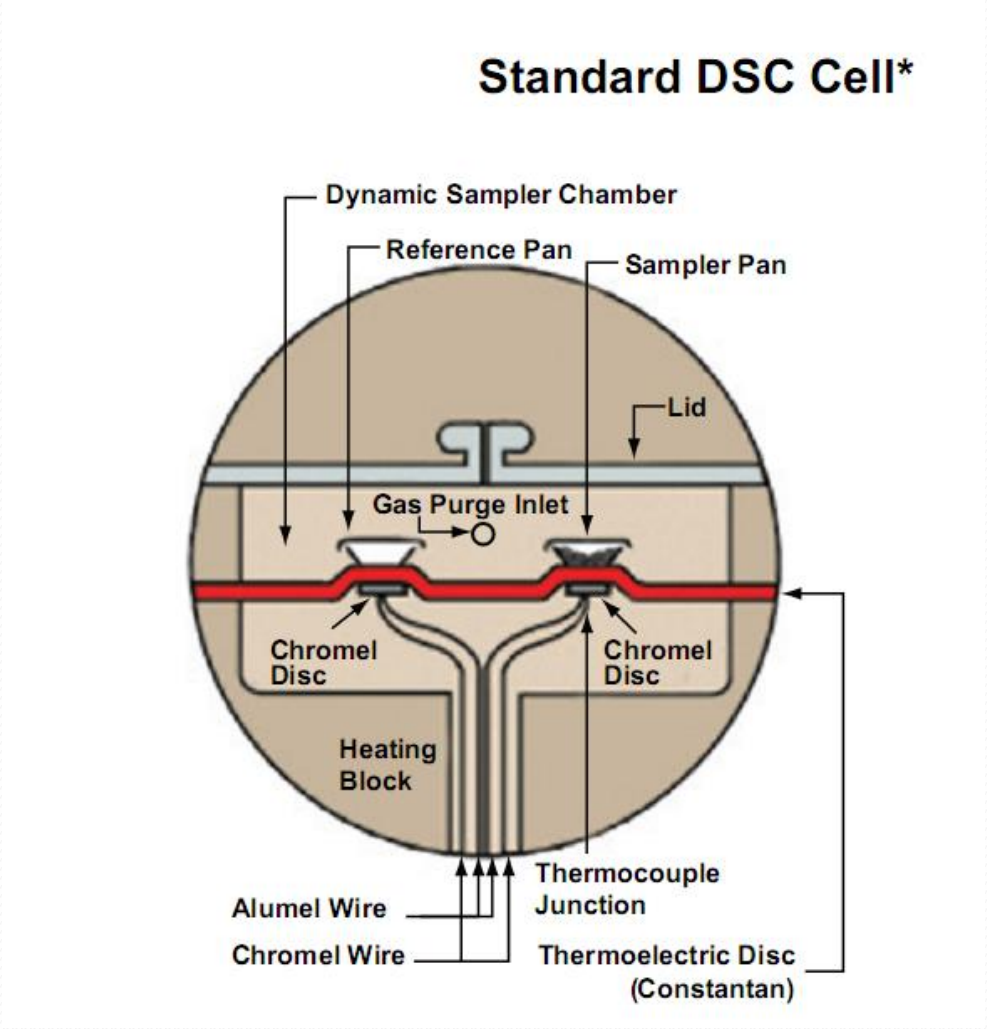
גישות אנליטיות בחקר של דבקים

יזהר הלחמי

אנליזה תרמית

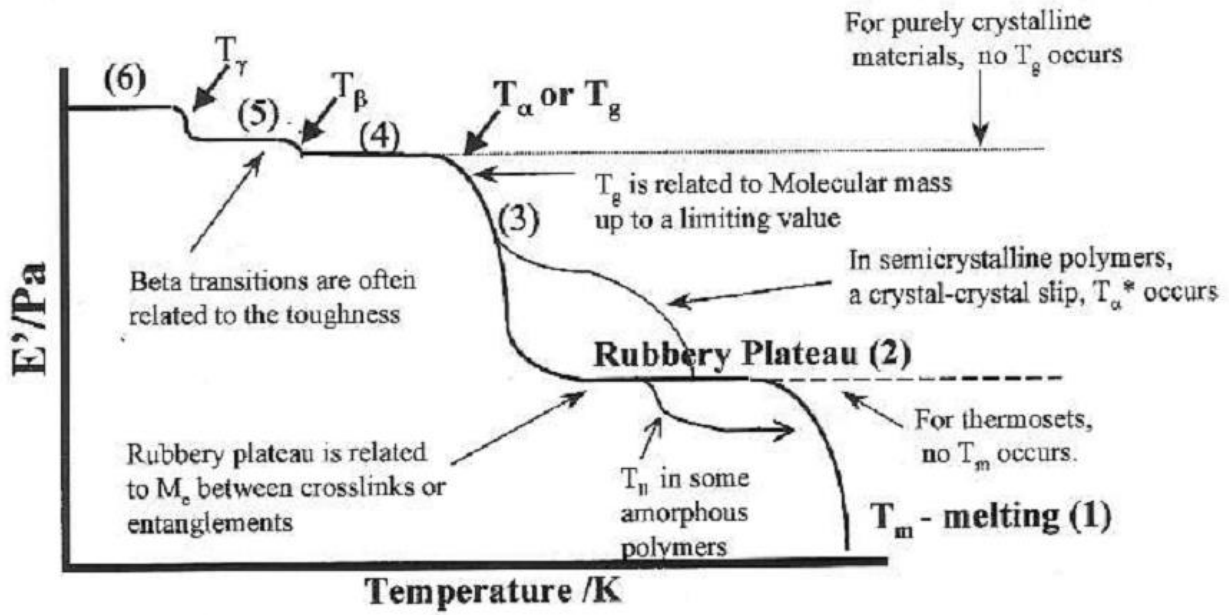
DSC



אנליזה תרמית

Figure 2. The double-furnace design pictured on the right allows very fast cooling and heating required for isothermal crystallization studies.

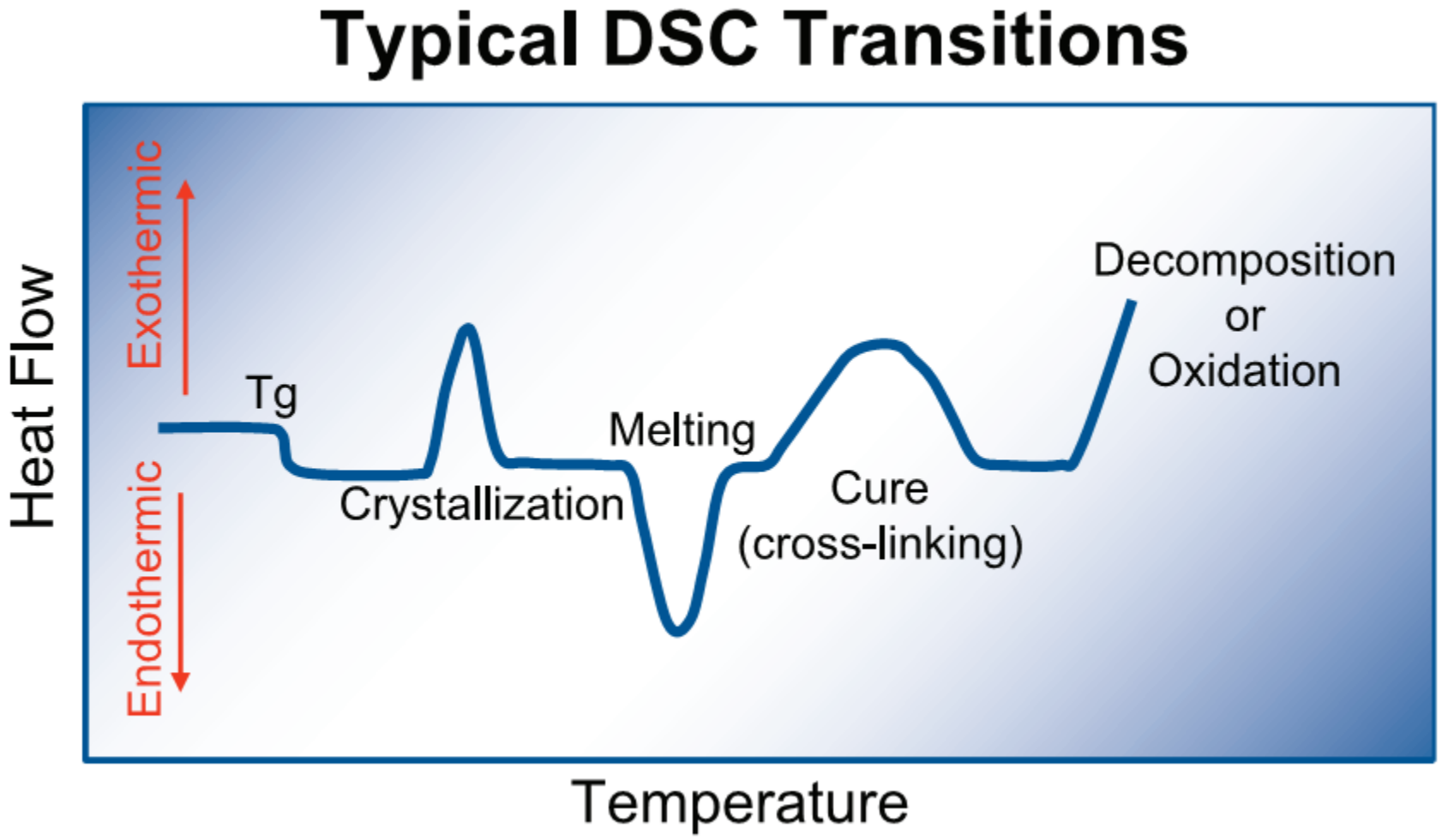
אנליזה תרמית



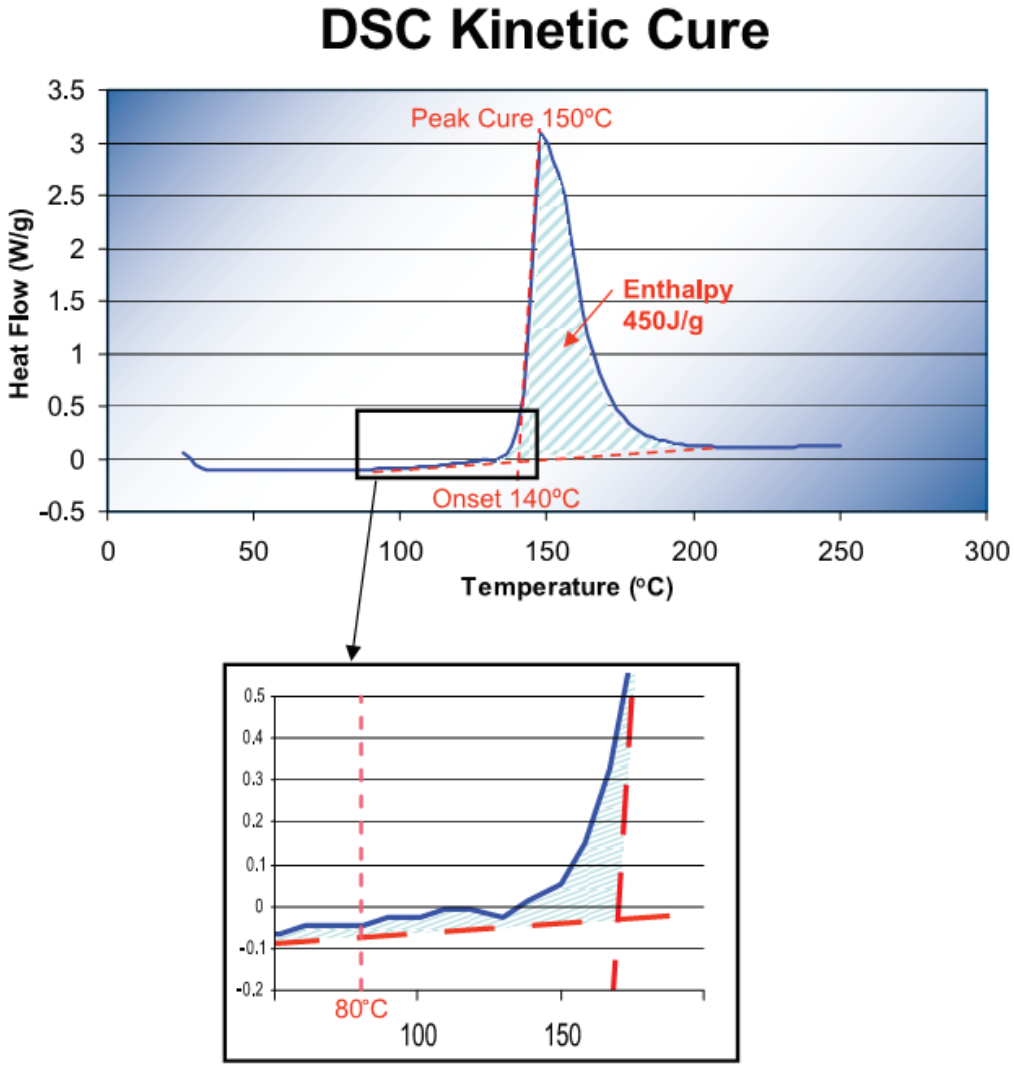
(6)	(5)	(4)	(3)	(2)	(1)
local motions	bend and stretch	side groups	gradual main chain	large scale chain	chain slippage

Fig. 8.2.2 An idealized polymer going through a set of transitions (for its storage modulus) as its temperature increases. Variations for different types of polymers are also shown. Used with the permission of CRC Press.

אנליזה תרמית

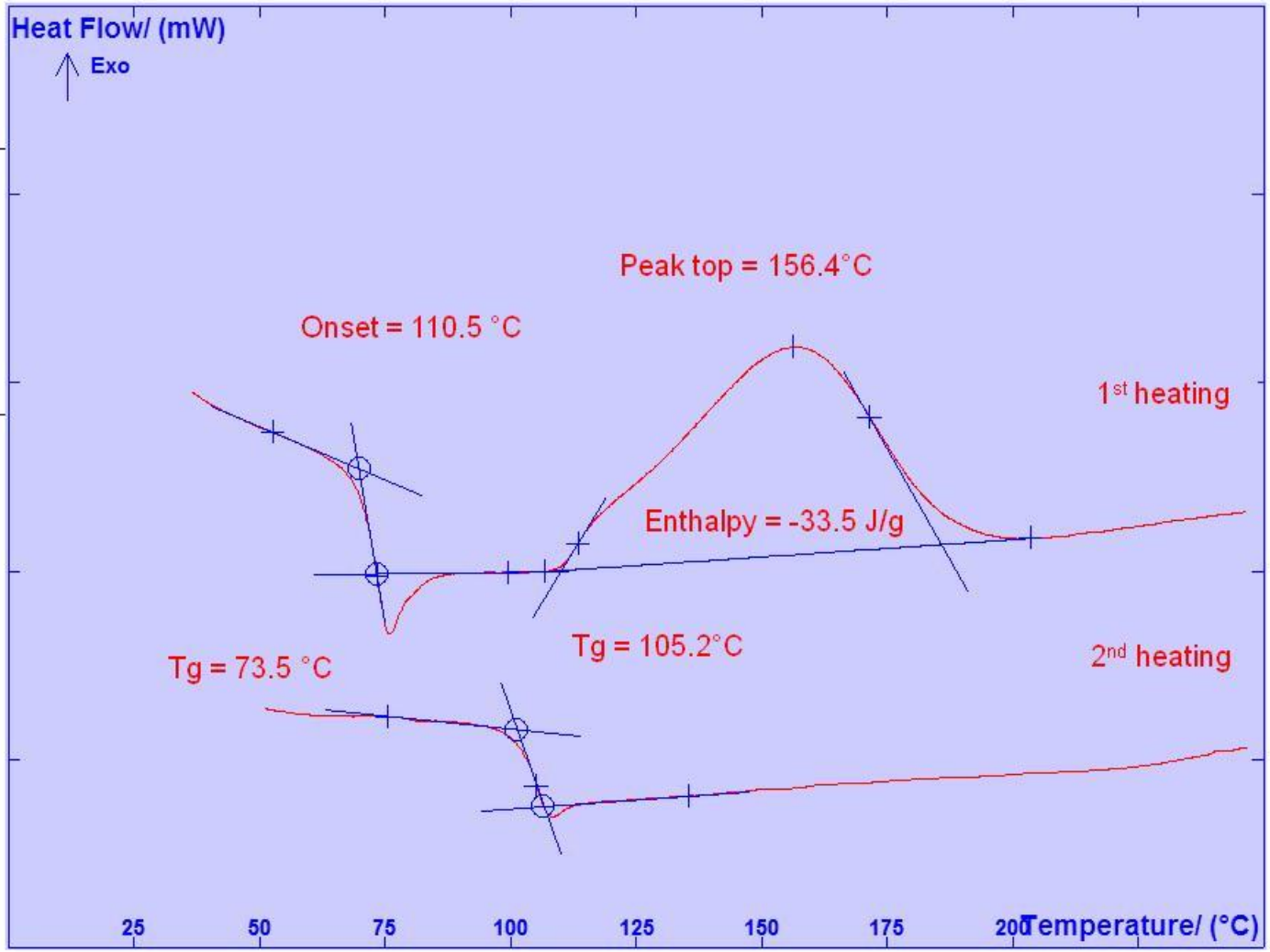


קינטיקה של מיצוק



Analysis of epoxy resin

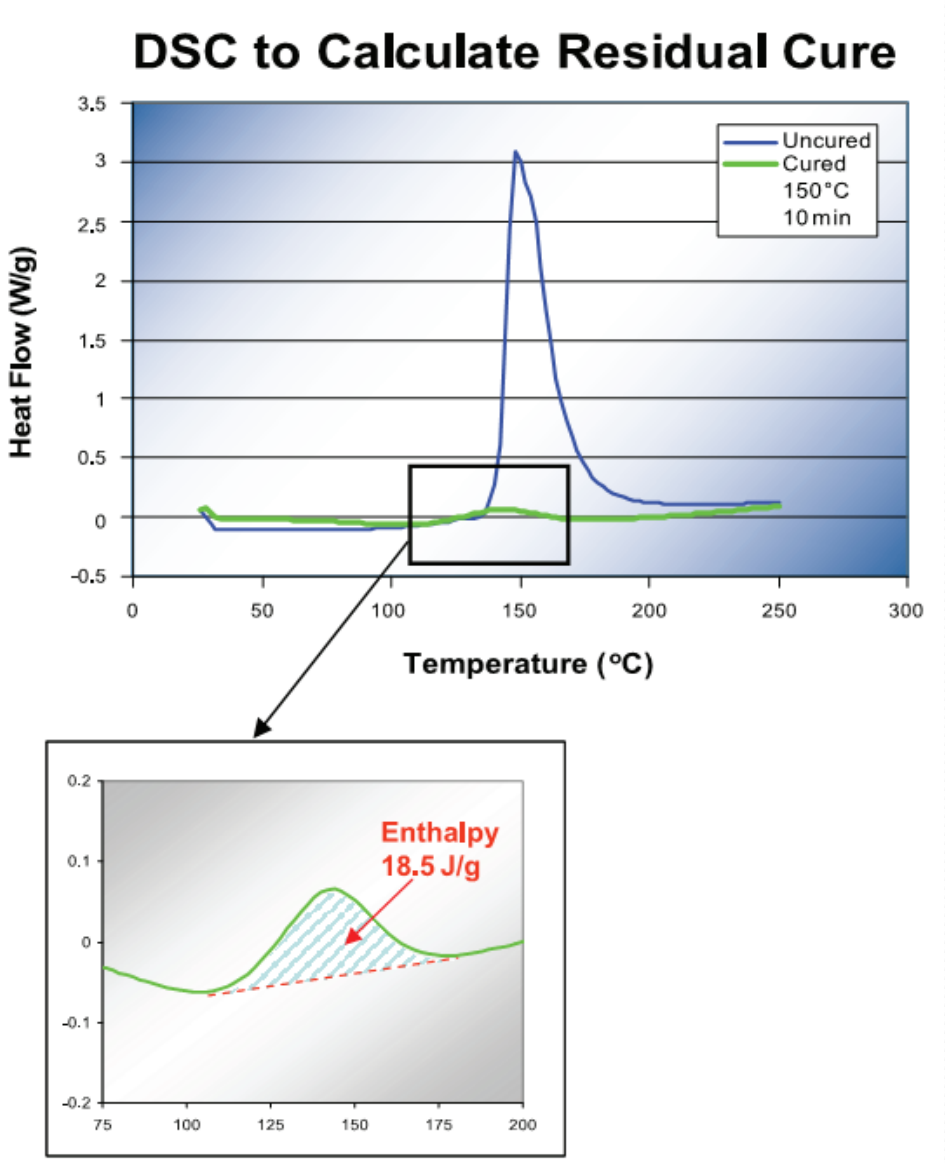
DSC131
Epoxy resin
6.7 mg
Crucible : Al
25°C → 250°C
@10 K.min^{-1}



קינטיקה ומעבר זכוכיתי – סטנדרטים בין לאומיים

The total change in enthalpy that the sample undergoes during cure can be calculated by integrating the area under the exotherm peak. For the material in the diagram above, the total heat of reaction is 450J/g. As specified in ASTM D3418, "*Standard Test Method for Transition Temperatures and Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry*", this total heat of reaction can then be used to determine the extent of reaction of the material after it is cured according to a desired cure condition. The

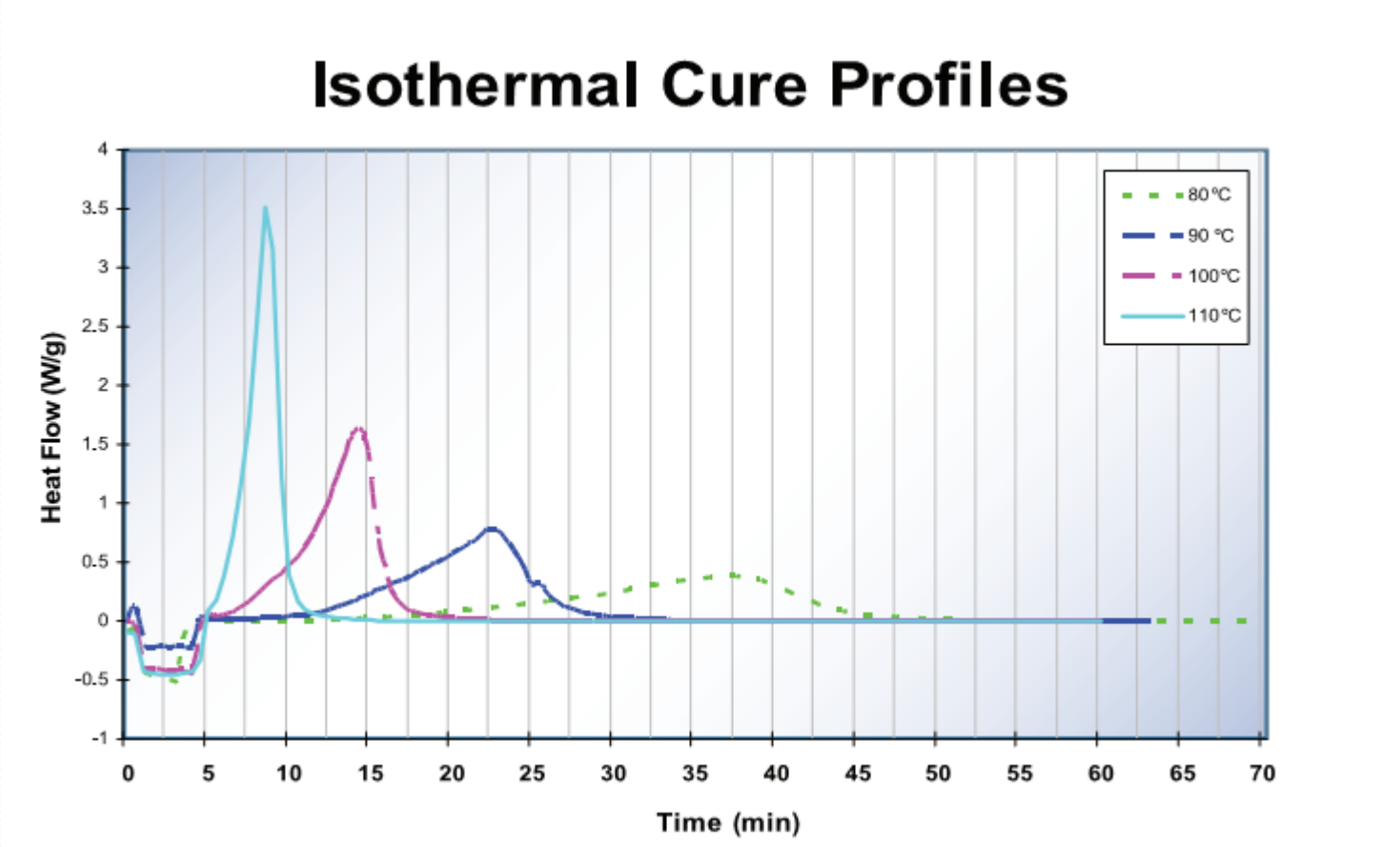
אנרגיה שיורית



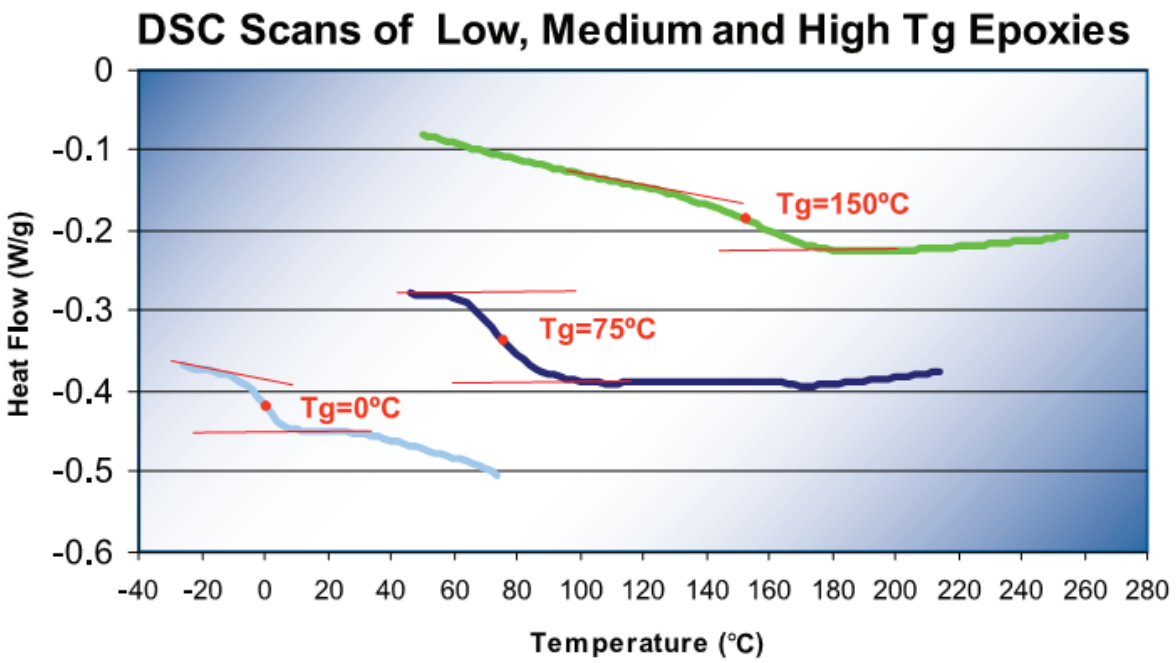
אנרגיה שיורית

The material cured at 150°C for 10 minutes exhibits only a very small residual exotherm peak. This indicates that most of the theoretical cross-linking reactions were completed during the cure. The enlarged view of the cured sample exotherm shows that only 18.5 J/g of reactivity remains of the original 450 J/g heat of reaction for this material. Thus, only 4.1% of the material is left unreacted by the imposed cure. Epoxies do not need to achieve a full 100% reaction in order to perform well as adhesives. Generally, systems that have been cured to at least 90% conversion will exhibit mechanical and physical properties that do not differ significantly from their fully reacted state. In addition, even lower degrees of conversion may produce properties that are perfectly sufficient for a given application.

מיצוק בטמפרטורה נתונה – השפעת זמן ההקשיה



נקודת מעבר זכוכיתית



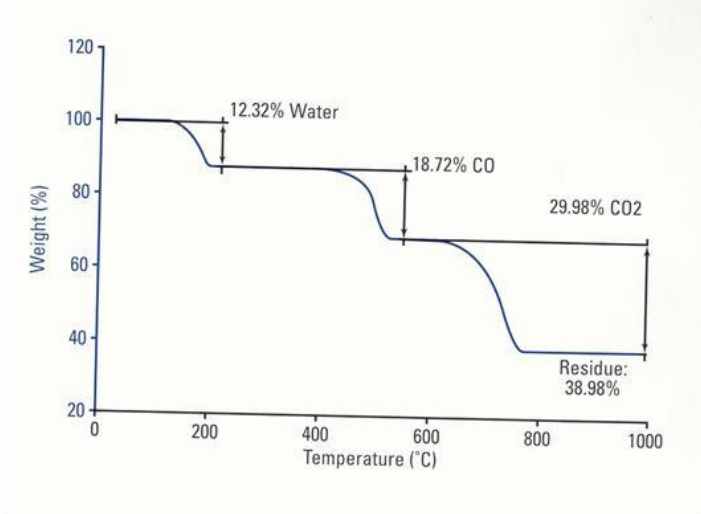
Some Typical Tg Ranges Are:

Very High:	> 200° C
High:	100° C – 150° C
Average:	50° C – 90° C
Low:	< 30° C

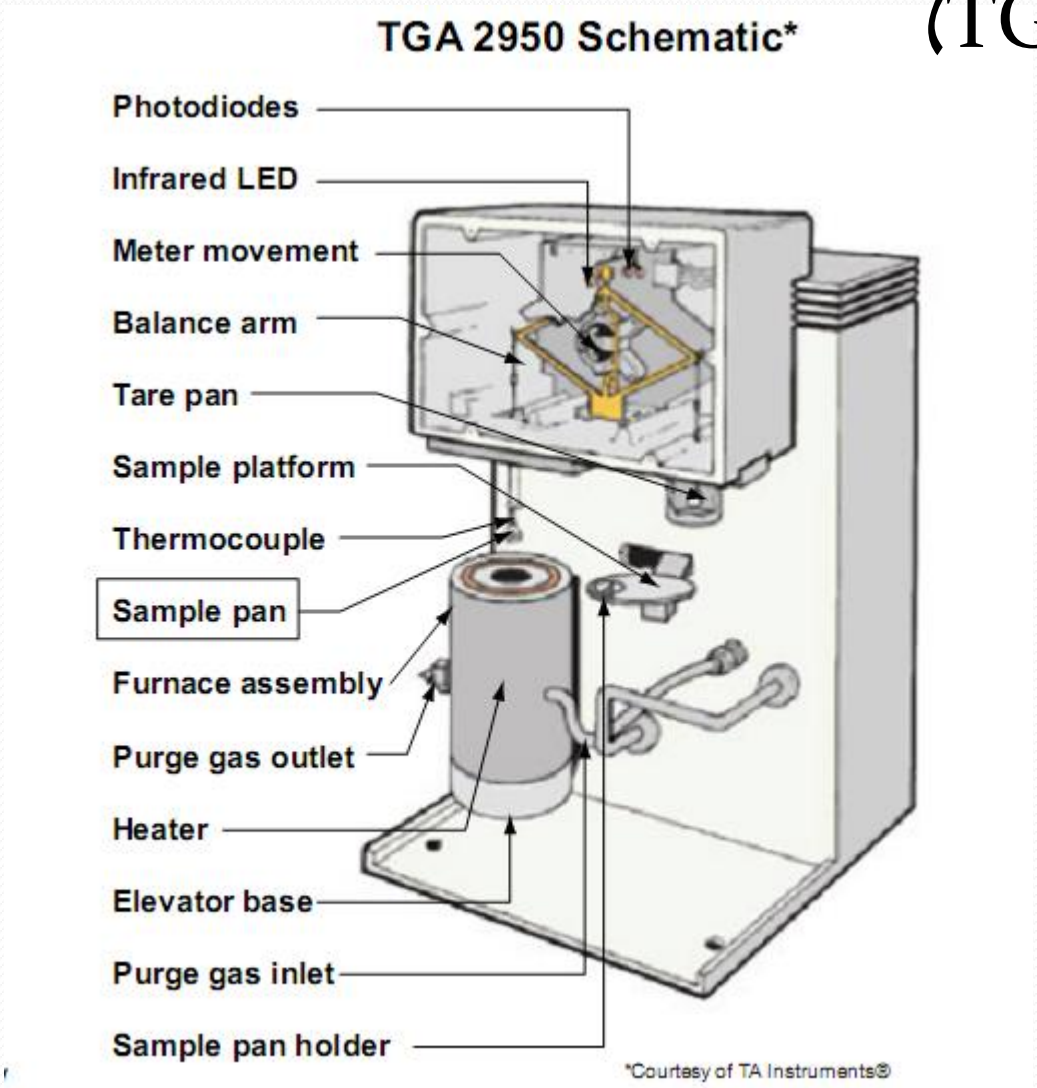
תרמוגרווימטריה (TGA)

TGA

- Constant Heating Rate
  - Initial Temp
  - Final Temp
  - Heating Rate (°C/min)
- Data
  - Weight vs Time
  - Weight vs Temp.
- Differential This Data (DTG)



תרמוגרווימטריה (TGA)



טמפרטורת שימוש מקסימלית

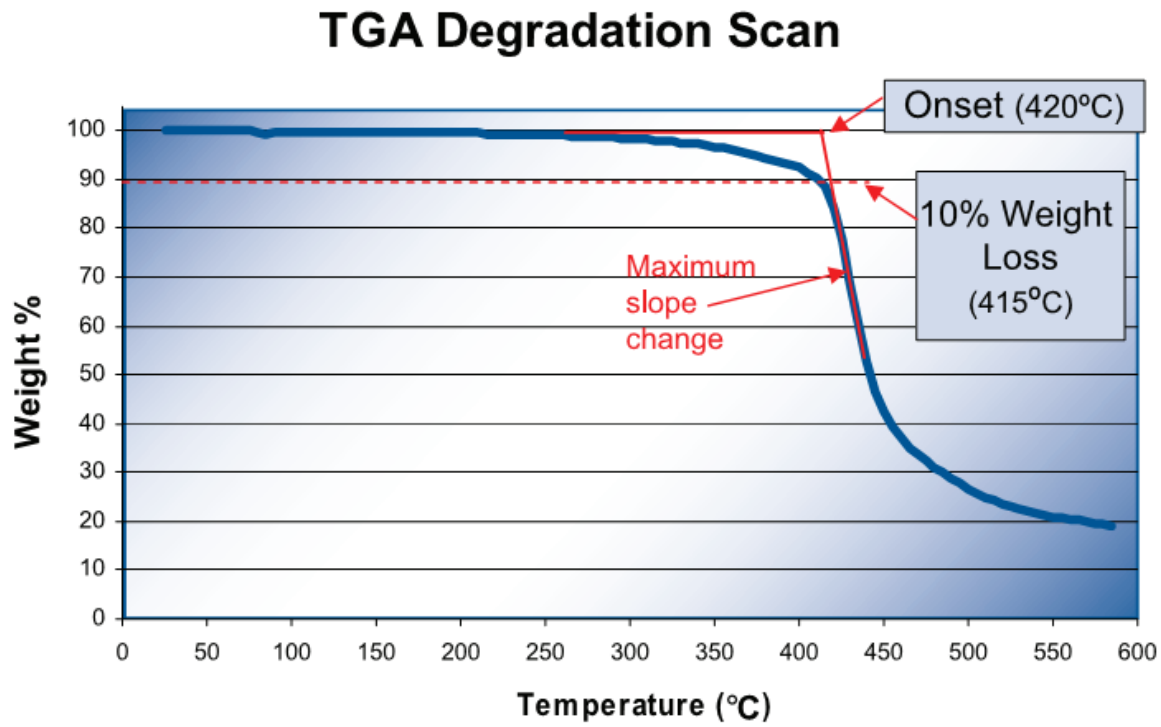


figure 2

As generally reported on data sheets, the upper ends of both the continuous and intermittent operating windows are calculated based on the degradation temperature. The upper end of the continuous operating window is calculated by subtracting 150°C from the degradation temperature. The upper end of the intermittent operating window is calculated by subtracting 50°C from the degradation temperature.

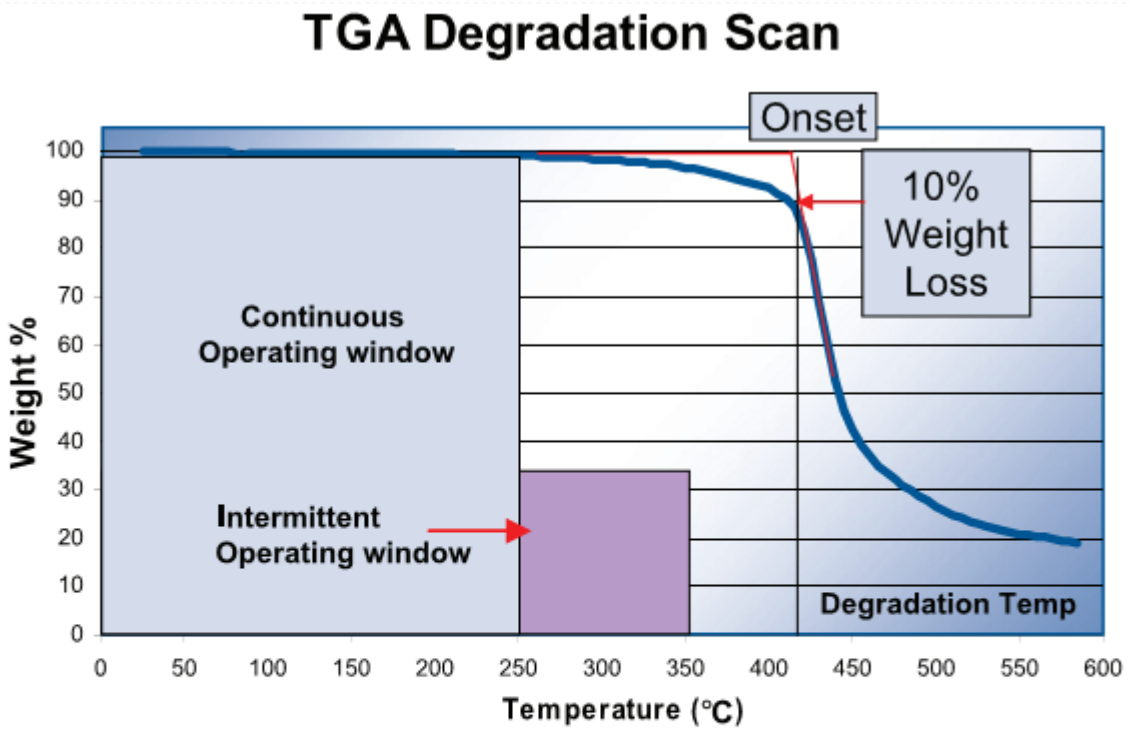


figure 3

For the example material in figure 3, the degradation temperature is approximately 420°C. Thus, 370°C would be calculated for the intermittent operating window and 270°C would be calculated for the continuous operating window. Generally, we would add a safety factor so that the datasheet would actually list 350°C and 250°C as the intermittent and continuous operating windows.

4.2 Outgassing (Thermal Stability)

The percent weight versus temperature curve is also used to determine weight loss at specified temperatures. This weight loss is often referred to as outgassing or thermal stability. Datasheets generally report outgassing levels at 200˚C, 250˚C and 300˚C.

<1.0% @ 200˚C is required by MIL-STD 883 Method 5011 (low outgas)

Figure 4 below shows an example of outgassing calculations.

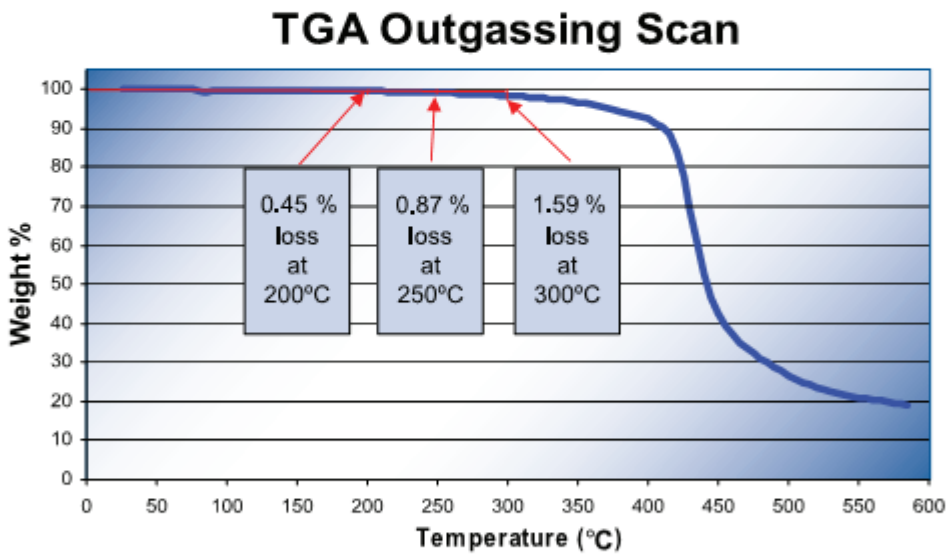


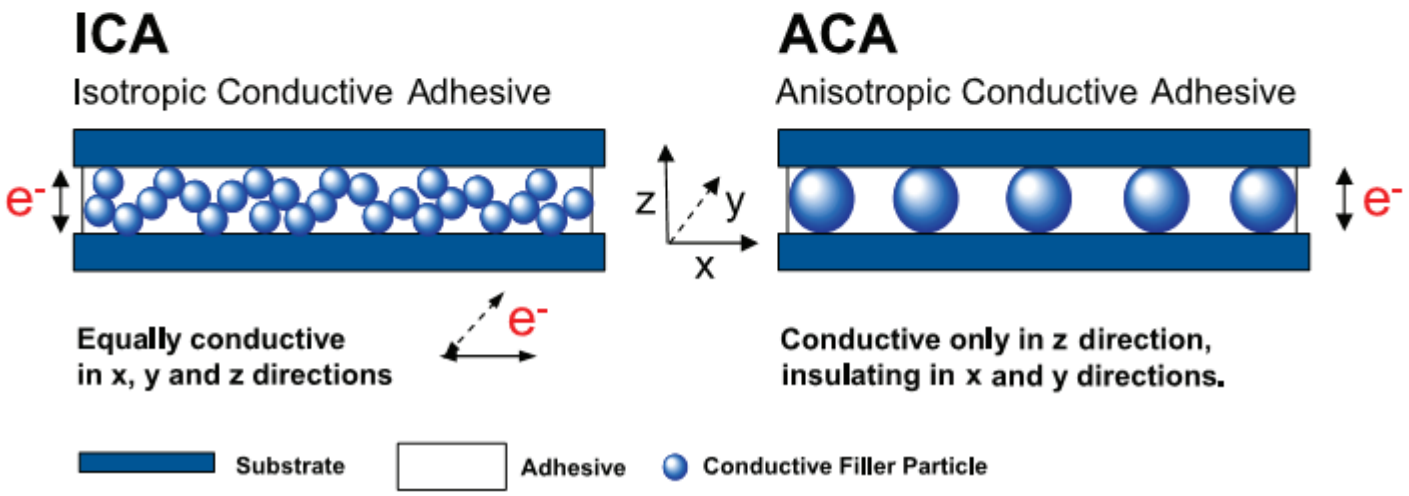
figure 4

One important industry specification is the NASA outgassing requirement. Products that meet this specification must exhibit less than 1.0% Total Mass Loss (TML) after being exposed to 125˚C for 24 hours in a vacuum. They must also contribute less than 0.1% Collected Volatile Condensable Materials (CVCM) during this exposure.

מוליכות חשמלית

A less-common type of electrically conductive adhesive is an Anisotropic Conductive Adhesive (ACA). As shown in figure 1 below, the amount of conductive filler particles used in an ACA is much lower than the levels in an ICA. In addition, the particle size in an ACA is designed to be the exact thickness of the bond line. As a result, these materials are electrically conductive in only one direction (through the bond line), and are actually electrically insulating in the remaining directions.

The majority of current applications are designed around ICAs.



Conductive Filler Geometries

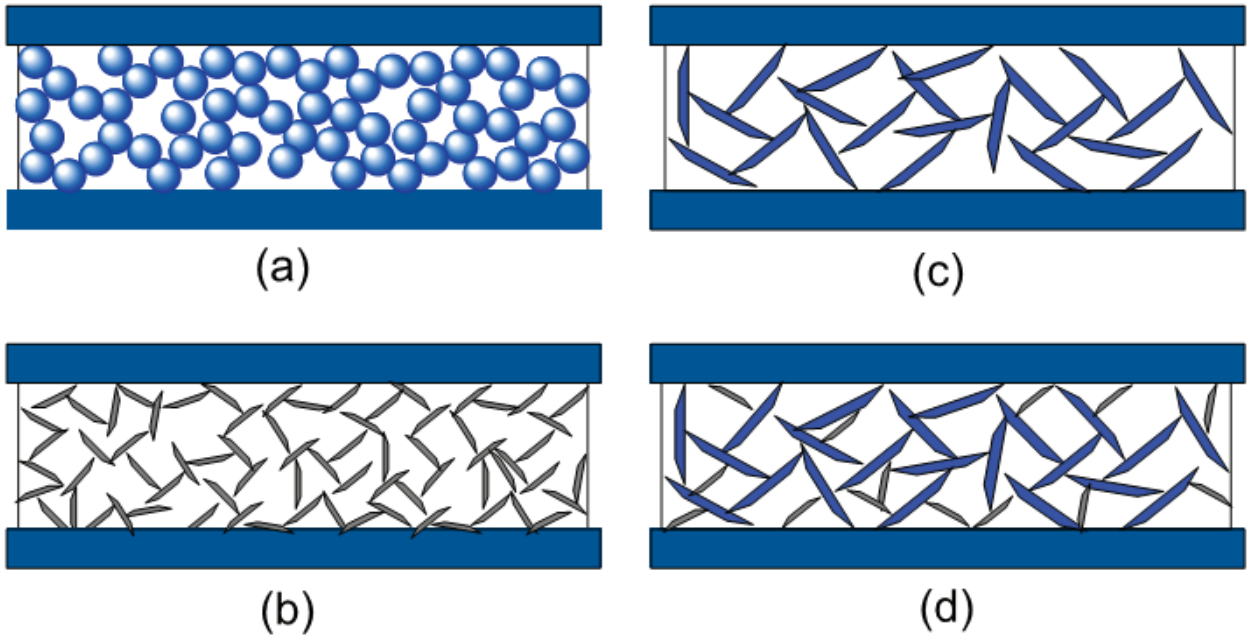
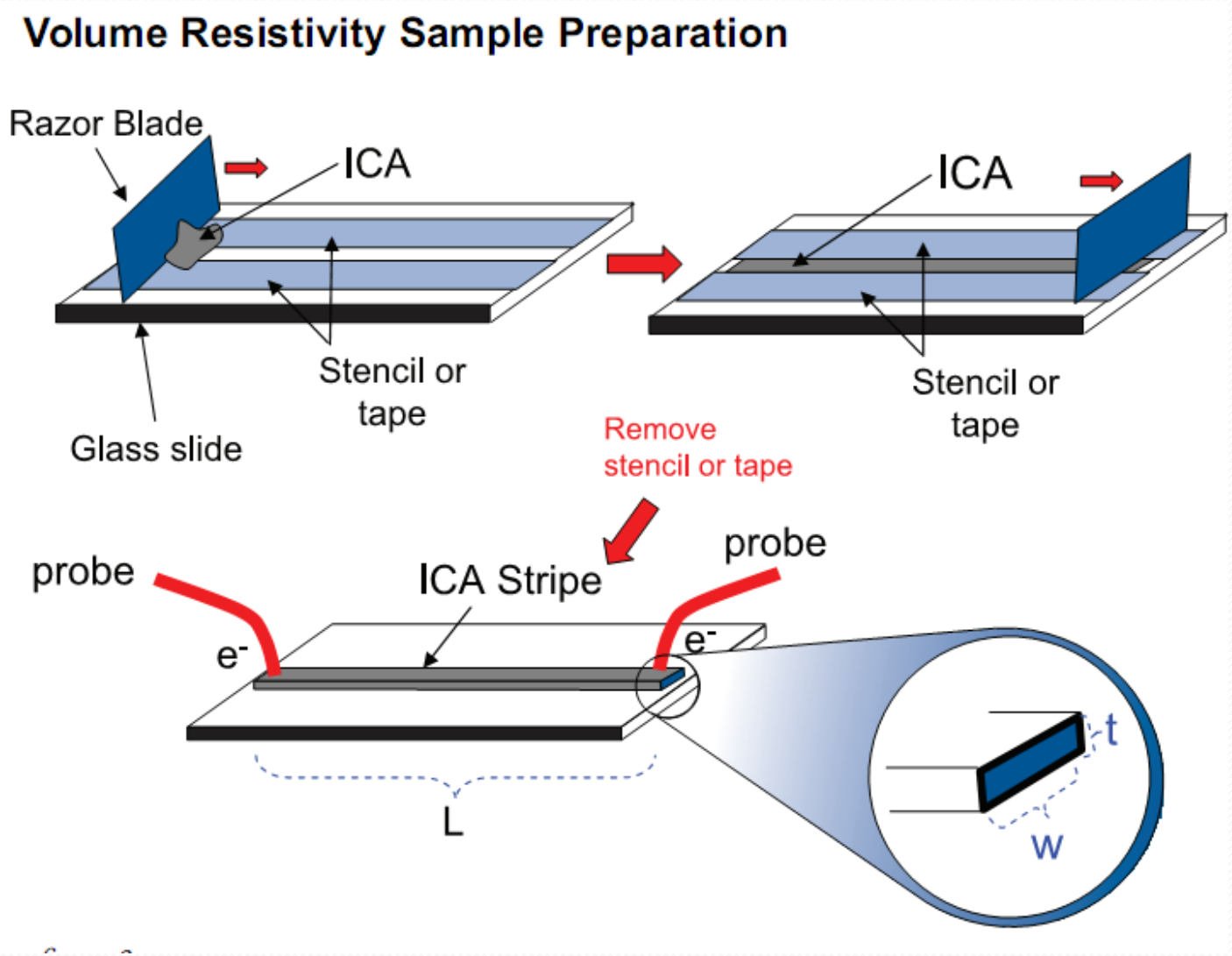


figure 2

The choice of flake size to impart conductivity to a resin system is also driven by the ICA's intended application. If the ICA is to be dispensed through a fine gage syringe needle, or screen-printed to very tight tolerances, there may be a limit to the maximum size of flake allowed. The required rheology of the ICA may also play a large role in flake size selection. Smaller flakes have much higher surface area per unit volume than larger flakes. As a result, adding smaller flakes will increase the viscosity of the ICA much more than the addition of the same loading content of larger flakes.

Volume resistivity of ICA



Volume resistivity of ICA

Once the sample has been prepared and cured, the two probes of a voltmeter are applied to the ends of the stripe to measure the resistance across the sample. Volume resistivity is then calculated according to the following equation:

$$\text{Volume Resistivity (ohm·cm)} = \frac{R * w * t}{L}$$

R = resistance (ohms)
w = width (cm)
t = thickness (cm)
L = length (cm)

מוליכות חום

Thermal conductivity, by definition, is equal to the quantity of heat that is transferred in a specific period of time through a known sample area when the sample's opposite faces are subject to an applied temperature gradient. Typical units of thermal conductivity are:

$$\frac{\text{Watts}}{\text{meter} * \text{Kelvin}} \left(\frac{\text{W}}{\text{m} * \text{K}} \right)$$

One method, ASTM E1461, "*Standard Test Method for Thermal Diffusivity by the Flash Method*", for measuring thermal conductivity is Laser Flash Diffusivity. Over the past few decades, this test method has evolved into one of the most widely used techniques for the measurement of the thermal diffusivity and thermal conductivity of polymeric materials in the adhesive industry. Using this technique, the front side of a small, usually disk-shaped sample, is placed into a horizontal fixture and heated by a short energy (laser) pulse. The resulting temperature rise on the alternate surface is measured versus time using an IR detector. Although this is a fairly quick test, the sample preparation and thickness are critical to the end result.

An advantage of this test is that it is non-contact and, is therefore non-destructive to the sample.

Method of testing thermal conductivity

Here is a schematic of the test apparatus:

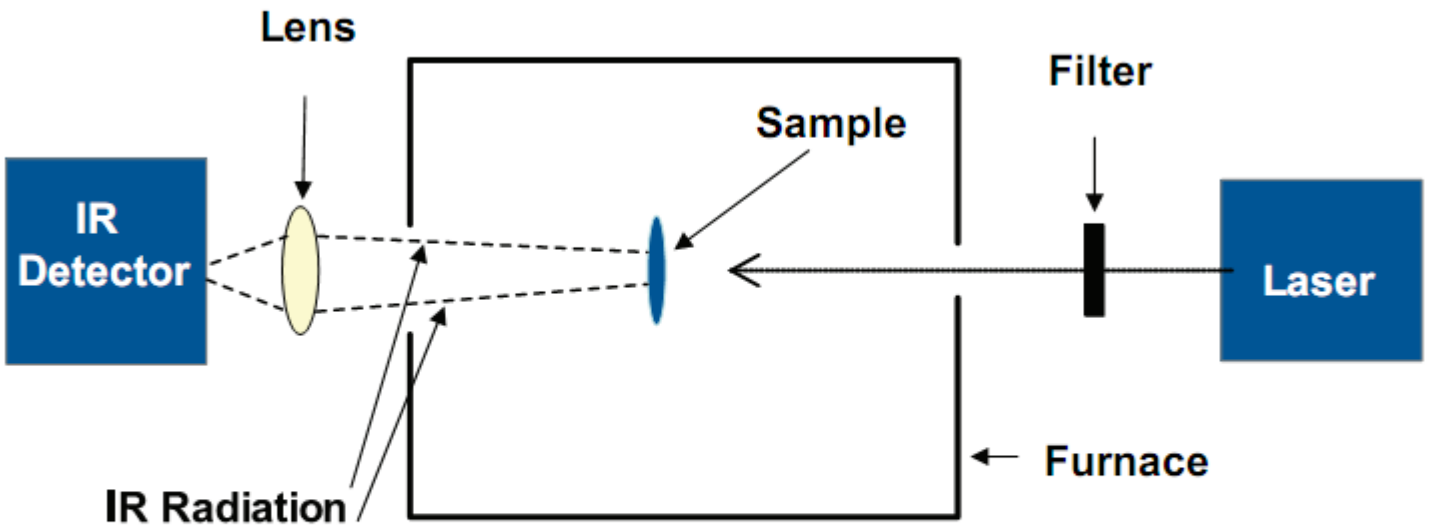


figure 1

Thermal conductivity (ThK) = Heat flow rate / (Area × Temperature gradient)

צמיגות וראולוגיה

Newton defined viscosity by the model in figure 2 below. Two parallel planes of fluid of equal area "A" are separated by a distance "dx", moving in the same direction, but at different velocities (V_1 and V_2). He assumed that the force to maintain this difference in speed was proportional to the difference in speed throughout the liquid. Also called the velocity gradient. To express this, Newton said that "η" is a constant for a given material and is called its "viscosity." The velocity gradient, dv/dx, is a measure of the change in speed at which the layers move with respect to one another. This describes the shearing a liquid goes through and is referred to as the "shear rate (S)" which is reported in "reciprocal second" (sec^{-1}). The term F/A indicates the force per unit area required to produce the shearing action. It is referred to as "shear stress" and will be symbolized by "F´". Its unit of measurement is "dynes per square centimeter" ($dynes/cm^2$).

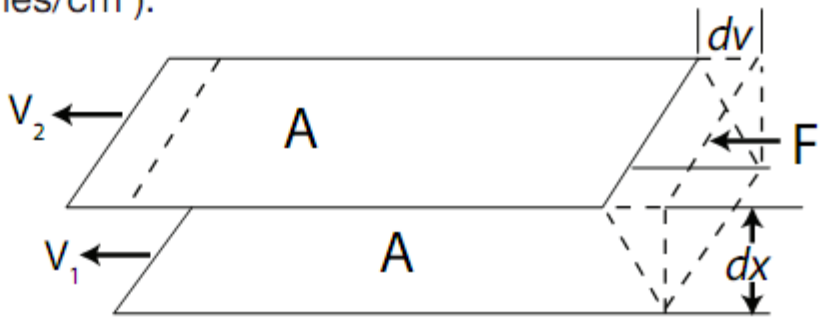


figure 2

צמיגות וראולוגיה

η = Viscosity = F´/S = shear stress/shear rate

ASTM Test Method D2393, "*Standard Test Method for High-Shear Viscosity Using a Cone and Plate Viscometer*", is based on the above definition and is followed for viscosity measurements.

The fundamental unit of viscosity is the "poise." If a material requires a shear stress of one dyne per square centimeter to produce a shear rate of one reciprocal second, it would produce a viscosity of one poise, or 100 centipoise. Viscosity can also be expressed in "milli-Pascal-seconds" (mPa·s). One milli-Pascal-second is equal to one centipoise. Newton assumed that all materials have, at a given temperature, a viscosity that is independent of the shear rate. In other words, twice the force would move the fluid twice as fast. This holds true for Newtonian fluids only. The following is a schematic (figure 3) of a cone and plate viscometer in action:

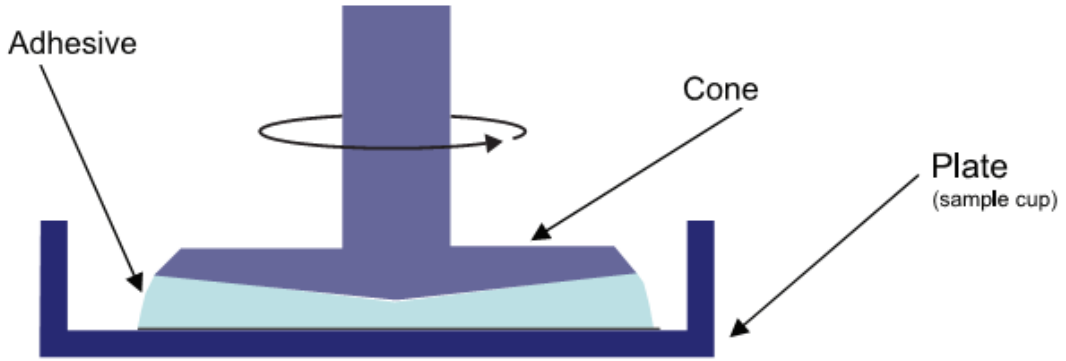


figure 3

צמיגות וראולוגיה

The type of flow described above is true for Newtonian fluids only. The following graphs show how this type of product behaves. Figure 4 shows the straight line relationship between shear rate (F´) and shear stress (S). Figure 5 shows how the viscosity remains constant (assuming temperature is held constant) with varying shear rates.

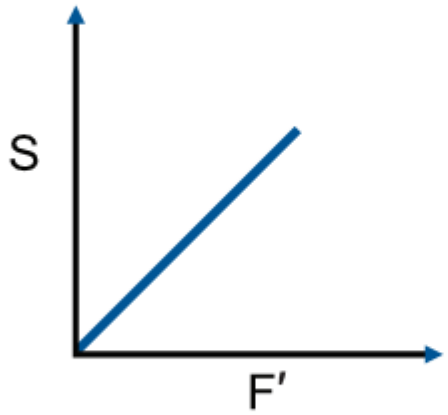


figure 4

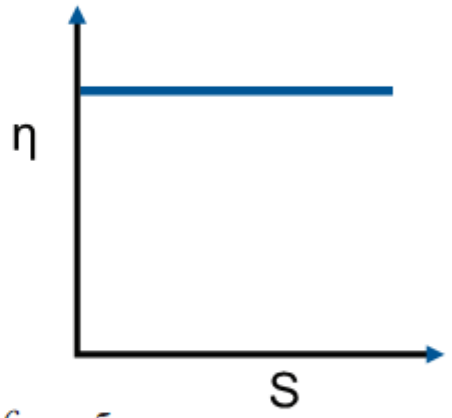


figure 5

But not all fluids are Newtonian in their flow characteristics. In fact, there are several types of flow behavior. These products are classified as Non-Newtonian. There are three subgroups within the Non-Newtonian classification: **Pseudoplastic, Dilatent** and **Plastic**.

צמיגות וראולוגיה

Pseudoplastic materials will decrease in viscosity with an increase in shear rate. This is sometimes referred to as shear thinning. Figures 6 & 7 depict this:

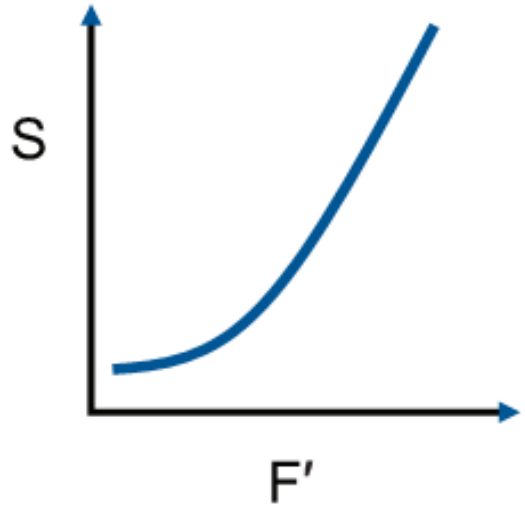


figure 6

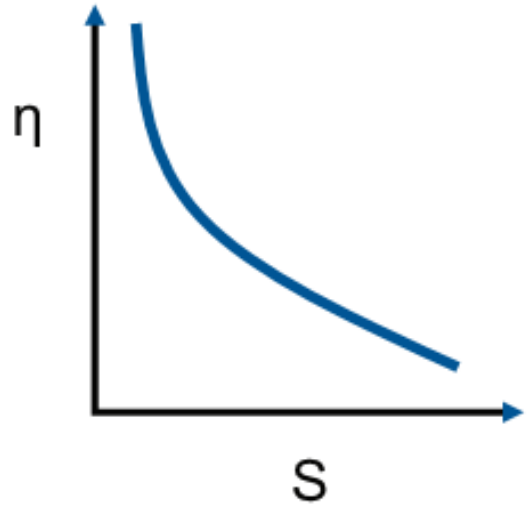


figure 7

צמיגות וראולוגיה

A **Dilatent** type of behavior as seen in figures 8 and 9 below, causes products to increase in viscosity with an increasing shear rate. This is also called shear thickening and is commonly seen with deflocculated solids such as clay.

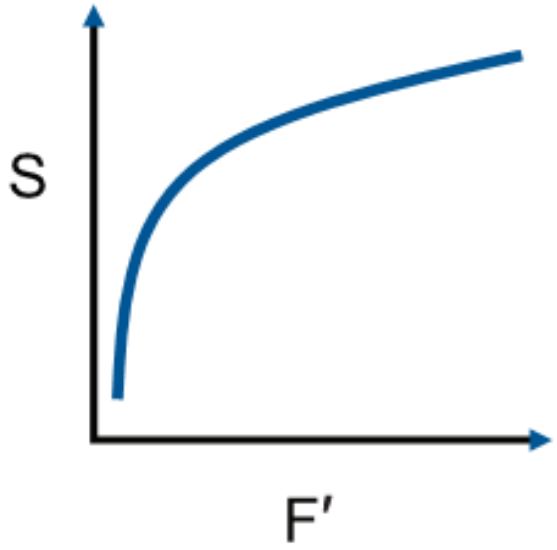


figure 8

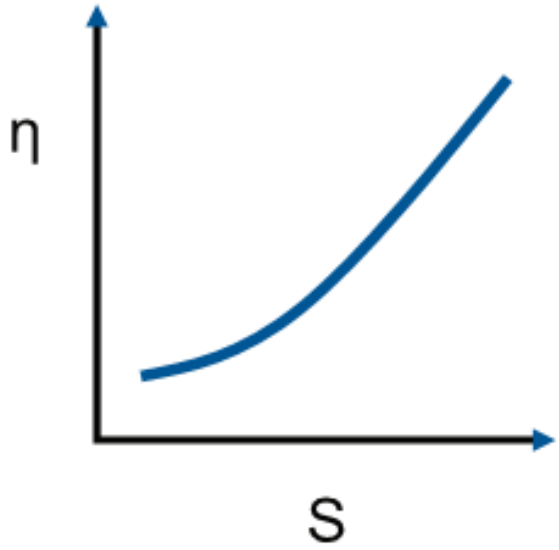


figure 9

צמיגות וראולוגיה

The third and final type of flow is **Plastic**. When a material exhibits Plastic behavior similar to figures 10 and 11 below, it will remain in a "solid" state until a certain amount of force (yield value) is applied to it before it will flow. A great example of this is ketchup.

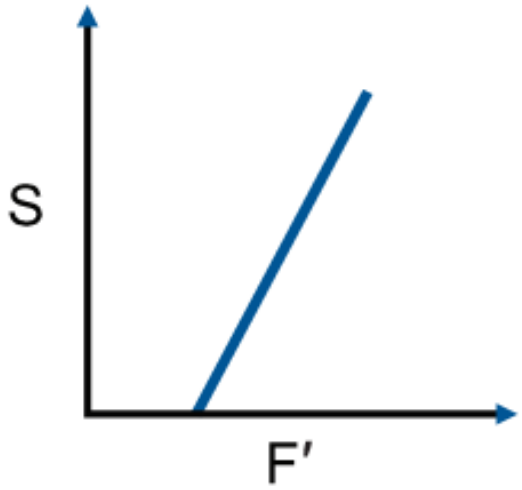


figure 10

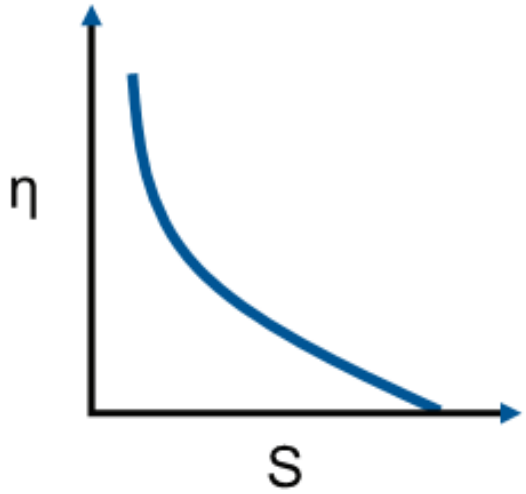


figure 11

צמיגות וראולוגיה

Epoxies can exhibit any or all of these flow behaviors which is important to consider when choosing an adhesive for a specific application. Thixotropy is another parameter that is related to viscosity and can be measured using a viscometer. A thixotropic fluid decreases in viscosity with time, while it is subjected to constant shearing as seen in figure 12. This type of behavior can occur in combination with any of the above flow types.

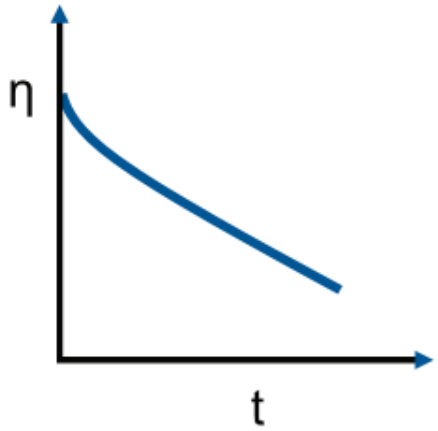
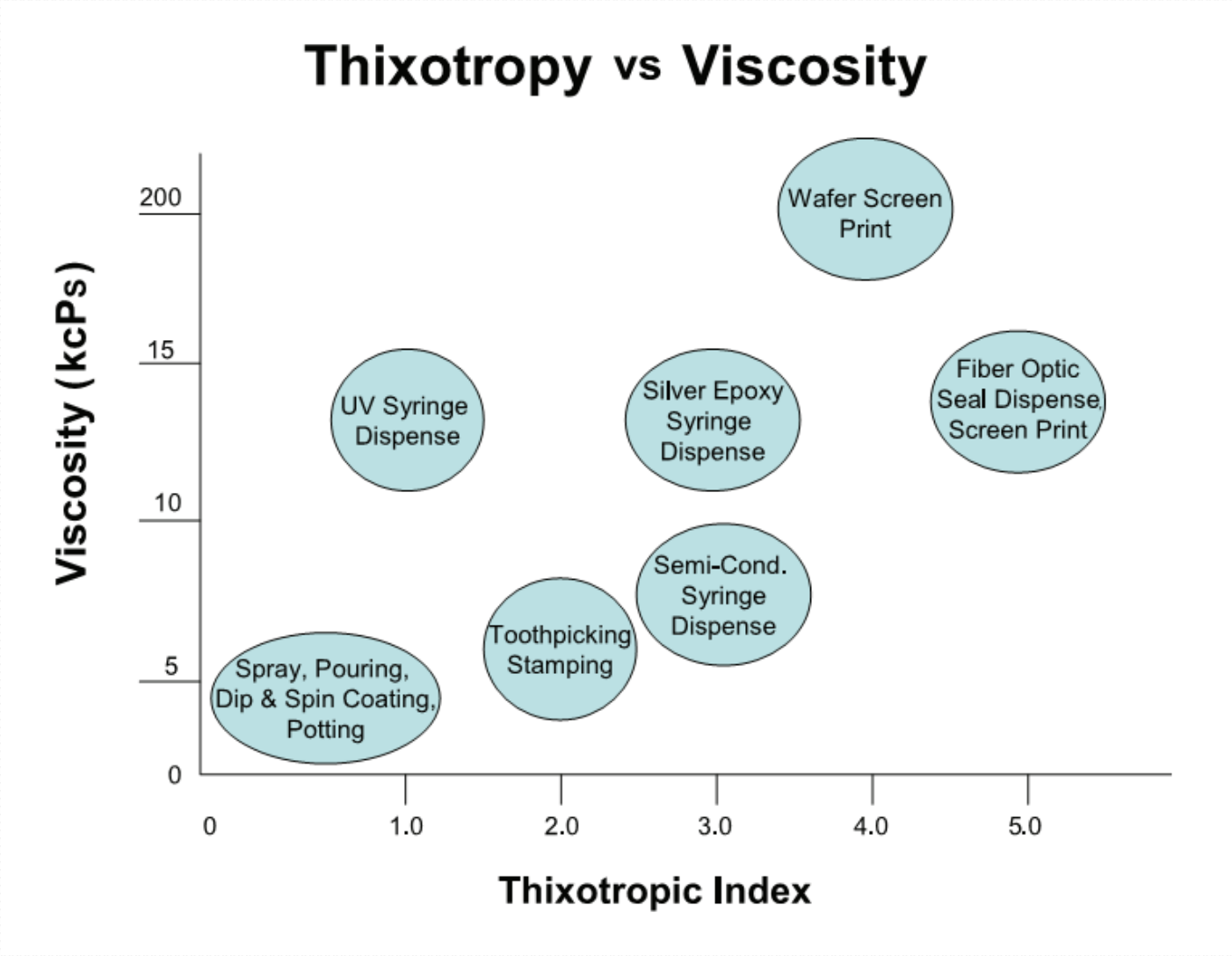


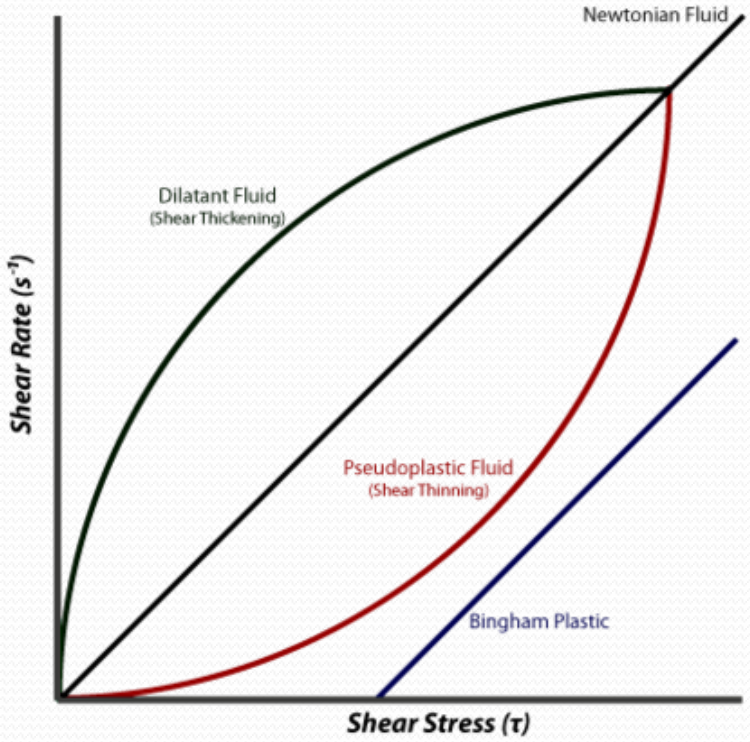
figure 12

When talking thixotropy, often we refer to Thixotropic Index (TI). This is a value reported by taking the ratio of two separate readings at different speeds on a viscometer. For example, if a material produces a reading of 15,000 cPs at 1 RPM and 10,000 cPs at 10 RPM, the thixotropic index is equal to 15,000/10,000 or 1.5. Usually, TI is calculated from viscosities measured at RPMs that are a decade apart (i.e between 1 and 10 RPMs or between 10 and 100 RPMs). This number is also key in choosing the proper type of material for a particular dispensing technique.

צמיגות וראולוגיה



צמיגות וראולוגיה



דוגמה לנוזל טיקסוטרופי

צמיגות וראולוגיה

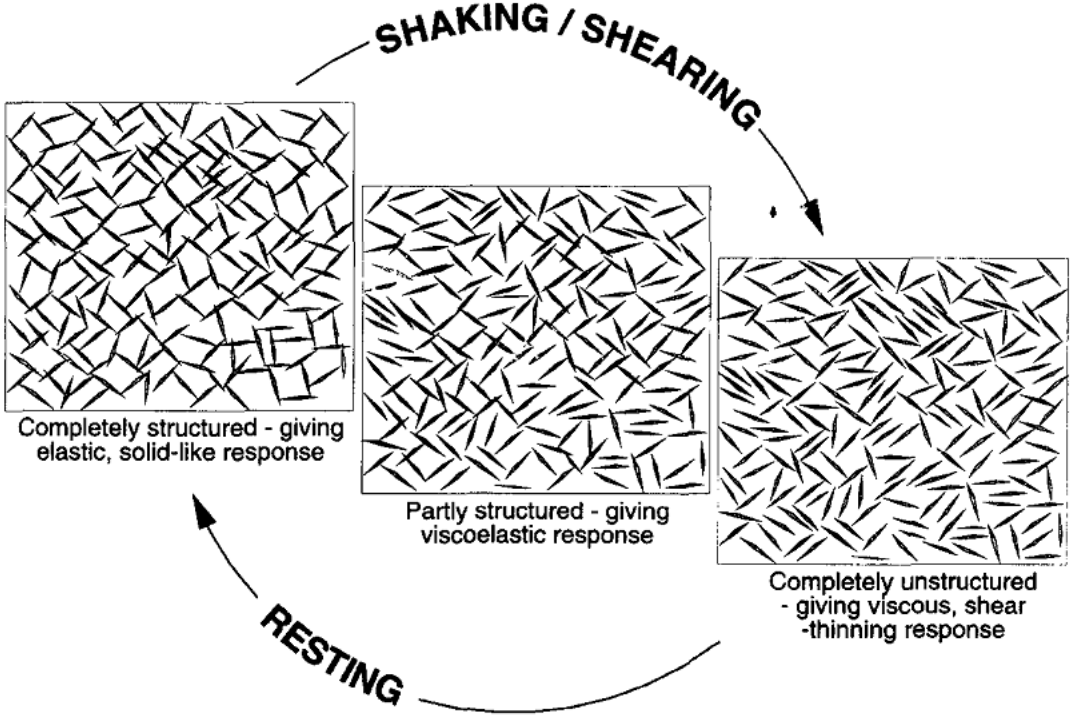
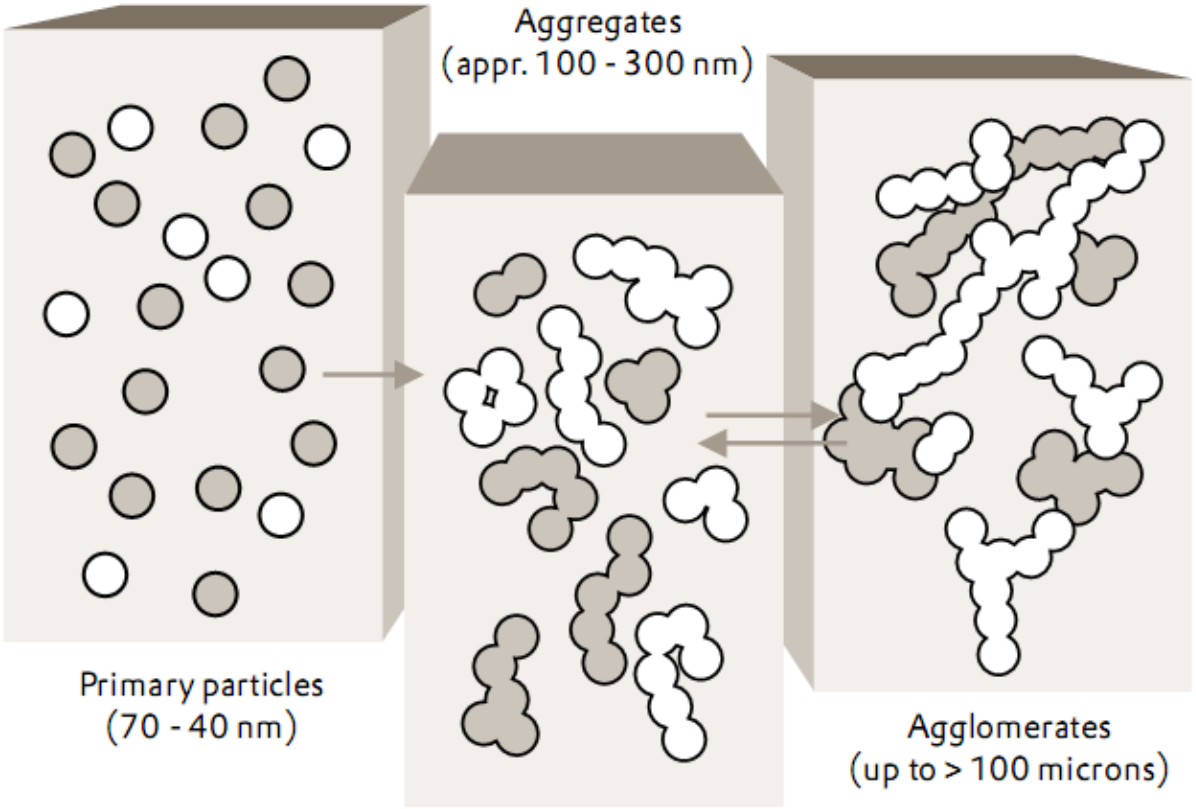


Fig. 1. Breakdown of a 3D thixotropic structure.

צמיגות וראולוגיה - סיליקה פירוגנית

Figure 2 Schematic representation of AEROSIL® fumed silica primary particles, aggregates, and agglomerates.



צמיגות וראולוגיה – מנגנון הפעולה של סיליקה פירוגנית

Figure 6 In liquids, AEROSIL® forms a three-dimensional gel structure by means of hydrogen bonds between the AEROSIL® particles. The gel structure is easily broken down again by shear forces.