Rheological Properties of Polyvinylacetate: Storage-Loss Modulus and Relaxation Stress

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Abstract: The dynamic viscoelastic properties of Polyvinylacetate with molecular weight 83000g/mol (PVA 83K) were determined by using a Rheometer operated in the dynamic mode and 8 mm parallel plate over a wide range of temperature as a function of frequency. The measurements were performed successively in the parallel plate geometry using 8 mm plate instead of 25 mm. The glass plateau regime is clearly observed because we could measure PVA 83K sample successively under its glass temperature. The storage and loss modulus and the relaxation stress are performed.

Keywords: The storage and loss modulus of Polyvinyacetate, Relaxation stress.

1. INTRODUCTION

Rheology is concerned with the description of the mechanical properties of the various materials under the various deformation conditions. Polymer rheology is in its various aspects intimately entwined with molecular physics, continuum mechanics, and the processing of polymeric materials. At present, rheological investigations of polymers are processing at an enormously rapid rate, embracing a wide range of materials: biological objects, paste-like substances such as lubricants. The applied aspects of rheology are tied up with the development of new technological processes for the processing of plastics, elastomers and fibers [1]. The understanding of the relationship between the rheological properties of polymers and their molecular structure has considerably improved in the past few years with the interest of physicists in the matter and particularly with the development of molecular dynamics theories [2]. Besides, rheological measurements are used now as an analytical tool of polymer characterization [3].

In this work the rheological properties are investigated in details for a commercial PVA 83K.

2. EXPERIMENTAL SECTION

Polydisperse PVA 83K sample was prepared for the Rheological measurements. In the disc form with 8 mm diameter and 1 mm thickness by using a press mould without vacuum at 50˚C under 10 bar for

20 min. The preparation steps and conditions are summarized as follows:
Approximately 0.1 g of the polymer is placed in a Teflon frame of dimensions 8 mm diameter and 1 mm thickness. This Teflon frame is introduced between two Teflon plates and positioned between two metallic plates in the mould. The sample is positioned on the lower plate followed by lowering the upper plate until just contact the upper Teflon plate. The sample is heated with heat rate 10˚C/min. and pressed under 8-10 bar by lowering the upper piston for 20

min. The mould is cooled to 30 ˚C , followed by taking the sample out.

After preparation the sample for the measurement, the sample is placed on the lower plate of the ARES-Rheometer followed by lowering the stage until the sample just contacts the upper fixture completely. The ARES-Rheometer, consists of a test station, a furnace and liquid nitrogen controller. The test station contains the motor and transducer between which the sample to be tested is placed. The furnace is a forced convection environmental chamber that encloses the sample. The gas temperature is controlled by two resistive heaters and the nitrogen gaseous is used during testing at or above room temperature. If test temperatures are below room temperature, liquid nitrogen is used. The temperature of the oven is maintained by a control loop that is closed around a platinum resistive thermometer.

The normal force of the instrument should be kept around zero and the actual gap size is read electronically to be around 1 mm. The measuring program is adjusted to measure the sample over a wide range of temperature from 25 ˚C up to 150 ˚C as a function of frequencies in parallel plate geometry and dry nitrogen atmosphere .The strain was kept inside the linear regime in the whole frequency range. The strain is applied to the sample and the resulting stress is measured by the transducer. The stress signal generated by the sample separated into two components; an elastic part which is in the phase with strain and a viscouse contribution which is 90° out of phase with the strain.

3. RESULTS AND DISCUSSION

The PVA83K sample was measured over a temperature range 25-150°C as a function of frequency. Different temperatures curves were shifted into single curve (Master curve) to a reference temperature T_0 (25 ˚C) by means of the time-temperature superposition principle as proposed by Williams, Landel and Ferry (WLF) [8].

Figure 1 shows the master curves of storage, $G'(\omega)$ and loss modulus, $G''(\omega)$ for PVA 83K . In Figure 1 $G''(\omega)$ and $G'(\omega)$ are plotted against the radian frequency with logarithmic scales . The storage modulus, $G'(\omega)$ is the ability of the material to store energy and the loss modulus represents the losses in the energy per cycle of the deformation. On the dependencies of G', G'' (Fig. 1) on frequency we deal with the following characteristic points and regions. The most important for the loss modulus are the points of intersection of its frequency curve with the curve of frequency versus the storage modulus. In the region of relatively low frequencies the point of their intersection corresponds to the maximum of the loss modulus. On the frequency scale this point is conveniently taken as the beginning of the rubbery plateau. In this way the extent of the plateau is determined on the frequency scale. The point of the minimum of the loss modulus is important. In the region of the terminal zone (which corresponds to the region of fluidity) the loss modulus is directly proportional to frequency. Figure 1 shows the glass plateau regime for PVA 83K at high frequency followed by the glass transition. The appearance of the glass regime because we could measure PVA 83K sample successively under its glass transition temperature with ARES rheometer. Since the glass transition temperature of PVA is $28°C$ [10] and the sample is measured at $25°C$. The glass transition relates to the movement of the segments. The flatness of the rubber-like (plateau) regime is not clear due to the insufficient high molecular weight sample. As the result we cannot determine accurately the plateau modulus, G_N° .

Since the rubber-like regime is the indication of the entanglements where the chains are entangled each other above a certain molecular weight that called critical molecular weight, Mc. The attainment of the critical molecular weight is usually tied up to the appearance in the polymer of a spatial network of junctions of the type of molecular entanglements, which are characterized by weak intermolecular interaction and accordingly, by a low potential energy barrier. This accounts for the very slightly dependence of Mc on temperature. Mc equals to nearly two times [10] the entanglement molecular weight, M_e which is the distance between the entanglement points can be determined as, $M_e = \rho RT / G_N^\circ$ [11]. ρ is the density of the material, R is the universal gas constant and T is the reference temperature which is taken to be the room temperature in this study. And G_N° is the plateau modulus that can be determined by different methods. From peak maximum in the loss modulus at the intersection point with the storage modulus as, $G_N^\circ = (4.60 \pm 0.06)G''_{max}$ [3].

G_N° could obtained also from the height of the plateau in Figure 1 at the point against to the minimum of loss modulus on the frequency scale. But these values of the plateau modulus are inaccurate because these points are not clear due to the insufficient high molecular weight (83000 g/mol) in addition to the large molecular weight distribution. The plateau regime is not clear also in the stress relaxation modulus (Fig.2) for the same reasons. The stress relaxation modulus, G(t) is defined as the stress divided by strain at constant deformation and is plotted versus time. The boundaries of the plateau are temperature-dependent At short time the corresponding region of the time scale is sometimes called glassy zone corresponds to the absence of any configurational rearrangements of the chain backbones It is clear from Figure 3 that at long time G(t) falls rapidly. In terms of mechanical models, this corresponds to the complete relaxation of all springs in an array. The region of time scale in which G(t) falls rapidly is often called the flow or terminal zone.

4. CONCLUSION

The rheological properties of PVA 83K are evaluated using an ARES Rheometer operated in the dynamic mode. The measurements were performed successively in 8 mm a parallel plate instead of 25 mm. The glass plateau regime is clearly observed because we could measure PVA 83K sample successively under its glass transition temperature. The storage and loss modulus and the relaxation stress are performed. The accurate value of the plateau modulus G_N° was difficult to obtain. Because of the insufficient high molecular weight and large molecular weight distribution.

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The Abbreviations and notation:

PVA 83K: Polyvinylacetate with molecular weight 83000g/mol.

ω : the angular frequency

G' : the storage modulus

G'' : the loss modulus

G_i : the relaxation strength

$G(t)$: The relaxation stress

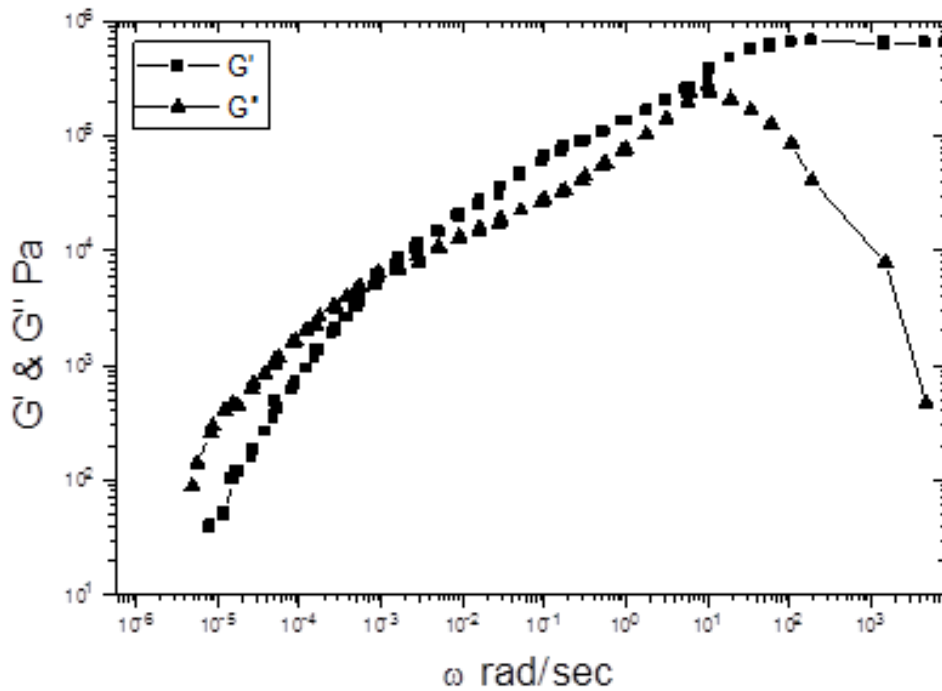T_0 : The reference temperature

G_N° : the plateau modulus

Figure 1: Master curve of storage and loss modulus as function of frequency for PVA 83K at T_0 =25C.
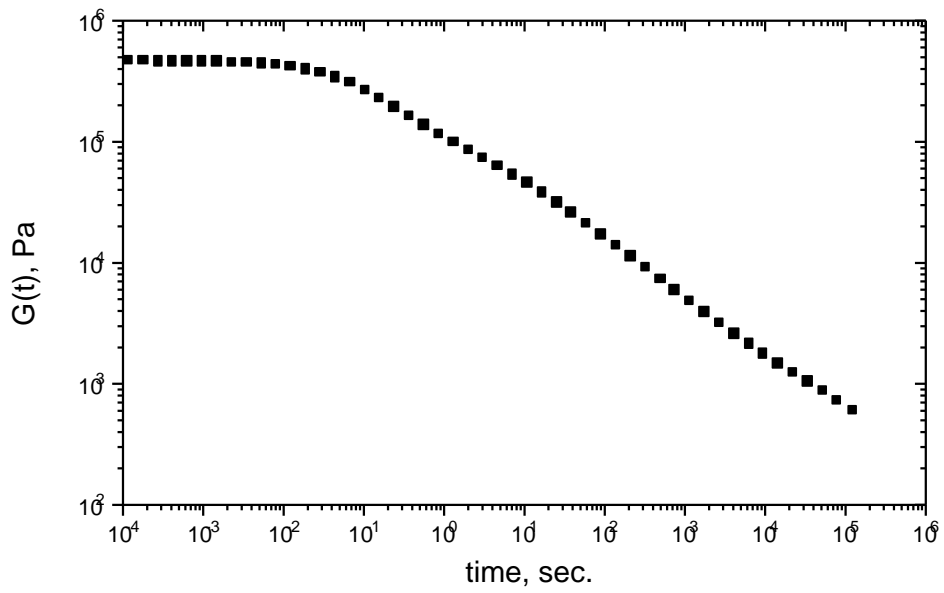
Figure 2: Master curve of the stress relaxation modulus for PVA 83K at T_0 =25C.