A Review on Dynamic Rheology for Polymers

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Abstract
An overview of Dynamic Mechanical Analysis (DMA) is provided with emphasis on fixtures and analyzers used in this technique. DMA can be employed to study thermal transitions of viscoelastic materials and the molecular motions associated with the transitions. The experimental setup for three point and four point bend test has been discussed. The DMA plots depict the two attributes i.e. storage modulus and tan delta, as a function of temperature and frequency. The variation of these two attributes can also be seen in glassy or rubbery region. As the heating continues, the glass transition (Tg) appears which indicates that the amorphous regions have begin to melt accompanied by the large scale motions in the chains of the amorphous regions. Tg is a temperature range where a material softens. All the transitions in material characterization by DMA are focused as these transitions are associated with the mechanical properties of the material under study.

Keywords: DMA; Glass transition; Storage modulus; Tan delta.

Introduction
It is well known that viscoelastic materials when subjected to dynamic loads manifest a phase lag in the deformation caused by the load. Dynamic mechanical analysis abbreviated as DMA is a technique used to study and characterize materials. It is used to calculate the tendency to flow (viscosity) and the stiffness (modulus). DMA does not require a lot of specialized training to use for material characterization [1]. It provides information about major transitions such as secondary and tertiary transitions. It allows characterization of those properties that directly affects the material performance [2]. DMA is also known as dynamic mechanical thermal analysis (DMTA) or dynamic rheology. It is used to study viscoelastic behavior of polymers. Certain materials, such as polymers exhibit viscoelastic behavior i.e. they show both viscous and elastic properties. However, the initial modulus and the change in modulus with applied stress/strain are directly related to material micro-structure [3]. The effect of both particle size and volume fraction on storage modulus, damping behavior and glass transition temperature is generally a primary consideration in testing of materials [4]. This visco-elastic behavior causes the shifting of corresponding stress and strain curves. Material characterization by DMA is done by applying a sinusoidal deformation to a sample of known geometry. The sample is subjected to controlled stress as input and deforms a certain amount, this results in sinusoidal deformation (strain) which is taken as output. This viscoelastic behavior causes the shifting of corresponding stress and strain curves [5]. Viscoelastic properties are shown by phase lag which occur during DMA tests.

Stress (σ) = σ' + sin(ωt + δ)
Strain (ε) = ε' + sin(ωt)
Where ω is the frequency of oscillation, t is time period,
And δ is phase lag between stress and strain.
Phase angle (∆) = tan (E'/E'')
The deviation is the phase shift, delta. The response signal (strain) is split into in phase response, which is the storage modulus (E') and an out of phase response, which is loss modulus (E'').

Storage modulus, (E') = (σ'/ε') cos δ
Loss modulus, (E'') = (σ'/ε') sin δ
And for purely elastic material,
Young modulus, (E) = (σ/ε)
For purely viscous material, phase angle is 90° and for purely elastic material, phase angle is 0°. DMA is applied to find the viscoelastic properties of viscous materials, in which phase angle lies between 0° to 90°. Loss factor, tan delta is the ratio of loss modulus to the storage modulus.

Instrumentation:
The instrumentation of a DMA consists of a displacement sensor such as a linear variable differential transformer (LVDT), which measures a change in voltage as a result of the instrument probe moving through a magnetic core, a temperature control system or furnace, a drive motor (a linear motor for probe loading which provides load for the applied force), a drive shaft support and guidance system to act as a guide for the force from the motor to the sample, and sample clamps in order to hold the sample being tested. Depending on what is being measured, samples will be prepared and handled differently [6]. A provision known as Temperature Modulated DMA (TMDMA) allows the investigation of reversible and non-reversible phenomenon in the crystallization and melting region of polymers [7].
Main types of dynamic mechanical analyzers currently used are:
1. Forced resonance analyzer
2. Stress and strain controlled analyzer
3. Torsional and axial analyzer
4. Free resonance analyzer

In forced resonance analyzers, the sample is forced to oscillate at a certain frequency and is reliable to scan a material performance across a temperature range [8]. These are the more common type of analyzers available in instrumentation today.

Analyzers are also used to control stress and strain. In stress control analyzer, a constant force is applied to the sample, by varying the time, temperature and frequency. A detector is used to control the constant applied force. In strain control analyzer, the deformation (strain) as a result of force is controlled by a force balance transducer [9].

In analyzers, force can be applied in twisting and axial motion. Force can be applied in twisting motion, to test the sample in torsion. In axial analyzer, force is applied axially along the axis of the sample.

Free resonance analyzers measure the free oscillations of damping of the sample being tested by suspending and swinging the sample. The samples are limited to rod or rectangular shaped samples [10].

The fixtures or the sample geometries have great influence on stress and strain values. Each of the geometries has a different set of equations for obtaining stress and strain values from force and deformation [11]. Fixtures help to increase the stress required for a set displacement and distortion is obtained. The four sides of the specimen to be tested should be true i.e.

opposite sides should be parallel and adjacent sides should be perpendicular:
1. Single/dual cantilever bending
2. Three point and four point bending
3. Tension
4. Compression/penetration
5. Shearing

In single/dual cantilever bending, the ends of specimen are clamped by the cantilever fixtures in place such that the clamps are perpendicular to the axis of specimen and a shearing component is introduced [12]. Dual cantilever and single cantilever are two types of fixtures. In dual cantilever, specimen is clamped by cantilever at both ends and in single cantilever; one end of specimen is clamped by cantilever [13].

In three-point fixture, specimen is placed as a freely moving beam and the specimen should be about 10% longer at each end of the edges. The specimen is loaded at three edges which are perpendicular to the axis of specimen. Figure 4 shows the specimen fixed at three edges. When the single edge at 1 is replaced by a pair of edges, it is known as four point bending. Four-point bending is equivalent to dual cantilever bending as the specimen is supported by two cantilever edges at edge 2 and 3 and a pair of edges at edge 1.
Figure 4: Three point bending

Figure 5: Four point bending

Table 1: Difference between three point and four point bend test

<table>
<thead>
<tr>
<th>Three point bend test</th>
<th>Four point bend test</th>
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<tbody>
<tr>
<td>In three-point fixture, peak stress is produced at specimen midpoint.</td>
<td>In four-point fixture, peak stresses are produced over an extended region.</td>
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<tr>
<td>Less volume under stress.</td>
<td>Large volume under stress, hence more potential for finding defects and flaws in material.</td>
</tr>
<tr>
<td>It is recommended for homogeneous materials like plastic.</td>
<td>It is suitable for non homogeneous material like composites, which are stiff and brittle so as to avoid premature failure.</td>
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</table>

The results measured by both the tests are however same but four-point bend test has more potential to detect internal flaws of material. Support spans used in these tests are different as these are used for different type of materials [14]. For testing of brittle materials, Four-point bend test is best suited [15]. The fixture for tensile test is usually applicable for films, fibers and thin rubber strips. The film or fiber specimen is loaded in extension, carefully keeping the specimen perpendicular to the bottom so that it may not twist [16]. Figure 6 shows the fixture for tension test with a specimen loaded in extension between top and bottom clamps.

Figure 6: Fixture for tension test

Compression test is applicable for soft materials like rubber. To compress the samples, generally circular plates are used but rectangular plates and samples can also be used. Plates required for compression test should be parallel and the samples should be same size as that of plate with no dips and bulges. Figure 7 shows the fixture for compression test.

Figure 7: Fixture for compression test

Fixture for shearing is applicable for adhesives and elastomers. Fixture for shearing test is shown in Figure 8.

Figure 8: Fixture for shearing test
Dynamic properties calculated by DMA:

DMA is not just limited to dynamic stress vs. dynamic strain but it is an analysis to measure properties like complex modulus, viscosity, compliance and damping characteristics. It is useful in characterizing the material structure and damping as a function of frequency, temperature, time, stress, atmosphere or a combination of these [17]. Applied sinusoidal stress, resulting strain and the phase lag between them are used to calculate all the dynamic properties [18]. The calculated dynamic properties are:

**Complex Modulus (E*)**

Modulus is defined as stress to strain ratio obtained under vibratory conditions (forced/free), when the sample is subjected to tension or compression. It is a property defined for viscoelastic materials. For a purely elastic material, no phase lag occurs between stress and strain and for a purely viscous material; there is 90° phase lag between stress and strain components. The behavior of the viscoelastic materials is identified by some phase lag between that of purely elastic and purely viscous.

For viscoelastic materials, the resulting strain splits into two components:

- **Storage Modulus (E')**: It is the in phase component of response signal (strain). Storage modulus refers to material stiffness or elasticity.

- **Loss Modulus (E'')**: It is the out of phase component of response signal (strain). It is the measure of oscillation energy transformed into heat. The complex modulus (E*) is the sum of in and out of phase components [19].

\[ E^* = E' + iE'' \]

**Damping (tan δ)**

Damping is defined as dissipation or loss of mechanical energy or internal friction and is denoted by tangent of phase angle (tan δ). As the material becomes elastic, phase angle becomes smaller. The amplitude of tan δ curve is directly related to materials ability to dissipate energy through segmental motion [20]. The Fiber matrix interface can be understood to a very good extent by damping curves [21]. Tangent of phase angle is the ratio of loss modulus to storage modulus.

\[ \tan \delta = E'' / E' \]

**Complex Shear Modulus (G*)**

Shear modulus is the stress to strain ratio obtained under vibratory conditions when the sample is subjected to shear. The in and out of phase components of complex shear modulus are:

- **Shear Storage Modulus (G')**
- **Shear Loss Modulus (G'')**

Complex shear modulus (G*) is the sum of these in and out of phase components.

\[ G^* = G' + iG'' \]

**Complex Viscosity (η*)**

Frequency scans are performed on DMA by keeping the temperature constant, to examine the viscous or unrecoverable regions of viscoelastic system which is also a major application of DMA. Frequencies vs. viscosity plots are obtained that are used to analyze the viscous portion of viscoelastic material in detail. Same as modulus, two components of complex viscosity are:

- In phase component (η') is energy loss portion of viscosity.
- Out of phase component (η'') is energy storage portion of viscosity.

The complex viscosity (η*) is the sum of these two components.

\[ \eta^* = \eta' - i\eta'' \]

**Relationship between E*, G* and η**

\[
G^* = E^* / 2(1 + \nu)
\]

\[
\eta^* = G^*/\omega
\]

Where \( \nu = \) Poisson’s ratio
And, \( \omega = \) Frequency

**Thermal Transitions:**

The two basic types of test modes performed in DMA are temperature and frequency sweep/scan. In temperature scan, frequency is held constant and temperature is varied to observe the behavior of polymer. Similarly in frequency scan, frequencies are varied isothermally. A polymer material, when subjected to temperature/frequency scan in DMA exhibit different behaviors at different temperatures or frequencies due to increase in molecular motions at higher temperature [22]. Mechanical properties are measure of what a polymer does when it is physically disturbed or tested. Initially when the temperature is low, polymer is characterized by solid state transitions. As the temperature is increased, the polymer material expands and it passes through gamma (T\( \gamma \)) and beta transitions (T\( \beta \)) where the free volume of material increases and localized molecular motions takes place. Toughening of polymer material is observed in beta transition. On further increase in temperature, the molecular chains start coordinating large scale motions accompanied with melting of amorphous phase. This stage is characterized by glass transition (T\( g \)). Further heating will cause melting and a melting temperature (T\( m \)) is reached [23, 24].

**Sub Glass Transition (T\( \gamma \) and T\( \beta \))**

These higher order transitions can be determined by DMA; however they are weak transitions but can be associated with the mechanical properties of the polymer. T\( \gamma \) and T\( \beta \) (solid state transition) are considered as sub glass transition. These
are considered as weak transitions as these are hard to observe because of small scale molecular motions in $T_r$. $T_g$ is accompanied with localized motions in main chain [25]. Region 5 and 6 in figure 9 shows the gamma and beta transitions respectively.

**Glass Transition ($T_g$)**

Glass transition is a major transition state in polymers in which material properties drastically changes from glassy to rubbery state [26]. This is the basic operating range of the polymer [27]. In temperature scans of DMA, $T_g$ can be seen as decrease in storage modulus accompanied by a peak in tan δ curve. $T_g$ is the temperature range where the material softens. Region 3 and 4 shows the glass transition state in figure 9.

**Rubbery Plateau ($T_o$)**

After $T_g$, the material starts to melt. The region after $T_g$ and before actual melting is known as rubbery plateau. A dramatic increase in modulus can be seen in the rubbery region. The change of state from glassy to rubbery is the main region for consideration to study the elastic properties of polymer material [28]. Rubbery plateau can be seen in region 2 in figure 9.

**Terminal Region ($T_m$)**

After rubbery plateau, a point is reached where the temperature leads to melting of amorphous phase, which is called terminal region. Here the material actually melts and flows away. Terminal region is shown by region 1 in Figure 9.

**Conclusion**

Currently in the field of materials, DMA is the most dominant tool to evaluate and characterize polymers. This review paper provides information about the fixtures and analyzers used in this technique and 3 point and 4 point bend tests are compared for better understanding. It allows detection of phase transitions to understand material behavior over a wide range of frequencies and temperature. This technique also determines the relevant damping factors and viscoelastic properties of neat and reinforced polymeric composites for various applications. DMA is a very useful tool to study mechanical behavior and for designing materials for specific applications.

**References**


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