

Viscoelastic and Rheological Properties of Polymers

By

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1. Viscoelastic properties

Polymers have unique viscoelastic properties because they consist of long molecular chains, which merge the properties of elastic solids and the Newtonian fluids [1]. Viscoelasticity nature makes the stress-strain response is a time dependent and the deformation is a partially reversible. Furthermore, Polymer melts are regarded as non-Newtonian fluids, which mean that there are variations in their viscosities and the relation between deformation rate and stress is not straightforward [2].

At temperatures lower than T_g , polymers behave like Hookean solids under small deformation, but near T_g temperatures their behaviors are viscoelastic without doubt. Along this temperature range, the phase angle (δ) between stress and strain will possess a value between 0° (completely elastic) to 90° (completely viscous) [3]. Temperature has a pronounced effect on the viscoelastic properties and this effect attributed to the chain molecular structure. Complex structures have the stronger the effect of temperature on their viscosities.

Polymer melts exhibit either linear or non-linear viscoelastic behaviors. Linear viscoelasticity occurs when the molecules have enough time to relax so that the entangled and the coiled state of the chains is not disturbed because the deformation rate is very slow. In contrast, non-linear viscoelasticity occurs when the deformation surpasses the limit of linear viscoelasticity and the melt structure is destroyed so that the entanglements of chains began to orientate along the flow [1]. To characterize the linear viscoelastic behaviors, there are some tests used,

such as small amplitude oscillatory shear (SAOS), stress relaxation, and creep / creep recovery.

For determining the viscoelastic properties of polymers, three test modes can be used. These modes are temperature sweep, frequency sweep and dynamic stress-strain tests (ASTM D4065, D4440, and D5279) respectively.

Temperature sweep is a common test method includes measuring the complex modulus (G^*) at low constant frequency whilst changing temperatures of the sample. A clear peak in the damping coefficient ($\tan \delta$) appears at the T_g of the polymer, as well as secondary transitions (β) can appear also.

In the "dynamic mechanical thermal analysis; DMTA", the mechanical responses of a viscoelastic materials are evaluated as a function of time, temperature and frequency, whilst they are subjected to a sinusoidal strain. This allowing one to calculate G^* , $\tan \delta$, loss modulus; G'' (represents the viscous portion) and storage modulus ; G' (represents the elastic portion). Furthermore, one can locate the T_g of the material, and specify transitions correlating to other molecular motions due to the variations in the G^* [3].

Results are commonly exist as a diagram (Figure 1) of $\tan \delta$, G' and G'' against temperature [4].

G^* combines the contributions of both viscous and elastic components to the material's stiffness (Equation 1) [4].

$$G^* = G' + G'' \dots\dots\dots(1)$$

$\tan \delta$ (also called loss tangent) (Equation 2) measures the damping ability of the material.

$$\tan \delta = G''/G' \dots\dots\dots (2)$$

There is a linear relation between G' data and the AUL over the rubber-elastic plateau .

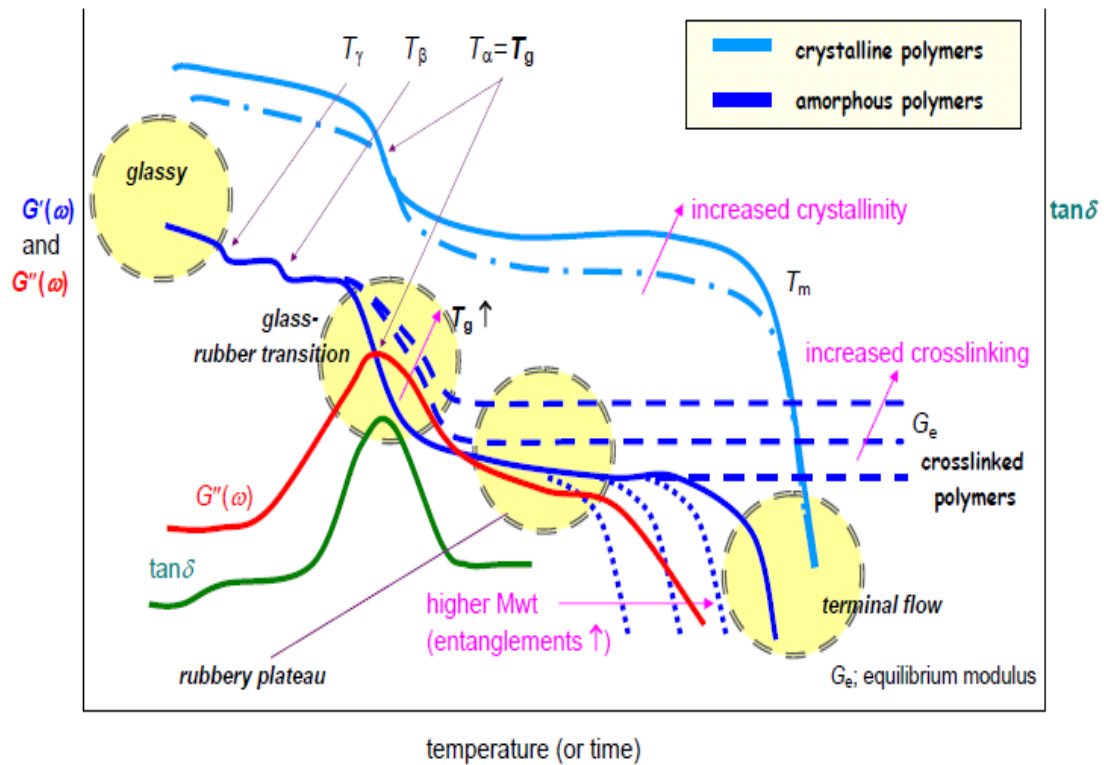


Figure 1: Dynamic viscoelastic behaviors as a function of temperature for typical polymers [4]

G' data can be utilized to calculate the degree of entanglement density (N) using the following equation [5]:

$$N = \frac{G'}{6RT} \dots\dots\dots (3)$$

Where G' is the storage modulus obtained from the plateau region, R is the universal gas constant and T is the absolute temperature.

G' and G'' together for the polymer solutions can be used to distinguish between cross-linked and uncross-linked polymer. When $G'' \gg G'$ the polymer solution is uncross-linked and it indicates that the viscous property is higher than the elastic one along the entire frequency range. If $G' > G''$ the solutions are partially cross-linked, and when both G' and G'' are very high and are roughly parallel to each other, the hydrogel is highly cross-linked network. For the uncross-linked hydrogel, the cross-over point appears when $G' = G''$ (where G' and G'' intersects

each other). This point denotes the gel-sol transition temperature as shown in Figure 2b [6].

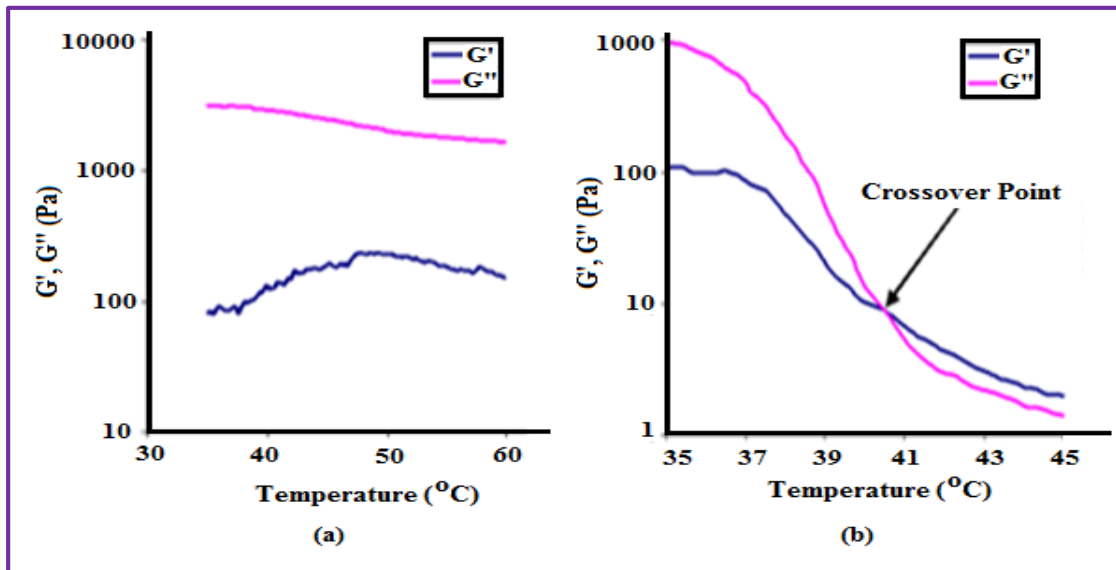


Figure 2: Rheological behavior of (a) cross-linked (b) uncross-linked hydrogel [4].

2. Rheological Properties

Since that the magnitude of the complex viscosity $|\eta^*|$ consists of viscous and elastic parts, the relation among storage modulus, loss modulus and frequency can be expressed as [7]:

$$|\eta^*| = \sqrt{(\eta'^2 + \eta''^2)} = \sqrt{\left[\left(\frac{G'}{\omega}\right)^2 + \left(\frac{G''}{\omega}\right)^2\right]} = \frac{|G^*|}{\omega} \dots\dots\dots (4)$$

Viscosity (η) is the ratio between shear stress (τ) to shear rate ($\dot{\gamma}$) as shown in Equation (5) and considers as the resistance property to the shearing effect.

$$\eta = \frac{\text{Shear Stress}}{\text{Shear Rate}} = \frac{\tau}{\dot{\gamma}} \dots\dots\dots (5)$$

The nature and shape of the viscosity curves depend on some factors, such as polymer molecular weight distribution (Figure 3 a), molecular weight, temperature, pressure, plasticizer and filler (Figure 3 b). Thus from the viscosity curve profile an important information can be obtained which reflects many polymer properties.

At low shear rate, the viscosity of the polymeric solution is independent on the shear rate (called zero-shear viscosity; η_0) and increases with increment of both density and the molar mass due to the enhancement of the intermolecular interactions [7].

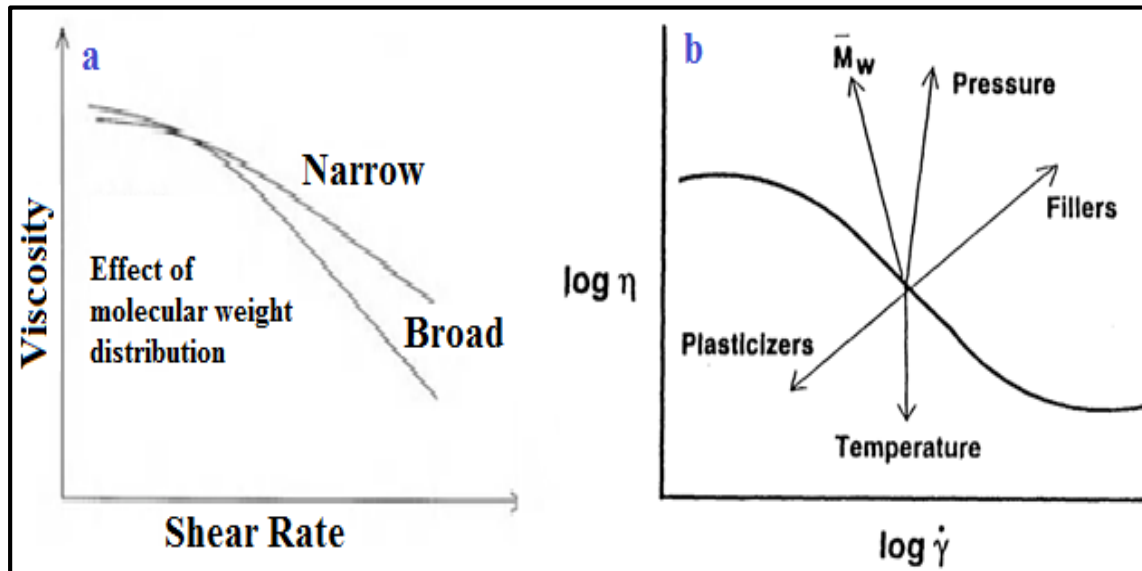


Figure 3: Dependency of polymer viscosity on various parameters [8]

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