

# DMTA: Dynamic Mechanical Thermal Analysis

by

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In the 50's, the term "thermal analysis" meant simply heating a sample in a capillary melting point tube to measure the melting point, or incinerating it to measure its ash content. And that was about all there was to thermal analysis.

Now the term is applied to a host of tests, including DSC (differential scanning calorimetry), TGA (Thermogravimetric analysis), and DMA (dynamic mechanical analysis).

DMA is a shortened form of Dynamic Mechanical Thermal Analysis (DMTA), which is another name for **Dynamic Mechanical Rheological Testing** (DMRT).

DMRT is the preferred name because this mode of thermal analysis is rooted in the science of rheology.

In the following sections, some of the features and benefits of DMRT are presented, relevant elements of rheology are defined, DMRT methods are explained, and some applications of DMRT to polymer studies are given.

## **Features and Benefits of DMRT**

Dynamic mechanical rheological testing (DMRT) is probably the most versatile thermal analysis method available, and no other single test method provides more information about a sample in a single test. Besides providing important material property data, DMRT provides a direct link between a material's chemical makeup and its mechanical behavior.

Materials can be characterized by DMRT regardless of their kind, their physical state, or the form in which they are used.

The material may be;

- A thermoplastic, a thermoset, or an elastomeric polymer.
- A polymer blend or "alloy";
- A liquid, a melt, or a solid;
- A soft solid such as cheese or toothpaste;
- A foam, wet or dry, soft or rigid;
- A dispersion, emulsion, or solution;
- "Neat" or with extenders, fillers, pigments, plasticizers, or fibers.

Usually, testing is nondestructive and only small samples are needed, an advantage for testing experimental materials.

And DMRT can extend beyond the present. Important as it is to know how a material behaves now, it is often more important to know how the material will behave weeks, years, even decades later. DMRT provides this ability. Using the Boltzmann superposition principle, time-temperature superposition, time-strain superposition, or time-concentration superposition and specialized computer software, rheological data generated in minutes or hours can be used to predict long-term material performance.

What DMRT is all about is described below, after a brief discussion of some relevant elements of rheology.

### What Is Rheology?

**Rheology.** Rheology is the science that studies the deformation and flow of materials in liquid, melt, or solid form in terms of the material's elasticity and viscosity. This is accomplished by applying a precisely measured strain to the sample to deform it, and accurately measuring the resulting stress developed in the sample. The developed stresses are related to material properties through Hooke's and Newton's laws.

**Elasticity.** Elasticity is the ability of a material to store deformational energy, and can be viewed simply as the capacity of a material to regain its original shape after being deformed.

**Viscosity.** Viscosity is a measure of a material's resistance to flow.

**Viscoelasticity.** Materials respond to an applied displacement or force by exhibiting either elastic or viscous behavior, or a combination of these, called viscoelastic behavior. Most polymers are viscoelastic, their mechanical properties showing a marked time- and temperature- dependence.

**Stress.** Stress is a distribution of forces over an infinitesimal area.

**Strain.** Strain is a measure of a body's change in shape. The change in strain with time is the shear rate. The change in strain with time is the shear rate.

**Hooke's law.** Hooke's law defines the mechanical behavior of an ideal solid, relating the applied strain ( $\epsilon$  or  $\gamma$ ) to the resultant stress ( $\sigma$  or  $\tau$ ) through a factor called the modulus ( $E$  or  $G$ ). Thus,  $\sigma = E\epsilon$  (tension, bending) or  $\tau = G\gamma$  (shear). The modulus is a measure of the material's stiffness (i.e., its ability to resist deformation). The linear region in which the modulus does not change when the strain is changed is called the Hookean region.

**Newton's Law.** Newton developed a relationship similar to Hooke's law for ideal viscous fluids, relating the stress ( $\tau$ ) linearly to the shear rate ( $dy/dt$ ). Thus,  $\tau = \eta dy/dt$ , where  $\eta$  is the coefficient of viscosity. A fluid is Newtonian if, when sheared, its viscosity does not depend on shear rate.

**Theory of Linear viscoelasticity.** The foregoing relationships are tied together by an elegant, overall theory of viscoelasticity<sup>1</sup>. So long as the measurements of stress and strain are made in the linear viscoelastic region, any of various viscoelastic functions can be calculated from another, and the various superposition methods can be employed.

**Newtonian Versus Non-Newtonian Flow.** Water and mineral oil are Newtonian, but not many other materials behave this way. Most fluids are non-Newtonian, their viscosity changing with changes in shear rate. This means the expression  $\tau = \eta dy/dt$  is only valid at a particular shear rate. Changing the shear rate changes the viscosity. Six types of non-Newtonian behavior are known, differing by how the viscosity changes with shear rate, and whether or not the flow pattern is time-dependent. The time-independent types are called Bingham, plastic, pseudoplastic, and dilatant; the time-dependent types are called thixotropic and rheopectic.

For Bingham fluids, a critical yield stress ( $\tau_c$ ) must be exceeded before flow begins. Until then, the material behaves as a Hookean solid; beyond  $\tau_c$ , it behaves as a Newtonian fluid. No-Drip paints and ketchup are Bingham fluids.

In contrast with Bingham fluids, most fluids show a curvature in their stress versus strain rate curves after exceeding the critical stress, and the apparent viscosity decreases, until a limiting value of ( $\tau$ ) is reached. Beyond this point, the shear rates varies linearly with stress and the viscosity becomes constant. This is known as plastic flow, exhibited, for example, by toothpaste, lipstick, and oil drilling muds.

For many materials, flow begins as soon as strain is applied. This is called pseudoplastic flow. Also, because the fluid's viscosity decreases with increasing shear rate, the phenomenon is described as being shear thinning.

Molten polymers, polymer solutions, bread dough, and a variety of suspensions, emulsions and other structured fluids used as pharmaceuticals and cosmetics exhibit pseudoplastic flow.

Moist sand, PVC plastisols, aqueous suspensions of penicillin powder, and other densely packed dispersions increase in viscosity when they are sheared at an increasing rate. After the altered structure stabilizes, the viscosity becomes constant. This shear behavior is called dilatancy. Since the viscosities of plastic, pseudoplastic, and dilatant fluids vary with shear rate, any measurement of their viscosity made at a single shear rate has little meaning. To compare meaningfully the flow properties of one non-Newtonian fluid with another, the viscosity of each must be measured over a range of shear rates - and the range must be the same for both. The sample temperatures must also be the same and be controlled during the test.

For the described non-Newtonian fluids, the shear stress, shear rate relation is time-independent. But dispersions stabilized by an internal network structure undergo a changing stress with time due to structure breakdown under an applied strain. If the shearing action is stopped and the dispersion is not disturbed, the structure redevelops. Such behavior is called thixotropy, a commercially significant property of materials such as paints, mayonnaise, and cough syrups.

Whereas a thixotropic fluid's viscosity decreases with time under a constant shear rate, rheopectic fluid's viscosity increases under these conditions.

The various types of non-Newtonian flow are illustrated in Figures 1 and 2.

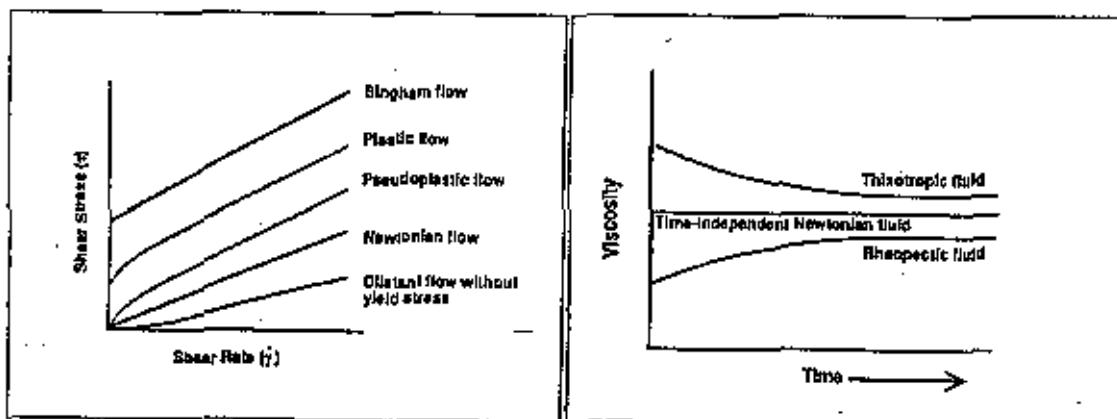


Fig. 1 Types of non-Newtonian flow

Fig. 2 Thixotropy versus Rheopecty

## What DMRT is ALL About?

**DMRT** is a laboratory test method in which rheological data for a material are generated using a rheometer (e.g., Rheometrics Mechanical Spectrometer RMS-800, Fluids Spectrometer RFS II, or Solids Analyzer RSA II) and sophisticated software. The material is characterized in terms of its modulus, elasticity, viscosity, damping behavior, and glass transition temperature, and the changes of these with strain, strain rate, temperature, and oscillatory frequency.

**How DMRT works.** In a dynamic mechanical rheological test, an oscillating strain (sinusoidal or other waveform) is applied to a sample and the resulting stress developed in the sample is measured. The output signals are analyzed, and, using established mathematical methods, the rheological parameters are computed.

**Ideal Solids.** For solids that behave ideally and follow Hooke's law, the stress is proportional to the strain amplitude, and the stress and strain signals are in phase.

**Ideal Fluids.** For fluids that behave ideally, the stress is proportional to the strain rate (Newton's Law). Here, the stress signal is out of phase with the strain signal, leading the strain signal by  $90^\circ$ .

**Viscoelastic Materials.** The stress signal generated by a viscoelastic material can be separated into two components: an elastic stress in phase with the strain, and a viscous stress in phase with the strain rate ( $90^\circ$  out of phase with the strain). The elastic stress measures the degree to which the material behaves as an ideal solid; the viscous stress, the degree to which the material behaves as an ideal fluid. This separation of the stress components vectorially allows the material's dependence on strain amplitude and strain rate to be measured simultaneously.

**Modulus.** The elastic and viscous stresses are related to material properties through the ratio of stress to strain, the modulus. The ratio of the elastic stress to strain is the elastic (or storage) modulus  $G'$ ; the ratio of the viscous stress to strain is the viscous (or loss) Modulus  $G''$ . When testing is done in tension or flexure rather than in shear,  $E'$  and  $E''$  designate the elastic and viscous moduli.

**Complex Modulus.** The complex modulus  $G^* = G' + G''$  reflects the contribution of both elastic and viscous components to the material's stiffness.

**Complex Viscosity.** The complex viscosity  $\eta^*$  is a measure of the material's

overall resistance to flow as a function of shear rate.

Damping Factor. The ratio of the viscous modulus to the elastic modulus is the tangent of the phase angle shift  $\delta$  between the stress and strain vectors. Thus,  $G''/G' = \tan \delta$ . This measures the damping ability of the material.

The Glass Transition. During measurement of the moduli ( $G'$ ,  $G''$ ) and damping behavior ( $\tan \delta$ ) of a polymer at a chosen oscillatory frequency over a sufficiently wide range of temperature, the effect of the polymer's glass transition can be clearly observed. The glass transition (sometimes called the  $\alpha$  transition) is a reversible change of the polymer between rubbery and glassy states, and the temperature at which this occurs, called the glass transition temperature  $T_g$ , can be measured accurately by DMRT. In fact, DMRT is considered the most sensitive method for measuring a material's glass transition temperature.

The glass transition is detected as a sudden and considerable (several decades) change in the elastic modulus and an attendant peak in the  $\tan \delta$  curve. This underscores the importance of the glass transition as a material property, for it shows clearly the substantial change in rigidity that the material experiences in a short span of temperatures. Accordingly, the glass transition temperature is a key factor in deciding the usefulness of a polymer.

But merely knowing the temperature at which the glass transition occurs (all that DSC and TGA provide) is not enough. Besides being a more accurate measure of  $T_g$ , DMRT tells much more about the material before and after the glass transition. DMRT also measures the rubbery plateau modulus which is much more sensitive than is  $T_g$  for detecting, for example, small differences in a thermoset polymer cure level.

Figure 3 shows that DMRT provides not only the  $T_g$  for an injection molded acrylonitrile-butadiene-styrene (ABS) plastic part and the change in modulus due to the glass transition, but also it sensitively detects residual strains in the unannealed part. The effects of the residual strains are seen in a higher  $\tan \delta$  over a range of temperatures and a shift in the secondary  $\beta$  transition.

Normal Stresses. When elastic materials are sheared, besides the shear stress that develops in a direction parallel to the shear force, other stresses develop in a direction perpendicular or "normal" to the shear direction. These are called normal stresses, and are involved in phenomena such as die swell and melt fracture.

Only differences between normal stresses are rheologically significant. The first normal stress difference  $\tau_{11} - \tau_{22}$  (called  $N_1$ ) can be calculated from measurements using cone and plate geometry. The second normal stress difference  $\tau_{22} - \tau_{33}$  ( $N_2$ ) is obtained from measurements using other geometries. Stress Relaxation and Creep. The foregoing discussion has been confined to dynamic rheological testing in which oscillatory strains are applied. Rheometrics rheometers can also apply a steady (non-oscillatory) strain to the sample. The stress required to maintain that strain over time is measured, and from these data a stress relaxation modulus  $G(t)$  or  $E(t)$  is calculated. Stress relaxation is the most fundamental manifestation of the viscoelasticity of polymers.

Creep tests are ran just the opposite of stress relaxation tests. Creep is measured by imposing a constant stress in torsion, compression, or tension on a sample and recording the deformational response (strain) over time. Both stress relaxation and creep can be measured routinely with Rheometrics rheometers.

Figure 4 shows a typical creep curve. If the stress and strain are in the linear viscoelastic region,  $J_e^0$  and  $\eta_0$  can be calculated from the data.  $J_e^0$  is the equilibrium creep compliance and  $\eta_0$  is the zero shear viscosity. The equilibrium creep compliance, a measure of stored energy, is important in extrusion, and is sensitive to molecular weight distribution.

The zero shear viscosity  $\eta_0$  is a sensitive measure of molecular weight. For low weight average molecular weights (no entanglements),  $\eta_0$  is proportional to  $M_w$  for high  $M_w$ ,  $\eta_0$  is proportional to  $M_w^{3.4}$ .

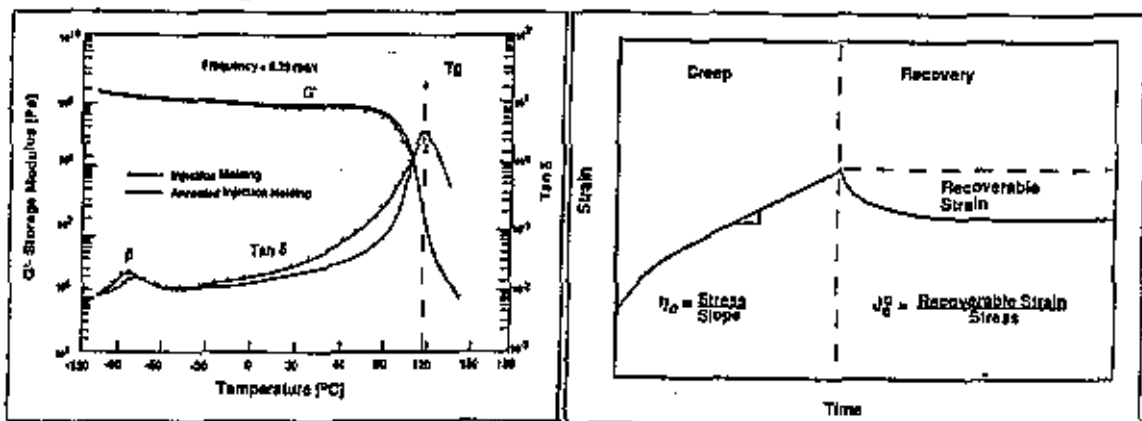


Fig. 3 Effects of residual strains

Fig. 4 Creep and creep recovery

This is shown in Figure 5.

To further illustrate the utility of DMRT, Figure 6 shows a frequency sweep of a typical polymer. Besides these data, information about  $M_w$  can be obtained from  $\eta^*$ , and the following calculations can be made:  $\eta_0$  from  $G''$ ;  $J_e^0$  from  $G'$ ; and  $\lambda_r$  (used to estimate die swell) from  $\eta_0 \times J_e^0$ .

Time-Temperature Superposition. Often, it is desirable to base the behavior of a material beyond the operational ranges of a given instrument, or at time intervals, short or long, that are difficult or inconvenient to measure. DMRT provides a solution to this dilemma. For example, data taken in the frequency domain over a range of temperatures can be connected automatically to a master curve in the time domain. This is possible because time and temperature effects are equivalent; also the aggregate effect of applying a series of stresses is the SUM of the effects of applying each stress separately (Boltzmann's principle). This provides a convenient way to predict, for example, long-term aging and dimensional creep of materials from short-term measurements.

### Applications of DMRT

DMRT can characterize the structure and flow properties of soft solids and structured fluids (emulsions, suspensions, and gels).<sup>2,3</sup> Tests can be ran at low deformations to measure the "at rest" structure, or at high deformations to simulate use (e.g., applying a coating, or silk-screening ink).<sup>4,5</sup>

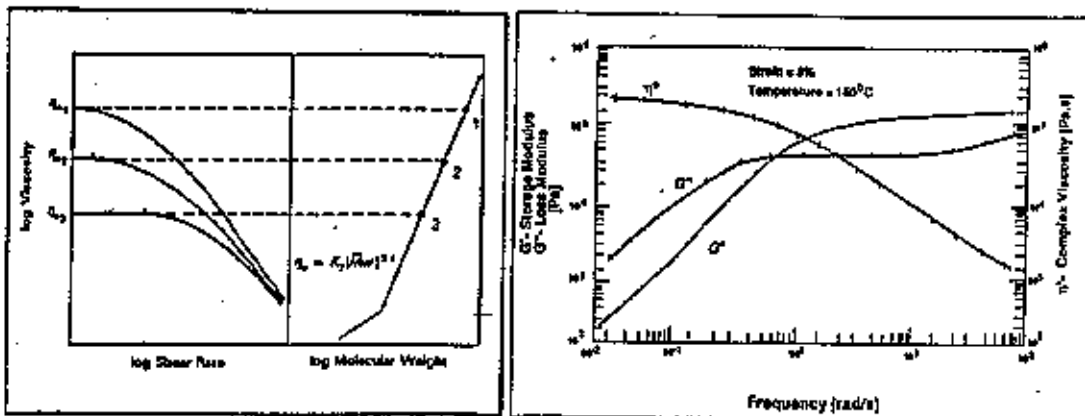


Fig. 5 Viscosity and molecular weight

Fig. 6 Frequency sweep



The behavior of thermoplastics during melt processing operations is governed mainly by the polymer molecular weight, molecular weight distribution, degree of branching, and filler content. DMRT data from molten samples can be used to relate the effects of these parameters to processability (e.g., die swell and extrusion ease), and data from solid plastics can be used to relate polymer morphology and structure to end-use performance. For example, measurements of a materials glass transition temperature and damping behavior can be used to predict use temperatures, impact properties and stiffness.<sup>6,7,8</sup> Also, DMRT data can be used to calculate the molecular weight distribution of polymers,<sup>9</sup> and, using Rheometrics software, this can be accomplished with a push of a button.

For thermosetting polymers, DMRT can measure the rheological changes occurring during the curing reaction as the resin transforms from a low melting solid to a low viscosity liquid, then through the gel point without disrupting the gel structure, and finally to a highly crosslinked, stiff solid.<sup>10,11</sup> In fact, the entire curing process can be simulated by the rheometer to provide production guidelines.<sup>12</sup>

For elastomers, DMRT has been used to study the effects of mastication during the processing of various grades of natural rubber;<sup>13</sup> to detect the effects of long-chain branching on processability of oil-extended rubber using time-concentration superposition, and to detect subtle differences in processing by making low frequency, low shear rate measurements rather than high frequency, high shear rate measurements;<sup>14</sup> to characterize cure behavior;<sup>15</sup> to linearize nonlinear data at large deformations using time-strain superposition;<sup>16,17</sup> to optimize tack and peel strength of pressure sensitive adhesives;<sup>18</sup> to predict the friction coefficient of tire rubber, and explain the mechanism of hysteresis friction;<sup>19</sup> to relate tire rubber compound DMRT data to tire performance (rolling resistance, traction, wear, handling, cornering);<sup>20</sup> to improve the solvent resistance of neoprene-epichlorohydrin;<sup>21</sup> to characterize elastomeric dental impression materials;<sup>22</sup> and to design and test elastomeric seals,<sup>23,24</sup> to cite just a few examples.

### **The latest Innovations in DMRT**

Simultaneous Multiple Frequency sweeps. Called MultiWave, this new test mode from Rheometrics provides the ability to test a sample at several oscillatory frequencies simultaneously, rather than sequentially at discrete frequencies.

MultiWave is advantageous for quickly testing materials that change (e.g., polymerize, or degrade thermally or oxidatively) as the test progresses. In fact, using MultiWave, the exact moment of thermoset gelation can be identified by measuring  $\tan \delta$  at several frequencies simultaneously.<sup>25</sup> Arbitrary Waveform Mode. Besides the standard sine wave oscillatory deformation normally used in dynamic tests, Rheometrics rheometers can impart deformations in virtually any user - selected waveform definable by a mathematical equation by means of an Arbitrary waveform Mode. This mode also speeds testing and, besides being useful for testing materials that may change rapidly with time, the Arbitrary Waveform mode can be used for modeling shear behavior in processes, and for increasing transient test sensitivity.

### **Required Instrumentation**

Hardware. Not all rheometers can make the foregoing measurements and some do not provide the precision and accuracy that workers at the leading edge of materials technology have become accustomed to. Suitable rheometers will:

- o Accommodate samples as liquids, melts, solids.
- o Apply both oscillatory and steady strains with direct drive actuators for maximum accuracy.
- o Apply strains at multiple frequencies simultaneously.
- o Apply strains sinusoidally and in any mathematically defined waveform
- o Resolve small strains precisely (0.0005 to 0.5 mrad for rotational rheometers,  $\pm 0.001\text{mm}$  for linear displacement rheometers).
- o Employ a low-compliance, non-hysteretic transducer to assure that only sample motion is being detected, and measure this motion with maximum accuracy.
- o Measure torques over at least a 1000-fold range to test a sample over a wide shear rate and temperature range without changing transducers.
- o Measure viscosity over a wide range ( $10^{-2}$  to  $10^6$  poises).
- o Measure normal forces.
- o Measure stress relaxation and creep.
- o Automatically control tension to compensate for material expansion and contraction during tests - and measure the coefficients of expansion and contraction.
- o Automatically control strain to increase the measurement range as a sample softens or hardens.

- o Compensate for fixture inertia in tests of fluids.
- o provide a sufficiently wide and stable sample temperature range (e.g., -150° to 600°C, with  $\pm 0.5^\circ\text{C}$  stability).
- o provide an inert gas atmosphere for sensitive materials.
- o have computer - controlled operation using advanced software.

**Computer Software.** The software for Rheometrics rheometers manages data collection, storage, transfer, and analysis.

Analytical and manipulative capabilities include;

- o Statistical analyses;
- o Cubic spline interpolation;
- o Curve approximations: polynomial, exponential, and Fourier series;
- o Model equations: power law, Bingham plastic, exponential, Ellis, Arrhenius, Herschel Buckley, Casson, user-defined;
- o Relaxation and retardation spectra; molecular weight distributions;
- o Multiple curve editing for automatic or manual time-temperature superposition to produce master curves;
- o Automatic test sequencing for round-the-clock, unattended testing.

Figure 7 shows the molecular weight distribution of a polystyrene sample calculated automatically from DMRT data using Rheometrics software. Figure 8 shows a master curve for a sample of PVC generated using time-temperature superposition. From tests made over only two and one-half decades of frequency at six temperatures, the behavior of PVC over seven decades of frequency was calculated automatically with Rheometrics software.

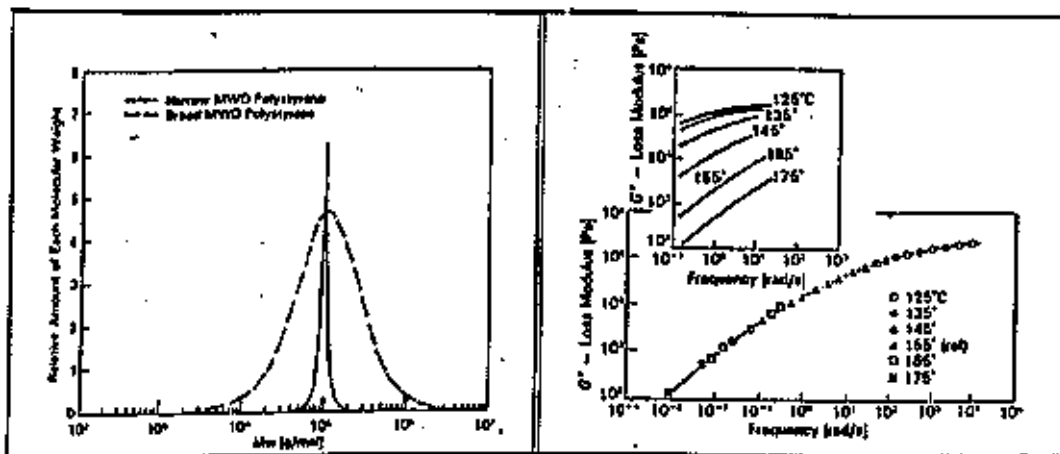


Fig. 7 Automatic calculation of MWD

Fig. 8 Automatic T-T Superposition

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