Thermal stability and melt rheology of poly(*p*-dioxanone)

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Abstract Melt viscosities of poly(*p*-dioxanone) (PPDO)
samples having different molecular weights were studied
using a controlled-strain rotational rheometer under a
nitrogen atmosphere. First, PPDO's thermal stability was
evaluated by recording changes in its viscosity with time.
The result, that samples' viscosities decreased with time
when heated, demonstrated that PPDO is thermally unstable:
its degradation activation energy, obtained by using a mod-
ified MacCallum equation, was a relatively low 71.8 kJ/
mol K. Next, viscoelastic information was acquired through
dynamic frequency measurements, which showed a shear
thinning behavior among high molecular weight PPDOs, but
a Newtonian flow behavior in a low molecular weight
polymer (M_w = 18 kDa). Dynamic viscosity values were
transferred to steady shear viscosities according to the Cox–
Merz rule, and zero shear viscosities were derived according
to the Cross model with a shear thinning index of 0.80. Then
flow activation energy (48 kJ/mol K) was extrapolated for
PPDO melts using an Arrhenius type equation. This activa-
tion energy is independent of polymer molecular weight. A
linear relationship between zero shear viscosity and molec-
ular weight was obtained using a double-logarithmic plot
with a slope of 4.0, which is near the usually observed value
of 3.4 for entangled linear polymers. Finally, the rheological
behaviors of PPDO polymer blends having bimodal molec-
ular weight distributions were investigated, with the results
indicating that the relationship between zero shear viscosity
and low molecular weight composition fraction can be
described with a Christov model.

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1 Introduction

Poly(*p*-dioxanone) is an absorbable aliphatic polyetherester
that has been commercialized for medical applications. A
semicrystalline biocompatible homopolyester, poly(*p*-di-
oxanone) has unique properties attributed to its low glass
transition temperature and rate of hydrolysis [1–4]. How-
ever, compared to other commercially available absorbable
polymers, such as polylactide or polyglycolide, literature
focused on PPDO is scarce. Most research dealing with this
polymer has been directed towards discussion of either its
structural characterization or biodegradation behavior
[1–17]. Few studies on the polymer's melt rheology have
been published [18].

Rheology has emerged as a valuable technique to
associate the macromolecular structure with thermal pro-
cessing behaviors and the final physical properties of
polymeric materials [19]. Because polymeric molecules
have long chain structures, their flow properties and vis-
coelasticity differ from those of low molecular weight
materials. Polymers' flow properties are characteristic of
molecular structures and phase structures, and are affected
by processing conditions. Flow properties also affect
polymers' responses to thermal processing, which play a
role in determining thermal, mechanical, morphological,
and optical properties of end products. For absorbable
polymers, even the absorption rate can be affected by
thermal processing conditions. Therefore, it is essential to
understand the flow properties of absorbable polymers
under thermal processing conditions.

The general thermal instability of absorbable polymers
presents an immediate challenge to measuring their melt
rheology. As PPDO reportedly starts to degrade at tem-
peratures above 80°C [20], which is well below its
melting temperature, degradation occurs during viscosity

measurement, or even during sample loading at elevated temperatures. Thermal degradation also is a concern during thermal processing as it decreases a polymer's viscosity, eventually altering end products' mechanical properties, and perhaps accelerating end products' post-implantation deterioration.

Previous thermal degradation investigations of PPDO have mainly based on pyrolysis tests to monitor weight loss isothermally or non-isothermally [21–25]. Such studies have concluded, based on observed weight loss and analysis of volatiles, that the main mechanism for thermal degradation is zero-order unzipping depolymerization. However, no direct correlation between thermal degradation conditions and viscosity data have been published so far.

In contrast, this study measured thermal stability and melt viscosity of a series of PPDO polymers having a variety of molecular weights, and two bimodally distributed PPDO polymers prepared by melt blending two grades of PPDOs: PPDO68 and PPDO18. Thermal stability was analyzed first according to some empirical relationships to derive the thermal decomposition activation energy. This value can be used to compare polymers' relative thermal stability. Next, flow activation energy was derived using an Arrhenius type equation. Finally, viscosity decrease with addition of low molecular weight PPDO was tested, and an attempt was made to correlate the results with some empirical equations.

2 Experimental

2.1 Materials

PPDOs with different molecular weights were synthesized in-house by ring opening bulk polymerization. The molecular weights of the PPDO samples were measured by gel permeation chromatography (GPC) coupled with on-line multi-angle laser light scattering (MALLS) and refractive index (RI) detectors. The GPC/MALLS system was comprised of a Waters Alliance 2695 separation module, a Wyatt Optilab rEX Refractometer, and a Wyatt EOS multi-angle laser light scattering detector. Two PL HFIPgel columns (9 μm, 300 mm × 7.5 mm i.d.) from Polymer Laboratories were used for separation. Hexafluoroisopropanol with 0.02 M sodium trifluoroacetate was used as the mobile phase delivered at a flow rate of 0.5 ml/min. The weight-average molecular weight results obtained for these samples were considered "absolute."

In this paper, the name of each PPDO sample reflects its molecular weight. For example, PPDO with an average molecular weight of 68 kDa was named PPDO68. All PPDO binary blends were first mechanically mixed using a PK tumble dryer, and then, extruded into pellets using a

Davis-Standard extruder. Both the extruder's pump and die operated at 115°C with the screw rotation varying from 20 to 35 RPM depending on blend composition. The resulting discharged pellets were devolatilized to eliminate any volatile composition. All polymers contained 0.2% of D&C violet No.2 dye, which we believe did not affect rheological behavior.

2.2 Rheology tests

All tests were performed between a pair of parallel plates on a controlled-strain rotational rheometer (Advanced Rheometric Expansion System (ARES), TA Instrument, Inc.) equipped with a 2 k FRTN transducer and a forced air oven. Nitrogen gas was used to prevent the oxidation of samples at elevated temperatures. First, dynamic strain sweep tests at 10 rad/s were performed to obtain the linear viscoelastic region for the following dynamic time sweep tests and dynamic frequency sweep tests. To keep the transducer in its measurement range, for the low molecular weight samples, the strain for all the tests was 10% and the diameter of the parallel plates was 50 mm; all other samples were run at 1% strain using 25 mm parallel plates. Then thermal stability was tested using dynamic time sweep tests at 1 rad/s to check the viscosity drop with time at several temperatures. Dynamic frequency sweep tests also were performed from 1 rad/s to 100 rad/s to collect the viscosity change with increased oscillation frequency. To minimize thermal degradation during loading and thermal equilibrium, fresh samples for each measurement were loaded at 120°C and then heated quickly to experimental temperature under constant nitrogen flow with the furnace closed.

3 Results and discussions

3.1 Thermal stability of PPDO

Absorbable polymers are known to be thermally sensitive. In general, high temperature thermal processing can degrade a polymer by decreasing its molecular weight and thus its melt viscosity. Thermal degradation that occurs at high temperatures will shape to some degree the physical properties and biodegradability of end products made from polymers that have undergone thermal processing. Therefore, before characterizing a polymer's melt viscosity, per se, it first is necessary to understand how exposure to investigated high temperatures changes that polymer's melt viscosity with time.

Rheological parameters commonly are acquired using sinusoidal oscillatory measurements at small deformation. When polymeric material is deformed sinusoidally, the resulted stress will oscillate sinusoidally at the same

frequency, albeit shifted by a phase angle with respect to the strain wave. Mathematical decomposition of the stress wave into in-phase and out-of-phase components enables characterization of complex viscosity, a dynamic parameter describing a material's resistance to flowing [26]. The degradation profiles of different polymers can be determined and compared by measuring complex viscosity data with isothermal time.

Isothermal degradation of PPDO68 at several temperatures was investigated under a nitrogen atmosphere. Figure 1a shows the relative viscosity decrease of PPDO68 with time at constant holding temperatures from 120°C to 180°C. These temperatures were chosen because they are above PPDO68's melting temperature and also within the reported range of thermal processing temperatures [20]. All of the viscosity measurements were taken over the course of 30 min.
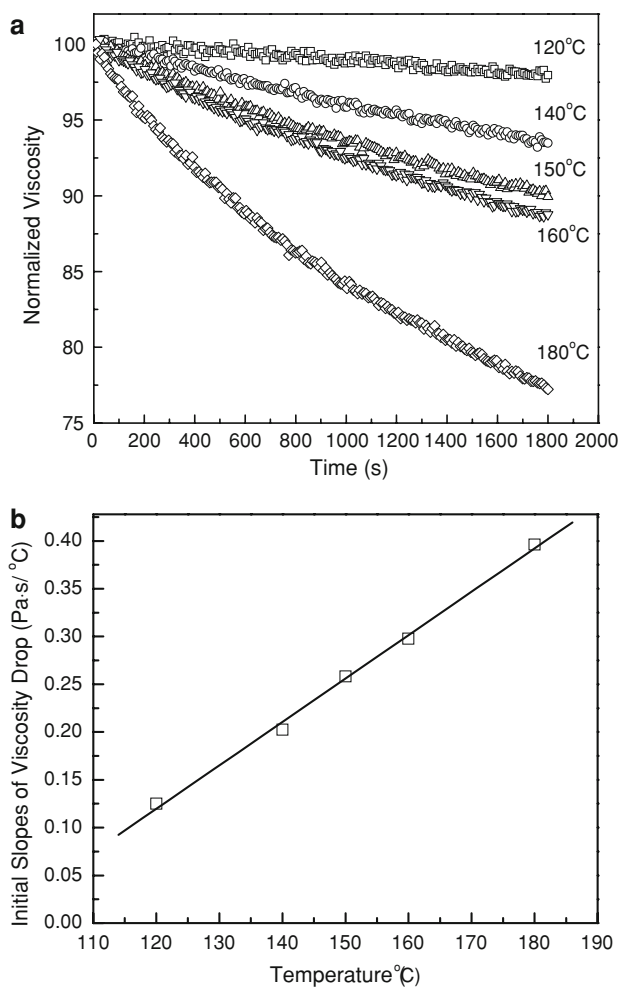

a

b

Fig. 1 (**a**) Thermal stability of PPDO68 at increased temperatures: decrease of normalized viscosity with heating time at different isothermal temperatures. (**b**) Thermal stability of PPDO68 at increased temperatures: viscosity drop speeds as a function of isothermal temperatures

At 120°C, viscosity dropped slowly with time in a linear pattern. Increasing temperature to 140°C speeded viscosity reduction, which remained linear. When the isothermal temperature was raised above 150°C, concave shapes in viscosity change were observed.

The viscosity change was first quantified by the initial slope change with isothermal temperatures in Fig. 1b. It was found that the initial slope increase with increasing temperature, which is reasonable because increasing temperature accelerates thermal degradation, leading to shorter chain products having lower flow viscosities.

To further quantify the thermal degradation, we attempted to analyze the results with some empirical relationships. Linearity failed when fitting the logarithmic melt viscosity as a function of time, a well-known relationship used to predict the thermal stability of random chain scission degradation. An equation recommended by MacCallum et al. [27], which previously was used to correlate the time for a weight loss to the isothermal degradation temperature, was modified to analyze our data quantitatively.

The original MacCallum equation is:

$$\ln t = \ln[F(1 - x)] - \ln A + \Delta E_d/RT$$

where t is time to achieve the weight loss x in measured temperatures, $F(1 - x)$ is an undefined function of X, and E_d is activation energy for thermal degradation.

In this paper, instead of measuring time to achieve a certain weight loss, we modified this equation to correlate the time at a certain viscosity decrease as a function of thermal processing temperature. This modification is justified because the viscosity reduction was induced by molecular weight decrease caused by thermal degradation. The correlation results are plotted in Fig. 2.
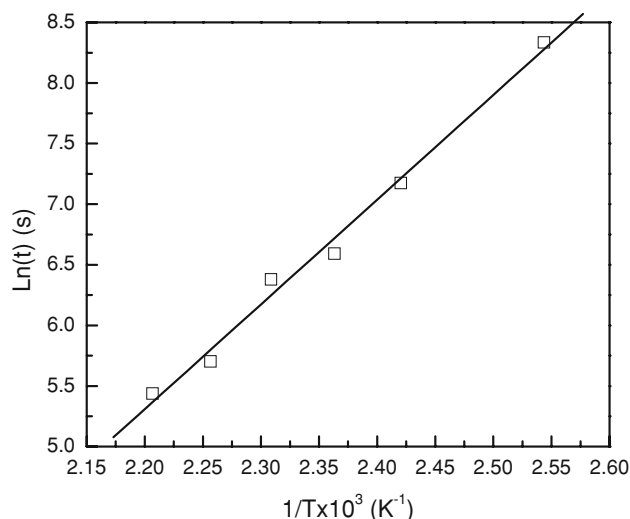

Fig. 2 Correlation of time at 95% viscosity with inversed isothermal temperatures using the MacCallum Equation

We observed that the logarithmic time for 5% decrease in viscosity increased in a linear fashion with the inverse of temperature (T^{-1}). The activation energy for PPDO68 was extrapolated from this relationship, and found to be 71.8 J/mol K. Measurements of the degradation profile of PPDO18 indicated that it was consistent with this relationship. However, a greater activation energy value (89.9 kJ/mol) was obtained for the lower molecular weight sample, indicating that it was slightly more thermally stable than the higher molecular weight sample.

3.2 Viscosity measurement

Because processing temperatures and shear rates affect polymeric melt viscosities greatly, rheological measurements of molten polymers can provide important parameters that help determine processing parameters. In most cases, thermal processing subjects polymeric melts to high steady shear under controlled pressure and temperature. However, when reproducing the measurements in laboratory rotational rheometers operated in steady shear mode, edge failure usually occurs at low shear rates, causing significant measurement error [26]. Therefore, small amplitude oscillatory shear tests generally were used to measure the melt complex viscosity. The measured complex viscosity can be directly transformed to steady shear viscosity by applying the Cox–Merz relationship [26]:

$$\eta(\dot\gamma) = |\eta^*(\omega)|; \quad \text{with } \dot\gamma = \varpi$$

where $\eta(\dot\gamma)$ is the steady shear viscosity and $\eta^*(\omega)$ is complex viscosity. The relationship between steady shear viscosity and shear rate can be described by some general viscous constitutive relationships. One commonly used relationship is the Cross model:

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

where η_0 is the zero shear viscosity, η_∞ is the viscosity at the high shear rate Newtonian limit, $\dot\gamma$ is shear rate, and k is a constant. By fitting the data with empirical mathematical models, two rheological parameters critical to thermal processing can be obtained: the zero shear viscosity (η_0) and shear thinning index (n).

Zero shear viscosity is the characteristic viscosity parameter obtained by extrapolating the shear rate to zero. It can be used to compare flow viscosities of different materials under identical conditions as an inherent parameter, and to calculate a material's flow activation energy, which is another important parameter to compare the flowability of different polymers.

Shear thinning index describes the strength of viscosity decrease with increased shear rates, where $n = 1$ indicates strong shear thinning and $n = 0$ indicates Newtonian flow.

This index is critical in the prediction of thermal processing parameters since most thermal processing occurs within a shear thinning zone at high shear rates [19].

Dynamic frequency sweep tests were used to measure PPDO's melt viscosity at intervals of 10°C between 110°C and 180°C. Results showed that PDS melts with high molecular weight (68 k) exhibited a shear thinning behavior typical of most polymer melts (Fig. 3a), while low molecular weight samples (18 k) exhibited a Newtonian flow behavior (Fig. 3b). The dynamic viscosity was transformed to a steady flow one using the Cox–Merz relationship, and the resulting steady shear viscosity was
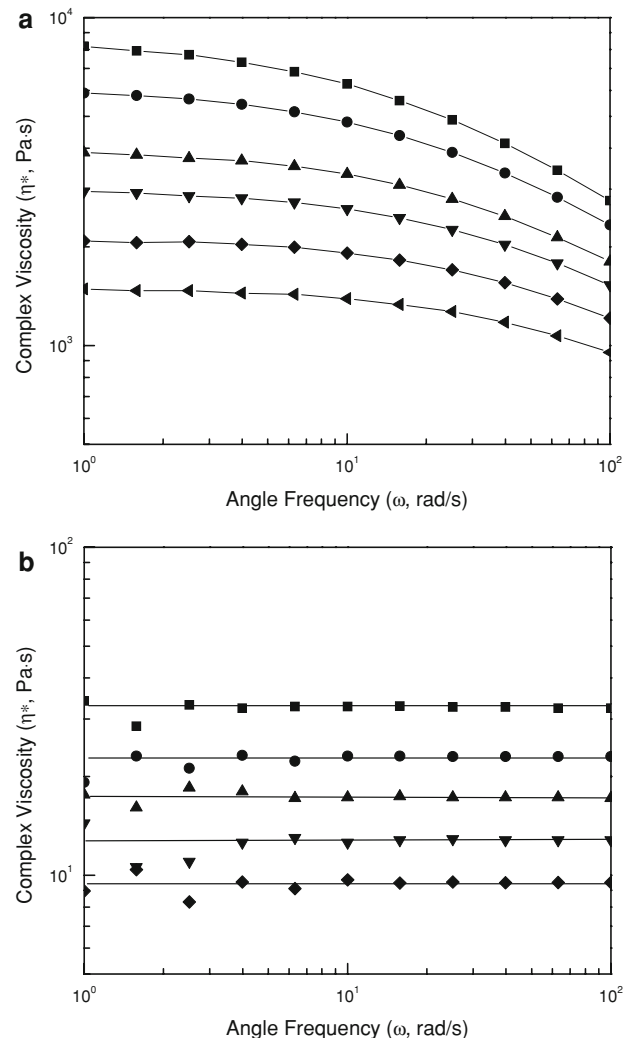
Fig. 3 (**a**) Change of PPDO melts' viscosities with oscillatory frequency at different temperatures: viscosity of PPDO68 showed shear thinning behavior. Solid lines are fit with a Cross model. Symbols: square, 120°C; dot, 130°C; up triangle, 140°C; down triangle, 150°C; diamond, 160°C; and left triangle, 170°C. (**b**) Change of PPDO melts' viscosities with oscillatory frequency at different temperatures: viscosity of PPDO18 showed Newtonian flow behavior. Solid lines are fit with the Cross model. Symbols: square, 120°C; dot, 130°C; up triangle, 140°C; down triangle, 150°C; diamond, 160°C; and left triangle, 170°C

fitted to several general viscous constitutive relationships. The Cross model was the best fit for the experimental data, and the zero-shear viscosities (η_0) and shear-thinning indexes (n) at each experimental temperature were extrapolated.

It should be noted that the polymer degraded with time during measurement at high temperatures as shown in Fig. 1. This degradation lowered high frequency viscosity values that were collected later, which could have introduced error into the calculation of the shear thinning effect, causing an overestimation of η_0 and n. However, since each dynamic measurement needed fewer than 100 s, we believe the effect of such degradation on our determination of shear thinning dependence and zero shear viscosity is negligible.

These calculated zero shear viscosities were correlated further with inversed temperatures using an Arrhenius type relationship, the result being a clear linear relationship (Fig. 4) from which the flow activation energy of each PDS melt was derived. Samples with different molecular weights showed similar slopes; and intercepts increased with increased molecular weight (Fig. 4). It was concluded from the plots that the activation energy for PPDO is 48 kJ/mol K. This result disagrees with previously reported results for poly(ε-caprolactone) (PCL) rheology, which hold that activation energy decreases with increased molecular weight [28]. Contradictory results also were reported for other polyolefins. Additionally, the reported activation energy of PPDO is higher than that of PCL, despite their similar structures.

Rotational rheometers are capable of measuring the linear viscoelastic properties of polymer melts at limited frequency ranges. If the oscillation frequency is too high, edge failure, which would result in underestimated values,
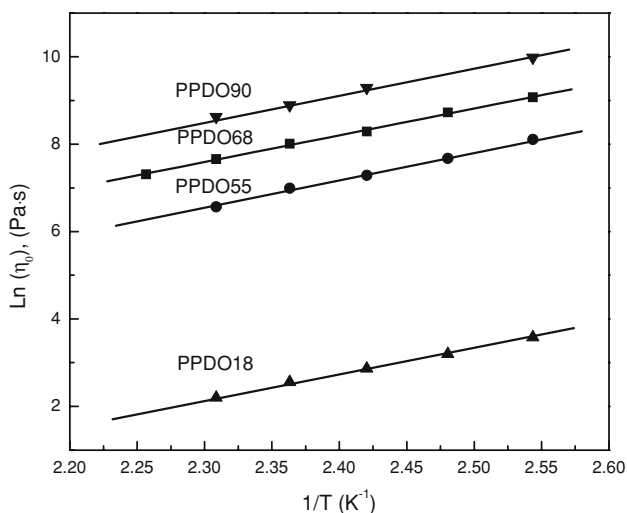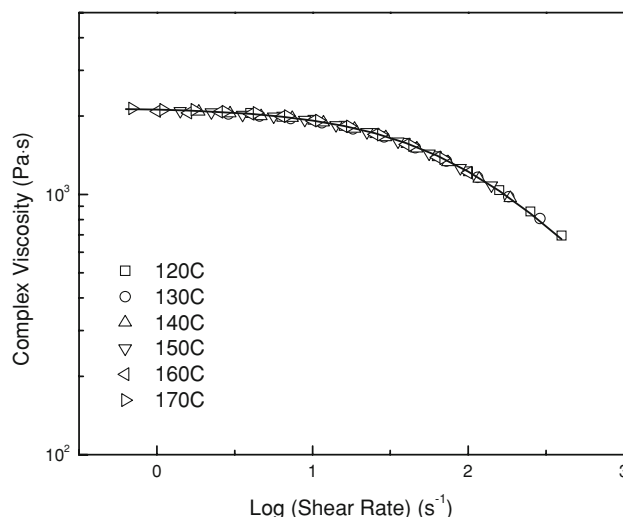

Fig. 5 Master viscosity curve of PPDO68 from time-temperature superposition using 160°C as reference temperature. The solid line is the best fitted equation for this curve: $\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1+(0.0076\dot{\gamma})^{0.8}}$

can occur. However, some thermal processing takes place at higher shear rates: extrusion may subject polymer melts to shear rates of 10^2–10^3 s^{-1}; during injection molding, more than 5,000 s^{-1} could be reached. So collecting viscosity data at high frequency is critically important for providing data for thermal processing at high shear rates, such as extrusion, molding, or melt spinning.

One way to expand the range of shear rates was to collect viscosity dependence to oscillation frequency at different temperatures, and then construct a master curve based on time temperature superposition (TTS). According to the Cox–Merz rule, dynamic viscosity as a function of frequency can be directly related to steady viscosity as a function of shear rate. We have superposed the viscoelastic results of PDS melts using the above obtained data and a good superposition can be obtained using TTS at a reference temperature of 160°C (Fig. 5). Complex viscosities in the broadened frequency range were calculated using its definition:

$$|\eta^*| = \frac{1}{\varpi}\left[(G')^2 + (G'')^2\right]^{1/2}$$

where G' is the in-phase elastic modulus, G'' is the out of phase viscous modulus, and ω is the angular frequency. It was found that the viscosity fit well with the Cross model and shear thinning index for PDS is $n = 0.80$.

3.3 Relationship between zero-shear viscosity and molecular weights

For linear polymers, a critical molecular weight (M_c) exists such that above M_c, polymer chains entangle together and the melt viscosity decrease with shear rates. When
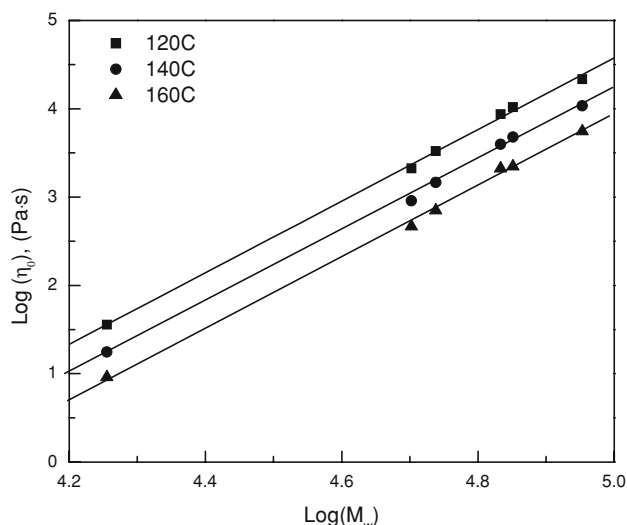

Fig. 4 Correlation of zero shear viscosity with inversed temperature and extrapolation of activation energy from experimental data

Fig. 6 Correlation of zero-shear viscosity (η_0) with PPDO molecular weight in a log-log plot

$M_w > M_c$, the measured zero shear viscosity is frequently observed to be proportional to the 3.4 power of molecular weight, $\eta_0 \propto M_w^{3.4}$; this index that could change slightly with molecular structures. While below M_c, the melt viscosity is usually independent of shear rates, and the measured zero shear viscosity is believed to be proportional to molecular weight, $\eta_0 \propto M_w$. Obtaining the relationship between zero shear viscosity and molecular weight, as well as the critical molecular weight, would be helpful in designing polymeric materials with particular thermal processability.

Viscosities of PDS with different molecular weights were measured using dynamic oscillatory sweep tests and transferred to steady shear viscosity using the Cox–Merz rule. The zero shear viscosities then were calculated using the Cross model. The results were correlated in a double logarithmic plot with their molecular weights at 120°C, 140°C, and 160°C (Fig. 6). A linear relationship having a 4.0 slope was found at each temperature, while the intercepts decreased with increased temperatures. The slope is close to the reported value (3.4) for most entangled linear polymeric material. It is interesting to note that according to the plot, the molecular weight of PPDO18 with M_w of 18 kDa was still above the critical entanglement molecular weight, although its complex viscosity did not appear to change with oscillation frequency in the frequency range tested (Fig. 3b), indicating a Newtonian flow behavior typically shown by short chain, unentangled materials.

3.4 Melt viscosity of PPDO blends

Polymers with bimodal molecular weight distribution could exhibit some unique advantages over mono-dispersed polymers. A small fraction of low molecular weight polymer could work effectively as a "plasticizer," lowering melt viscosity significantly for easier thermal processing. These polymers have additional advantage that they do not introduce new chemistry to a polymer. Besides, the bimodal distributed polymer have been reported to offer other preferred properties, such as more favorable crystallization kinetics, and increased bioabsorbability [29].

Homologous polymer blends prepared from the same chemical composition but having differing degrees of polymerization (i.e. molecular weight) were believed to be miscible down to the molecular level. The viscosity could be best described by the log-additivity rule:

$$\log \eta_b = \sum (w_i \log \eta_i)$$

where η_b and η_i are the viscosity of polymer blend and the ith composition, respectively, and w_i is the weight fraction of the ith composition. However, in many cases, positive or negative deviations were observed from experimental data. These deviations could have been caused by the interaction occurring in the blend system, by mixing that was by inadequate, and/or some concentration fluctuation in the blends. Some other empirical relationships were used to predict viscosity of those blended systems. Christov et al. proposed one relationship to describe the viscosity of polymeric blends with positive deviation [30]:

$$\eta_b^{\alpha} = \sum w_i \eta_i^{\alpha}$$

where α is an empirical parameter that can be derived from experimental data.

Melt viscosities of two polymeric blends prepared from PPDO60 and PPDO18 were measured using a dynamic
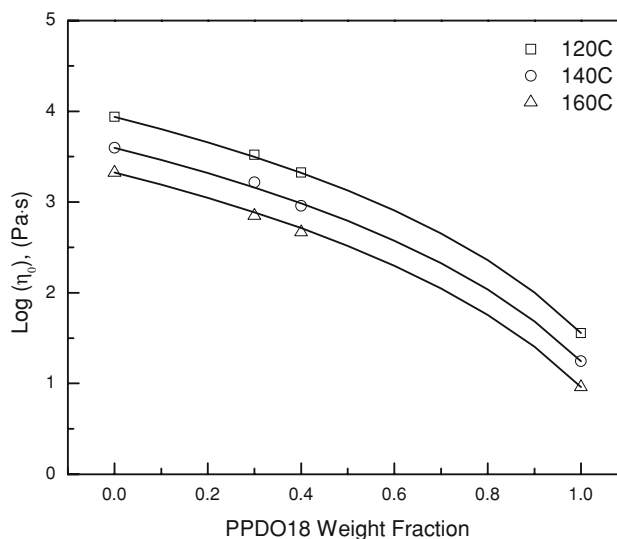

Fig. 7 Decrease of zero shear viscosity with increased low molecular composition incorporation at 120°C, 140°C, and 160°C and fit with the Christov equation with an $\alpha = 0.25$

frequency sweep test. The calculated zero shear viscosities derived from the Cross model were plotted versus the blends' compositions in Fig. 7. Results showed that at experimental temperatures of 120°C, 140°C, and 160°C, all data did not follow the log-additivity rule, but showed a positive deviation. Further analysis of these data showed that the Christov model best described our blend system at all three temperatures with a single index of $\alpha = 0.25$. This deviation implies that the mixing of this blend system is not homogenous at the molecular level; some concentration fluctuation could exist in the blends.

4 Conclusion

Thermal stability and melt rheology tests of poly(*p*-dioxanone) (PPDO) samples having different molecular weights showed the material's thermally instability in the melt. Increasing isothermal temperature accelerated thermal degradation as indicated by quickening viscosity reduction. Degradation activation energy was calculated from thermal degradation profiles by correlating degradation time at certain viscosity retention to inversed isothermal degradation temperature. Results showed that a lower molecular weight sample (89.9 kJ/mol K) was slightly more thermally stable than a higher molecular weight sample (71.8 kJ/mol K).

Experiments correlating viscosity dependence to oscillation frequency showed the shear thinning behaviors of higher molecular weight samples. The dynamic results then were transformed according to the Cox–Merz rule and fitted with the Cross model to derive zero shear viscosity and flow activation energy. Results showed that independent of molecular weight within the range tested, PPDO melts have a flow activation of 48 kJ/mol K. Fitting melt viscosity and shear rate with a Cross model gave a shear thinning index of 0.80. Plotting logarithmic zero shear viscosity with molecular weight revealed a linear relationship with a slope of 4.0, agreeing with the index for entangled linear polymers.

Finally, PPDO polymer blends from two different molecular weight samples also were tested. The relationship of composition to viscosity did not follow the log-addition rule, showing instead a positive deviation with a Christov model index of 0.25.

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