



Application Note

#1549

Nanomechanics of Pressure-Sensitive Adhesives

Pressure-sensitive adhesives (PSAs) form bonds under light pressure, making them invaluable for a wide range of applications. Nanomechanical testing of PSAs is essential to understanding their viscoelastic and adhesion properties at relevant structural length scales. In this application note, the viscoelastic and adhesion properties of two commercially available PSAs are investigated using a Hysitron® TI 990 TriboIndenter® equipped with nanoDMA® IV and an xSol Cryo low-temperature setup. This advanced system provides precise control over testing parameters, making it an ideal testing solution in such sectors as electronics, automotive, aerospace, and construction.

Characterization of Adhesives

The increased demand for high-performance adhesives in technically challenging applications for today's advanced products—cell phones, large-panel displays, and even modern construction materials—has led to several key developments in adhesive technology. These have increasingly come at small length scales, from hundreds of nanometers to tens of micrometers. Effective nano- to microscale characterization methods for these materials must be able to access specific force, length, temperature, and strain-rate scales. Nanoindentation is primary among these characterization methods, able to assess a high-performance adhesive's tackiness and mechanical properties by quantifying storage modulus, loss modulus, tan delta, and near-surface work of adhesion under a range of conditions.

There are many categories of adhesives, each classified according to type, chemistry, and structure. For this application note, we will focus on pressure-sensitive adhesives (PSAs), which are low-modulus elastomers that deform easily under low pressures. Deformation is required to maximize the contact area between PSA and substrate, since the adhesive contact relies on van der Waals forces to maintain this interface.

Time dependency in PSA properties is described by viscoelastic behavior, which can be measured by dynamic mechanical analysis (DMA) at larger length scales. Bruker's nanoDMA is a corresponding technique at the appropriate nanometer to micrometer length scales, ideal for measuring the surface properties of PSAs. NanoDMA IV with CMX is Bruker's latest dynamic nanomechanical testing capability with displacement feedback control, automated displacement amplitude tuning, force amplitude control, and dual lock-in amplifiers for second-harmonic measurements to provide powerful characterization of mechanical properties as a function of depth, frequency, and time.

The nanoDMA technique can be combined with variations in temperature to perform thermomechanical analysis and measure transition temperatures. Short time periods (high frequencies) can be correlated with low temperatures and vice versa. This principle can be quantitatively applied via the Williams-Landel-Ferry model, and is commonly referred to as time-temperature superposition (TTS).¹ Viscoelastic property data can be used in conjunction with TTS to create a master curve at a specified reference temperature, allowing the TI 990 TribolIndenter to provide frequency-dependent information beyond the testing capabilities of any traditional DMA instrument.

Nanoindentation Procedure

Dynamic and tack properties of two PSAs (Adhesive A, a commercially available restickable mini tab, and Adhesive B, an outdoor construction tape) were measured using a Hysitron TI 990 TribolIndenter with Performech® III controller (equipped with nanoDMA IV, xR transducer, xSol Cryo temperature stage, and a standard diamond Berkovich indenter probe). The xR transducer is Bruker’s extended-range transducer, capable of displacements up to 150 μm , with a force range of nN to 10 mN. Reference frequency sweep tests from 9 Hz to 100 Hz were performed at temperatures between -20°C to 40°C .

A displacement-controlled methodology was used to ensure similar contact depth. Dynamic and adhesion tests both consisted of large lifts to ensure the probe was completely out of contact prior to approach on a fresh surface. The indenter was loaded into the sample at $0.5 \mu\text{m/s}$ and unloaded at the same rate. Adhesion tests consisted of a two-second hold segment at the maximum depth before unloading. It is important to note that many indentation variables will have an effect, since greater contact time, larger area, and higher pressures will increase the number of van der Waals bonds that are formed.

Adhesive Testing Results

Figure 1 shows a strong frequency and temperature dependence in storage modulus for both the adhesives tested. However, the difference in properties at various temperatures has a larger variation in Adhesive B when compared to Adhesive A. It is also evident that the storage modulus is increasing with decrease in temperature (for all frequencies). This can be explained by the fact that polymer chains become stiffer at lower temperatures, thus restricting their movement. The flexibility of PSAs reduces as the temperature decreases, causing the adhesive polymer to become harder and stiffer.

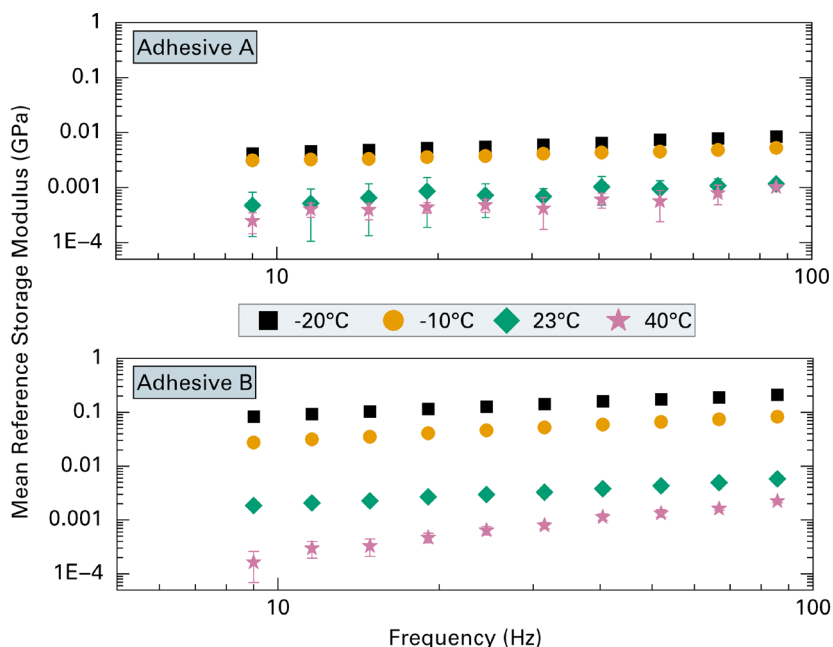


FIGURE 1.

Frequency sweep tests measuring mean reference storage modulus for Adhesives A and B at -20°C , -10°C , 23°C , and 40°C .

Dynamic data from frequency sweep tests was used to create a master curve (Figure 2, with reference temperature of -20°C) using TTS and the Williams-Landel-Ferry equation. This analysis shows the frequency dependence of Adhesive B from 10^{-3} Hz to 10^3 Hz, covering six orders of magnitude in frequency.

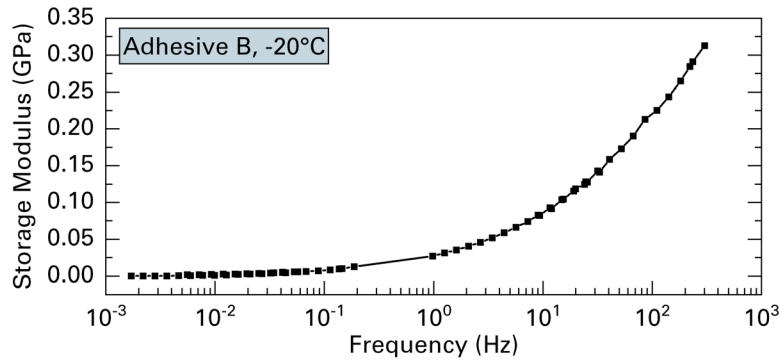


FIGURE 2.

Storage modulus master curve for Adhesive B at -20°C .

Table 1 summarizes the results from basic quasi-static indentation tests on Adhesive B. Maximum negative force is obtained from the unloading portion of the curve, and work done (energy required) to separate the indenter from the sample was calculated by integrating the force-distance curve where the force is negative, i.e., area under the curve (see Figure 3).

Temperature ($^{\circ}\text{C}$)	Max Negative Force (μN)	Work (μJ)
-20	-277.0 ± 13.4	378.6 ± 16.5
23	-39.6 ± 1.3	232.8 ± 4.7
40	-29.7 ± 2.2	152.0 ± 28

TABLE 1.

Maximum negative force and work done to separate the indenter from the sample surface, at different temperatures for Adhesive B.

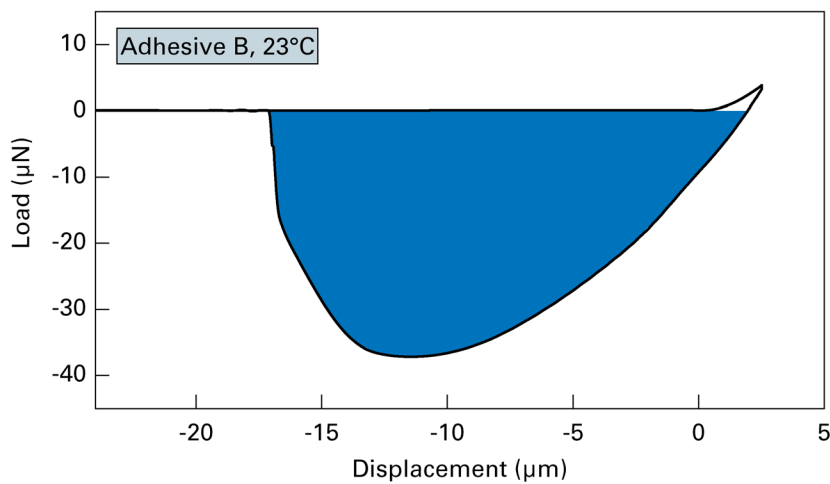


FIGURE 3.

Load versus displacement curve for Adhesive B at 23°C , showing the maximum negative force required for separation. Area under the curve (shaded) indicates the work done to separate the probe from the sample.

As mentioned, the polymer's stiffness increased as the temperature decreased and it became more brittle, producing less tack. Figure 4 demonstrates this theory, where the unloading portion of the curve at -20°C suddenly snaps out of contact, compared to 23°C and 40°C, which both show adhesion over a 10–20 µm pull-off distance.

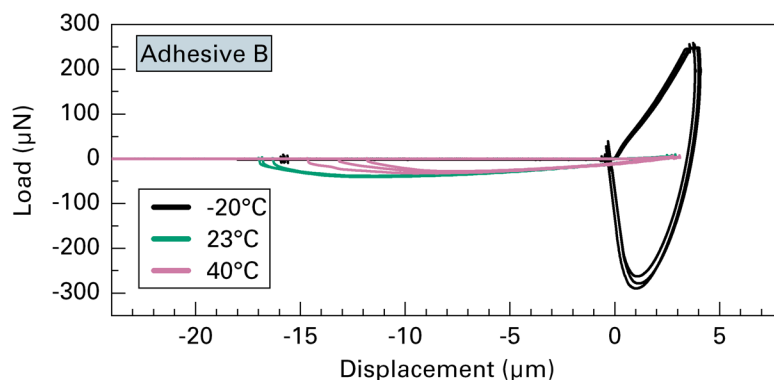


FIGURE 4.

Load versus displacement for Adhesive B at -20°C, 23°C, and 40°C.

Superior Control to Evaluate PSAs

With Bruker's Hysitron TI 990 equipped with nanoDMA IV and the xSol Cryo setup, both adhesive and viscoelastic properties of two pressure-sensitive adhesives were quantitatively measured. Full control was retained over the indenter loading and unloading rates, peak loads and displacements, along with other test parameters. The samples showed distinct dynamic and adhesive properties at various temperatures. These types of testing methods are suitable for a variety of soft and/or sticky materials, including biologicals, pharmaceuticals, gels, and polymers. Such nanoindentation-based dynamic and work-of-adhesion tests can provide chemists and materials scientists quantitative measures of material performance.

Authors

Douglas Stauffer, Sr. Manager of Applications Development, Bruker (douglas.stauffer@bruker.com)
Radhika Laxminarayana, NRL Development Engineer, Bruker (r.laxminarayana@bruker.com)

References

1. M. L. Williams, J. D. Ferry, and R. F. Landel. The Temperature Dependence of Relaxation Mechanisms in Amorphous Polymers and Other Glass-forming Liquids. *Journal of the American Chemical Society*. **77**(14). 3701-3707, 1955. DOI: 10.1021/ja01619a008

Bruker Nano Surfaces and Metrology

Minneapolis, MN • USA

Phone +1.952.835.6366

productinfo@bruker.com



www.bruker.com/TI990