Dynamic mechanical analysis in materials science: The Novice’s Tale

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ABSTRACT
There are a few useful textbooks and online materials available on dynamic mechanical analysis (DMA) but no short and succinct article that will be useful for a beginner. Here we are providing a brief introductory overview of DMA, followed by details of the different types of measurements possible with a typical DMA instrument. Some of the important measures needing to be taken in these analyses are also summarized, along with the possibilities of designing new experiments with the help of a DMA instrument. Oscillatory stress/strain-assisted studies of two different types of membranes—a polymer membrane and a membrane which consists of assembled ultra-thin oxidized graphene flakes—are discussed at the end. These studies show the vast possibilities of DMA in understanding the different aspects of solids, such as their phase transitions, microstructure, damping, complex interactions in the composite matrix, and also about the mechanical modulus of the solid membrane. Hence this article discusses the new avenues for DMA in different fields and takes the reader from the fundamentals to its advanced applicability.

Key Words: dynamic mechanical analysis; graphene oxide; micro-structure; polymers; solid electrolyte, complex modulus.

INTRODUCTION
Dynamic mechanical analysis (DMA) has become an important materials characterization tool which can unveil the complex elastic modulus of solids and thus becomes an inseparable component of any materials science laboratory to correlate the structure and property of solids [1, 2]. Elastic modulus or modulus of elasticity is a measure of material’s resistance or response towards external stress, where stress is defined as the applied force per unit cross-sectional area. Elastic modulus is defined as the slope of the stress–strain curve in the linear response region (elastic) of the plot. There are different modulus based on the type of deformation, such as Tensile modulus (uniaxial deformation normal to the cross-sectional surface of the material, where the strain is measured as the change in length due to the deformation per unit length of the material), Compressive modulus (measure of the contraction of the material upon a compressive force normal to the cross-sectional surface), Shear modulus (the modulus calculated with a force vector parallel to material’s cross section), etc. Understanding the response of solids to dynamic stimulus is important in different fields such as paint industry, adhesive development, plastic hip joints and dental fillings, contact lenses, heart valves, mechanical dampers, airbags, etc., to name a few, where the frequency-dependent modulus variations is an important measure. The importance of frequency-dependent modulus calculations in some of these fields will be clear from the later discussions.

Static force-assisted mechanical studies cannot unravel the complex modulus of a material, though those can give insight about the yielding strain (stress) and linear stress–strain
response of the material. The complex modulus of a material contains both storage (recoverable energy, elastic) and loss (thermally dissipated, viscous) parts and hence it is a complex quantity [1]. Evaluation of complex modulus is important to unravel the viscoelastic properties of a solid, where no material is ideally elastic (ideal solid) or viscous (ideal liquid) in nature. As the applied frequency becomes higher, the material becomes more like a solid (higher storage modulus) and at lower frequencies liquid-like (lower storage modulus) behaviour will dominate. Hence the modulus response to the variations in frequencies is an important measure to find the applications of solids in different fields. But, the temperature dependency of modulus in contrast, at higher temperatures behaves like a liquid. Further, it can also give information about the major and minor (secondary and tertiary) phase transitions in materials such as polymers. Such transitions are occurring due to their inter-molecular rearrangements as a response to the applied frequency or temperature. Those minor transitions are quite difficult to probe with other methods such as differential scanning calorimetry (DSC) [3]. Though DMA and DSC reveal quite similar information, both vary significantly depending on the analysis, sample preparation, sensitivity, and applied stimulus. It is known that mechanical changes are more pronounced than changes in the heat capacity. DMA can detect the short-range motion more efficiently and the onset of chain motion implies temperature transition. Studies on those phase transitions are discussed in the later part of this article. But such phase transitions of materials with frequency are important to be studied in fields they are being used. For example, airbag works at extremely high frequencies (~10,000 Hz) and the material made of such airbags should have a glass transition frequency higher than this operational range. In such cases, studies such as dielectric relaxation spectroscopy (DRS) will be highly useful. In case of paints, the coating should be able to withstand the same level of deformation its substrate is undergoing without peeling off or crack. Hence viscoelastic studies on paints are also essential to obtain the optimum paint formulations.

DMA can also be used to study composites and mixtures, and the complex interactions among their constituents. Though most of the materials respond elastically or inelastically to the applied stress, repeated loading can lead to the mechanical fatigue. For example, biological systems such as bones and tissues get stiffen with recurring elastic stress [4]. Though most of the synthetic materials do not have this property, certain composites matrices such as poly(dimethylsiloxane) impregnated to vertically aligned carbon nanotubes show such self-strengthening under cyclic loading [4]. This has been proven as a result of complex interactions between matrix materials and nanostructures. Such active materials can lead to the development of adaptable structural materials and artificial biological tissues and bones, and DMA is an efficient method to unravel stress or strain hardening or softening due to cyclic loading [4, 5]. Hence DMA is highly resourceful in different fields where materials properties are assessed in terms of operational temperature, load, frequency, other external parameters, and intermaterial interactions.

This article discusses some of the essential knowledge one has to start dealing with DMA and introducing different modes of operation and methods available in a DMA instrument. The methods and principles discussed here are common to any DMA instrument make, though some of the photographs shown in the later sessions are taken from that of TA Q800. Last part of the article includes some of the interesting experiments designed with this analyser (DMA, the instrument is also named as DMA from hereafter). DMA-assisted analyses on two different materials are shown here: a polymer membrane [polyethylene oxide (PEO)] which is highly explored as a solid electrolyte for lithium (Li⁺) transportation and a graphene oxide (GO) membrane, a highly researched macroscopic structure of oxidized graphene sheets. Evaluation of the melting temperature (Tm) of the semi-crystalline PEO membrane is very much essential to find its use as a solid electrolyte and the details of such studies using DMA are discussed here. GO membranes have high potential in various fields, from solid electrolytes to water desalination [6, 7], and the intercalated small molecules decide the mechanical robustness of the film [8]. This article discusses how DMA is used in understanding the role of intercalated molecules in mesoscopic membranes such as GO, and explores the possibilities in designing some novel experiments with different modes of a DMA to understand the microscopic structure of GO membranes. The advancements in the design and sensitivity of the DMA over the last several years are also helpful to explore its potential in unexplored territories of material’s characterization, and some of such milestones in DMA are briefed in the below section.

Rheology is the study of deformation and flow of materials, and its scientific history starts from Poynting’s first attempt to measure the elasticity of a material using oscillatory experiments, dated back in 1909 [9]. Such interests gradually translated in making commercial instruments to measure the ‘normal force’ and the Weissenberg rheogoniometer was such initial attempt in this venture [10]. Moreover, such developments in the instrumentation of mechanical properties using oscillatory forces had helped to develop theories on polymer viscoelasticity. Among sporadic efforts in the instrumentation, the modern age of DMA has been started in the year of 1966 when J. Gilhams first developed the Torsional Braid Analyzer [11]. It was DuPont and Perkin-Elmer credited for the development of a controlled stress analysers in the early 1980s [1]. Current DMA technology has been evolved to measure the strain of as small as 1 nm with a load (force) range of 0.0001N–18 N in a wide temperature range (say –150°C–600°C), in different humid conditions, and can mimic the mechanical relaxations of solids in different environments [12]. Hence the present DMA based experiments can simulate the real-time performance of materials [13]. For example, an advanced tool in DMA has the ability to conduct dynamic mechanical studies in liquid environment. They can be used to study or simulate the performance of biological membranes in actual physiological conditions. Here the use of such methods in identifying the microscopic structure GO membrane is discussed towards the end.

**EXPERIMENTAL**

Basic working principles

The viscoelastic behaviour of a material needs to be evaluated as a function of time, temperature, and frequency [14]. In a DMA, typically a sinusoidal oscillatory force is applied to the material and the resulting deformation or strain is measured in response to the applied stress in the linear viscoelastic region of the material. Hence it is important to note that the linear response of the material has to be evaluated before advancing to the dynamic force (strain) based experiments. Further, the amplitude of the dynamic perturbation should be so small that it should not go beyond the linear Hookean region of the material. Hooke’s law states that strain in a material is proportional to
the applied stress within the elastic limit of the material. This has been schematized in Fig. 1A. This is analogous to other types of dynamic measurements such as DRS or linear electrochemical impedance spectroscopy (EIS), where the applied alternating voltage should lie within the linear current-voltage characteristics of the material [15]. DRS studies are important in characterizing the materials phase transitions in large frequency windows where DMA has limitations, as stated before. EIS is a potential tool in electrochemistry to quantify different parameters namely ionic conductivity, corrosion, catalytic charge transfer efficacy, etc.

The response of the material to the dynamic stimulus will not be in-phase with the stimulus in case of a viscoelastic material. The phase difference is 0° for a perfectly elastic material, 90° for a pure viscous material, and intermediate for a viscoelastic material, as shown in Fig. 1B. Hence by evaluating the phase lag (δ), one can calculate the material’s properties such as the ability to flow (viscosity) and the stiffness (modulus) from recovery.

Let us assume that the strain lags by a phase angle δ. In general, for a viscoelastic material, strain is defined as,

\[ \varepsilon = \varepsilon_0 \sin(\omega t + \delta) \]  
(1)

where \( \omega \) = angular frequency, (rad/s); 2\( \pi f \). Then, stress

\[ \sigma = \sigma_0 \sin(\omega t + \delta) \]  
(2)

or

\[ \sigma = \sigma_0 \cos \delta \sin(\omega t) + \sigma_0 \sin \delta \cos(\omega t) \]  
(3)

Here the stress component \( \sigma_0 \cos \delta \) is in phase with strain while stress component \( \sigma_0 \sin \delta \) is out of phase with the strain by a phase angle of \( \pi/2 \) rad. Hence the dynamic modulus which is in phase with the strain is,

\[ E_1 = \frac{\sigma_0 \cos \delta}{\varepsilon_0} \]  
(4)

It is called storage modulus and it measures the stored energy and represents the elastic portion.

Dynamic modulus which is \( \pi/2 \) rad out of phase with the strain is,

\[ E_2 = \frac{\sigma_0 \sin \delta}{\varepsilon_0} \]  
(5)

It is called loss modulus and it measures the energy dissipated as heat, represents the viscous portion.

Hence Equation (3) can be written as,

\[ \sigma = \varepsilon_0 E_1 \sin(\omega t) + \varepsilon_0 E_2 \cos(\omega t) \]  
(6)

and loss factor tan δ is defined as (which is depicted in Fig. 1C):

\[ \tan \delta = \frac{E_2}{E_1} \]  
(7)

The complex modulus is defined as,

\[ E = E_1 + i E_2 \]  
(8)

or

\[ E = \frac{\sigma_0 \cos \delta}{\varepsilon_0} + i \frac{\sigma_0 \sin \delta}{\varepsilon_0} \]  
(9)

Figure 1: (A) A typical stress-strain curve of a polymer obtained via controlled force mode, (B) the dynamic stress-strain curves of different materials namely, elastic, viscous, and viscoelastic [1]. (C) Representation of complex modulus: real (\( E_1 \)) and imaginary (\( E_2 \)) parts of modulus and loss tangent [1]. A simple block diagram of a typical DMA is shown in (D). The displacement sensor will be either a linear variable differential transformer-based detector or an optical encoder having high-precision displacement measurements over a large range.
A block diagram of a typical DMA is shown in Fig. 1D. The sample placed in a holder (clamp) is shown in green and the dynamic force is applied using a force motor. The displacements are measured using linear variable differential transformer or optical encoders having high-precision in measuring linear displacements over a wide range. Details of different types of modes and methods available are discussed in the following sections.

With this background, the different modes of DMA can be discussed now, where the mode of operation will decide the unveiled component of the modulus (E/E\prime/E\prime\prime or tan δ). It has to be noted that temperature is an important parameter in deciding the mechanical properties of materials, particularly soft materials such as polymers, and hence the sample (chamber) needs to be kept at a constant temperature (if not it is a temperature sweep experiment) before conducting the different modes discussed below. The failure in ensuring the temperature stability can cause large deviations in the frequency-dependent mechanical measurements since temperature is another control parameter in deciding the elastic modulus of the material, as discussed before. The temperature ramp rate is also important in temperature sweep experiments. The temperature ramp is an important parameter in deciding the curing behaviour of thermosetting resin where the minimum viscosity obtained can be varied with the temperature history and ramp. Increasing the rate of temperature decreases the minimum viscosity attained and the resin gets softer faster. But it can also make the curing faster and the degree of flow depends on the type of mould used and the amount of pressure applied. Hence temperature ramp rate needs to be optimized depending upon the use of the material concerned and a typical temperature ramp used is 10 degrees/minute. There will be two thermocouples associated with DMA, where one measures the chamber temperature and the other measures the samples. The alignment of these thermocouples prior to the experiment is very important in the measurement procedure. Furthermore, the mechanical properties can also get affected by other external parameters such as humidity (if not it is a humidity-controlled experiment where it has to be monitored systematically) and hence a closed chamber experiment is always recommended to get reproducible modulus parameters and phase transition temperature. Humidity controlled experiments are particularly important while dealing with hygroscopic samples such as PEO and GO, two materials discussed in the last part of the article.

### Modes of operation

DMA can be operated in different modes with different control parameters.

#### Multi-frequency

The multi-frequency mode (Fig. 2A) can evaluate stress/strain variations as a function of frequency while oscillation amplitude is kept constant.

These tests can be run at single or multiple frequencies in temperature ramp, time sweep or temperature step/hold experiments. It helps to determine glass transition (Tg) and melting temperatures (Tm) of a polymer material [12]. But it has to be noted that in single-frequency temperature scan experiments to find the phase transition temperatures, the selection of frequency is an important parameter. As stated before, at higher frequencies, the material becomes more solid-like and at lower frequencies liquid-like behaviour will be dominating. Hence, a large scale variation in the operational frequency may affect the phase transition temperatures in a broad range. Normally such experiments are conducted in 1 Hz. The frequency range of DMA Q800 is 0.1–200 Hz and hence it can probe the three decades variation in properties of a material and most of the applications of materials lie in this range, except cases such as airbag operation [1]. Resonance of a material with the instrument is another issue with frequency-based experiments where it can affect the modulus calculations. Such issues are discussed in detail elsewhere [1], and hence not elaborating here.

#### Iso-strain mode

In this mode, stress or strain is ramped at a constant rate while temperature is kept constant. The stress/strain is assessed with varying strain/stress (Fig. 2B). The linear viscoelastic (Hookean) region can be predominantly identified using this mode.

#### Creep-recovery

Creep recovery test is one of the most rudimentary tests to study the relaxations of materials such as polymers [17]. Creep testing is performed by applying a constant stress to the sample and the deformation is monitored as a function of time (Fig. 4A). After the removal of stress, the material is allowed to relax, which is called a recovery test. These two tests are often executed sequentially. The ratio of the time-varying strain and the
constant stress is called the creep compliance (inverse of stiffness):

\[ C_{\text{creep}}(t) = \frac{e(t)}{\sigma(t)} \ldots (10) \]

An ideal creep–recovery curve (Fig. 3A) manifests four distinct regions: (i) initial deformation, (ii) a transition zone, (iii) equilibrium region and (iv) the recovery region. Multiple creep–recovery cycles are also performed to check whether the properties of the sample deteriorate over cycles or not.

The creep–recovery cycle has the advantage to simulate the real-life circumstances with utmost accuracy because of two reasons:

i. Creep–recovery cycle can be repeated multiple times.
ii. The variation in temperature is independent of stress.

Creep experiments can be executed over a variety of samples, where the deformation mode can be chosen based on its modulus and viscosity. Here the sample geometry is not at all a constraint. In general, the total strain is the summation of three distinct parts [18], namely:

i. the immediate elastic deformation \( e_1 \)
ii. the delayed elastic deformation \( e_2 \)
iii. the Newtonian flow \( e_3 \) similar to the deformation of a viscous liquid which obeys Newton’s law of viscosity.

The magnitudes of applied strain \( e_1, e_2, \) and \( e_3 \) are directly proportional to the magnitudes of the applied stress. So a creep compliance can be designated as [18],

\[ J(t) = \frac{e(t)}{\sigma(t)} = J_1 + J_2 + J_3 \ldots (11) \]

where, \( J_1, J_2, \) and \( J_3 \) are parallel with, \( e_1, e_2, \) and \( e_3.\)
Stress relaxation

Stress relaxation is conceptually the reverse of creep recovery test. Here the strain is held constant and the stress is recorded as a function of time (Fig. 3B). Stress relaxation modulus is defined as [1],

\[ G(t) = \frac{\sigma(t)}{e} \quad \ldots (12) \]

In the absence of viscous flow, the stress decays to a finite value. The area under the stress–relaxation curve plotted as E(t) versus t is the viscosity, where E(t) is the stress–relaxation modulus. At very low strain, the viscosity of a colloid can be measured without ruining its structure. This is one of the compelling implications of the stress–relaxation experiment. Creep and stress relaxation data are complimentary, and can be related as [1],

\[ \left( \frac{\sigma_c}{\sigma_r} \right)_{\text{creep}} \approx \left( \frac{\sigma_c}{\sigma_r} \right)_{\text{stress relaxation}} \quad \ldots (13) \]

The relaxation studies also help to understand the molecular structure of the solid and hence will be helpful in molecular modelling. One such study with GO membranes is shown in the later part of the article.

Different types of clamps are available in DMA and the nature of the clamp decides the nature of modulus exploring. Such different clamps available and the sample requirements (type and dimensions of the sample) are discussed below.

Different methods in DMA experiment

There are different types of experimental modes in DMA depending upon the type (dimension and geometry) of sample and modulus (Young’s modulus, Shear Modulus, Bulk modulus, etc.) needs to be determined. These different modes use different types of clamps for mounting the samples. Schematic of those clamps and their functioning are shown in Fig. 4. One end of the clamp (blue parts in the figure) is fixed and the other end moves according to the programmed methodology of the measurement. It has to be noted that the modulus determination needs the dimensions of the sample and hence properly shaped samples are important in all the different clamps. Different clamps and their functions are briefed below.

Tension. Thin films are normally tested with this clamp where Young’s (complex modulus having real and imaginary parts) modulus can be unravelled. In this clamp, the sample is kept in tension (with a small preload to make sure the absence of any wrinkles/folding/air gaps) between a fixed (top part) and moveable plate (Fig. 4F). This mode is suitable for gels, high viscosity resins, adhesives, and highly damped materials.

Submersible clamps. This mode enables samples to be analysed in a submersible clamp equipped with a liquid environment, where the measurements can be conducted in different temperatures up to the evaporation temperature of the liquid being used (Fig. 5 A1, A2 and A3). The presence of surrounding fluid medium can affect the mechanical properties of membranes (biological membranes to solid electrolytes) and this clamp will help to understand such properties in in vitro conditions. One such study is discussed in the later part.

There are other modes associated with DMA such as dual/single cantilever (for the measurement of thermoplastics and highly damped materials), three-point bend modes (for studying stiff and flexible samples), etc. It has to be noted that the choice of a clamp is very crucial in the measurement. Thin samples can be tested in tension mode with great accuracy. More than 1 mm thicker samples prefer to be measured in bending mode, while gels and weak elastomers are perfect for compression clamp.

The clamps need to be properly calibrated before each experiment. There are different calibrations needed to be performed for different clamps (it may vary depending on the clamp, and details will be available with the concerned make’s DMA instrument operation manual) and this includes mass, position, etc. of the concerned clamp. Successful calibration should be ensured prior to the experimental procedure in order to ensure the reliability of the data. Further, the dimensions of the sample need to be accurately measured prior to the experiment and should be clamped with the proper tightening.

DISCUSSIONS

DMA-based studies can be conducted to monitor strain/stress variations in solids with different control parameters such as stress/strain, frequency, temperature, humidity, etc. Table 1 summarizes some of the important DMA test modes, the extractable parameters from these modes, and the physical significance of the results. The basic principles behind each of these modes are already given in the experimental section. Some of these modes and their analyses are discussed with specific examples briefed in the following sections.

DMA analyses of membranes

Now we will be discussing the DMA-assisted studies on two different types of samples: (i) a semi-crystalline polymer–PEO thin film and (ii) GO membranes developed via vacuum-assisted assembly process from the GO dispersions. The detailed synthesis will be discussed later [19].

Polymers undergo different types of transition, depending on the nature of the polymer, extent of cross-linking, and molecular assembly. Crystalline polymers show latent heat involved transition at their melting (melting temperature, \( T_m \)) and the melting drastically lowers the storage modulus of the material. Hence DMA can be used to identify this phase transition in polymers, either via temperature sweep (Fig. 6) or frequency sweep. Amorphous polymers will have a lower modulus value (than crystalline ones) and they undergo a glass transition (\( T_g \)) from their glassy to rubbery nature with a subsequent decrease in the modulus (Fig. 6). It can be considered as a second-order phase transition while the melting transition is first order. Semi-crystalline polymers have both crystalline and amorphous
regions (as schematized in Fig. 6B) with intermediate modulus values, and hence have both the transitions. High-molecular weight PEO (600 kDa in the present case) is a semi-crystalline polymer.

More precisely, the modulus variation with the secondary transitions (γ and β) is shown in Fig. 6C. As the material is heated, the free volume increases, resulting in the initiation of bending, stretching (localized bond movements), and side-chain movements. This corresponds to the Tγ transition. The Tγ to the movement of whole side chains and localized groups comprised four to eight backbone atoms. With the continual heating, the amorphous region starts to develop large-scale coordinated motion. It represents a major transition in polymer as the material enters into a rubbery state from a hard glassy state.
with a drastic change in modulus ($T_g$). One has to keep in mind that glass transition only happens in amorphous material while a 100% crystalline material will never give a $T_g$. As discussed before, the frequency has a high influence on the $T_g$ measurements as it has a contrary influence on the viscous and elasticity parts of the material [1].

Frequency scan in DMA has limitations of small range and hence measurements beyond the range of instrument become difficult as mentioned in case of air bag’s characterization. One of the ways is to adopt other similar phase transition study tools (say DRS) or there are methods available in DMA itself to address such issues. One such method is time-temperature superposition (TTS) which is being extensively used to overcome such difficulties associated with DMA [1].

DMA studies on PEO membranes

Details of the PEO membrane preparation can be seen elsewhere [20]. PEO films of thickness ~0.01 mm, length ~6 mm, and width 5.3 mm are made via proper cutting from a larger film. The storage modulus variations in pure PEO (at a frequency of 1 Hz) with temperature (ramp 2°C) are shown in Fig. 7 (dynamic temperature scan mode from Table 1 is used here). It can be concluded that the transition temperature is ~74°C (found from the storage modulus drop in accordance with the discussion in the previous section) and it matches well with the reported values [21].

One of the important applications of PEO is as a solid electrolyte for lithium (Li) ion transport. We have developed a solid electrolyte of PEO and Li salt having a low content of Li ions [20]. The inclusion of Li salt in this high dielectric constant PEO matrix solvate the Li ions and this shifts the $T_m$ of the PEO, as shown in Fig. 7 (LiPEO10) [22]. The microstructure imaging of the membrane (one such Li incorporated membrane (LiPEO10)) using scanning electron microscope (SEM) is shown in Fig. 8A, where the details of the experiment are described later [23]. The spherulitic parts represent the crystalline portions and it can be seen that the PEO has large number of spherulites with a very small separation among them. The same film is then subjected to a tensile stress beyond its yielding point (in the necking region, the non-linear region in stress–strain curve before the film failure) and further imaging of the same film is shown in Fig. 8B, details are published elsewhere [23]. It can be seen that spherulitic parts got separated and an intermediate amorphous region has been developed.

This microstructural deformation has after-effects in ionic (Li) conductivity of the PEO based solid electrolytes [20], but here we want to emphasize that the external stress can affect the microstructure of soft materials such as polymers and hence can affect their physical properties. The stress within the linear stress-strain region will not affect the crystallite spherulitic arrangements. In other words, the polymer relaxes to the original structure soon after the removal of external stress and hence is found to be not affecting the ionic conductivity of the film [23].

The in situ variations in the ionic conductivity with dynamic external stress can give further insight into to the microstructural...
variations in the membrane, and such experiments can be designed with DMA along with the coupling of optical spectroscopy or Raman scattering. Such in situ electrochemical and mechano-optical studies will be highly useful not only in studying the materials properties but also in the bulk characterization of the membranes for their applications, but not many studies have undergone in these aspects.

**Mechanical analyses on GO membranes**

GO membranes are large-scale structures of ultra-thin GO flakes of several nanometre lateral width and they form randomly arranged macro-scale structures while assembling them via flow-assisted membrane-based vacuum filtration [24]. Their mechanical strength is mainly governed by the inter-flake hydrogen bonding interactions and also due to the hydrogen bonding with other intercalated molecules such as water [25]. Such membranes are found to be viscoelastic in nature [26], and their viscoelasticity can be largely tuned by the intercalated molecules [19]. In one such study, we had shown that removal of water from GO membrane was achieved using a solvent drying technique and the intercalated ethanol used for the water removal has enhanced the viscoelasticity of the membrane several times [19]. Apart from the dynamic studies of individual membranes [GO_water (original membrane) and GO_ethanol (after the removal of loosely bound water inside the GO_water membrane)], we have carried out in situ measurements of solvent extraction and the resultant enhancement in the viscoelasticity (tan δ value) using a submersible clamp-assisted experiment. Schematic of the experiment and the result are shown in Figs 5 A3 and 9.

In the experimental procedure, frequency sweep with GO_water in air is conducted with the submersible tensile clamps and the tan δ variation is monitored. Further, the tank is filled with ethanol (99.9%) without disturbing the GO_water attached to the tension clamp. A frequency sweep is conducted again after equilibrating the system at 29°C for 5 min [19]. It has been observed that GO_water in ethanol has a higher tan δ than that of its original values in all the sweep frequencies and these values match with those of GO_ethanol, where the GO_ethanol is synthesized by flow-assisted filtration of ethanol sonicated GO followed by diethyl ether washing [19]. These experiments show that loosening the hydrogen bonding network inside GO membranes by controlling the water content has a critical role in deciding the net viscoelastic properties of the membranes. Such studies are important in studying the mechanical properties of biological membranes too where they have to expose in to different physiological fluids of different surface tension [27]. Their properties can be simulated with these of in vitro experiments.

Another advantage of DMA is the possibility of molecular structure modelling of solids using relaxation studies. Here we are reporting such an interesting study on two different membranes: GO_water and GO_ethanol, which helped to develop a molecular model of those macroscopic GO membranes.

As discussed before, stress relaxation of a solid is an essential characteristic of any structural material where it governs the dynamic load bearing capacity [28, 29]. It is the time-dependent decrease in stress in response to a constant strain. It has been shown that the stress relaxation behaviour of graphene-based membranes fits well with a modified Maxwell–Wiechert model where the interlayer cross-linking is mainly responsible for the stress relaxation phenomenon [28]. A polymer viscoelasticity can be depicted by a simple Maxwell–Wiechert model where a dashpot and a spring are combined to model the viscous and elastic portion of the material, respectively, as

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**Figure 8:** SEM images of lithiated PEO (LiPEO10) (A) before and (B) after tensile stretching [23]. The semi-crystalline spherulites in Fig. 8A have displaced due to the tensile stretching (Fig. 8B).

**Figure 9:** The tan δ variation of the GO_water measured in a submersible clamp of DMA, with and without ethanol [19]. These data are conducted with the experimental mode (dynamic stress–strain) explained in Table 1.
where $\sigma_0$ is the initial applied stress at the beginning of relaxation and $t$ is the characteristic relaxation time.

The GO membrane has a multilevel lamellar structural framework, similar to other reported graphene membranes [28], hence a ternary Maxwell–Wiechert model has been proposed instead of simple model. It is the combination of a spring parallel with two Maxwell series units, as shown in Fig. 10. This modified model describes stress relaxation by the following equation,

$$\sigma(t) = \sigma_\infty + \sigma_1 e^{-t/\tau_1} + \sigma_2 e^{-t/\tau_2} \ldots \ (15)$$

where $\sigma_\infty$ is the residual stress for the spring, $\sigma_1, \sigma_2$ and $\tau_1, \tau_2$ are initial stresses and characteristic relaxation times of each Maxwell unit, respectively. When the Equation (15) is divided by $\sigma_0$, one can get the following equation,

$$A(t) = A_\infty + A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \ldots \ (16)$$

where, $A_\infty, A_1, A_2$ represent $\sigma_\infty/\sigma_0 \times 100\%$, $\sigma_1/\sigma_0 \times 100\%$, $\sigma_2/\sigma_0 \times 100\%$, respectively.

Each term has its characteristic significance: $A_\infty$, the term depicts the graphene piled network with sufficiently high strength which acts as the opposing force against slippage and relaxation. The $A_1$ corresponds to the laminates which are easy to flow. The $A_2$ denotes the stretchable wrinkles in the graphite network. So, it is quite obvious that the $A_1$ and $A_2$ parts must be immobilized by escalating the interlayer attraction. Thus the viscous flow between adjacent nanosheets of the graphene matrix regulates the stress relaxation. The increased interlayer attraction decelerates sheet slippage and hence restrains the stress relaxation. The stress relaxation study has been conducted on GO_water and GO_ethanol membranes and the results are shown in Fig. 11. It has been found that in GO_water, the stress was found to be relaxed to 63% of its initial value and this relaxation retention for GO_water is found to be significantly higher than that of GO_ethanol (stress retention is ~50%), which indicates higher cross-linking in GO_water (Fig. 11). Further fitting this relaxation behaviour with Maxwell’s model helps to find the different parameters namely, $A_1, A_2, A_\infty$, etc., in which the model is found to be exact with the observed relaxations behaviours of the membranes. The fitting shows that $A_1$ and $A_2$ term for GO_water is lower than the GO_ethanol whereas $A_\infty$ is higher for GO_water indicating stronger cross-linking in GO_water (the data are summarized in Table 2). Hence this stress relaxation also provides enough evidence for higher viscoelasticity of GO_ethanol, as observed by other dynamics studies reported elsewhere, but along with the molecular (micro) structure of the GO membranes. Hence DMA brings a plethora of opportunities in studying the properties of solids with different modes, methodologies, and clamps.

### CONCLUSIONS

This article discusses the basics of DMA, where it is identified as an unavoidable materials characterization tool to explore structure-property analyses. The basics of DMA are discussed in the initial part, followed by different types of static and dynamic measurements possible with a DMA instrument in depth. Samples of different dimensions and shapes can also be tested using DMA, where different types of clamps and modules of a typical DMA instrument are discussed with their detailed usages. Nowadays most of the dynamic mechanical analysers are computer-guided, and procedures and precautions, such as temperature and humidity control, preload force, amplitude of dynamic stimulus, etc., taken during the measurements, can highly affect the results. Finally, two types of membranes are discussed for studies using DMA. First, it is a semi-crystalline polymer (PEO) membrane, where the melting temperature is shown to be extractable from the dynamic measurements. The effect of introducing lithium salt into this PEO is shown further, which affects the melting transition, where it can be traced using a DMA. Further, the effect of mechanical deformation in PEO like soft matrix is the change in their microstructure, which has been shown with the help of an optical microscope. Secondly,
macroscopic structures of graphene flakes—GO membranes—are studied using DMA and have shown that the effects of intercalated molecules and removal of water are traceable with DMA-based measurements, and relaxation studies such as stress–relaxation can help to model the microstructure of such macro-scale structures. In a nutshell, we discussed DMA not only as a fundamental tool for materials characterization but also as a potential platform for exploring the microstructure, other environmental effects, phase transitions including secondary and tertiary transitions, etc. of different types of membranes ranging from biological membranes to synthetic ones.

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AUTHORS’ CONTRIBUTIONS

S.P. has conducted the DMA experiments and T.N.N. supervised the work. S.P. and T.N.N. analysed the data and wrote the first draft. P.M.A. has vetted the manuscript and P.M.A., S.P. and T.N.N. jointly finalized the manuscript.

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