

Rheological Studies on Radiation Modified Polyethylene Resins

Song Cheng and Ed Phillips*

Sterigenics Advanced Applications, 7695 Formula Place, San Diego, CA 92121-2418

* Corresponding author. Email address: scheng@sterigenics.com

Abstract

Radiation modification of polyethylene resins prior to end product conversion has brought about significant improvement of various properties of the resins and products made from them using extrusion based processes where the products are formed in the melt phase at different shear rates and extensional rates. Rheological characterizations including Rheotens measurements, capillary viscosity and melt flow stability were carried out on radiation modified HDPE and LLDPE resins and their un-irradiated base resins. It is shown that electron beam irradiation of the resins has significantly enhanced the melt strength due to long chain branching. This effect would be very beneficial to the processability of the radiation-modified resins for applications that demand higher melt strength.

Keywords: rheology, melt strength, polyethylene, radiation, long chain branching

1. Introduction

Over the recent years Sterigenics Advanced Applications has developed the RAPREX[®] family of radiation modified polyethylene (PE) resins, which are produced through pre-conversion radiation processing of PE resins in combination with additional proprietary processing. The irradiation is carried out at low radiation dose and under ambient conditions before the resin is converted to any formed part. It has been shown that despite the very low crosslinking degree it incurred, such modification could bring about significant improvement of properties on the resins and products made from them [1, 2]. The base resins were selected from a wide range of commercially available PE resins including high density polyethylenes (HDPEs) and linear low density polyethylenes (LLDPEs). Our previous fundamental characterizations of the radiation-modified PE resins indicated that radiation gives rise to long chain branching and oxidation on the polymer chains [3].

It is well known that the melt strength of polyolefins is related to the molecular structure of the polymers, including the molecular weight distribution and the degree of branching. Long chain branching in polyolefins is known to decrease the melt flow rate and enhance the melt strength of the polymers [4]. Long chain branching was created in polypropylene (PP) to increase the melt strength and produce commercial high-melt-strength (HMS) PP resins [5]. One of the methods for inducing long chain branching in PP was by ionizing radiation [6]. Branched HMS PP was blended with linear PP to obtain good foamability that came from a good balance of high melt strength and high

melt extensibility [7]. Low density polyethylene (LDPE) was shown to have higher melt strength than HDPE and LLDPE because LDPE had higher branching degree and broader molecular weight distribution [8]. Higher melt strength of PE was related to improved bubble stability for film blowing [8]. Blending LDPE with LLDPE brought up the enhancement of the melt strength for LLDPE, and synergistic effects were found for the blend [9].

With the understanding that the low dose radiation modification of PE resins results in long chain branching in the polymer, it is expected that the melt properties of the modified PE resins would be modified accordingly. In this paper the results from rheological characterization including Rheotens measurements, capillary viscosity and melt flow stability are reported for radiation-modified HDPE and LLDPE and the results are compared with those for the un-irradiated control resins.

2. Experimental

2.1. Materials

R-100A and R-200A are radiation-modified HDPEs and R-300A is a radiation-modified LLDPE. All three contain additional antioxidants and stabilizers. R-100 Control, R-200 Control and R-300 Control are the un-irradiated HDPE and LLDPE base resins, which are all commercially available. Some of the basic properties of all the resins are listed in Table 1.

Table 1. Basics properties of the resin samples

| Property | R-100 Control | R-100A | R-200 Control | R-200A | R-300 Control | R-300A |
|--|---------------|--------|---------------|---------|---------------|---------|
| Melt Flow @190°C, 2.16 kg (g/10min.), I ₂ | 0.08 | --- | 8.7 | 0.85 | 1.0 | 0.24 |
| Melt Flow @190°C, 10 kg (g/10min.), I ₁₀ | 1.7 | 0.26 | 48 | 14 | 7.7 | 3.5 |
| I ₁₀ / I ₂ | 21 | --- | 5.6 | 16 | 7.7 | 15 |
| Density (g/cm ³) | 0.947 | 0.948 | 0.947 | 0.951 | 0.920 | 0.921 |
| Mn (Dalton, by GPC) | --- | --- | 15,500 | 11,100 | 50,100 | 47,400 |
| Mw (Dalton, by GPC) | --- | --- | 112,000 | 158,000 | 197,000 | 206,000 |
| Mw/Mn | --- | --- | 7.3 | 14.3 | 3.9 | 4.3 |

2.2. Rheological Characterization

2.2.1. Rheotens melt elasticity

Rheotens is a technology developed to quantitatively characterize the melt strength and extensibility of polyolefins. The instrument measures both melt strength and extensibility simultaneously by combining the capillary rheometer with a device that pulls the melt away from the capillary die at increasing strain rates and draw ratios. Drawing force (in cN) is measured by a force balance as melt strand extruded from the die is accelerated on take-away wheels. The maximum drawing force at rupture is defined as the melt strength. The velocity (in mm/s) at rupture is defined as the extensibility. The throughput from the

die remains constant. It is a relatively simple, fast but elegant way to relate rheological properties to melt processability [10]. A Geotfert Rheotens instrument was used. The test conditions are listed in Table 2.

Table 2 Test conditions for Rheotens

| | |
|--------------------|--------------------------|
| Wheel Position | Approx. 114 mm below die |
| Wheel Temperature | Ambient |
| Barrel Diameter | 12 mm |
| Die Entry Angle | 180° |
| Die Inner Diameter | 2 mm |
| Die Length | 30 mm |
| Dwell Time | 6 min. |
| Barrel Temperature | 190 °C |

2.2.2. Capillary rheology

Capillary rheology characterization of R-200A and its control resin was carried out using a RPA2000 instrument manufactured by Alpha Technologies. The melt viscosity was measured as a function of shear rate.

Capillary rheology characterization of R-300A and its control resin was carried out using a Geotfert capillary rheometer. The melt viscosity was measured as a function of shear rate according to ASTM D 3835-96. The test conditions are listed in Table 3.

Table 3 Test conditions for capillary rheology for R-300A

| | |
|--------------------|--------|
| Test Temperature | 190 °C |
| Initial Pressure | 0 MPa |
| Barrel Diameter | 12 mm |
| Die Entry Angle | 180° |
| Die Inner Diameter | 1 mm |
| Die Length | 20 mm |
| Preheating Time | 6 min. |

2.2.3. Melt flow stability

The melt viscosity was measured as a function of time at a fixed shear rate according to ASTM D 3835 - 96 Appendix X-1 using a Geotfert capillary rheometer. The test conditions are listed in Table 4.

Table 4. Test conditions for melt flow stability

| | |
|--------------------|-----------------------|
| Shear Rate | 92.46 s ⁻¹ |
| Test Temperature | 190 °C |
| Initial Pressure | 0 MPa |
| Barrel Diameter | 12 mm |
| Die Entry Angle | 180° |
| Die Inner Diameter | 1 mm |
| Die Length | 20 mm |

3. Results and discussion

3.1. Rheotens curves

Fig. 1 shows the Rheotens curve of R-100A as compared with that of the R-100 Control. As the more linear R-100 Control is extended, it exhibits an apparent increase in melt tension as the extensibility is increased. However, the slope of the curve starts to decrease at the extensibility of about 65 mm/sec. In the curve for the branched R-100A, the increase in melt tension continues as the extensibility increases and the slope of the curve does not decrease but increases instead until the melt strand comes to the break (i.e., strain hardening). The melt strength of the branched R-100A at break (at the same extensibility of about 85 mm/sec) is two times that of the melt strength of its more linear precursor (37 cN vs. 18 cN).

Fig. 2 shows the Rheotens curve of R-300A as compared with that of the R-300 control. The comparison is even more dramatic between the branched R-300A and its more linear precursor R-300 Control. At 70 mm/sec the LLDPE R-300 Control begins to exhibit melt instability in the form of a sinusoidal, undulating, thick-and-thinning draw resonance. R-300A does not have any such melt resonance before the break at about 105 mm/sec. The melt strength of the branched R-300A at the breaking point is about 5 times that of its linear precursor before the draw resonance occurs (20 cN vs. 4 cN).

It is known that the melt strength of PE increases with the decrease of the melt flow [4, 8, 9]. The most striking change for the radiation-modified PEs is the drastic decrease of the melt flow index (Table 1). So the increase of melt strength is expected.

The significant enhancement of melt strength may be translated to improved processability for various melt processes [4]. Some processes require adequate melt strength at high extensibility, i.e., strain hardening. For example, in extrusion coating, the melt curtain is pulled from the die onto the substrate at draw ratios greater than 100:1 and at line speeds greater than 1,000 ft/min (5,000 mm/sec). Linear polymers usually exhibit neck-in and sometimes show melt resonance at draw ratios and extensibilities far below the process requirements for economic production rates. In foaming applications, enhancement of melt strength and extensibility would mean improved foamability [7]. In thermoforming and blow molding, after the mold closes and forming pressure is applied, extensional rates are accelerated and the polymer must resist thinning as material is distributed into the far corners of the part. Polymers exhibiting strain hardening or high extensional melt strength deform uniformly as stress is applied to the melt. The R-100A and R-300A resins in this study clearly possess such strain hardening behavior and should show good processability.

3.2. Melt Viscosity vs. Shear Rate

Fig. 3 shows the melt viscosity vs. shear rate curves on a logarithm scale for R-200A and R-200 Control. Both samples show typical shear-thinning behavior. The melt viscosity

was increased drastically after the radiation modification at lower shear rate, and the difference is greater when the shear rate is lower.

Fig. 4 shows the melt viscosity vs. shear rate curves for R-300A and R-300 Control. The melt viscosity was also higher after the radiation modification, but the difference before and after irradiation is smaller. This is consistent with the fact that R-300A has significantly less drastic increase of molecular weight distribution after irradiation than R-200A, as can be seen from the polydispersity (M_w/M_n) changes listed in Table 1.

It is important to view melt strength not only over a broad extensional rate range but also over a broad shear rate range. Different melt processes require different melt performance levels at low shear rates or high extensional rates. In some processes the melt polymer is required to exhibit high melt strength at low shear rates. For example, in melt phase thermoforming, when a large, heavy extruded sheet is heated to above its melting point in preparation for thermoforming, it is the high melt strength at the low shear rate that allows the material to support its own weight and not sag into the heating bank. For blow molding of large parts, the hanging parison will resist sagging if the polymer possesses such melt characteristics, which is also called sag resistance. R-200A has demonstrated such melt behavior.

3.3. Melt Flow Stability

Fig. 5 shows the melt viscosity vs. time curves for R-100A and R-100 Control. R-100A has higher melt viscosity than the R-100 Control. Both resins show slight decrease of the viscosity with time in the first 4 minutes or so, probably indicating some initial degradation. R-100A may have slightly more drop than the control. But both resins showed good melt flow stability from about 4 min. to about 20 min.

Fig. 6 shows the melt viscosity vs. time curves for R-300 and its control. R-300 has higher melt viscosity than the control. Both resins show slight decrease of the viscosity with time in the first 4 min. or so, but both resins showed good melt flow stability from about 4 min. to about 20 min. The curve for R-300 parallels that for its control very well, indicating very similar stability.

The melt flow stability of the radiation modified PEs may be a concern because there might be residual radicals in the polymer, which at melt temperature and with the existence of oxygen might cause thermal oxidative degradation. If that were to happen, there would have been significant decrease of the melt viscosity. Our results here indicate that that is not the case, at least for R-300A. We believe the good melt flow stability comes from the stabilizing effect of the additional antioxidants and stabilizers.

Conclusions

It is shown by this study that pre-conversion radiation modification of HDPE and LLDPE resins can bring about significant rheological changes despite the low crosslinking degree. Melt strength at high extensibility and melt viscosity at low shear can be enhanced. Melt

flow stability can be maintained. The rheology changes may be translated to improved processability for practical conversion processes, such as strain hardening and sag resistance. One subject this paper has not studied is the blends of irradiated PE resins with un-irradiated PEs. Blending may yield good balance of melt properties or may even exhibit synergetic effects. It would be interesting to characterize the rheology of the blends in future studies.

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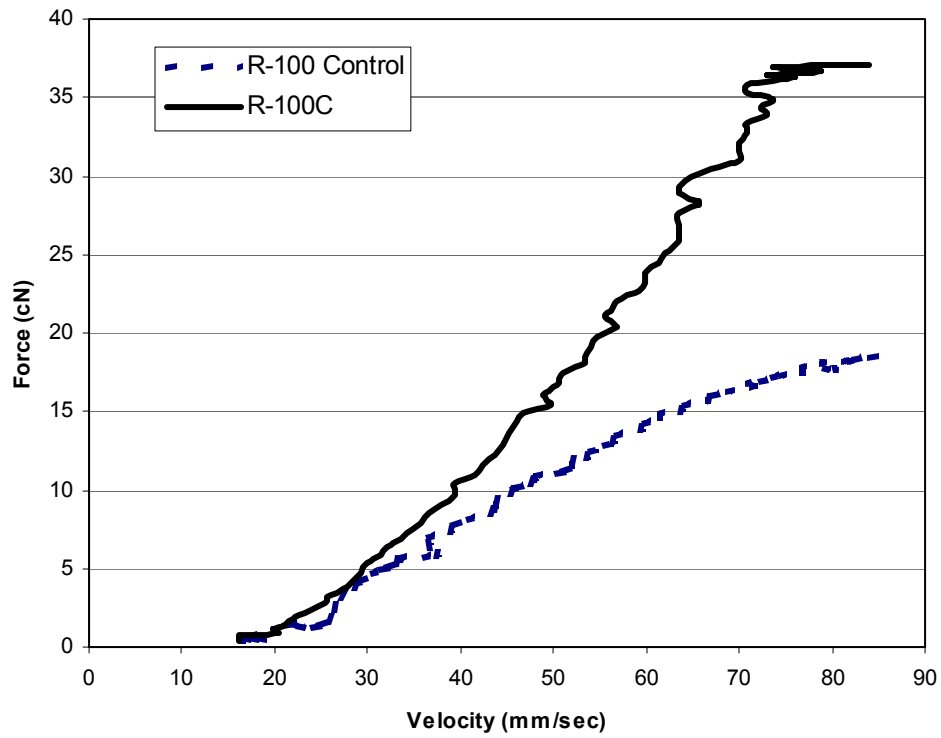


Fig. 1. Rheotens curves of R-100 and its control

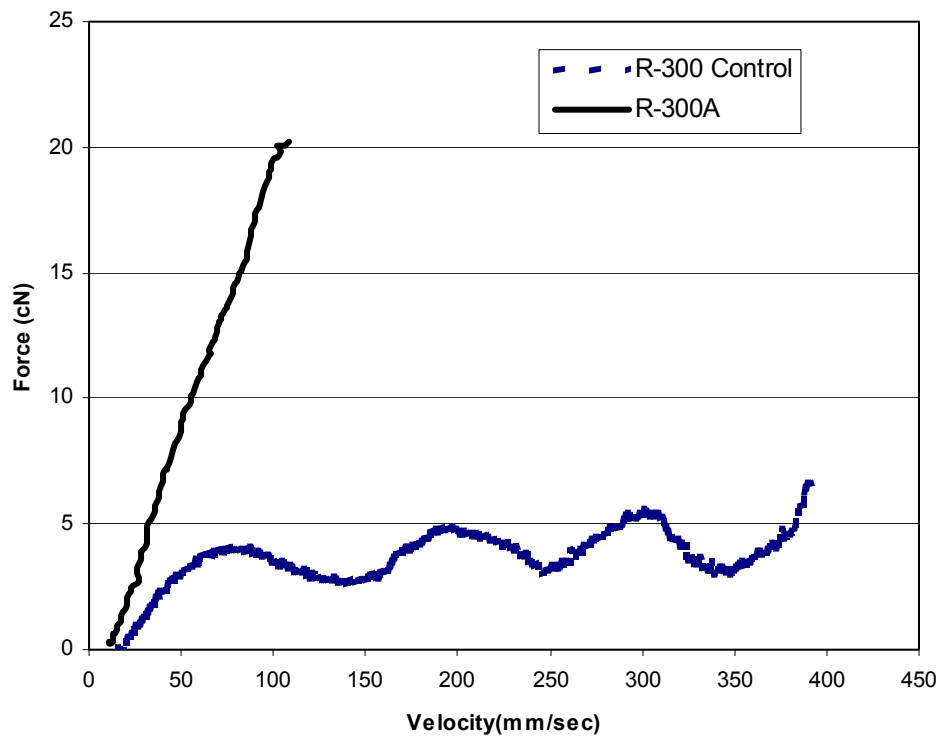


Fig. 2. Rheotens curves of R-300 and its control

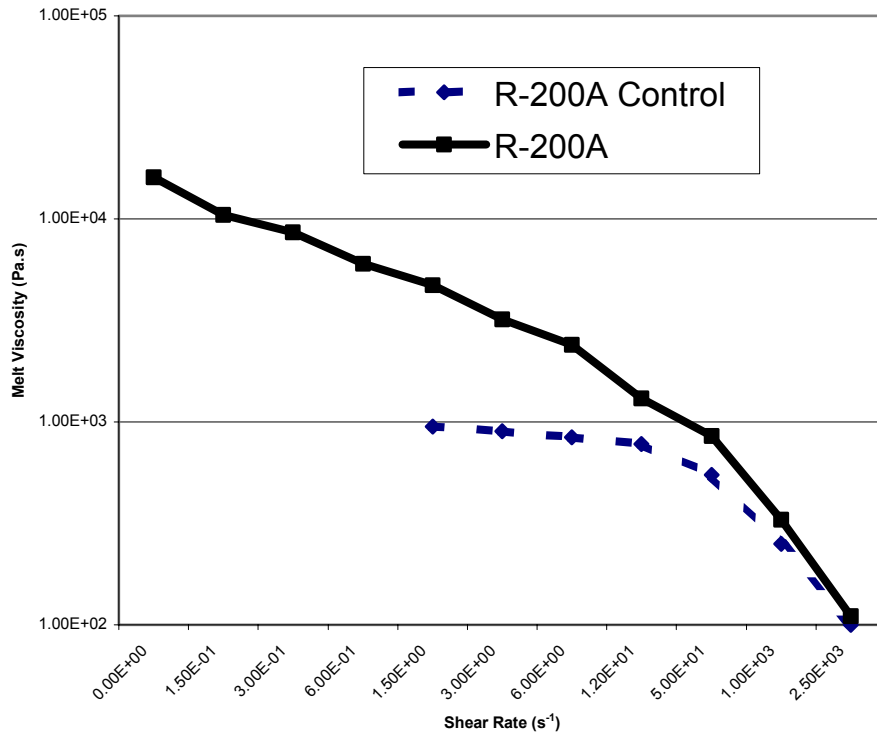


Fig. 3. Melt viscosity vs. shear rate for R-200A and its control

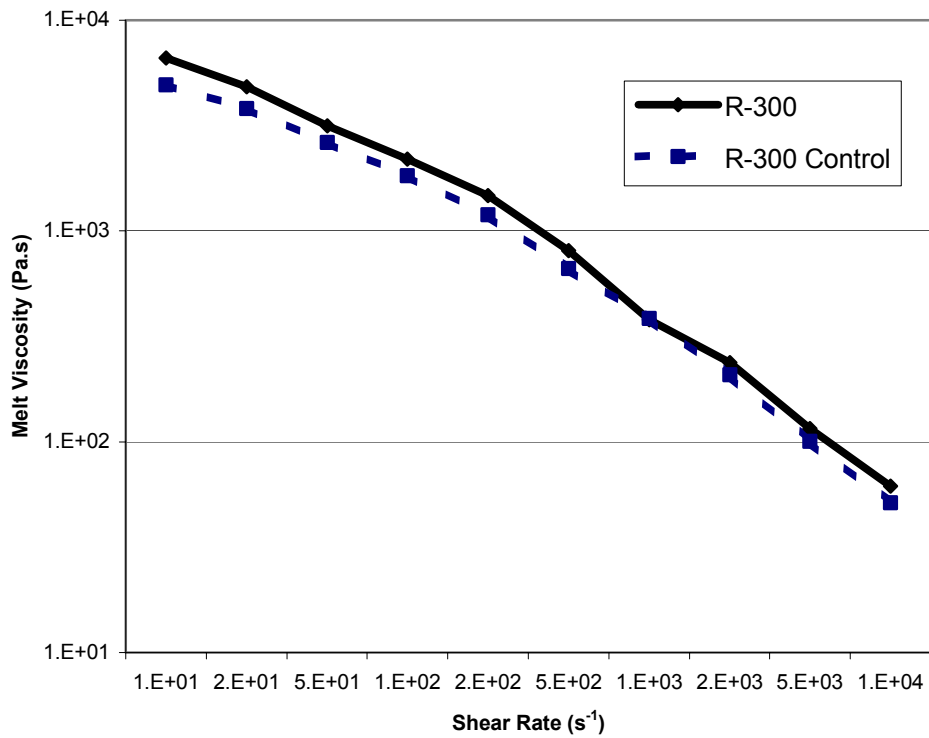


Fig. 4. Melt viscosity vs. shear rate for R-300A and its control

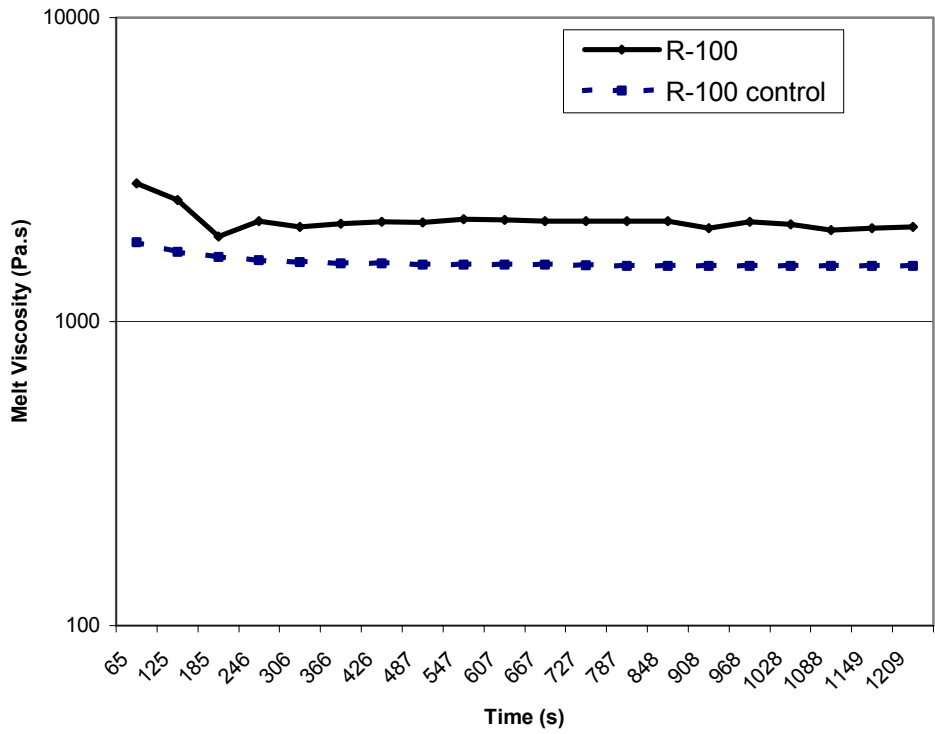


Fig. 5 Melt Flow Stability for R-100 and its control

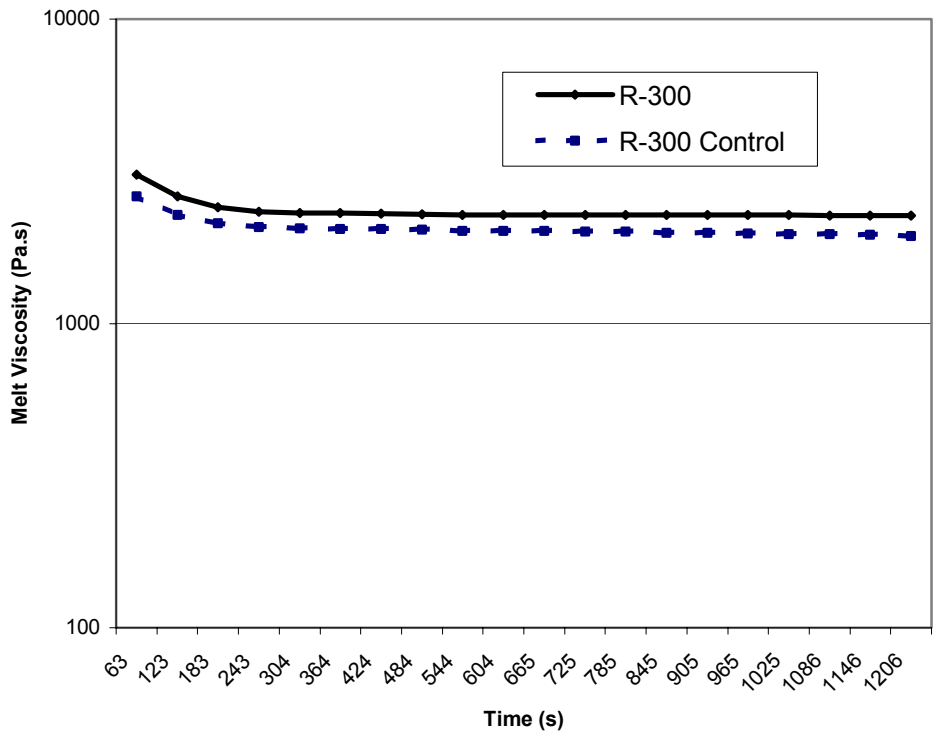


Fig. 6 Melt Flow Stability for R-300 and its control