

Methods for characterising surface tension of hot melt adhesives

Summary

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J S Nottay and M Rides

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Measurement Note

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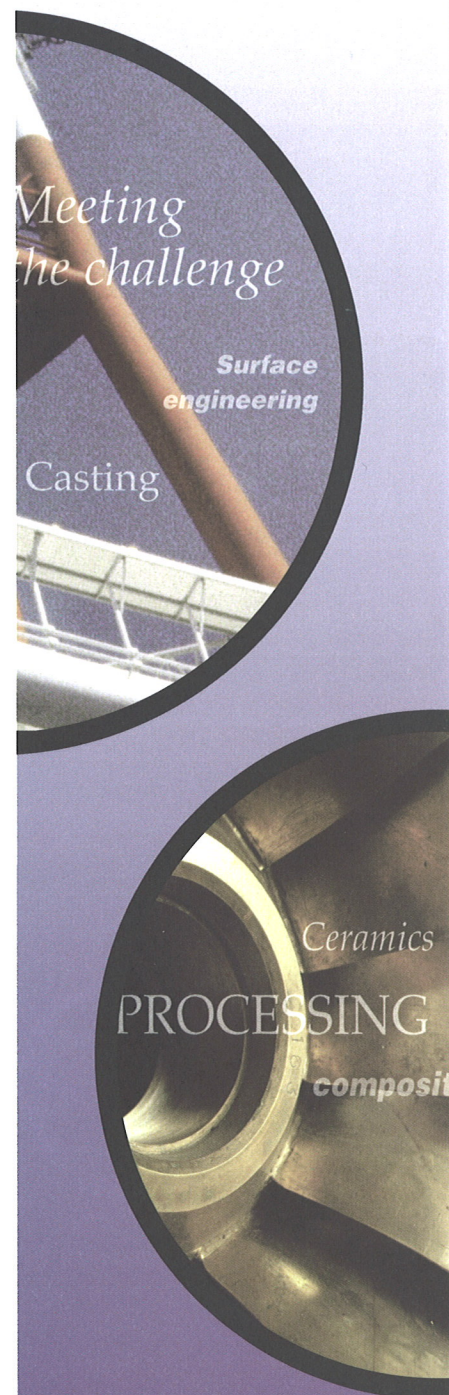
This Measurement Note describes a pendant drop shape analysis method that was used to determine the surface tension of a range of hot melt adhesives under typical elevated temperature processing conditions. As part of these measurements, densities for the liquid adhesives were measured using Archimedes' principle.

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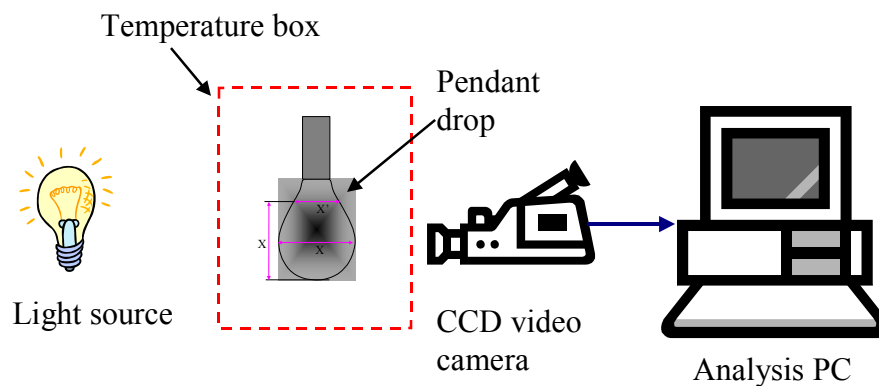


Figure 1: Automated drop shape analysis method for determining surface tension from pendant drops

Introduction

The surface tension, or more accurately the liquid-air interfacial tension, of a liquid adhesive is a key property for bond formation [1]:

- Interfacial tension of the adhesive and the surface energy of the substrate determine the wetting of the adhesive on the surface, good wetting promotes intimate contact and higher adhesion.
- The penetration of the liquid into craters and pores in rough and porous substrate, which enhances bond strength through mechanical ‘keying’ is a surface tension driven process.
- Surface tension is one of the properties controlling the stability of adhesive jets or sprays during dispensing; it may be an important parameter in effects such as stringing or drop break-up

Hot melt adhesives, polymeric materials applied to substrates in a molten form that develop mechanical strength on cooling, are a widely used class of adhesive. The drive to increase production rates is leading to the introduction of high speed dispensing processes, which push current understanding of adhesive behaviour.

Surface tension can be measured many ways. The challenge for determining the properties of hot melt adhesives is that they are only liquid at elevated temperatures and are typically processed at temperatures $> 100\text{ }^{\circ}\text{C}$. This Measurement Note describes the use of the “pendant” drop method to measure the surface tension of various hot melt adhesives under realistic process temperatures, Figure 1.

Pendant Drop Shape Technique

The equilibrium shape of a hanging pendant liquid drop is due to a balance between the forces acting on the drop. The principal forces are:

- Gravity – pulls the drop down, elongating the drop; and
- Surface tension – acts to prevent the growth of surface area and pull the drop into a spherical shape.

The shape of the drop therefore contains information on both the density and surface tension of the liquid. Building on the work of Laplace, theoretical relationships between shape, density and surface tension have been derived. The Young-Laplace equation [2], which relates the surface tension (γ_l) to the drop shape, is

used in automated drop shape analysis (ADSA) techniques:

$$\gamma_l = \frac{\rho_l g X^2}{f\left(\frac{X'}{X}\right)}$$

where g is the acceleration due to gravity, X is the diameter of the drop at its fullest width, X' is the diameter of the drop a distance X above the maximum width (Figure 2).

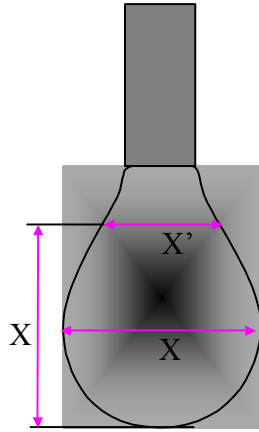


Figure 2: Pendant drop shape

The density of the liquid (ρ_l), in this case the adhesive, was unknown at the measurement temperatures and needed to be determined. $f\left(\frac{X'}{X}\right)$ is the shape parameter of the drop and can be calculated by the ASDA software or found in look-up tables.

Figure 1 shows the ADSA equipment used to measure surface tension. The shape of the pendant drop is projected onto the camera using back lighting. The captured video image is analysed using an imaging/software system, “CAMTEL, FTA 100 in this work [3], in order to calculate the shape parameter. The sample is enclosed in a temperature chamber where an elevated temperature can be maintained.

Materials

Nine hot melt adhesives were supplied by National Starch and Chemical Ltd. Four of the adhesives (Instant-Pak 2600, Varnimelt X10, Novacol 90 and Ultra-Melt 201) are grades used in packaging. These are collectively referred to as packaging adhesives in this report. These

were supplied as solid granules. The remaining five adhesives were different grades of Dispomelt pressure-sensitive hot melt adhesive (DM727, DM747, DM505, DM2000 and DM3000A) used in garments. These were supplied as solid blocks. The Dispomelt adhesives are, under ambient conditions, visco-elastic and very tacky. The removal of small samples from the blocks was very difficult owing to the nature of these materials. Unlike the packaging grades, the Dispomelt adhesives did not exhibit a sharp melting transition.

Density Measurements.

The densities of the adhesives were measured using the Archimedes principle - the apparent weight of an object immersed in a liquid decreases by an amount equal to the weight of the volume of the liquid that it displaces. The decrease of mass of an object of known volume on immersion can be used to calculate the density of the fluid, ρ_l [4].

Using this principle a steel ball, suspended by a spot-welded Nichrome wire was lowered into a beaker of molten adhesive, Figure 3. For a sphere the density of the liquid ρ_l is determined:

$$\rho_l = \frac{m_a - m_i}{\frac{4}{3}\pi r^3}$$

where m_a is the mass of the ball in air, m_i is the mass of the immersed ball and r is the radius of the ball. The radius of the ball was measured at room temperature and corrected using the known coefficient of thermal expansion for the steel to obtain values for r at each temperature.

Density measurements were made for 9 grades of hot melt adhesive. Once immersed in the adhesive, the samples were allowed to reach temperature equilibrium before the mass was recorded. Tests were performed at several typical

process temperatures (110 °C, 130 °C and 150 °C). The calibration of the technique was checked using distilled water, (density 0.9877 g/cc) and the measured value was within 0.112% of the reference value.

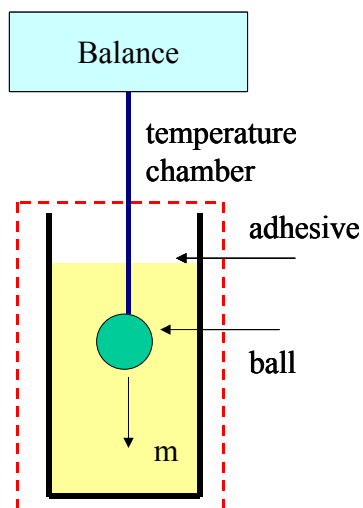


Figure 3: Density measurement by Archimedes' principle

The determination of density of visco-elastic polymer melts at elevated temperatures presents several problems not encountered with Newtonian liquids at ambient conditions.

- Attachment of air bubbles to the ball, causing an increase in buoyancy.
- Convection currents in the liquid are possible if there are temperature variations.
- The visco-elastic nature of the materials may lead to 'drag' forces imposed on the ball that persist after the ball is immersed.

In order to accurately measure the densities the adhesive was heated up to the test temperature and allowed to stabilise for approximately 1 hour to ensure that any residual air within the melt was allowed to escape. Once this had occurred (through visual indication), the temperature was rechecked using a calibrated thermocouple and the steel ball and wire were lowered into the melt. The weight of the steel ball in the adhesive melt was recorded after a period of stabilisation (which allows convection currents and visco-elastic effects to decay). Figure 4 shows the values obtained. These density values were used in the calculation of surface tension.

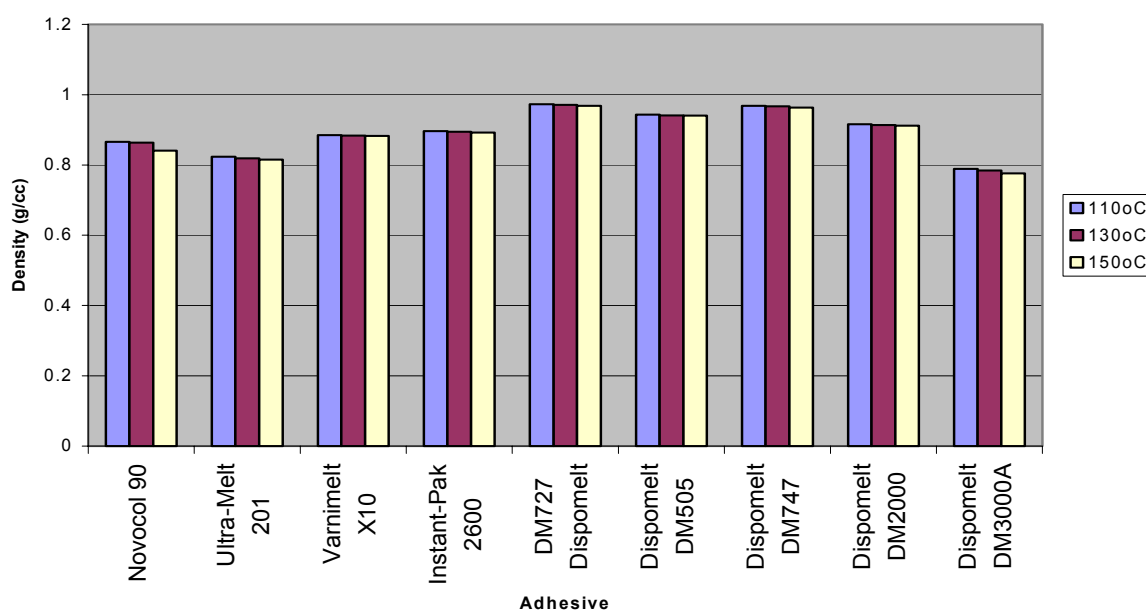


Figure 4. Density values for hot melt adhesives

Surface tension measurements.

Surface tension measurements were made using the ADSA method described earlier. The heated box was required to keep the adhesive melt at a constant temperature during the measurements.

The hot melt adhesive samples were provided in either pellet or block form. It was first necessary to prepare the adhesive melt in pipettes by cutting the adhesive pellets/ blocks into smaller pieces and inserting them into the glass pipettes. The adhesive is then melted in the heated box prior to measurement. Figure 5 shows a disposable glass pipette that has been prepared for measurement. The plug at the top ensures that adequate control of the adhesive drop is maintained during measurements.

The ADSA software relies on dimensions determined from the drop image and therefore requires accurate calibration of the magnification factor of the camera in order to produce reliable results. Optical calibration of the field of view in the x and y directions is performed using a steel ball of 6.000 mm diameter at 21 °C. During measurements, the pipette tip diameter (measured before the test) is used as a reference to adjust the magnification factor. The syringe was securely mounted to a retort clamp and lowered into the chamber of the heater box.

The system calibration can be checked using a syringe of known diameter and a fluid of known density and interfacial tension, for example glycerol.

The pipette is clamped in a retort stand within the heated box and positioned so that the pipette is aligned vertically. Once the pipette is correctly aligned the temperature is then increased to the desired value and allowed to stabilize. As the pendant drop formed the camera zoom lens was adjusted to ensure precise to

obtain the best focus of the drop for maximum clarity and contrast. The image of the drop was then captured and transferred to the PC for analysis using the Young-Laplace equation [2]. Figure 6 shows the software interface and a typical pendant drop.

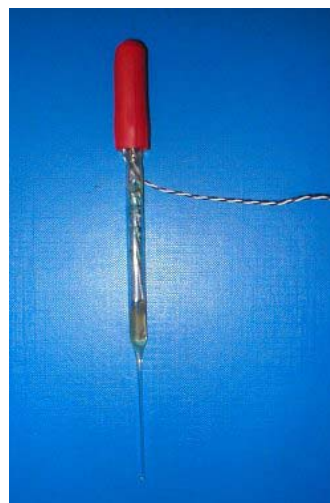


Figure 5: Glass pipette containing adhesive melt/ thermocouple and control plug

The Laplace method, once a drop has formed, produces surface tension values that are independent of the volume of the drop. A series of images captured at different stages of the drop extrusion were analysed for surface tension. These confirmed the invariance of calculated surface tension with drop volume.

Ten readings of the surface tension were taken for each packaging adhesive at the 110 °C, 130 °C and 150 °C. The Dispomelts adhesives were insufficiently molten at 110 °C and data were obtained at 130 °C and 150 °C only.

Figure 7 shows the results that were obtained for the surface tension measurements on the packaging adhesives. Figure 8 shows the results for the Dispomelt materials at 130 °C and 150 °C. The scatter bars represent the spread in the calculated surface tension values.

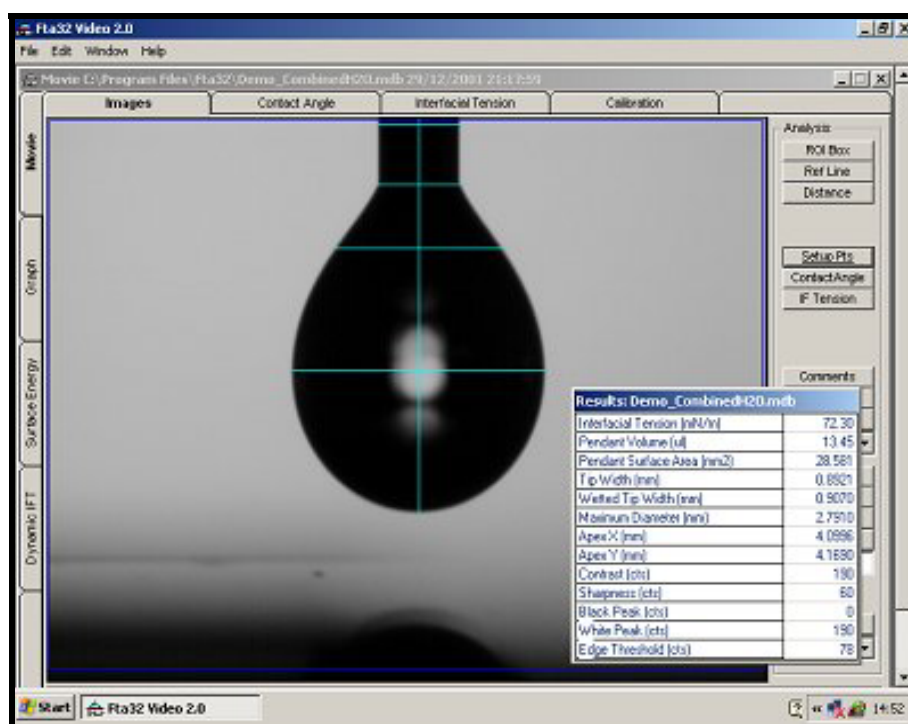


Figure 6 Screenshot of Pendant drop and software interface.

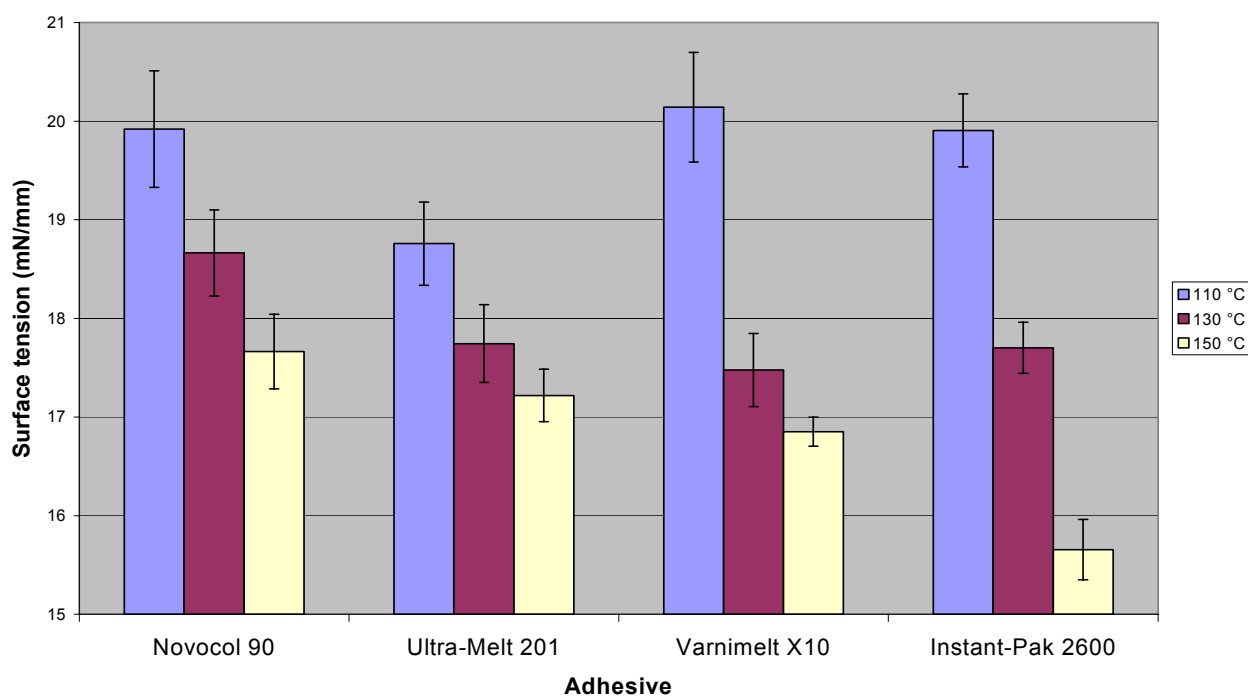


Figure 7 Surface tension measurements of packaging hot-melt adhesives

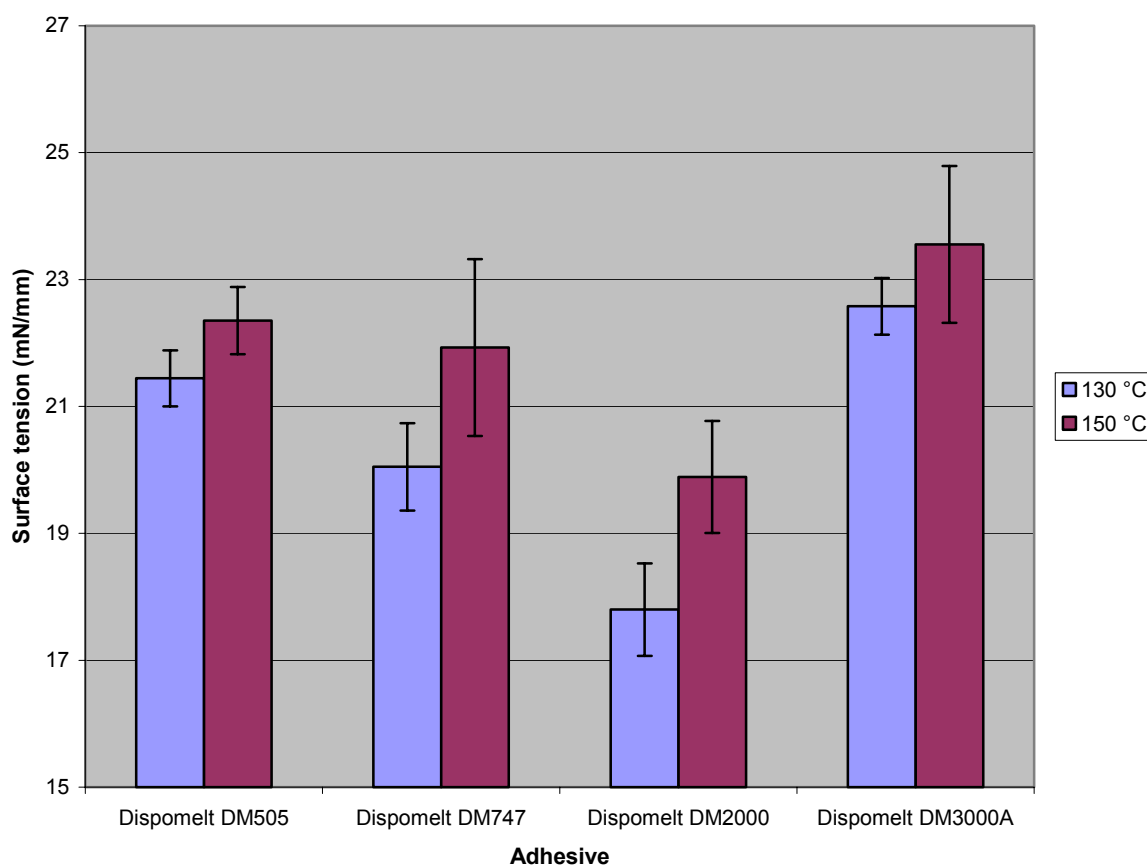


Figure 8 Surface tension measurements of Dispomelt adhesives at 130 and 150°C

Discussion.

The surface tensions of several different hot melt adhesives under realistic processing conditions have been determined using an automated drop shape analysis technique based on the Laplace method. As part of this work, densities for the liquid adhesives were determined using the Archimedes principle. Densities were in the range 0.788 to 0.972 g/cc.

The surface tension values obtained were around 20 mN/m, typical values for liquid hydrocarbons. Surface tension measurements showed that there was a gradual decrease in the surface tensions of the packaging adhesives with increasing temperature. This is expected as the increasing thermal agitation of the molecules and decreasing density will lead to reduced inter-molecular forces. The different adhesive systems show differing

sensitivity of surface tension to temperature.

The surface tensions of the Dispomelt adhesives all appear to increase with temperature. The reasons for this are unclear but as these materials have complex formulations there may be some phase changes occurring in the adhesive as the temperature increases.

The Dispomelt materials were troublesome to work with due to their high degree of “tack” at ambient temperatures. The Dispomelt melts were more viscous than the packaging adhesive melts and they were more able to retain air within the melt at elevated temperatures. This led to problems when carrying out density measurements. In order to counteract this problem the adhesives were allowed to stabilise for long periods.

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The authors would like to thank Dave Carter and Wei Kong of National Starch and Chemical Ltd for supplying the adhesives and Rob Brooks, Bruce Duncan Richard Mera and Crispin Allen at NPL for their help and contributions to this Measurement Note.

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