TECHNISCHE FAKULTÄT DER CHRISTIAN-ALBRECHTS-UNIVERSITÄT ZU KIEL	**Scientific Methods**
Dynamical-Mechanical Analysis (DMA) of polymers	**Test No. M306**

Aim: Determination of the mechanical properties of a typical polymer under alternating load in the elastic range and relation to microscopic polymer properties.

1. Introduction

In this experiment the response of a polymer to an alternating load in the elastic range will be determined. Due to the viscoelastic behavior of polymers, the mechanical properties are determined by a mixture of elastic (following Hookes law) and viscous (following Newtons law) behavior. Therefore the strain will be partly in phase and partly out of phase with the stress. This difference is the phase angle δ and can be measured by DMA, giving information about the glass transition temperature. The obtained data can then be related to microscopic properties like entanglement or cross-linking of polymer chains.

2. Theory

2.1 Mechanical Properties

2.1.1 Elastic and Plastic Deformation

In general, deformation, i.e. change of the shape of a sample due to an external force F, can take place in two different ways:

a) Elastic behaviour

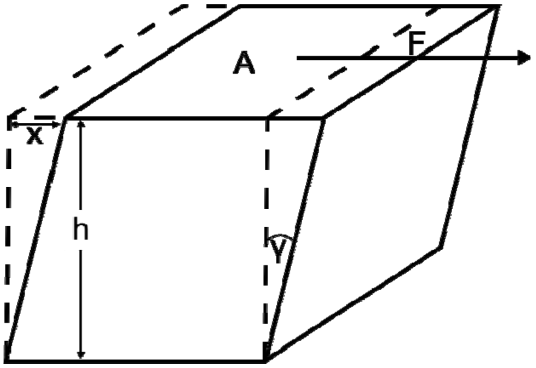

Fig. 2.1: Schematic drawing of elastic shearing

Figure 1 shows a schematic for elastic shearing, where *A* is the area, *F* is the force, *h* is the height, *x* is the shearing distance and γ is the shear strain.
The strain is given by the following relation:

$$\tan\gamma = \frac{x}{h} \tag{2.1}$$

For small values of *tan*(γ), i.e. x << h, which is normally fulfilled, the strain is given by

$$\gamma = \frac{x}{h}. \tag{2.2}$$

The applied stress σ is proportional to the shear strain γ with the shear modulus *G* as proportional constant (Hookes law)

$$\frac{F}{A} = \sigma = G\gamma . \tag{2.3}$$

b) Viscous behavior

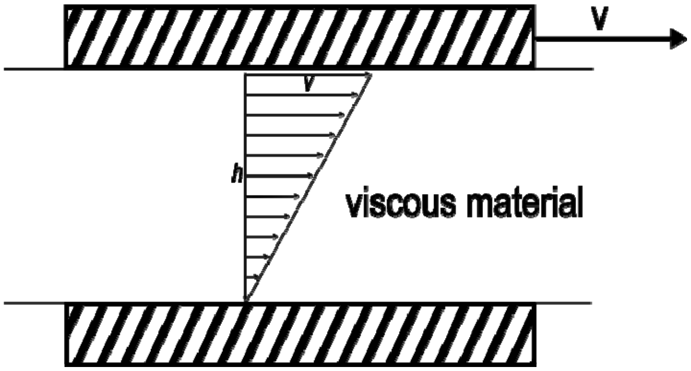

Fig. 2.2: Schematic drawing of viscous flow.

Figure 2 shows a schematic for viscous flow. The two plates are separated by a viscous material with the viscosity η and the upper plate moves with a velocity v induced by a stress σ.

In a Newtonian liquid the velocity gradient $\frac{dv}{dh}$ is proportional to the stress σ

$$\frac{F}{A} = \sigma = \eta \frac{dv}{dh} \tag{2.4}$$

and the velocity gradient $\frac{dv}{dh}$ is equivalent to the strain rate $\frac{d\gamma}{dt}$, resulting in Newtons law

$$\sigma = \eta \frac{d\gamma}{dt} \tag{2.5}$$

2.1.2 Viscoelastic behavior

Polymers normally combine elastic and viscous behaviors, which is called viscoelasticity. This is theoretically described by different combinations of spring- (ideal elastic) and dashpot- (ideal viscous) models. The simplest combinations are the Maxwell and the Voigt-Kelvin models. Their symbols and response to a rectangular external force are shown in figure 2.3. The Voigt-Kelvin model is more suitable for predicting creep, since there is a strain maximum for a given stress on a infinite time scale. Nevertheless the Maxwell model predicts stress relaxation more realistically.

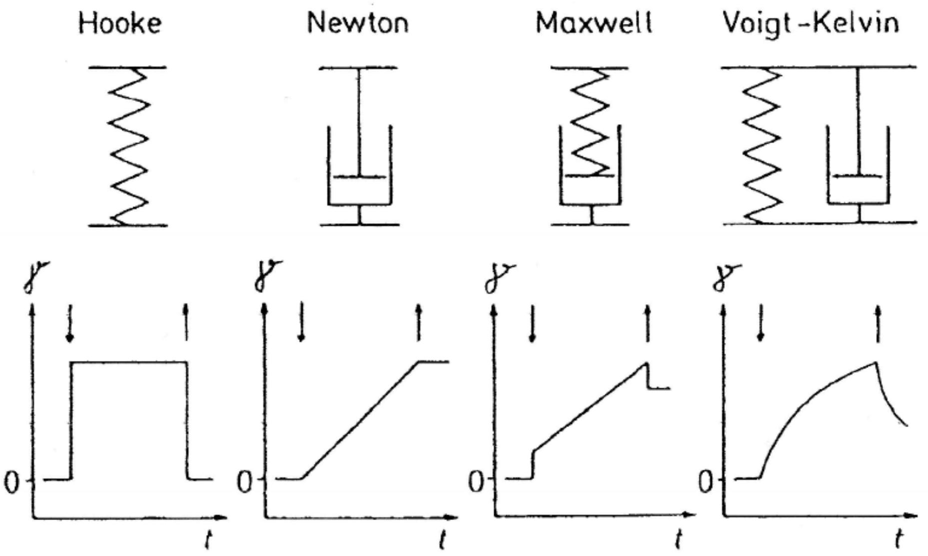

Fig. 2.3 Models for Hooke, Newton, Maxwell and Voigt-Kelvin behavior and corresponding response to a rectangular force.

Figure 2.3 shows only the response to one rectangular external force. In order to state the strain or stress for a system one has to take all deformation history into account. This is done by the Boltzmann superposition principle, which is here shortly demonstrated. In order to do this clearly, a parameter known as time dependent creep compliance $J(t)$ has to be defined. It relates the strain after a given time $\varepsilon(t)$ to the applied stress σ for a linear viscoelastic material.

$$\varepsilon(t) = J(t)\sigma \tag{2.6}$$

The superposition principle can now be demonstrated by a series of loading steps causing a creep deformation as shown in figure 2.4. For instance the strain at the time t for a loading step $\Delta\sigma_1$ applied at a time τ_1 is given by

$$\varepsilon_1(t) = \Delta\sigma_1(t-\tau_1) \tag{2.7}$$

If further increments of stress, which can be either positive or negative, are applied then the principle assumes that the contributions to the overall strain $\varepsilon(t)$ from each increment are additive, resulting in.

$$\begin{aligned}\varepsilon(t) &= \varepsilon_1(t) + \varepsilon_2(t) + \ldots \\ &= \Delta\sigma_1 J(t-\tau_1) + \Delta\sigma_2 J(t-\tau_2) + \ldots \\ &= \sum_{n=0}^{n} J(t-\tau_n)\sigma_n\end{aligned} \tag{2.8}$$

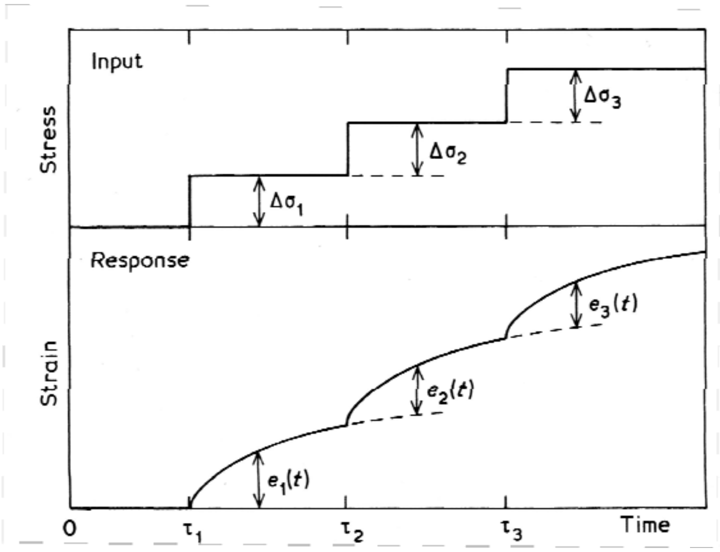

Fig. 2.4 The response of a linear viscoelastic material to a series of loading steps.

It is possible to show this in integral form

$$\varepsilon(t) = \int_{-\infty}^{t} J(t-\tau)d\sigma(t)\,. \tag{2.9}$$

The integral has to be taken from -∞ because the entire deformation history has to be taken into account. The equation can be used to determine the strain after any general loading history. It is normally expressed as a function of τ which gives

$$\varepsilon(t) = \int_{-\infty}^{t} J(t-\tau)\frac{d\sigma(\tau)}{d\tau}d\tau\,. \tag{2.10}$$

The equation for determining the stress by knowing the deformation history is similar

$$\sigma(t) = \int_{-\infty}^{t} G(t-\tau)\frac{d\varepsilon(\tau)}{d\tau}d\tau\,. \tag{2.11}$$

2.1.3 Frequency Dependence

The deformation of a material, which is periodically strained, can be calculated in the following way.
The applied stress will then vary as a function of time

$$\sigma = \sigma_o \sin(\omega t) \tag{2.12}$$

For an elastic material, which obeys Hooke's law the strain would vary in a similar manner.

$$\varepsilon = \varepsilon_0 \sin(\omega t) \tag{2.13}$$

For a viscoelastic material this is not the case, because the strain lags somewhat behind the stress. This can be considered as a damping process and the result is that when a strain as in Eq. (2.13) is applied the stress also varies in a sinusoidal manner, but out of phase with the applied strain.

$$\begin{aligned} \varepsilon &= \varepsilon_0 \sin(\omega t) \\ \sigma &= \sigma_0 \sin(\omega t + \delta) \end{aligned} \tag{2.14}$$

In these equation a phase angle δ is introduced, which is the relative angular displacement of the stress and the strain. By using simple mathematical rules, the equation for the stress can be expanded to

$$\sigma = \sigma_0 \sin(\omega t)\cos(\delta) + \sigma_0 \cos(\omega t)\sin(\delta) \tag{2.15}$$

So the stress can be considered as being resolved into two components; one which is in phase with the strain ($\sigma_0 \sin(\omega t)\cos(\delta)$) and one which is $\pi / 2$ out of phase with the strain ($\sigma_0 \cos(\omega t)\sin(\delta)$). So it is possible to define two dynamic Young's moduli; E_1 in phase and E_2 out of phase.

$$\begin{aligned} E_1 &= \frac{\sigma_0}{\varepsilon_0}\cos(\delta) \\ E_2 &= \frac{\sigma_0}{\varepsilon_0}\sin(\delta) \end{aligned} . \tag{2.16}$$

The phase angle δ is then given by

$$\tan(\delta) = \frac{E_2}{E_1} . \tag{2.17}$$

A complex notation is also possible, the result would be

$$E^* = E_1 + iE_2 \tag{2.18}$$

where E* is the overall complex modulus. E_1 is the real part of the dynamic Young's modulus, which relates stress and strain and determines elastically stored and released energy (reversible), while E_2 is the imaginary part and represents the loss due to friction and generated heat. The calculation of the dynamic shear moduli G^*, G_1 and G_2 are similar, just displacing the strain ε with the shear γ.

2.2 Polymers

2.2.1 Mechanical Properties

In this chapter the mechanical behavior of polymers in general and its relation to the molecular structure will be discussed. Due to the fact that polymers have a chain-like structure, they have some characteristic features, e.g. rubber elasticity (entropy elasticity). For low temperatures, polymers behave like ordinary solids, i.e. the chains are frozen in and there is no relative movement of chains and molecules with respect to each other. Elastic behavior is only possible, if the atoms move relative to each other. However, the Young's moduluscan be much lower than theoretically calculated. This is due to the fact, that, besides at the cross-linked points, the forces between the chains are much smaller, usually van der Waals Forces.

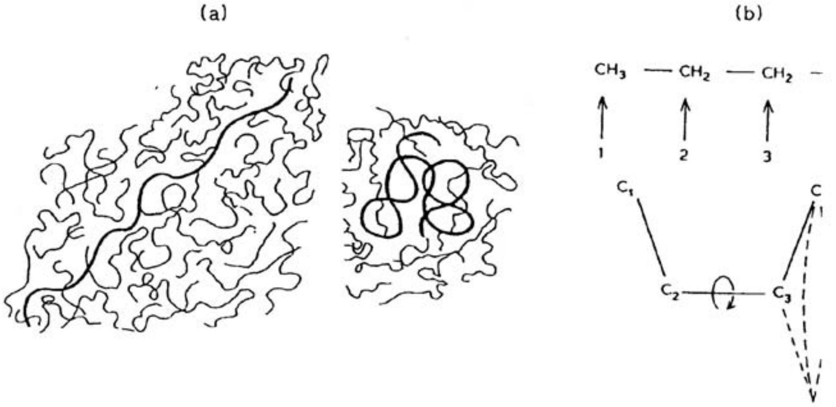

Fig. 2.5 (a) Chain molecule, stretched and squeezed, (b) sketch of the degrees of freedom of rotation along the polymer backbone

At temperatures above the glass temperature T_g the free volume is large enough and the molecule can be rotated along bindings at the backbone, so that polymer chains can be stretched. As there are more possible arrangements for the squeezed than for the stretched form, the entropy of the squeezed form is higher and it is more likely for the polymer being squeezed. Due to that fact there is an entropic restoring force for stretched polymer chains and in a closed system stretching of a polymer leads to an increase in the temperature.

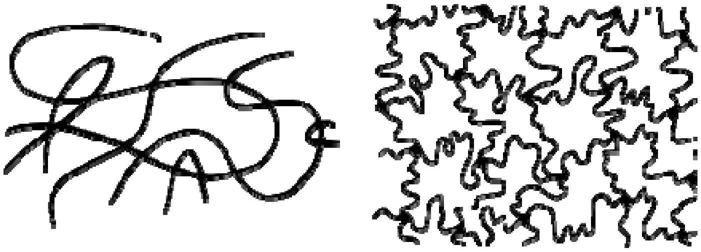

Fig. 2.6 Entanglement (a) and cross-linking (b) of polymer chains.

The polymer chains can be interconnected either physically by entanglement (Fig.2.6. a) or chemically by cross-linking (Fig. 2.7. b). It is obvious that more cross-linking will lead to higher restriction to stretching of polymers. To distinguish linear (non-crosslinked) thermoplastic polymers and elastomers one has take variation of the Young's or shear modulus with temperature into account.

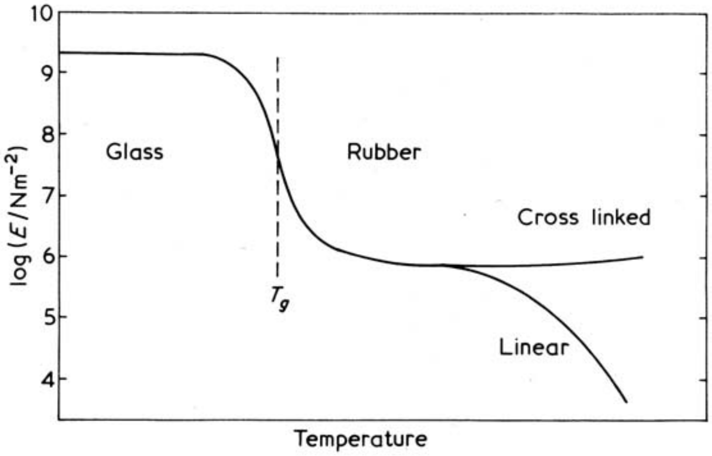

Fig. 2.7 Typical variation of Young's modulus, *E*, with temperature for a polymer showing the effect of cross-linking upon *E* in the rubbery state. Please note the log scale for the E-Modulus.

For temperatures below the glass temperature T_g polymers should be stiff, sometimes even brittle. At higher temperatures around T_g the Young's modulus decreases strongly by 3 orders of magnitude for non crystalline polymers. For semi crystalline polymers only minor changes, in dependency of the order of crystallization, are expected. In non crystalline polymers the chains become mobile and the free volume raises to values above polymer chain sizes around T_g. This leads to these drastic changes. These polymers will even physically dissolve at higher temperatures. Cross-linking of chains can inhibit the mobility, so at a certain rate of cross-linking, polymers are showing at values above T_g a plateau for *E*. Very high cross-linked polymers are chemically dissolved before reaching T_g and show therefore no rubber elasticity. These polymers are called thermosets.

2.2.2 Time-Temperature Superposition

It is possible to interrelate the time and temperature dependence of the viscoelastic properties of polymers. It is thought that there is a general equivalence between time and temperature. For instance a polymer which shows rubber elasticity for a given temperature and testing rate (which correlates with the time) can show glassy behavior for lower temperatures or higher testing rate. So curves, which relate an elastic modulus of a polymer (such as E, G,...) to time (or testing rate), measured at different temperatures, can be combined to one master curve at a reference temperature. An example of such a superposition is shown in figure 2.7.

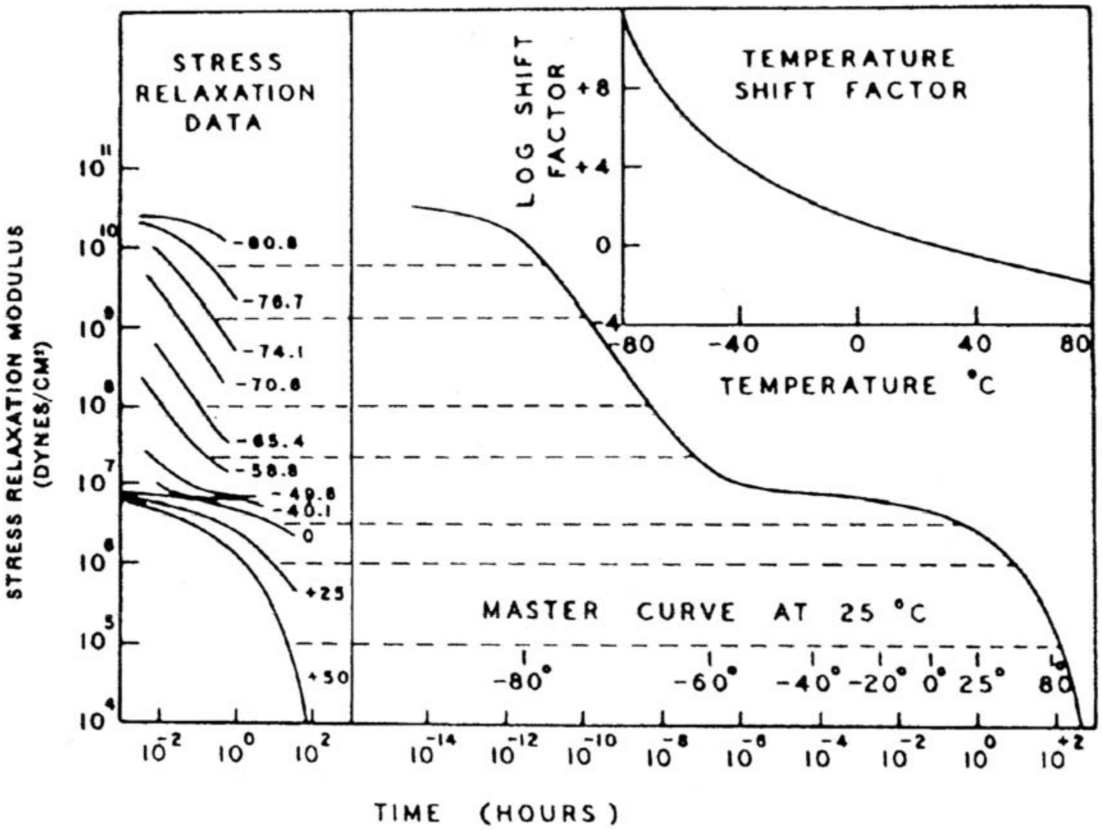

Fig. 2.7. Curves which relate stress relaxation modulus to time, measured at different temperatures can be combined to one master curve for a reference temperature.

The time dependent shift factor a_T can be calculated using the semiempirical Williams-Landel-Ferry (WLF) equation.

$$\log(a_T) = -\frac{C_1(T - T_g)}{C_2 + (T - T_g)} \tag{2.19}$$

The constants are empiric and have values of $C_1 = 8.86$ and $C_2 = 101$ K. Using this equation the shift can be calculated by

$$t_r = \frac{t_T}{a_T} \tag{2.20}$$

where t_r is the time correlating to the reference temperature and t_T the time correlating to the measured temperature. Using this equations one can form a master curve at one reference temperature from measured data at several different temperatures.

So it is possible to determine glass transition temperature by measuring elastic properties over temperature and/or time range and combining these to one curve.

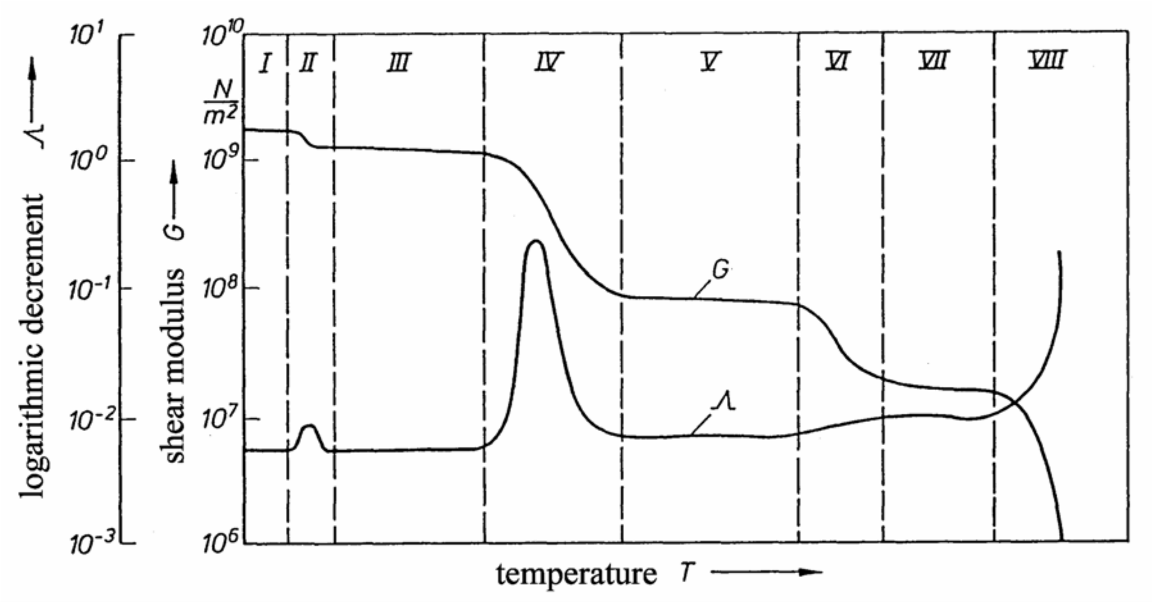

Fig. 2.8 Temperature dependency of shear and loss modulus on a logarithmic scale

In figure 2.8. the temperature dependency of the *G* and *Λ*, which were introduced in chapter 2.1.3 as G_1 and G_2 is shown. T_g lies in section IV. There one can see a relaxation of G_1 and a resonance peak of G_2. *Tanδ* shows a similar peak in the range of the glass transition.

3 Experimental

3.1 Aim

The shear modulus, the loss modulus and the phase factor should be determined for different temperatures and frequencies (testing rates). The glass temperature should be determined and the master curve for the shear modulus should be calculated and discussed.

3.2 Equipment

- DMA Setup with integrated furnace
- Power supply for heating
- Power supply for motor
- Frequency counting unit
- PVC samples

3.3 DMA Setup

In the DMA Setup the PVC samples can be heated rotated at measurable frequencies. The temperature can be measured by an integrated thermocouple while the frequency is counted by the frequency counting unit and measured by a multimeter. Still the real PVC rotational frequency is different from the measured one due to two facts: The frequency counter has eight measuring marks and there is a 4,75 to 1 transmission between the motor and the sample. So the measured frequency has to be divided by 38 to get the real rotational frequency.

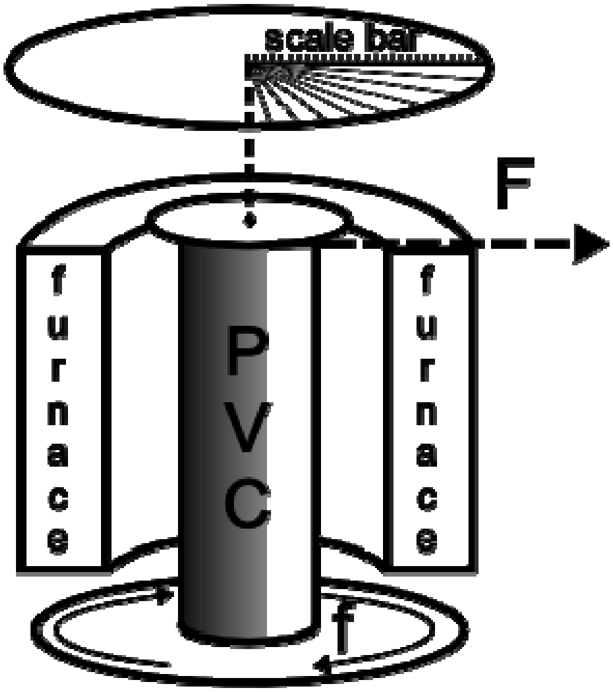

Fig. 3.1 Sketch of the DMA Setup

Figure 3.1 shows a sketch of the DMA Setup, the force will be applied by a spring and the deflection and the phase angle can be measured by a scale bar.

3.2 Sample

PVC samples with 6 mm diameter, total length of 38 mm and experimental length of 35 mm are used for the experiment.

3.3 Experimental Sequence

3.3.1 Sample and Apparatus Preparation

The sample has to be mounted to the DMA apparatus. At the lower and its fixed by a screw and at the topper the force acts.

Next a slow frequency has to be applied and the furnace should be heated to 70 °C and kept there for a while to equilibrate it. Typical values for the power supply are 3.1 V. 3.6 A for a temperature of 70 °C. Then a slight force should be applied until a small deflection can be seen.

3.3.2 Experiment

The range of 70 °C to 110 °C 6 temperatures should be selected and for each temperature five experiments with frequencies in the range of 50 to 250 Hz should be performed. The phase angle and the total deflection should be determined for every frequency and temperature.
Note: Due to the softening of the sample in the glass transition range, the force has to be reduced during heating. Heat the furnace modestly to avoid overheating and to allow sufficient equilibration.

4 Analysis of the Experiment

- Calculate G_1, G_2 and $tan\delta$ from your data.
- Plot G_1, G_2 and $tan\delta$ vs. temperature.
- Determine the glass temperature T_g and compare it with literature values.
- Calculate and plot the master curve for G_1 using the WLF equation.
- Try to estimate if the polymer is linear, cross-linked or semicrystalline.

5 References

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