Predicting Polyolefin Foamability Using Melt Rheology

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Abstract:

Many different polyolefinic foams and effectively nonfoamable polyolefinic resins were studied by ASTM D-4440, "Standard Test Method for Plastics: Dynamic Mechanical Properties Melt Rheology" techniques [1]. The sensitivity of this test method to chain branching of the polymeric molecule was maximized by optimization of the test setup parameters. With the optimized test set-up, the melt viscosity, which is also known as complex viscosity, and the viscoelastic properties of storage and loss modulus were measured for the various materials. The functional relationship between the loss tangent, tan δ, which is defined as the damping of the material from the loss modulus divided by the storage modulus, and the complex viscosity characterizes each polyolefin material. Comparison of the loss tangent vs. complex viscosity relationship functionality for foams and nonfoamable resins has identified a "processibility window" for the polyolefinic foaming process. Applying ASTM D-4440 techniques to determine whether the functional relationship between the loss tangent and complex viscosity passes through the processibility window for polyolefinic resins from new or recycled sources or even resin blends can thus be employed to predict their foamability and thereby avoid costly process upsets or needless process trials.

Introduction:

Rheology is the study of material flow. Thermoplastics flow behavior during melt processing is governed mainly by the polymers molecular weight, molecular weight distribution, and degree of branching [2].

Rheological studies measure these properties effectively and are widely published [3, 4]. For example, the zero shear viscosity is directly related to the molecular weight and measured using either a frequency sweep or creep experiments. Studies from linear polymers developed theories to transform frequency sweep data into the molecular weight distribution curves. Creep data can be transformed into molecular weight curves, as depicted in Figure 1. The degree of branching is easily measured using frequency sweeps. When the complex viscosity decreases with frequency the degree of branching is increasing, Figure 2.

Past examples of optimizing the melt strength of talc filled polypropylene foam was published by Rheometrics Scientific Corporation [5]. The study was about polypropylene melts using different talc levels from foam samples as good versus bad samples. The melt elasticity and melt strength as the talc level changed was reported as changes in the viscosity and storage modulus versus the frequency, and increased in sensitivity as the frequency decreased.

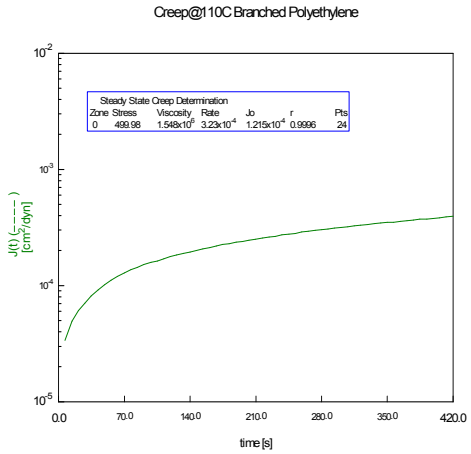

Figure 1, Creep Data from Branched Polyethylene

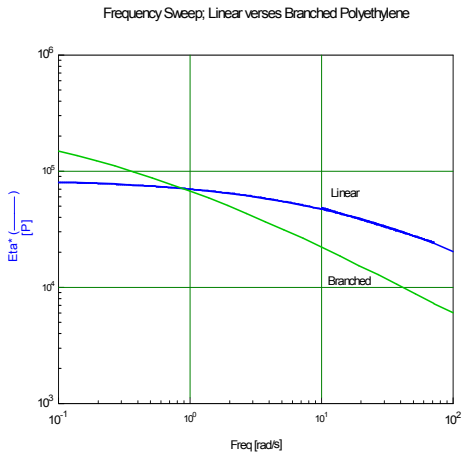

Figure 2, Frequency Sweep, Linear and Branched Polyethylene

Melt strength is a property of the polymer melt which indicates its ability to withstand drawing without breaking. Melt strength is improved by the presence of a high molecular weight tail or long chain branches.

A popular method to measure melt strength is using a capillary rheometer equipped with a haul off device and a force transducer to measure the strength of the polymer melt. The results are typically presented as graphs of force/melt strength versus drawdown speed. The graphs enable interpretation of degree of melt strength for different linear polymers.

Melt elasticity produces memory and is related to the die expansion. Melt strength of the molten polymer determines whether the polymer remains foam after exiting the die or collapses onto itself. During the polymer processing the flow properties are determined by the viscosity versus temperature curve.

The three rheological test modes; Creep (Transient), Frequency Sweep (Dynamic), and Capillary (Steady) are

distinguished by the way the strain is applied, and are currently used to evaluate zero shear viscosity, molecular weight, branching, and melt strength of polyolefins. All three methods are all performed at isothermal conditions. The processing of polyolefin foams covers a wide temperature range, from melting, processing, cooling, and die conditions. To cover the entire process many isothermal tests are performed which takes time. Each of the isothermal tests is 15 to 30 minutes; to cover the entire temperature range requires 4-8 hours per sample material.

Frequency sweep data measures the zero shear viscosity and provides information about a polymers molecular weight, and the branching. We saw an increase in sensitivity as the testing frequency decreased. The foam processing is directly influence by temperature. Combining the two, frequency and temperature relationship, we need to define a new point of view, the foam processibility window. The functional relationship between tan δ and the complex viscosity characterizes and fingerprints every polyolefin material.

Experimental:

The dynamic mechanical analysis was conducted using a Rheometrics SR5 Rheometer. The instrument was equipped with electrically heated plates, Pyrex glass outer chamber, nitrogen gas purge, and the test fixtures (tooling) were parallel plates. The plates were 25 mm in diameter and the distance between plates was 1.0 mm. The plate distance (gap) and upper plate were set and calibrated at 190°C.

The ASTM D-4440 (similar to ISO 6721-10 [6]) test method was modified by decreasing the frequency while increasing the measurement time.

Data analysis was performed using Orchestrator™ software. Calculations and data conversion were programmed into the software.

The materials selected for this study were either virgin or recycled materials.

Results and Discussion:

Temperature ramp data is reported as storage and loss modulus and complex viscosity as a function of temperature [1], Figure 3. From the basic data we calculate the tan δ, which is the loss modulus divided by the storage modulus, then the log of tan δ and log of the complex viscosity.

The functional relationship between tan δ and the complex viscosity provides information about the molecular structure and a "fingerprint" of the polyolefin melt behavior during processing.

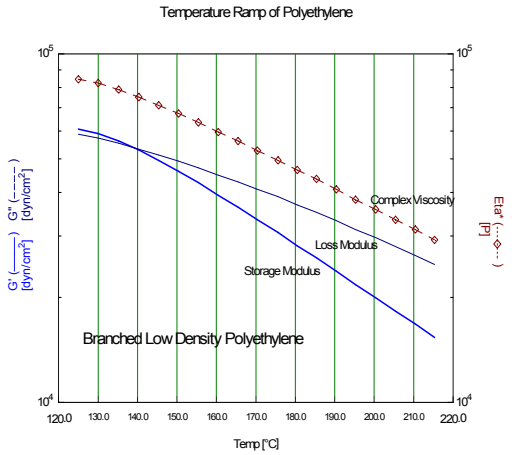

Figure 3, Storage and Loss Modulus and Viscosity versus Temperature

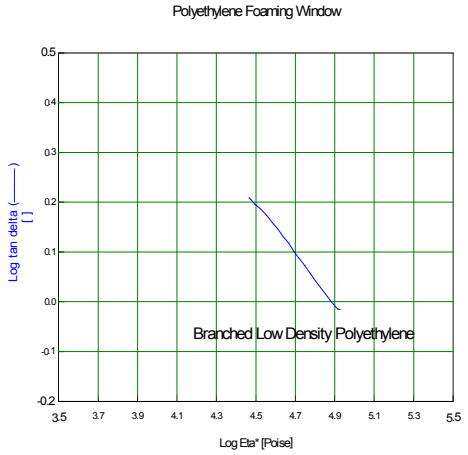

Figure 4, Polyethylene Processibility Window

The processibility window is the plot of tan δ versus the complex viscosity. The graphs can be in either liner or log formats, Figure 4. The most preferred format is Log-Log data on a linear scale because the linear relationship is easily expressed.

Comparison of the tan δ vs. complex viscosity relationship functionality for foams and nonfoamable resins has identified a "processibility window" for the polyolefinic foaming process, Figure 5.

The processibility window is typically a parallelogram shape and the most important part is the tan δ value. Secondly note the testing temperature range. Polyethylenes temperature range is 120°C to 220°C, and polypropylene temperature range is 180°C to 260°C. Viscosity is a function of the temperature. Tan δ is a function of the melt elasticity and strength. The polyolefin processibility window is the view of a material melt elasticity and strength as a function of viscosity.

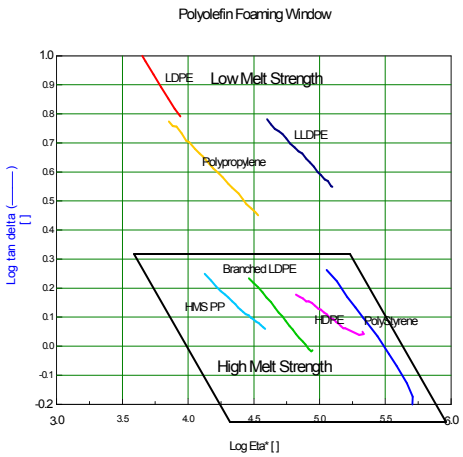

Figure 5, Polyolefin Processibility Window

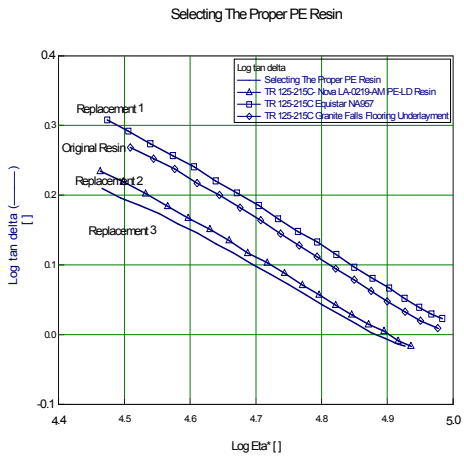

Figure 6, Selecting a Polyethylene Resin

Foam densities are controlled by numerous parameters and variables like processing conditions, additives, type of blowing agents, nucleating agents, resins and rheology modifiers, etc [7]. One phenomenon that most foaming experts will agree upon is when the foaming agent is increased the foam density decreases to a plateau. Then as the foaming agent increases the cell size increases and voids are formed. This plateau is related to the tan δ value in Figure 5. In order to reach a foam density of 16.0 kg/m^3 (1.0 pcf) the log (tan δ) value must be negative at the lower temperature values. For a foam density of 64.0 kg/m^3 (4.0 pcf) the log (tan δ) value would start around 0.06 at the lower temperatures then increase, based on experience.

Whether or not a polyolefin resin will make foam is determined by where the plot lies on the log (tan δ) versus log (complex viscosity) curve. Higher tan δ values limit the foaming to producing very high density foam. The lower the tan δ value, the higher the melt elasticity and melt strength and thus the increased ability to produce lower density foam. The preferred and ideal direction is lower viscosity (log complex viscosity) and low tan δ values. The ideal resin system plot would be in the lower left hand corner, Figure 5.

Finding a suitable replacement resin or using recycled material(s) can be costly using a trial and error method on production lines. Utilizing this rheological technique, we measure the current resin and establish target values. Figure 6 has data of the original resin and three possible replacements.

Figure 6 recommends replacement Resin 2 and 3 over Resin 1. Both Resins 2 and 3 had increased melt strength and decreased viscosity. Using the log-log plot to calculate the linear trend line, and solve the temperature difference for a similar viscosity value. If we choose replacement resin 2, the process temperature would decrease by 8.18°C to obtain the equivalent complex viscosity.

Conclusion:

Applying the rheological technique of a temperature ramp expressed as tan δ versus the complex viscosity provides invaluable information about the resin viscoelastic properties in a timely and efficient manor.

Comparison of current or original resin with proposed replacements, recycled material, or blends, can be employed to determine the best match and/or the temperature shift necessary. By knowing the direction to change the temperature and amount before starting pilot or plant trials saves time and resources.

References:

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