

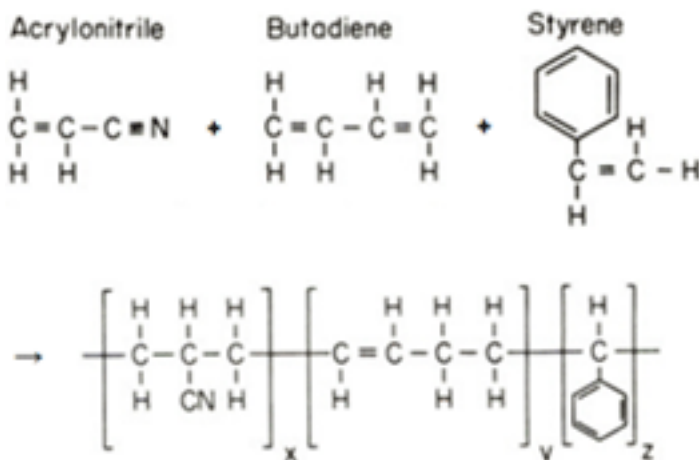
Effects of Temperature and Concentration on the Rheological Properties of Acrylonitrile-Butadiene-Styrene Polymer Solutions and Melts

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ABSTRACT Acrylonitrile-Butadiene-Styrene (ABS) is a ubiquitous polymer used throughout industry. The rheological properties of ABS are extremely important to know if one is designing a system that will extrude the polymer into various shapes, as it can help in determining what temperature the polymer should be, or how much force must be applied to the polymer to force it through a die. ABS is manufactured and processed in volatile solvents at high temperature and pressure. Thus, its rheological properties, or a measurement of how easily it flows, are highly sought after information. The rheological properties of ABS at 25 degrees Celsius and 1 atmosphere are well known. However, industry often requires for the temperature and pressure to be much higher, at around 100 atmospheres and 50-100 degrees Celsius, and concentrations varying from 40 to 70 weight percent. Solvents often used to synthesize ABS are also quite volatile; that is, they vaporize easily, which is only exacerbated by the high temperatures required, as the high temperatures cause the already volatile solvents to vaporize more easily at higher temperatures. This research seeks to quantify the rheological properties at high temperatures and at various concentrations. In order to determine the properties, a unique high-pressure rheometer will be used. The rheometer exerts a torque on the liquid at various shear rates, and measures the resistive force the liquid exerts on the rheometer to calculate viscosity. The rheometer also allows a pressure to be put over the polymer, which assists in preventing the solvent from vaporizing. The results obtained will be compared to theoretical models that require pressure, temperature, concentration, and molecular weight as input.

INTRODUCTION

Acrylonitrile-Butadiene-Styrene (ABS) is a polymer used all throughout industry. Thus an understanding of the behavior of ABS solutions would be significant in manufacturing, as the polymer is used in many high-volume applications including automotive components, plastic building blocks, and extrusion 3D printers. The plastic also serves countless other functions in many small volume applications, such as the casing for electronic devices, piping, musical instruments, and golf clubs. [1] ABS is generally synthesized by the polymerization of acrylonitrile and styrene in the presence of



polybutadiene, all of which are present in a solution of acetone and butanone, as seen in the reaction below. It can also be synthesized by grafting an acrylonitrile-styrene copolymer onto polybutadiene, which would produce a polymer with different mechanical properties. [2][3][4][5][6]

The rheological behavior of ABS at room temperature and pressure is well known, however the conditions present during manufacturing of ABS are far more extreme. Thus the behavior of the dissolved ABS/solvent solution must be observed at temperatures ranging from 50-100 degrees Celsius [3], which in turn requires higher pressures. This complicates the process, as ABS is synthesized in highly volatile solvents, which tend to evaporate before a test can be completed on the sample, skewing any results obtained. In order to prevent the solvent loss, and thus to prevent the ABS from becoming too concentrated, the rheometer being used must be sealed and pressurized. This presents a great challenge, since most rheometers are not designed for the temperatures and pressures present in commercial polymerization processes.

Further challenges are presented by the polymer itself, as it is extremely viscous at elevated temperatures, as can be seen in Figure 1; for comparison, the viscosity

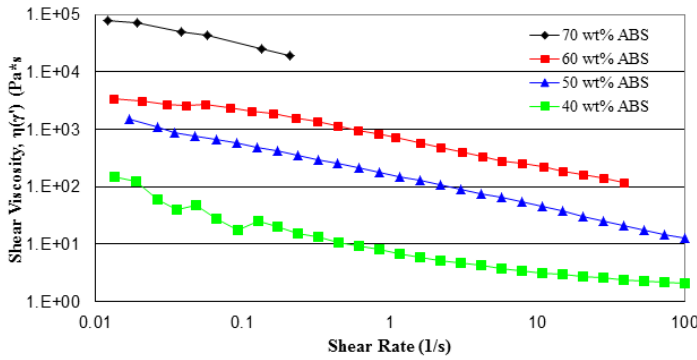


Figure 1: Shear Viscosity as a function of shear rate for un-sheared ABS/Acetone solutions at concentrations ranging from 40 to 70 wt. % ABS, temperature of 25°C, and pressure of 1 atm. of water at 25°C is 10-3 Pa*s. This presents difficulty for many rheometers, as the machines are usually rated for a maximum torque at which they can no longer analyze an ABS fluid. Figure 1 illustrates this phenomenon; during testing with the 70 weight percent ABS dissolved in acetone, the rheometer used was unable to rotate the fluid at a high shear rate, limiting the data that could be obtained.

It stands to be noted that the rheological behaviors of ABS solutions at high temperatures are not well documented, possibly due to the difficulties that must be overcome in order to analyze the polymer in these conditions. Because of the challenges presented, it would be of great benefit to manufacturers for the rheological behaviors that ABS solutions exhibit at industrial temperatures and pressures to be studied. The data would allow manufacturers and processors of ABS to predict pressure drop-flow rate relationships, design better solvent devolatilization systems, and better predict mechanical performance properties of ABS resins.

The next section, titled Experimental Methodology, describes how data were collected, and gives some equations that were used to analyze the data. The following section, titled Results and Discussion, comments on the results and illustrates constitutive models that fit the data so that extrapolation and interpolation may be done. The final section, titled Conclusions, summarizes the experiment as well as the important results.

EXPERIMENTAL METHODOLOGY

A unique rheometer developed by Anton Paar, the MCR 500, was used to determine how the rheological properties of ABS vary with temperature, pressure, time, and concentration. [7] The rheometer shears the fluid in a sealed vessel, which prevents solvent loss by allowing pressurization. A cross section of the rheom-

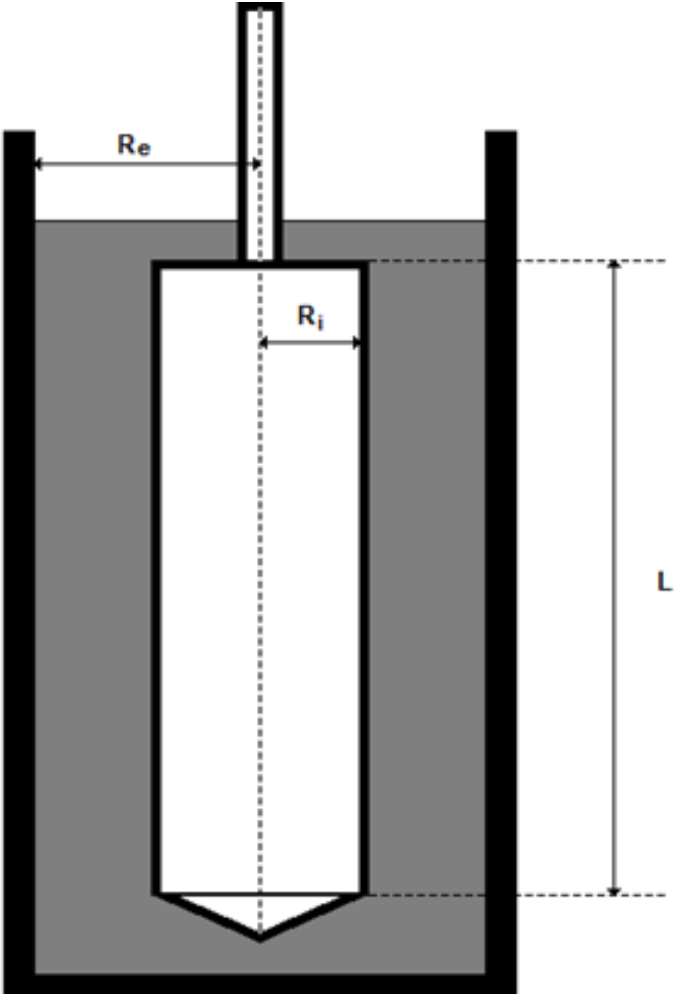


Figure 2: Rheometer cross-section view

eter can be seen in Figure 2, where the dark shaded region represents the fluid being sheared. When the fluid is sheared, a velocity profile is generated, with the fluid flowing faster closer to the bob, and slower closer to the edge of the container. From this velocity profile and the torque generated by the rotating bob, the viscosity of the fluid, defined as shear stress (τ) divided by shear rate (γ'), can be calculated from equation 1 [8], shown below. The variables Re, Ri, and L are illustrated in Figure 2, while η represents the viscosity of the fluid, M represents the torque the fluid exerts on the rheometer, and ω represents the angular velocity of the bob.

$$\eta = \frac{\tau(r)}{\dot{\gamma}(r)} = \frac{M / (2\pi * L * r^2)}{2 * \omega * R_i^2 * R_e^2 / r^2 * (R_e^2 - R_i^2)}$$

$$= \frac{R_e^2 - R_i^2}{4\pi * L * R_e^2 * R_i^2} * \frac{M}{\omega}$$

Equation 1

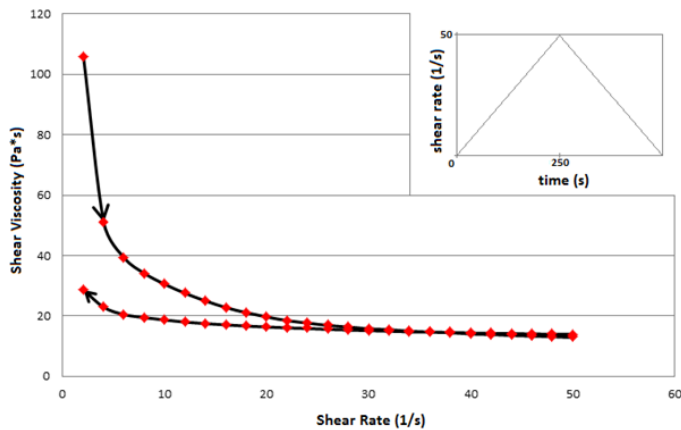


Figure 3: Demonstration of Thixotropy, 50 wt. % ABS in Acetone, 25 deg. C

The shear-thinning property of ABS manifests itself through the exponential decrease in viscosity as a function of shear-rate, and can be directly observed from the viscosity shear-rate plots. Figure 1 is a compilation of such results, illustrating the shear viscosity data for four different concentrations of ABS dissolved in Acetone at 25 degrees Celsius.

During the collection of data for the shear viscosity, it was observed that ABS is a thixotropic material; that is, upon shearing the material and seeing a viscosity drop due to shear thinning, the material's viscosity remains low once the shear is lifted. This phenomenon is demonstrated in Figure 3, which shows a hysteresis test of an unsheared 50 wt. % ABS polymer in Acetone at 25°C, and 1 atm. During a hysteresis test, the shear rate is increased linearly to a maximum of 50/s, and then decreased linearly back down to 0.01/s. Because of the thixotropic nature of ABS, the shear viscosity does not return to its initial unsheared value, but instead dramatically lowers, as can be seen by the bottom curve in Figure 3. A non-thixotropic material, such as polystyrene, would have zero area between the two curves, as the structure of the polymer does not degrade at high shear rates. This phenomenon will be commented on

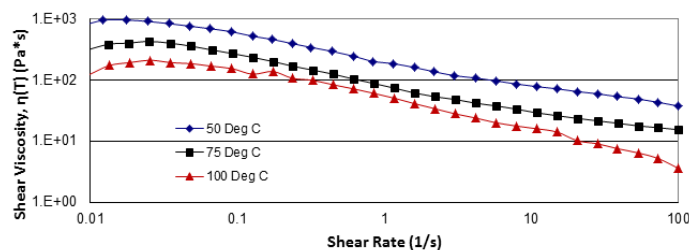


Figure 4: Shear viscosity as a function of temperature, temperatures ranging from 50°C to 100°C, 60 wt. % ABS in Acetone, pressure of 1 atm, unsheared samples

later, in the Results and Discussion section.

The dependence of the viscosity of ABS on temperature can be analyzed by heating the rheometer while simultaneously pressurizing it to prevent devolatilization of the sample. The cell was pressurized with carbon dioxide, an inert gas, so as to prevent a potential reaction taking place between either the gas and the polymer or the solvent. Figure 4 illustrates dependence of viscosity of ABS on temperature: as the temperature increases linearly, the viscosity drops exponentially.

RESULTS AND DISCUSSION

The shear viscosity data obtained from the Anton Paar rheometer were modeled using the Cross Model, with equation shown in equation 2 below [9].

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + (\kappa^2 \dot{\gamma})^{\frac{1-n}{2}}}$$

Equation 2

In this model, η_0 is the zero-shear viscosity, η_{∞} is the infinite-shear viscosity, typically taken to be the viscosity of the solvent, K and n are fitting parameters, and $\dot{\gamma}$ is the shear rate. Figure 5 illustrates the fitting of the cross model to shear viscosity as a function of shear rate. In Figure 5, the points represent experimental data, and the solid lines represent the prediction for the model. As can be seen, using the fitting parameters given in Table 1, the model found accurately predicts viscosity as a function of shear rate of ABS at 25 degrees C, demonstrating that the Cross Model can be used to extrapolate the viscosity data to different shear rates.

To further illustrate the dependence on concentration that viscosity exhibits, Figure 6 shows viscosity as a function of polymer concentration, for a constant shear

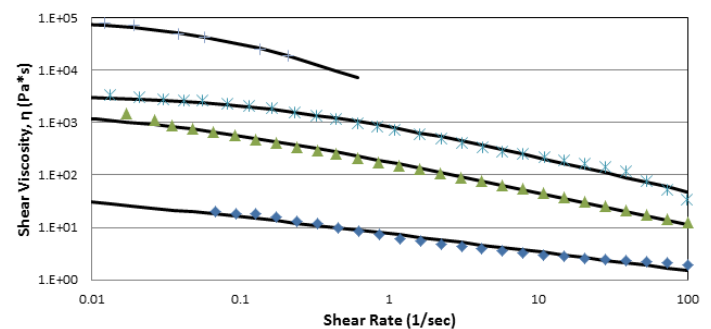


Figure 5: Cross Model fitting of ABS Shear Viscosity as a function of shear rate, 25 deg. C, 1 atm. Concentrations range from 70 wt. % to 40 wt. % ABS in Acetone, unsheared samples. Points are experimental data, lines represent the Cross Model.

| Polymer Concentration (wt. %) | η_0 (Pa*s) | η_∞ (Pa*s) | n | k |
|-------------------------------|-----------------|----------------------|------|-------|
| 40% | 100 | $3.1 \cdot 10^{-4}$ | 1.27 | 31.34 |
| 50% | 1800 | $3.1 \cdot 10^{-4}$ | 0.77 | 6.03 |
| 60% | 3500 | $3.1 \cdot 10^{-4}$ | 0.66 | 2.41 |
| 70% | 90000 | $3.1 \cdot 10^{-4}$ | 0 | 4.28 |

Table 1: Parameters used to fit the Cross Model to ABS/Acetone Solutions as a function of Shear Rate

rate, with trial 1 being an unsheared sample, and trial 2 being a sheared sample. The two trials indicate that after being sheared (thus inducing thixotropy), the polymer exhibits a larger dependence on concentration. Trials 1 and 2 have trend line equations given by the following: $\eta = (6 \times 10^{-15}) \cdot (C_{ABS})^{10.2}$, and $\eta = (5 \times 10^{-22}) \cdot (C_{ABS})^{13.9}$, respectively. As can be seen, trial 1, the unsheared sample, depends on the concentration of polymer as a 10.2 power, and trial 2, the sheared sample, depends on the concentration of polymer as a 13.9 power, indicating a higher dependence on concentration. Although these trends are based on just four data points, the trends hold very strongly, with r^2 values above 0.9.

The thixotropic behavior illustrated by the gap between the two curves in Figure 3 is possibly caused by the structure, which consists of rubber particles suspended in the polymer. This decrease is not permanent however, as the polymer will eventually relax and return to its former state. Equations 3 and 4, stated below, model this behavior of structure degradation and subsequent reformation.

In this model, τ_s is the yield stress, $\dot{\gamma}$ is the shear rate, η_∞ is the infinite viscosity, χ is a fitting parameter, t_a is the structure buildup or aggregation time, t_s is the structure breakdown or segregation time, and λ is a number between 0 and 1 that represents the amount of structure within the material, with 0 representing no

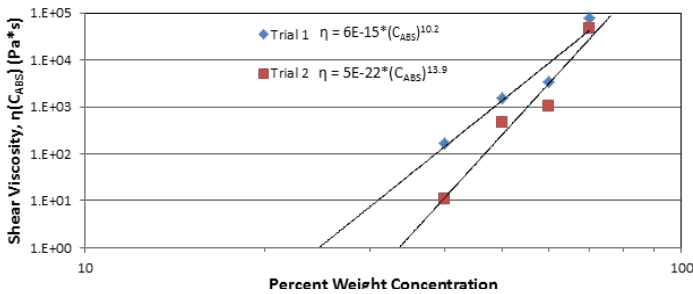


Figure 6: Shear Viscosity of ABS as a function of polymer concentration. Shear viscosities taken at a constant shear rate of 0.1/s, 25°C, 1 atm. Trial 1 used unsheared samples, trial 2 used sheared samples.

$$\eta = \frac{\tau_s * \lambda}{\dot{\gamma}} + \frac{\eta_\infty}{[1 - (1 - \chi) * \lambda]^2}$$

$$\frac{d\lambda}{dt} = \frac{(1 - \lambda)^2}{t_a} - \frac{\lambda^2}{t_s}$$

Equations 3 (top) and 4 (bottom)

structure, and 1 representing fully structured. [10] For ABS this would mean no interaction between individual polymer strands. In order to calculate η_∞ , the shear rate would need to be increased until the fluid's viscosity levels off. This value is the infinite viscosity, and is usually taken to be the solvent's viscosity. [10][11] The constant t_a can be calculated by shearing the polymer at a very high shear rate, then decreasing to a selected shear rate, and measuring the time the polymer takes to reach equilibrium. Similarly, to calculate t_s , the polymer is sheared at a very low shear rate, then increased to the same selected shear rate, and the time required for the polymer to reach equilibrium is measured. The selected shear rates should vary across the range of shear rates offered by a particular rheometer, and the times averaged. [10]

An additional model of this thixotropic behavior is the Maxwell Model, governed by equations 5 and 6, shown below. [9]

Here, τ is the shear stress, $\dot{\gamma}$ is the shear rate, and

$$\tau(t) = \int_{-\infty}^t G_0 * e^{-\frac{-(t-t')}{\lambda}} * \dot{\gamma}(t') dt'$$

$$\eta(t) = G * \lambda_t * (1 - e^{-t/\lambda})$$

Equations 5 (top) and 6 (bottom)

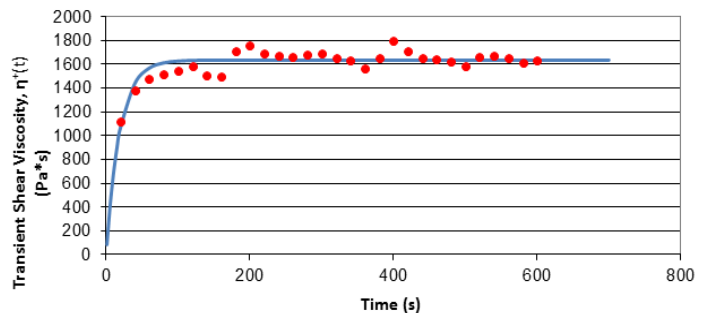


Figure 7: Maxwell Model to predict time dependent behavior of 50 wt. % ABS, 25 deg. C, and shear rate is 10/s

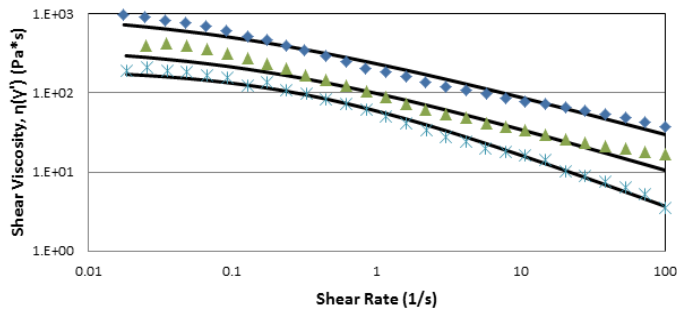


Figure 8: Cross Model fitting of ABS Shear Viscosity as a function of temperature, 60 wt. % ABS in Acetone, 1 atm. Temperatures range from 50°C to 100°C, unsheared samples. Points are experimental data, lines represent the Cross Model.

G and λ_t are fitting parameters, with values of 86.9 Pa and 18.8 sec respectively. Figure 7 illustrates this type of test, with experimental data as points and the model as a solid line. At a constant shear rate and temperature, viscosity as a function of time is measured. As can be seen, the viscosity rapidly increases from its decreased state and levels off at a steady state viscosity.

| Polymer Solution Temperature (°C) | η_0 (Pa*s) | η_∞ (Pa*s) | n | k |
|-----------------------------------|-----------------|----------------------|------|------|
| 50 | 1100 | $3.1 \cdot 10^{-4}$ | 1.01 | 3.75 |
| 75 | 400 | $3.1 \cdot 10^{-4}$ | 0.92 | 2.79 |
| 100 | 200 | $3.1 \cdot 10^{-4}$ | 0.65 | 1.90 |

Table 2: Parameters used to fit the Cross Model to 60 wt. % ABS polymer in Acetone Solutions as a function of Temperature

The cross-model, given by equation 2, was also used to model shear viscosity as a function of temperature, as can be seen in Figure 8. The parameters used to produce these curves are given in Table 2. As can be seen, the cross-model again accurately predicts the shear viscosity as a function of shear rate for different temperatures, indicating that the model could be used to predict shear viscosity at shear rates beyond what a rheometer is capable of reproducing.

In order to compare the experimentally determined viscosity as a function of temperature with a theoretical model, equation 7, the William-Landel-Ferry

$$a_T = \frac{\eta(T) * T_{ref} * \rho_{ref}}{\eta(T_{ref}) * T * \rho}$$

$$= \exp \left[\frac{-c_1 * (T - T_{ref})}{c_2 + (T - T_{ref})} \right]$$

Equation 7

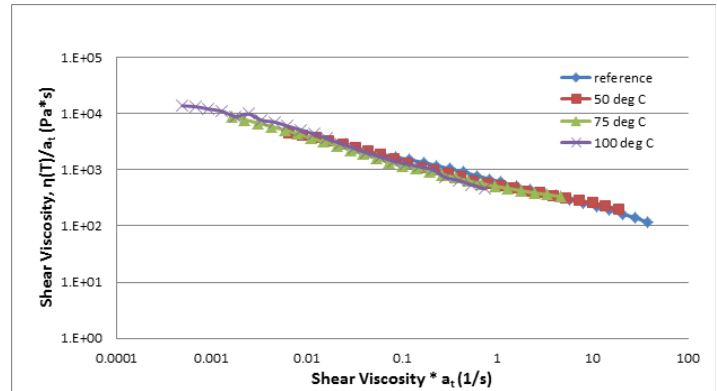


Figure 9: WLF Shifted Viscosity as a function of temperature plot, 60 wt. % ABS in Acetone at 1 atm, reference is 25°C.

(WLF) time-temperature superposition, shown below as equation 7, was used. [9]

| Temperature (°K) | a_t |
|------------------|-------|
| 298 | 1 |
| 323 | 0.19 |
| 348 | 0.046 |
| 373 | 0.014 |

Table 3: WLF Shift Factors used to produce Figure 9

To utilize this model, at least two data points in addition to the reference temperature are required. Tests were performed from 50 to 100 degrees Celsius in 25 degree increments. With the data from the 3 temperatures and the reference of 25°C, the shear viscosity curves were shifted to form a master curve, seen in Figure 9. The master curve was generated by dividing shear viscosity and multiplying shear rate by the a_t values found in Table 3. By convention, the a_t value for the reference temperature of 25°C was taken to be 1.

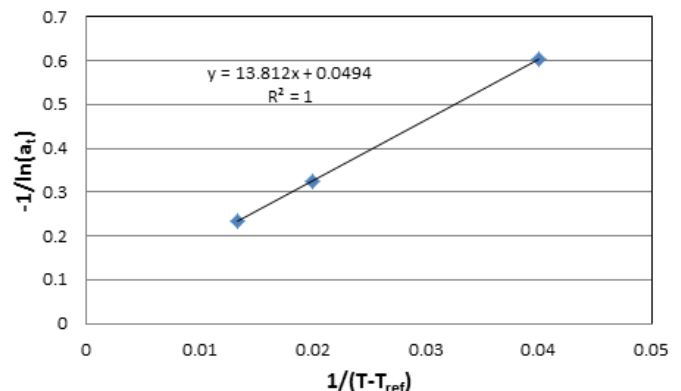


Figure 10: Graphical Determination of constants c_1 and c_2 via linearization of WLF relation

Since the other three at values are less than one, this results in the upward shift of shear viscosity, allowing for the master curve to be generated. Then, equation (7) was linearized in order to calculate the constants c_1 and c_2 , which were determined to be 20.2 (unitless) and 279.6°K, respectively. This linearization is shown in Figure 10, where the slope of the trend line represents the ratio c_2/c_1 , and the y-intercept represents $1/c_1$, as determined from the linearization of equation (7).

CONCLUSIONS

Samples of Acrylonitrile-Butadiene-Styrene (ABS) were sheared in a unique sealed rheometer in order to determine the viscosity of the polymer as a function of time, pressure, temperature, and concentration. This information is extremely important, as ABS is a high volume use polymer, meaning that manufacturers would greatly benefit from viscosity information, as it would allow them to better predict mechanical properties, as well as pressure drops in piping systems that transport the material. While the viscosity of ABS at room temperature and atmospheric pressure are well known, the conditions present during the manufacturing process are far more extreme. Further complicating the process are the solvents used to synthesize ABS, which are highly volatile and thus vaporize easily at atmospheric pressure. The sealed Anton Paar rheometer prevents solvent loss by allowing the cell to be pressurized.

There was found to be a strong relationship between shear viscosity and polymer concentration, as well as a very strong relationship between shear viscosity and temperature. During the data acquisition, it was also found that the viscosity is a function of shear history, meaning that if the sample had been recently sheared, the thixotropic behavior of ABS would temporarily cause a decrease in viscosity.

Models were then fit to the shear viscosity plots as a function of time, concentration, and temperature, to allow for extrapolation and interpolation of the viscosity data to the needs of the manufacturer.

ACKNOWLEDGEMENTS

I would like to thank my research advisor, Dr. Kurt Koelling, for the advice he has given me throughout this project. I would also like to thank the Department of Industrial and Systems Engineering at Ohio State University for providing the pure polymer used in my studies.

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