STRATEGIES FOR RHEOLOGICAL EVALUATION OF PRESSURE SENSITIVE ADHESIVES

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Abstract

Pressure sensitive adhesives (PSA) have been widely used in industries. A quantitative understanding of the physical performance of such materials, such as adhesiveness, cohesiveness, tack and peel performance, are important for quality control and for guiding formulators. Rheology is a powerful tool that provides direct measurement of a material's viscoelastic properties, which can be directly correlated to their end use performance. In this paper, we discussed strategies for comprehensive rheological analysis using a rotational rheometer. Specific analytical methods include the following: temperature ramps for predicting application temperature range and Dahlquist criterion, frequency sweeps for evaluating tack and peel performance, and creep tests for monitoring adhesive cold flow. A Time-Temperature Superposition (TTS) technique was also introduced for predicting the viscoelastic behavior of a PSA over several decades of magnitude of shear rate or time scale.

Introduction

Pressure sensitive adhesives (PSAs) are widely used in many industries ranging from pressure-sensitive tapes, labels, electronic circuits, automotive parts, as well as medical products such as dermal dosage systems. PSAs are composed of a mixture of polymers, copolymers, tackifying resins, plasticizers, and some antioxidant stabilizers in various amounts according to the properties desired (1-4).   When applied between two substrate layers, pressure-sensitive adhesives can provide strong cohesion strength with the application of light pressure (5-6).   Traditionally, pressure-sensitive adhesives are processed in two major methods: solvent coating or hot melt coating. Both methods have their pros and cons depending on specific applications. The hot-melt coating process leads to a significant savings in cost, a simplification of the process, and an abatement of air pollution. The solvent coating process results in better shear strength than melt coating and is preferred for use in applications requiring durability and exposure to high temperatures (7).   In addition to their formulations, the applications performance of PSAs is also significantly affected by their processing methods. There are many literature articles that have been devoted to characterizing the viscoelastic behavior of PSAs and their applications performance. Examples include failure analysis (8-9), tack-peel measurements (10-12), and rheological viscoelastic characterizations (7, 13-16).

Rheology is defined as the science of flow and deformation of matter. It addresses the relationship between a given deformation and the stress response for a measured material. Rheological techniques are commonly used to evaluate a material's viscosity and viscoelastic properties as a function of time, temperature, and shear. Adhesives are viscoelastic materials. In recent years, rheology has become

more and more popular for evaluating the performance of PSAs and troubleshooting formulation problems. Initially, rheology was applied to measure the shear viscosity of PSA solutions and hot melts, since viscosity is critically important to the PSA coating process. In their applications conditions, PSAs are viscoelastic solids. Typical rheological analyses are conducted in oscillatory modes. A small sinusoidal amplitude (strain) is applied to the material within its linear viscoelastic region. The material's rheological response (stress) is measured. In addition, the phase angle (delta) between the input strain and output stress signals is also determined. From these raw signals, the viscoelastic parameters (G*, G', G" and tan delta) can all be calculated. The elastic or storage shear modulus (G') is commonly used to describe or compare the cohesive strength and tan delta (i.e. the ratio of G"/G') can be used to describe the elasticity behavior of the adhesives.

Rheology is a powerful tool for evaluating the viscoelastic behavior of PSAs. For example, a dynamic temperature sweep test is commonly used to evaluate the applications temperature window. A dynamic frequency sweep over a wide range of frequency can be used to correlate with PSA tack and peel performance. A creep TTS analysis can help predict the cold flow behavior of adhesives. However, due to the complications of rheological techniques, any inappropriate experimental settings may lead to wrong results, which may result in misleading the formulation and process engineers. In this paper, we highlighted several technical tips on strategies for good rheological test methods. Specifically, we focused on the three most commonly used rheological tests: temperature ramps; axial tack testing, and time-temperature superposition (TTS). We will discuss the interpretation of the rheological data, techniques for identifying and minimizing experimental errors, and for pushing the experimental limits of rotational rheometers.

Experimental

Two example pressure sensitive adhesive samples are used for this study. One is a non-crosslinked adhesive, which melts and flows under higher temperatures; the other is a slightly crosslinked adhesive, which does not melt. The goal of this work is to develop good test methodology that would correctly reflect the viscoelastic behavior of adhesive materials. A TA Instruments DHR-3 rotation rheometer with the environmental test chamber (ETC) is used for all tests. The measurement geometries are 8mm parallel plates. The adhesive sample was loaded at 100°C, at which it was in the molten state or at least soft and easy to trim. Then with the axial force being controlled at 0 +/- 0.1N, the sample was cooled down to the starting measurement temperature. Cooling the sample without controlling the axial force could cause the sample to detach from the plate due to shrinkage. Dynamic strain sweeps were performed at different temperatures below and above the glass transition of the material. The temperature ramp experiment was programmed from -30°C to 100°C with a heating rate of 3°C/min. The test frequency was 6.28 rad/s. The oscillation strain was actively adjusted during the test using either non-iterative sampling or the auto-strain function to ensure being in the linear viscoelastic region and obtaining good torque signals. The axial force was controlled at 0 +/- 0.1N. The tack testing was performed using 8mm parallel plate geometry at ambient temperature. The pull-off speed was at 0.1mm/s. The time-temperature superposition (TTS) test was programmed by setting up a series of frequency sweeps (0.1 to 100 rad/s) from -30°C up to 100°C with a 10°C interval per step. Again, both strain and axial force were actively adjusted with the same method described in the temperature ramp test. TTS analysis and data transformations were conducted using TA Instruments TRIOS software.
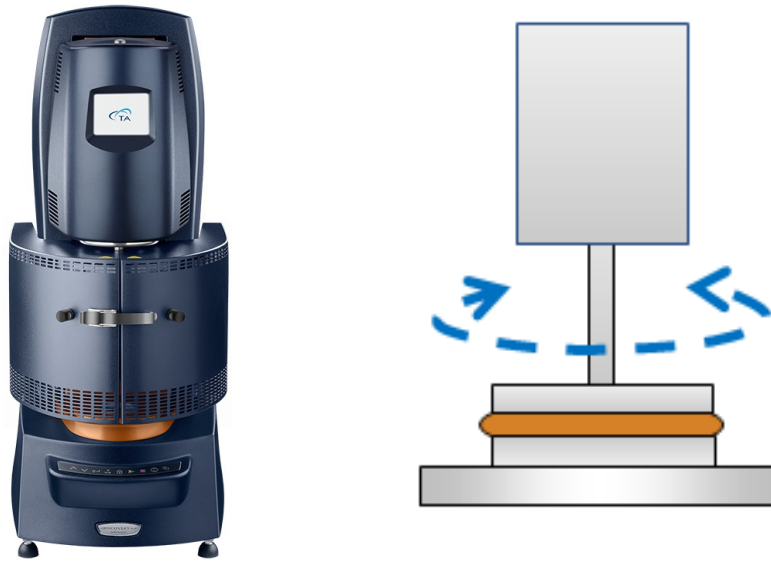
Figure 1. TA Instruments DHR-3 rheometer with ETC oven and parallel plate geometry

Results and Discussions

1. **Tack and peel evaluations**

The most important parameters for evaluating the performance of PSAs are tack, peel and shear adhesion. A variety of performance tests have been developed to directly measure these properties (ASTM D2979, ASTM D3121, PSTC-6, PSTC-5, PSTC-101 etc.). One of the most commonly used methods for evaluating the tack performance is defined by ASTM D2979. This test can be conducted on a rotational rheometer using parallel plate geometry. One places the PSA sample between two parallel plates with a certain pressure for a short time, and then pulls off the plates with a speed of 0.1mm/s. The maximum force required to pull the plate away is defined as the sample's tackiness. In this type of test, breakings may occur in 3 different ways: (1) if the bond force at the interface is stronger than the cohesion strength of the adhesive, breakage will occur between adhesive layers; (2) if the cohesion strength is much stronger than the adhesion bond at the interface, then breakage will occur at the plate interface; (3) sometimes, there will be a mixed breakage of both cohesion and adhesion. Figure 2 shows the tack testing results of the non-crosslinked and crosslinked PSA samples. The crosslinked PSA shows significantly higher cohesion strength due to the introduction of a crosslinking network. Therefore, the failure occurred at the interface. The non-crosslinked PSA has weaker cohesion bond so failure was observed between the adhesive polymers. Since the adhesive strength is strongly dependent on the substrate that the adhesive is attached to, the tack and peel measurements must take the surface properties of the substrate into account.

Rheology is a powerful technique that measures the viscoelasticity of a material. The parameters that rheology measures, such as G', G" and tan delta are directly related to the cohesive strength of the adhesive. It provides important information on the mechanical properties of the adhesives themselves as a function of time, temperature and shear rate. In the following, we will discuss how to extract useful information out of a rheological a dynamic temperature ramp, dynamic frequency sweep and TTS analysis.
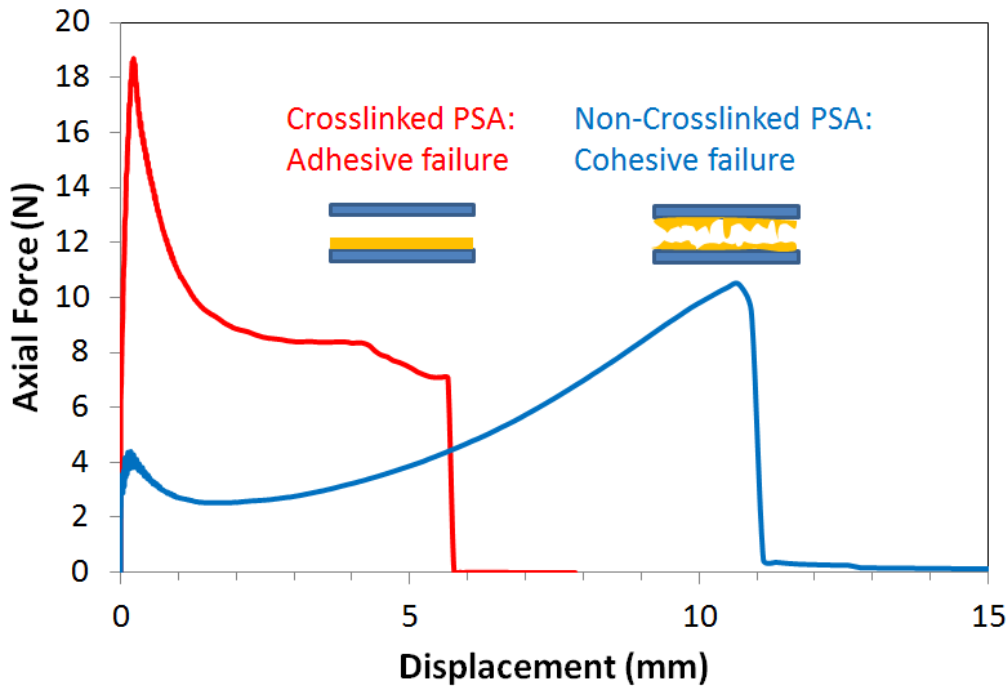
Figure 2. Tack testing results on non-crosslinked and crosslinked PSAs.

2. **Dynamic temperature ramp analysis**

Figure 3 shows the dynamic temperature ramp results on the linear non-crosslinked PSA. This temperature ramp test conveys information regarding the rheological performance of the adhesive over a broad temperature range. First, the glass transition temperature (Tg) is observed at 16.3°C based on the location of the tan delta peak. Below Tg, the sample is hard and brittle and has no tackiness. The glass transition temperature is usually considered as the lowest applications temperature of a PSA. Above Tg, the sample softens, and the modulus drops significantly. The sample behaves in a viscoelastic manner. At very high temperatures, non-crosslinked PSA melts. This can be observed as the G'/G" crossover temperature (Tx). For this measured adhesive, the Tx is observed at 75.9°C. Above this temperature, adhesive flows like a liquid and loses adhesive strength. In general, the application temperature window of a PSA can be described as between Tg and Tx. In the adhesive industry, people also use the Dahlquist temperature (Td) to help evaluate the performance of PSAs (17-18). The Dahlquist temperature is the temperature where the modulus (G' or G*) drops below 300 kPa. The Dahlquist criterion states that the modulus of an adhesive should be between 50 to 300 kPa. When higher, the adhesive has difficulties wetting the substrate; if lower, the adhesive has low shear resistance. In certain applications, Td is considered as the lower temperature limit for the application of an adhesive to a substrate. In addition to temperatures, this temperature ramp test results also provide information on the

modulus of adhesive. The rubbery plateau modulus (G' or G*) is also commonly used to evaluate the cohesive strength of an adhesive.
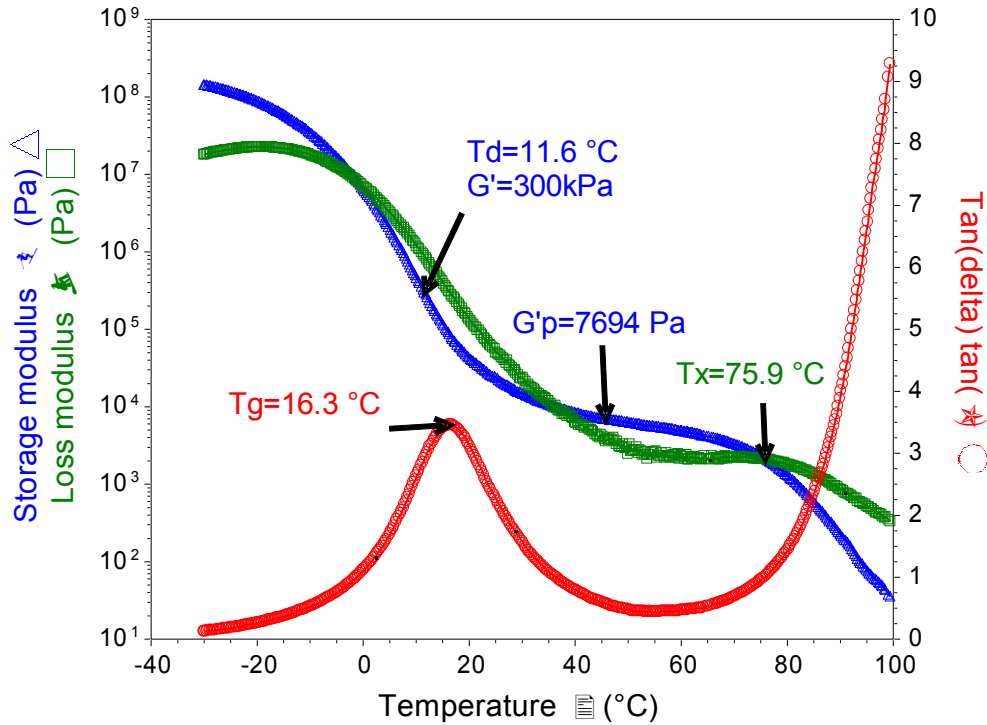
Figure 3. Dynamic temperature ramp of non-crosslinked PSA

As can be seen form the above discussion, a dynamic temperature ramp analysis provides important information about the applications temperature window and the viscoelastic performance of an adhesive. However, during a temperature ramp test, the physical properties of the sample undergo huge changes from high stiffness solid to low viscosity liquid. Figure 3 shows that the modulus (G') of the sample drops over 7 decades from -30°C up to 100°C, which creates challenges to the experimental design. Figures 4 shows the strain sweep results performed at different temperatures. At temperatures below Tg (e.g. -30°C), the adhesive shows high modulus and a short linear viscoelastic region (LVR). At strain above 1%, the measurement reached the instrument torque maximum. However, at higher temperatures when the adhesive was in the molten state (e.g. >50°C), a higher strain (e.g. 5-10%) is preferred in order to obtain better measurement signals. A good design for this type of test should allow the auto changing of strain during the temperature ramp experiment. The TA Instruments DHR rheometer provides 2 methods for altering the strain during temperature ramp tests. One method is called "Auto-strain", which is under "Conditioning" – "Options" in TRIOS control software. This method is generic and can be applied on both the DHR and ARES G2 rheometers. The second approach is "non-iterative sampling", which is applicable when using the controlled stress (DHR or AR) rheometers (Table 1). Both methods require the operator to select a reasonable torque window during a test. Figure 5 shows an example of how strain changes in response to the measured oscillation torque. In this measurement, a minimum test torque was programmed at 2 μNm. The initial measurement strain was set at 0.05%, which was within the linear region of the sample below Tg. At higher temperatures, when the sample passed its Tg and became soft, the torque at 0.05% strain was reduced significantly. When the measured
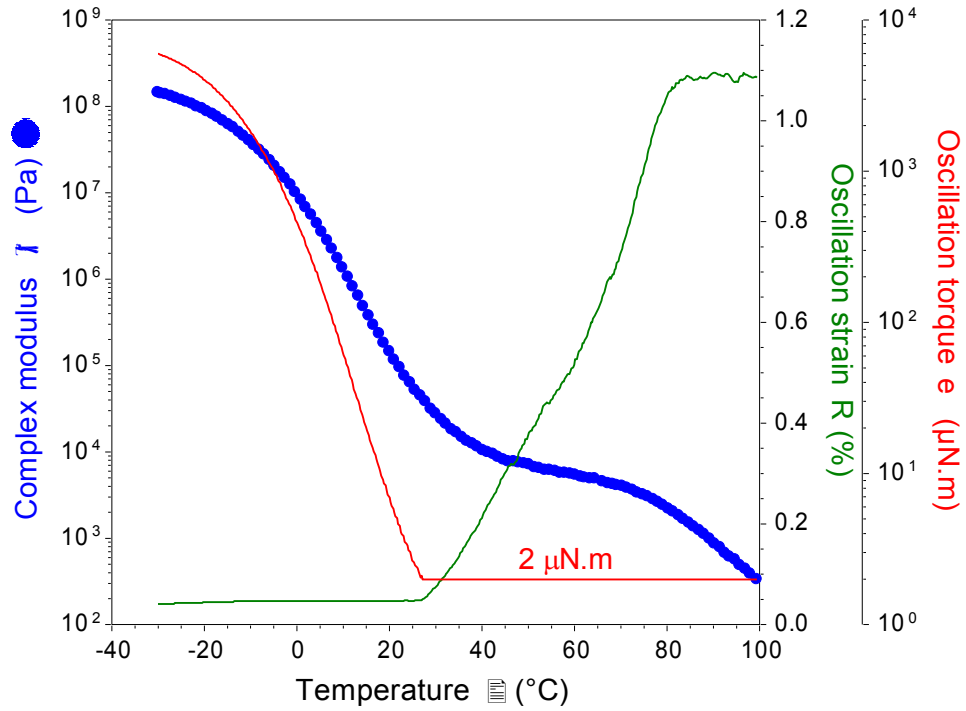
torque dropped below 2 μNm, the rheometer automatically switched to torque control to maintain the minimum torque at 2 μNm. In this case, strain was increased, but still remained within the linear region of the material at the measurement temperature.
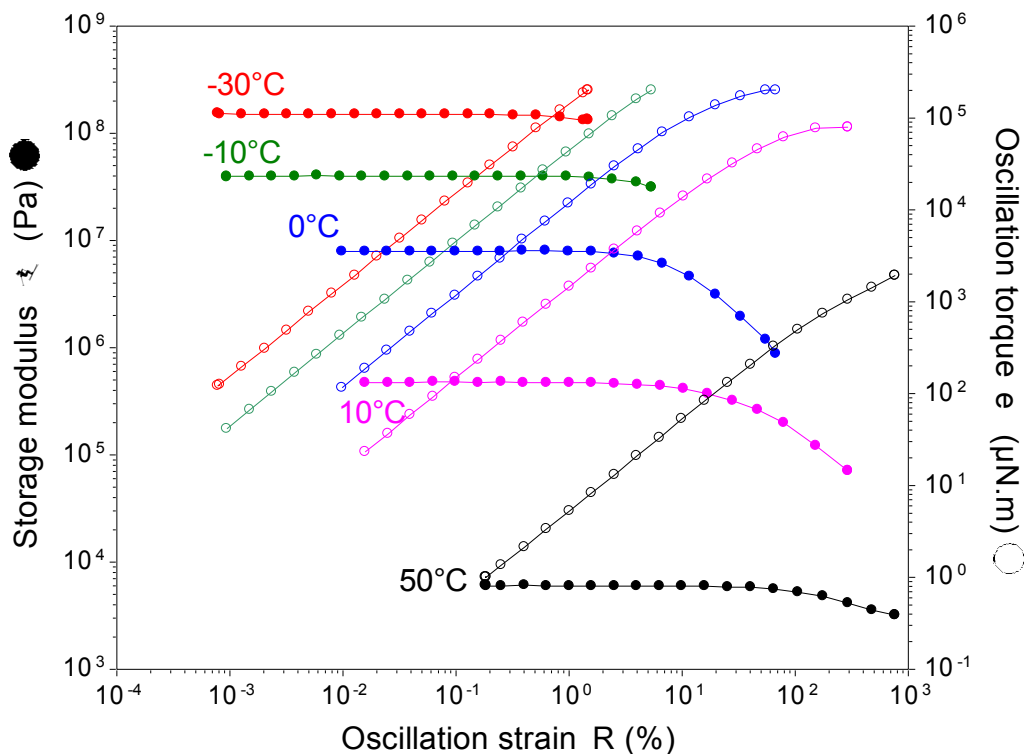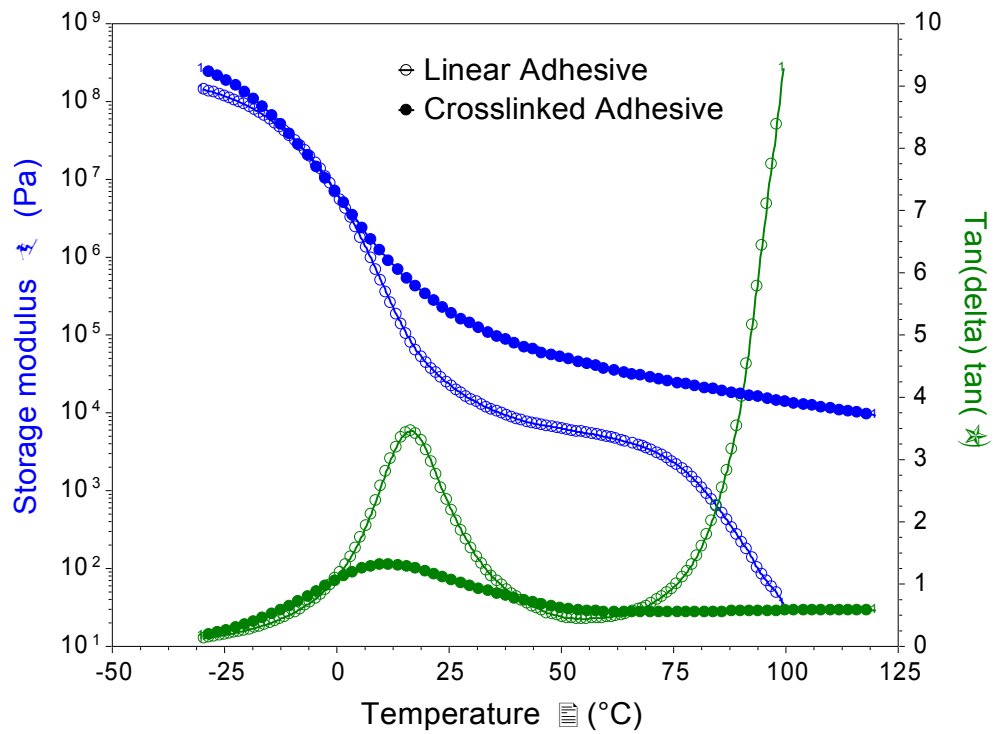

Figure 4. Dynamic strain sweeps of non-crosslinked PSA at different temperatures

Table 1. Example setups of "auto-strain" and "non-iterative sampling"

Figure 5. Demonstration of strain changes in response to measurement torque in a temperature ramp test

Figure 6. Temperature ramp results of a non-crosslinked and a crosslinked PSA

During a temperature ramp test, both sample and the testing fixture will undergo thermal expansion and/or shrinkage. A good experimental design should find ways to actively adjust and release this axial force due to thermal expansion. On a DHR rheometer, this axial force control feature is under "Conditioning" – "Options". When testing a non-crosslinked PSA, it is recommended to control this axial force at around zero (e.g. 0 +/- 0.1N). For testing crosslinked PSA, depending on its rubbery plateau modulus, it may be beneficial to apply a slight positive force to ensure good contact between plates and sample and also to avoid slipping during test. Figure 6 shows the comparison temperature ramp results of a non-crosslinked and a crosslinked PSA. With the introduction of a crosslinking network, the adhesive shows much higher cohesion strength (i.e. higher modulus within rubbery plateau region). Its applicable temperature window can also be significantly extended.

3. **Time-temperature superposition (TTS) and rheology transformations**

Dynamic rheological measurements provide good correlation to the cohesive strength of PSAs. The modulus (G' and G") measured under different frequencies is directly related to the tack and peel performance. Since frequency is inverse of time, G' measured from the mid to low frequencies at the applications temperature is related to the tack cohesive strength and shear resistance. G' measured at high frequencies is related to the peel strength. According to the Cox-Merz rule, the dynamic complex viscosity versus frequency can be transformed to shear viscosity versus shear rate. Figure 7 shows a frequency sweep example of the non-crosslinked PSA at 30°C, and figure 8 shows the result of this frequency sweep after Cox-Merz transformation.
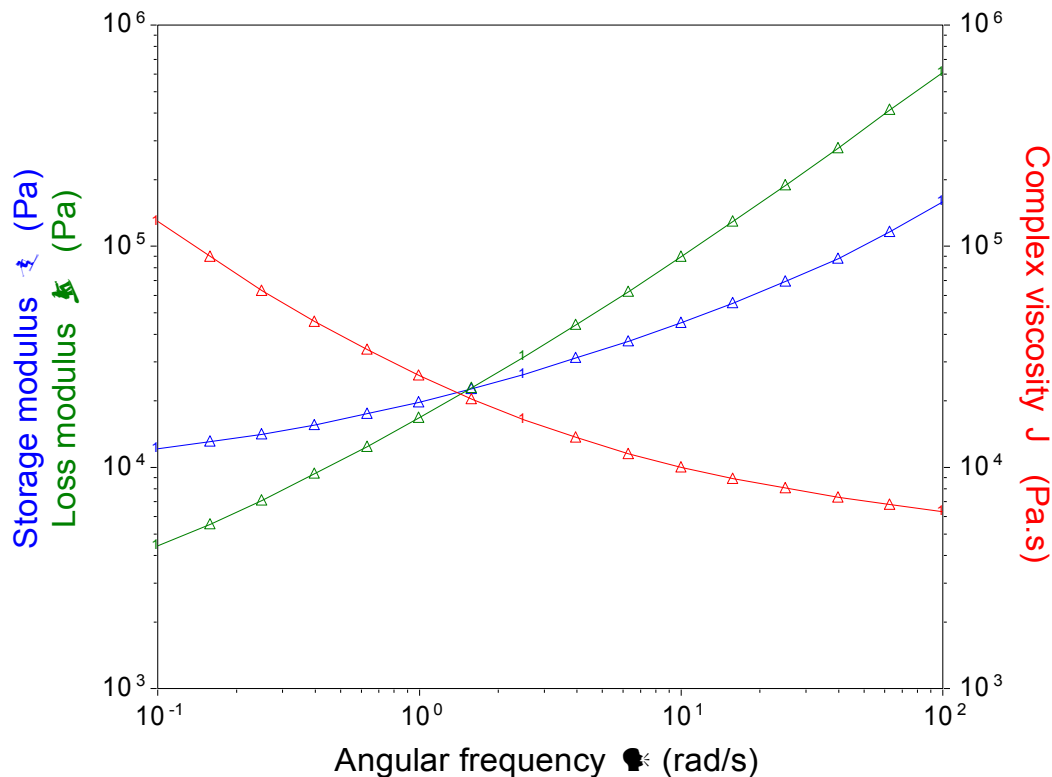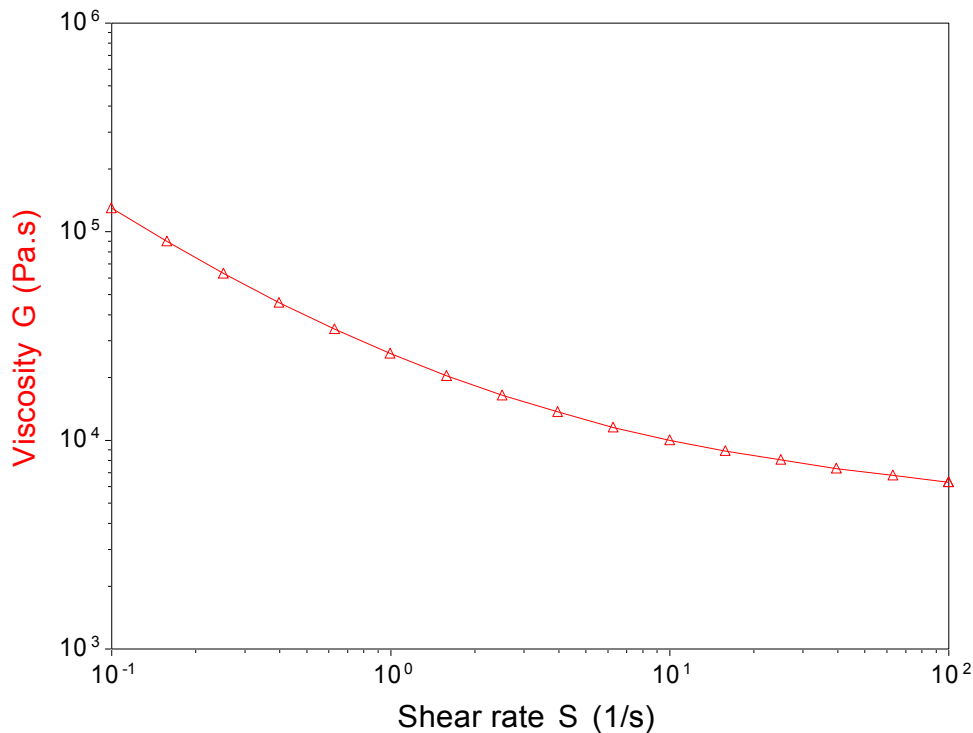

**Figure 7.** Frequency sweep of non-crosslinked PSA

Figure 8. The Cox-Merz transformation result from figure 7

However, the maximum frequency a rotational rheometer can reach in a single test is 628 rad/s, which may not be high enough to mimic certain high shear situations. Also, the low frequency data may require days or years to collect, which makes the measurement practically impossible. In this case, a Time-Temperature Superposition (TTS) technique can be explored to extend the frequency range. TTS is an empirical theory, which is based on the observation that for a thermo-rheologically simple material, its viscoelastic properties generated at different temperatures are equivalent to the properties measured over a broad time or frequency scale. The data measured under low temperatures can be shifted to high frequencies or short times; the data measured under high temperatures can be shifted to low frequencies or longer times. Figure 9 shows the TTS master curves generated on the non-crosslinked and crosslinked PSAs. The reference temperature selected in each test was 20°C. Comparatively, a good PSA should have lower modulus at higher frequencies (high shear) so that it is easy to peel; and higher modulus at lower frequencies (long time) so it will show good resistance to creep or cold flow.
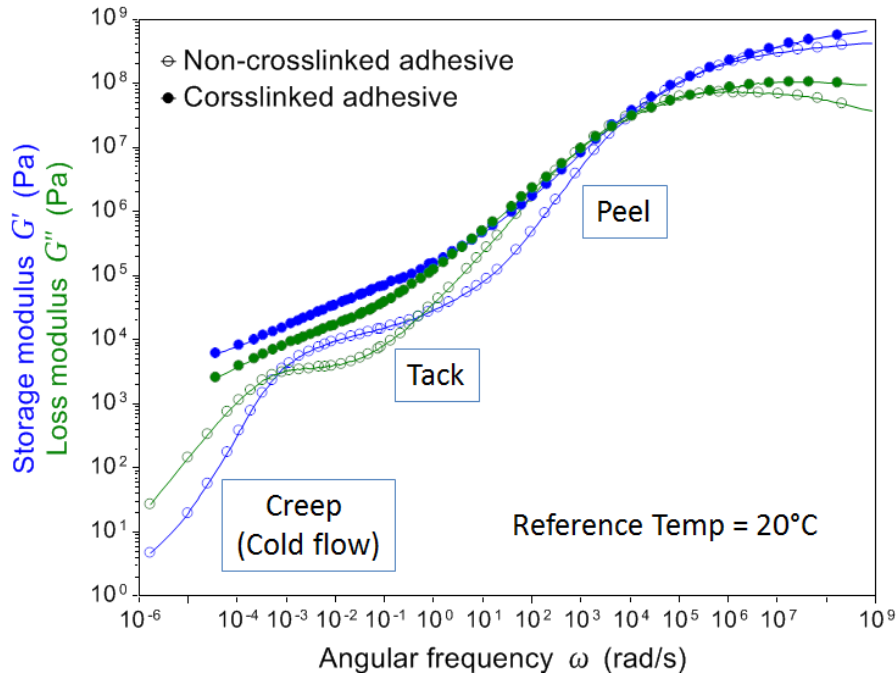
Figure 9. Time-Temperature Superposition master curves using 20°C as reference temperature

Another important performance evaluation of PSA is to monitor the ability to resist cold flow under load. A transient creep test is commonly used for this analysis. If one wants to make long-term predictions regarding the behavior of a PSA, the creep TTS technique can be explored. Creep tests collected at higher temperatures can be shifted to long time scales (13). However, if the cold flow behavior is investigated within the linear viscoelastic region of the material, then the dynamic oscillation data can be interconverted with transient data through relaxation spectrum calculations. In this case, additional creep TTS analysis is not necessary. Figure 10 shows the creep curves of the non-crosslinked and crosslinked PSAs, which were converted directly from the dynamic TTS master curves shown in figure 9. The dynamic data was first transformed into a relaxation spectrum, and then converted a retardation spectrum. From there, it can be further transformed to creep. The creep results in figure 10 show that the non-crosslinked adhesive has significant creep over time, thus displays poor resistance to cold flow.
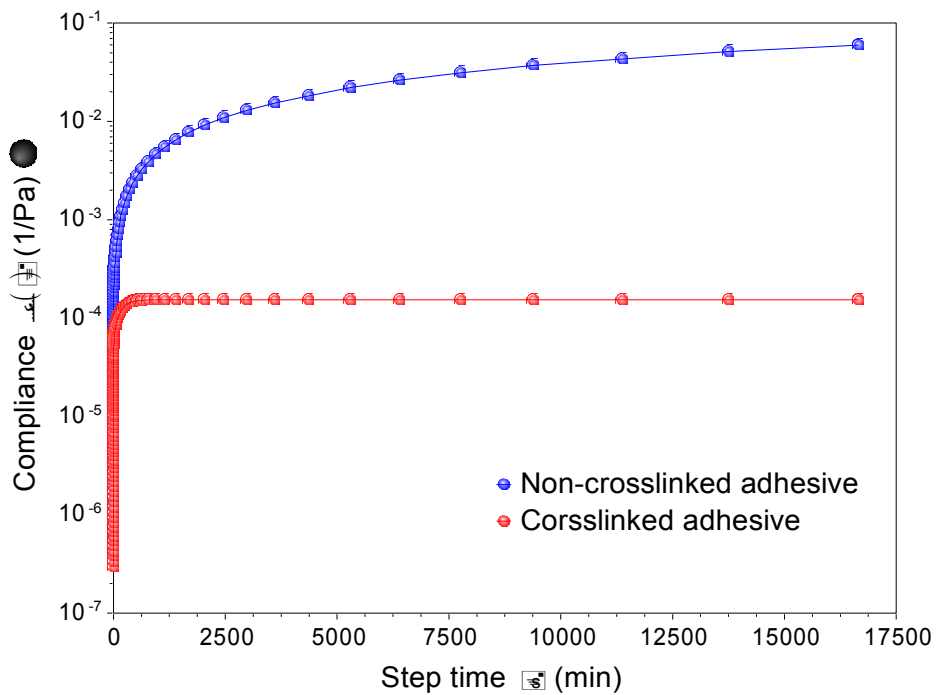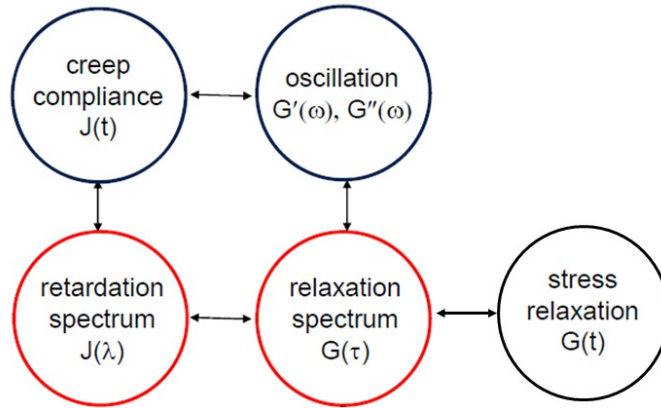
Figure 10. Creep curves transformed from dynamic testing

Conclusion

With appropriate method development, rheological measurements can provide useful information for processing, product development, and applications of pressure sensitive adhesives. Practical parameters, such as application temperature, flow, tack and peel, cohesive strength and shear resistance, can be directly obtained from rheological measurement results. In a dynamic temperature ramp test, the glass transition temperature (Tg), melt temperature (for linear non-crosslinked PSA), modulus, and Dahlquist criterion can be determined. The results of TTS measurements provide direct information on a PSA's

tack and peel performance and cohesive strength over a wide shear range and time scale. Rheological interconversion is a powerful technique that converts rheological data between dynamic and transient modes within a material's linear viscoelasticity region.

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