RS043

Characterizing Melt Viscosity of Rigid PolyVinyl Compounds using a Dynamic Strain Rheometer

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ABSTRACT

Injection molding big parts and complex shapes with rigid PVC is probably the most demanding PVC process in terms of melt viscosities. PVC is a material with physical and chemical characteristics that make it process slightly more difficult in comparison with other thermoplastics. The high viscosity contributes to the development of a high amount of heat when the material is subjected to the shear applied by the screw during the plasticization. The thermal instability of the compound results from the breakdown either when it is heated at temperatures higher than admissible or when it remains for too long at high temperature. Hence evaluating the material behavior in terms of its thermal stability and melt viscosity is important for end-users of PVC compounds. This paper attempts to assist engineers who are faced with the task of screening compounds from various suppliers, prior to full-scale evaluation of the compound in production machines.

INTRODUCTION

Traditional tests for polymers focus on the amount (mass) of material passing through a known diameter orifice in a given time frame, usually 10 min. This type of test, known as Fluidity Index or Melt Index (MI), provides a single point measurement of the flowability of a material. The standard measurement for Melt Flow of PVC compounds is generally not done according to ASTM D 1238[(1)]. An extension, ASTM D 3364 [(2)]is used specifically for flow rate measurements of PVC compounds while detecting and controlling various polymer instabilities associated with the flow rate. In this test, no control or knowledge of the material flow pattern exists, and thus the strain history is different for each material studied. This single point value is a composite of both the viscosity and elasticity in the sample. This empirical value is not defined in terms of a particular deformation, but represents a single point value which typically serves to rank or screen materials. Due to the nature of the measurement, it is not possible to determine the effect of the viscosity contribution independent of the elasticity. Many times, samples with the same MI value, process drastically different from each other. This method is best used as quality control[(3)] for the flow behavior of molten thermoplastics. It does not provides a fundamental property measurement and may or may not correlate with processing behavior.

Dynamic measurements, on the other hand, obtained with Strain/Stress Controlled Rheometers provide a valuable means of characterizing information regarding the material's thermal and flow behavior. These instruments have the ability to rigorously determine both the elastic and viscous response of a sample in a single experiment. The strain-controlled instrument applies a controlled shear strain in the form of displacement and measures the stress through a torque transducer to calculate the modulus, viscosity etc.

The materials under investigation comprised three rigid PVC compositions labeled as Sample A, B and C. Each composition is markedly different in their composition with variations in the thermal stabilizer type and concentration, apart from differences in the type of the base PVC resin.

SOLUTION

The complex viscosity is evaluated using the strain controlled Rheometer RDA III with a parallel plate geometry. The experiments were conducted in accordance with ASTM D 4440/ISO 6721-10[4, 5]. The samples for the test are compression molded into 25 mm circular discs, after appropriate pre-drying.

Linear visco-elastic behavior is defined, for the purpose of the standard requirement, wherein the modulus is independent of the applied strain. This assumption is necessary for the comparison of the test data. Therefore the amplitude of oscillation is set such that the deformation of the specimen occurs within the linear-viscoelastic region. Figure 1 shows a strain sweep performed on samples A from 1% to 100 % strain to define this linear viscoelastic region. All samples A, B, C showed a linearity onset at ~ 10% strain.

A frequency sweep was done on the samples A, B and C to compare the complex viscosity of each sample and to check the validity of Cox-Merz rule[6]. Sample A exhibits the lowest complex viscosity (1173.2 Pa s) at 100 rad/sec. The overlaid results of the measured complex viscosity on the strain-control rheometer for samples A, B, C are shown in figure 2.

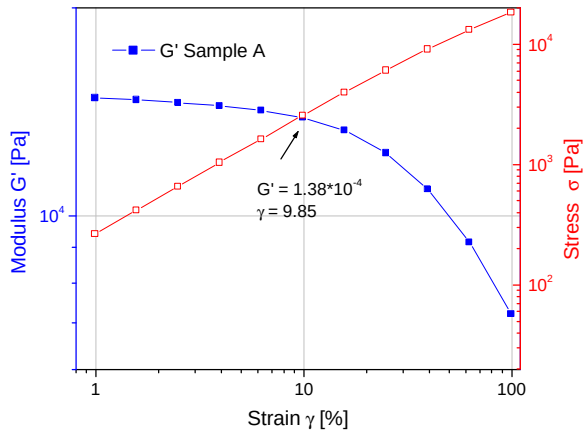

Figure 1: Strain Sweep @ 200°C of PVC sample A

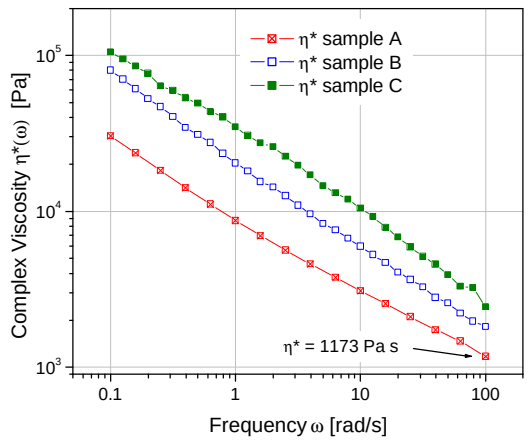

Figure 2: Frequency Sweep @ 200°C of PVC sample A, B, C

A capillary rheometer[7] was used to evaluate the apparent viscosity over the practical range of shear rate from 100-10000 s^{-1}. The test conditions were: - die with L/D of 1/30; - temperature of 200 °C. The shear viscosity was recorded for all samples. As can be seen from the figure 3, sample A exhibited a lower viscosity profile (1131.12 Pa s at 100 s^{-1}) across the shear rate range of 100-10000 s^{-1}) compared to the sample B and C.

This observation[8] on the capillary rheometer reflects similar trends as observed in the viscosity profile obtained from the RDAII as shown in table 1.

A time sweep was performed to evaluate the melt stability under the following test conditions: Geometry 25 mm parallel plate; Gap 1.93 mm; Frequency 6.2832 rad/sec; Temperature 200ºC; Strain of 10%; Time 1200 seconds.

Dynamic viscosity values were compared after ~ 215 seconds and shown in figure 4. Sample A exhibited a dynamic viscosity of 3894.1 Pa s; Sample B of 7656.2 Pa s and Sample C of 11430 Pa s. The complex viscosity for all three samples is slighly increasing with time.

To further augment the observed viscosity profiles, the 'K value' or the 'Viscosity Number' defined by ISO/R 174-1961 [9] for the PVC resins A, B and C were analyzed. Solution with different concentrations of the PVC resins in cyclohexanone were prepared. The flow times of the solvent and the solutions of resin were measured at 27°C by Ubbelhode

VISCOSITY COMPARISON

Sample	@ 100 (rad/sec) Complex Viscosity, eta*(Strain Control)	@ 100 (1/sec) Steady Shear Viscosity (Capillary)
Sample A	1173.2	1131.12
Sample B	1817.7	1849.36
Sample C	2434.3	2580.95

Table 1: Viscosity comparison of PVC samples A, B, C

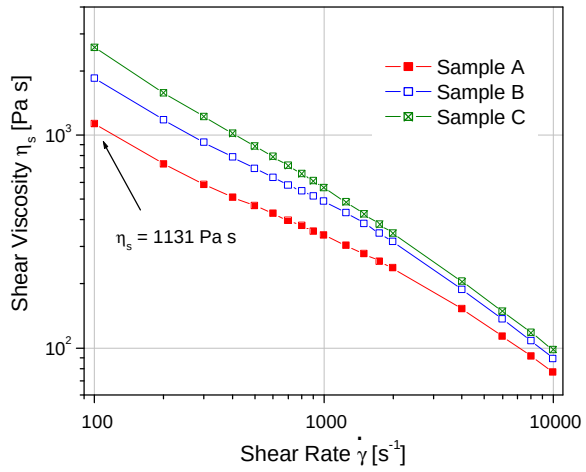

Figure 3: High Shear Viscosity @ 200°C measured in a capillary rheometer

viscometry and the viscosity number was calculated by extrapolating to zero concentration.

The viscosity number (K) as defined by ISO/R 174-1961[9] is calculated as:

$$K = (t-t_0)/t_0 * C$$

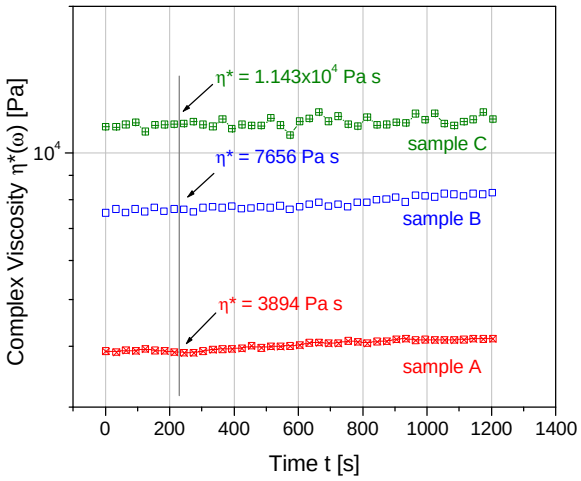

Figure 4: Time Sweep @ 200°C for sample A, B C

where t = time of flow in seconds of the solution, t_0 = time of flow in seconds of the redistilled cyclo-hexanone and C = concentration in g of resin per ml of solution.

The viscosity number is reported to the nearest whole number. Sample A shows a markedly low K-value of 53, sample B exhibits a K-value of 56 and sample C of 59. This correlates qualitatively with the differences in the viscosities observed on the strain controlled rheometer & the capillary rheometer.

CONCLUSION

Sample C exhibits a relatively lower viscosity profile compared to sample B and C. The viscosity trend observed can be considered as an indirect measure of the material's intrinsic melt viscosity. This parameter defined by the solution techniques (K-Value) for linear polymers, correlates with the polymer average molecular weight. The Strain Controlled Rheometer thus provides a valuable, reliable and fast method to evaluate the melt-stability compared to traditional test methods. The melt viscosity serves a useful purpose of characterizing new compounds, screening multiple formulations or providing protocols for quality control. Supplementary techniques such as torque rheometer testing, static dynamic testing on the 2-roll mills will provide information on the degradation rate, thermal instability, etc. A combination of these techniques generates multiple indicators on the PVC proces/ sability prior to full-scale production trails.

REFERENCES

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6. (Cox Merz Rule)- A well-known empiricism in the rheology of polymer melts is the Cox-Merz rule, which relates the linear dynamic moduli as functions of frequency to the steady shear flow viscosity curves. This relationship is very useful because it allows to estimate steady flow viscosity curves from the more readily obtainable from dynamic mechanic rheological measurements.
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