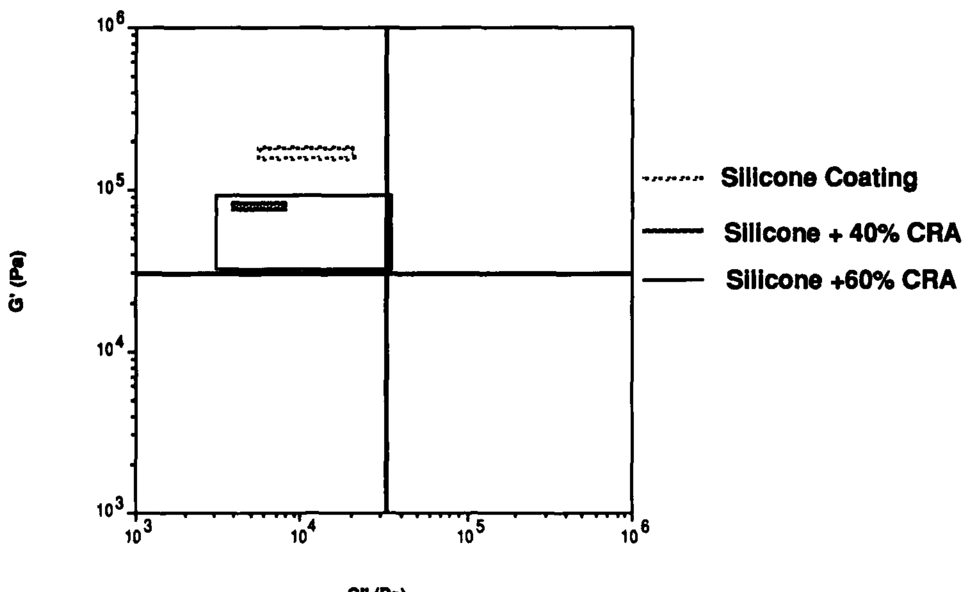

FIGURE 4 Viscoelastic windows of release coatings,⋯⋯silicone coating,——silicone + 40% CRA,——silicone + 60% CRA.

a polydimethyl silioxane (PDMS), PDMS + 40% control-release additive (CRA), and PDMS + 60% CRA. It can be observed that because of the high modulus (G′) and low dissipation (G″), PDMS is not a PSA, but rather is a release coating. However, with the incorporation of an increasing amount CRA, the modulus is progressively reduced together with a progressive increase of flow or dissipation. Such progressive decrease in G′ and increase in G″ results in a progressive increase in the tackiness of the samples. Thus, PDMS when modified with 60% CRA is tacky. It can be anticipated that, with further increase in the CRA concentration, the viscoelastic window of the resulting sample will move towards the central region which is the location for general purpose PSA's or, in this case, a general purpose silicone PSA.

IV.a.2 High Shear PSA's (Quadrant 2)

Figure 5 shows the viscoelastic windows of three high-shear PSA's; HSPSA-1, 2, and 3. It can be observed that the viscoelastic windows for all of these adhesives occupy the top-right hand corner which means that these adhesives have comparatively high modulus (G′) and high dissipation (G″) within the application rates (*i.e.* between 10^{-2} to 10^2 sec^{-1}). The operative rheological region for debonding is the transition region while that for bonding is the plateau region. In general, these adhesives have comparatively high Tg's and are comparatively highly crosslinked to achieve the high shear performance.

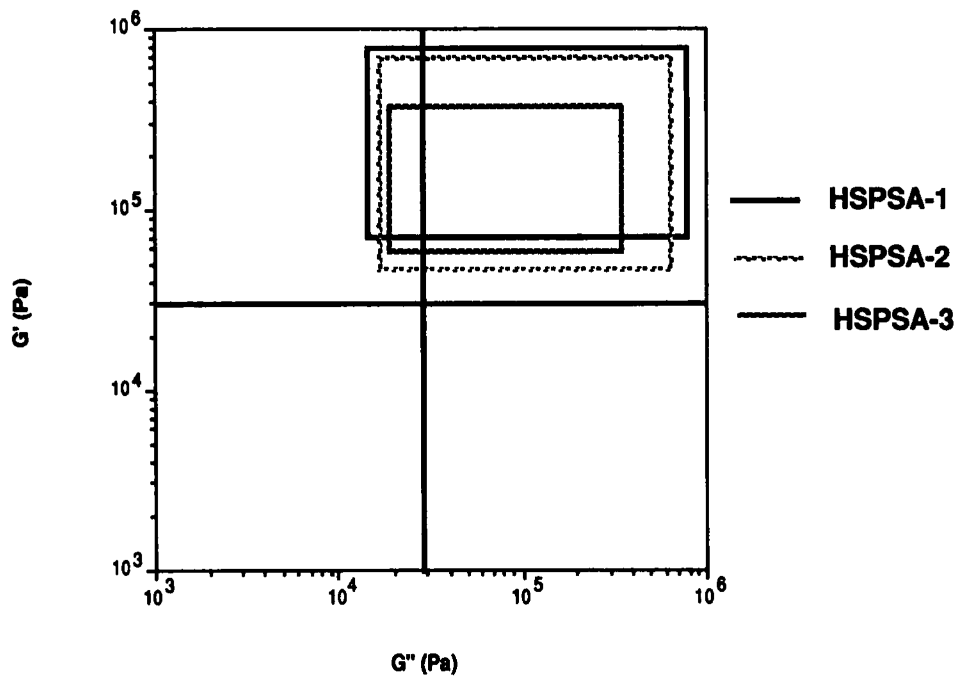

FIGURE 5 Viscoelastic windows of high-shear PSA's, —— HSPSA-1, ------ HSPSA-2, —— HSPSA-3.

IV.a.3 Removable PSA's (Quadrant-3)

Figure 6 shows the corresponding viscoelastic windows for removable adhesives. RPSA-1, 2 and 3. For these adhesives, their operative rheological region for debonding is the plateau region, while that for bonding is the onset of the flow region.

The distinct characteristics of this type of adhesive are:

- Low bonding modulus so that it is very contact efficient.
- Low dissipation which implies more elastic or better removability.

IV.a.4 Medical Type PSA's (Lower Right of Quadrant-3)

Figure 7 shows the viscoelastic windows of some of the removable from skin (bandage) PSA's. Compared with the viscoelastic windows of the removables, they tend to occupy the lower (better conformability) and further to the right (better flow) area of Quadrant 3. Some of the noteable differences between the removable and the bandage adhesives are:

- The reference temperature for the medical adhesive is the body temperature of 37°C instead of 23°C in the removable case. This makes the bonding modulus of the medical adhesives even lower (more conformable) than the removables because of the higher reference temperature. This is desirable for contact area considerations because of the rough and frequently contaminated nature of the skin.

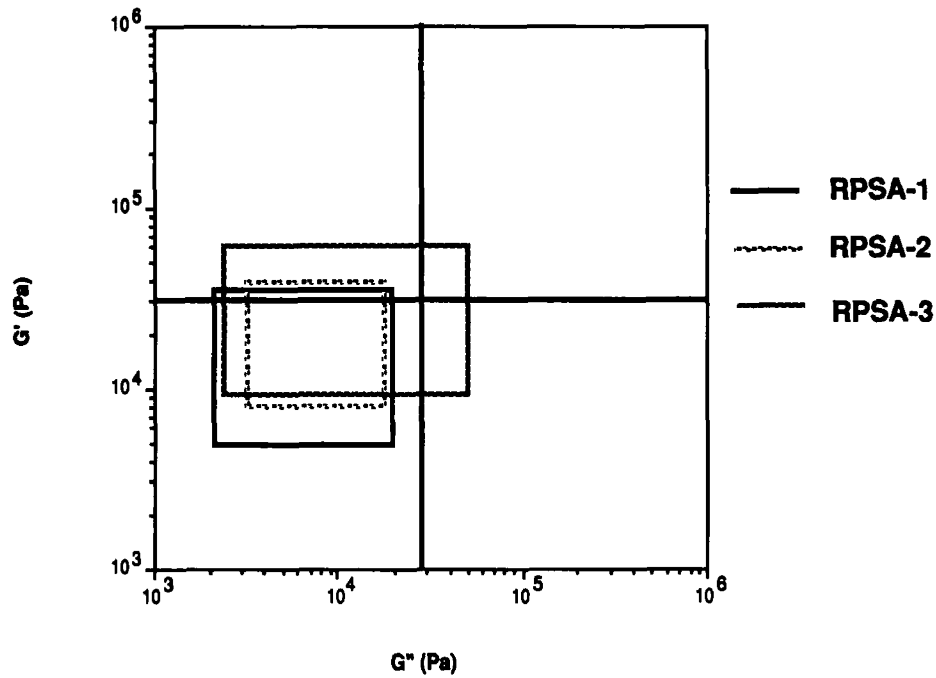

FIGURE 6 Viscoelastic windows of removable PSA's, —— RPSA-1, ······ RPSA-2, —— RPSA-3.

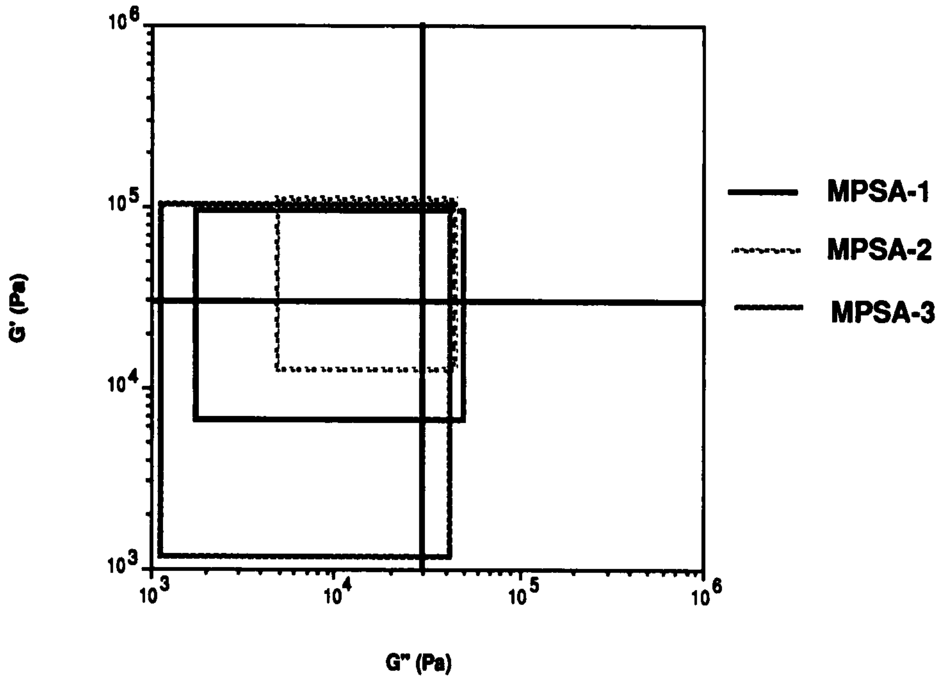

FIGURE 7 Viscoelastic windows of medical PSA's. ——— MPSA-1, - - - - MPSA-2, ——— MPSA-3.

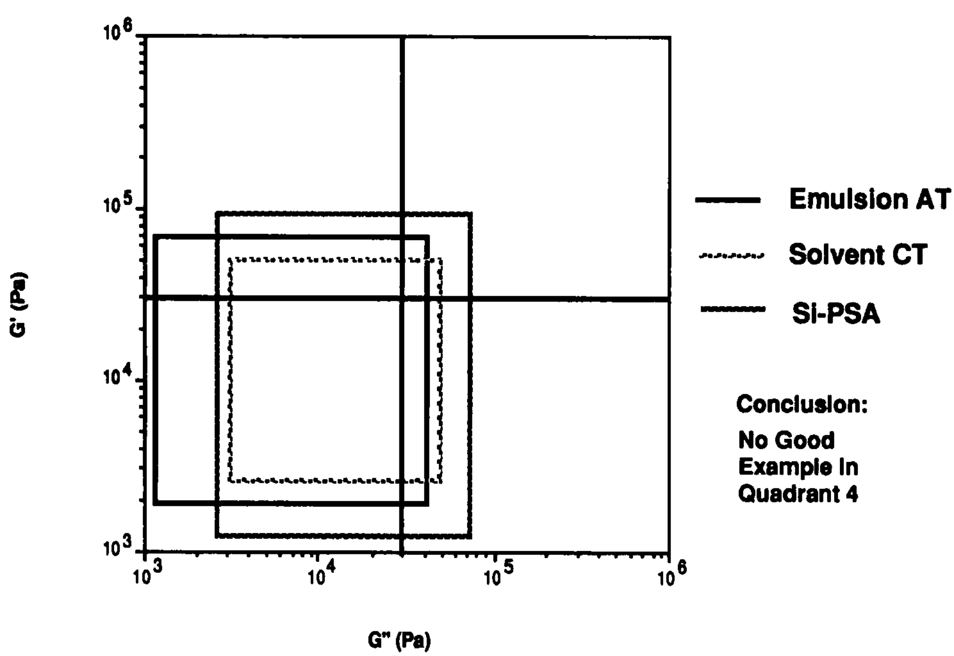

FIGURE 8 Viscoelastic windows of selected all-temperature and cold temperature PSA's, ——— emulsion AT, - - - - solvent CT, ——— silicone PSA.

- The debonding moduli (top right hand corner of the window) are usually higher than those of the removables. This again is necessary to prevent lift or detachment because of frequent movement of the skin especially on curved areas like the knee and elbow.

IV.a.5 All Temperature/Cold Temperature PSA's (Right of Quadrant-3 and Left of Quadrant-4)

Three adhesives that have a significant portion of their viscoelastic windows into the 4th quadrant are (1) an emulsion all-temperature adhesive, ATPSA-1; a solvent cold temperature adhesive, CTPSA-1; and a silicone PSA. Their windows, which indicate low bonding modulus as well as good flow nature, fall somewhere between the 3rd and 4th quadrants (Figure 8). So far, no good example of a PSA has been found with its viscoelastic window located completely in the fourth quadrant.

IV.a.6 General Purpose PSA's (Central Area)

Figure 9 shows the corresponding viscoelastic windows for three general purpose acrylic PSA's: GPPSA-1, 2 and 3. The operative rheological region for debonding is in the onset of the transition region, while that for bonding is in the onset of the flow region. It can be observed that they all occupy the central region (overlapping part of the four quadrants) illustrating the general purpose nature of this type of PSA.

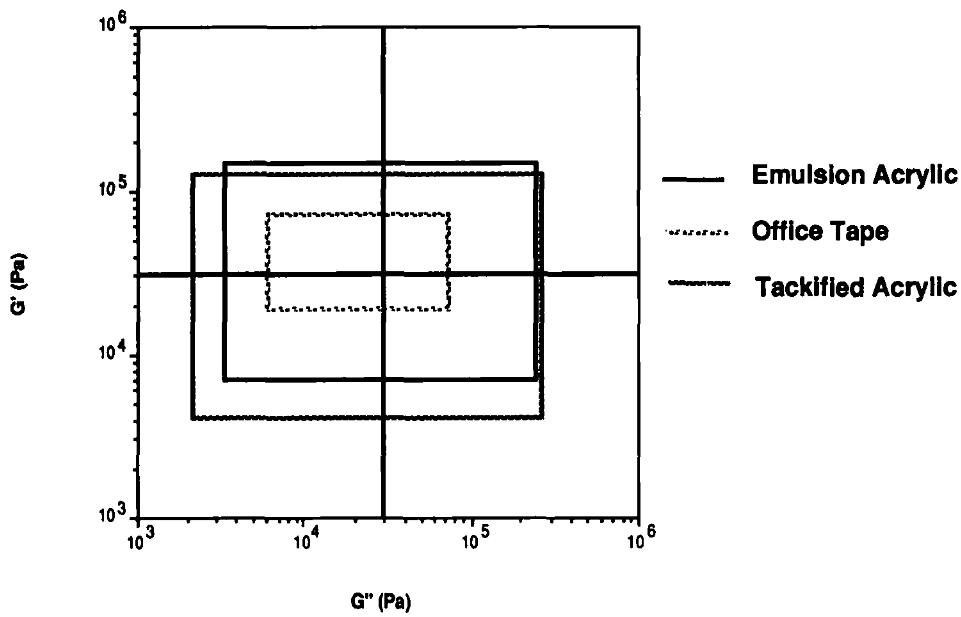

FIGURE 9 Viscoelastic windows of general purpose PSA's, ━━ emulsion acrylic, ----- office tape, ━━ tackified acrylic.

V CORRELATION AND PREDICTION OF ADHESIVE PERFORMANCE WITH THE VISCOELASTIC WINDOW

Figure 10 illustrates the relative position of the viscoelastic window with respect to the Dahlquist Contact Criteria line[1] as well as the diagonal line where $G' = G''$ or $\tan \delta = 1$.

V.a The DAHLQUIST'S CONTACT CRITERIA LINE

The Dahlquist line is an important reference line as it indicates whether a material would be contact efficient (PSA) or deficient (non PSA).[1] It is quite evident that except for the release coatings, all the different types of the adhesives described in this paper have bonding modulus (*i.e.* the base of the window) much below the Dahlquist line (which means good conformability). In other words, by comparing the position of the base of the window with the Dahlquist line, immediately we know whether the material is a PSA.

V.b The G′-G″ CROSS OVER LINE ($\tan \delta = 1$)

The diagonal $\tan \delta = 1$ line is another important line of demarcation as it separates regions where the elastic or storage modulus (G′) is greater (*i.e.* $\tan \delta < 1$) or smaller

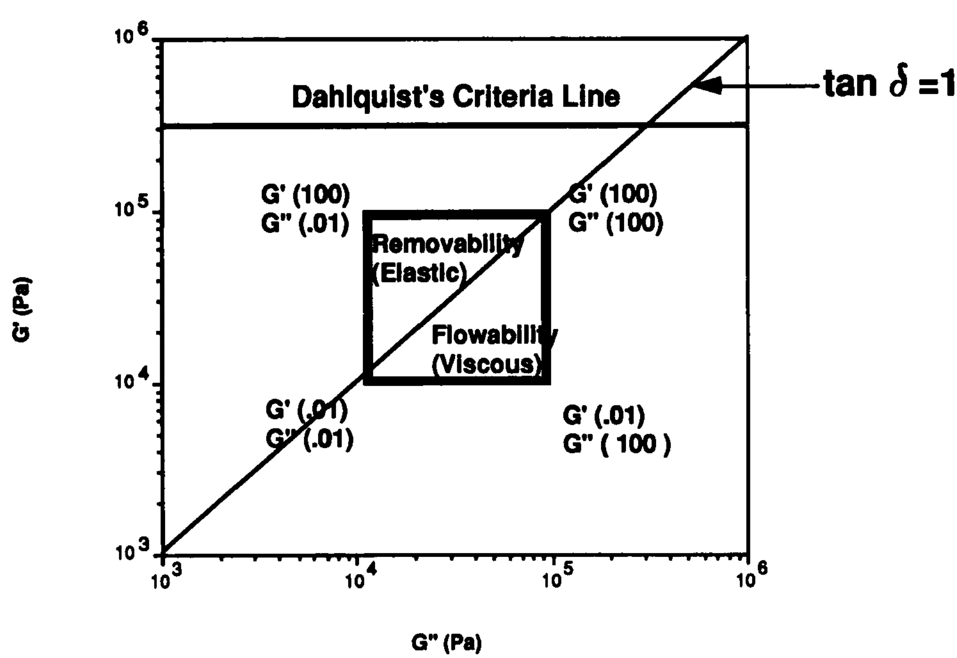

FIGURE 10 Relationship of the viscoelastic window with the Dahlquist contact criteria and tan δ.

(tan $\delta > 1$) than the loss modulus G″. The portion of the window to the left of the line (*i.e.* tan $\delta < 1$) indicates the more elastic region. In other words, the closer the viscoelastic window is towards the top-left hand corner of the G′-G″ plot, the more elastic (or better removability) will be the material characteristics. Conversely, the closer it is towards the lower right hand corner of the plot, the more viscous (or cohesive failure) will be the material characteristics.

Assuming that the adhesive is the only variable in the construction, and that the surface effect is negligible, the following adhesion and convertibility performance can be correlated with the shape and location of the viscoelastic window.

V.c Shear Performance

The shear performance can be correlated with the following features of the window. The base of the window (*i.e.* G′ at 0.01 rad/s.) usually indicates the value of the plateau modulus because of the subambient Tg of PSA's. In general, the higher the plateau modulus or the base of the window (provided that the Dahlquist Contact Criteria is still satisfied), the better will be the shear. The high shear type of adhesive is a good manifestation of this correlation. In addition, if the base of the window or the plateau modulus is the same, the more extended the plateau, (*i.e.* the difference between G′ at .01 and 100 rad/sec is smaller), the shorter will be the window, hence, the better is the shear prediction. This is because a more extended or flatter rubbery plateau is indicative of either higher degrees of entanglement, or higher chemical or physical crosslink density.

V.d Peel Performance

Peel performance is dependent upon the efficiency of the bonding step as well as the separation resistance in the debonding step. The bonding efficiency can be correlated with the plateau modulus at the bonding frequency (~0.01 rad/s). In other words, the lower the G′ value at 0.01 sec^{-1} (or the base of the window), the more favorable is the bonding. The debonding strength comes from two contributing terms, the cohesive strength which is indicated by the storage modulus, G′, and the energy of dissipation term which is indicated by the loss modulus, G″, both measured at the debonding frequency (~100 rad/s). Thus, the higher the debonding G′ and G″ values (*i.e.* the top right-hand corner of the window), the higher will be the debonding strength.

V.e Tack Performance

The correlation of tack performance is similar to that of peel, except that the bonding frequency for tack is about 1 rad/s, which means that the bonding efficiency relates approximately to the inverse of the half-height of the window. The debonding resistance can be related again to how high is the top-right hand corner of the window (*i.e.* G′ and G″ values at 100 rad/s).

VI SUMMARY

The usefulness of the viscoelastic window concept is:

(1) It can be obtained without constructing the master curve of the adhesive, which usually takes several hours to obtain. In fact, it can be obtained by making two measurements at two frequencies (*i.e.* 10^{-2} sec^{-1} and 10^{2} sec^{-1} at the specified temperature). Such simple and rapid measurements will immediately identify the nature and type of the adhesive, even though one lacks the details of the master curve which is the recommended method for more quantitative information, if time is available.

(2) With the viscoelastic window defined, qualitative information regarding the adhesion performance and the mode of failure of PSAs can be obtained as described. This is particularly useful for comparing, evaluating and screening different adhesives since the shape and location of their viscoelastic windows provide comparative qualitative performance information prior to measuring their peel, tack, and shear performances. It is the prime objective of this paper to illustrate how such information can be extracted from the viscoelastic windows.

On the other hand, the limitation of the viscoelastic window method is that it only gives the G' and G'' values at those two frequencies. There is no information of G' and G'' at the in-between frequencies (*e.g.* 10^{-1}, 10^{0}, 10^{1} sec^{-1}, etc.) or other frequencies. It is evident that, occasionally, two adhesives could have the same viscoelastic window although their frequency dependence of G' and G'' or their master curves are different. When such a situation occurs, running a frequency scan between the viscoelastic window frequencies or, better still, a master curve for each of the adhesives, would be the recommended method for more quantitative comparison.

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