ABSTRACT: Earlier published rheological data of methyl methacrylate (MMA) heated and isothermally polymerized at temperatures between 50 and 80 °C have been reanalyzed using three semiempirical models of viscosity advancement including a modified Boltzmann sigmoidal model, a microgel model for cure, and a first-order isothermal kinetic model. These alternative models possessed few fitting parameters and could be used without requiring more experiments to be run. For each dataset as a function of temperature, the analysis resolved time constants associated with both the induction time for polymerization and the rate of viscosity rise, which were inversely related to the polymerization temperature. We found the sigmoidal model the most robust to accommodate nonlinearities in viscosity advancement with radical polymerization of MMA.

INTRODUCTION

Characterizing polymer advancement is industrially relevant, and the development of both mathematical and physical models to describe the physics of conversion, molecular weight changes, and heat transfer has been advanced. Recent reviews have treated dynamic conversion in bulk radical polymerization,\(^1\)–\(^3\) and specific models have been developed for polypropylene,\(^4\) polyphenylene oxide,\(^5\) polymethyl methacrylate (PMMA),\(^6\)–\(^8\) other acrylates,\(^9\) polyamides,\(^10\) epoxies,\(^11\) norbornenes,\(^12\)–\(^15\) and low density polyethylene,\(^14\)–\(^15\) with the focus on plant efficiency and safety.\(^16\)–\(^17\) Similar rheological assessments during chemical reaction have also been performed with reactive extrusion.\(^16\)–\(^18\)

Simple phenomenological models have described these correlations, based on dynamic thermophysical property measurements. An excellent review article highlighted a range of different models of polymerization both in terms of viscosity advancement and thermodynamic heats of evolution.\(^19\) Regimes of fluid viscosity have been linked to the physical structure of the monomer and the gel as conversion progresses, which has been characterized in recent efforts by Cioffi using mixtures of styrene and butyl methacrylate.\(^20\) Much of the analysis is based on determining the Trommsdorff effect, the autocatalytic, polymerization-induced, conversion with intermediate stages defined primarily by diffusion and convection constraints.\(^3\)–\(^20\) The rate of change in viscosity at specific viscous ranges, and the induction times needed to trigger transitions from one zone to another are all measureable parameters and factors that can be included in the reaction engineering kinetics of polymerization.

Polymer sensitivity to the Trommsdorff effect has been sensed by differences in reactivity that are linked to dynamic viscosity changes. Determinations of dynamic viscosity parameters are achieved from fitting a power law model shown in eq. (1), where \(b\) is the power law exponent.\(^21\)

At low values of \(b\), there are no entanglements between polymerizing monomers; as \(b\) reaches intermediate ranges, polymerization is interpreted as constant with no diffusion limitations, and at high values of \(b\), the Trommsdorff region is observed where rising viscosity blocks both heat transfer and mass transfer effectively.

\[
\log \eta = \log a + b \times \log t
\]  

From an industrial processing perspective, the linkage between dynamic viscosity and material conveyance is a key for controlled polymerization.\(^20\)–\(^22\)

One reality with the power law model is that multiple regressions are required to characterize a single
dynamic viscosity curve, particularly if thermal runaway exists. As a result, interpretation is needed to resolve the individual stages of growth, and some resin mixtures clearly show a delineation in modes of behavior, whereas other filled resins with higher initial viscosity only show one slope in dynamic viscosity. Formulation influences clearly affect reaction kinetics as well as how fast viscosity changes during conversion and can be resolved. Although the power law is simplest, the dynamic viscosity influences from a reaction exotherm or branching during conversion may have stronger influence on dynamic viscosity complicating its broader use. Alternative mathematical relationships to define dynamic viscosity might be also worth considering.

Halley and McKay comprehensively summarized a large group of viscosity advancement models and provided links of what resins best fit these different empirical, semiempirical, and molecular conversion relationships. Alternative dynamic models include a first-order isothermal model [Eq. (2)] and the microgelation model [Eq. (3)], which is obviously quite similar to the power law model. Both models also yield a time constant associated with conversion, and a second parameter tied to the initial viscosity.

\[
\ln \eta = \ln A + t/\tau \tag{2}
\]

\[
\log \eta = \log A' + b \log(1 + t) \tag{3}
\]

A third model we have deployed is a phenomenological sigmoidal model [Eq. (4)] that captures not only the nonlinear trend in polymerization but also can be adjusted using form fitting parameters to include an initial viscosity and an end-point asymptotic viscosity limit as shown in Eq. (4).

\[
\log \eta(t) = \log \eta_\infty + \frac{\log(\eta_0) - \log(\eta_\infty)}{(1 + \frac{t - t_0}{\Delta t})} \tag{4}
\]

The Boltzmann model has four fitting parameters, several with physical significance. \(\eta_0\) is attributed to the initial viscosity of the resin. The terminal viscosity \(\eta_\infty\) is an upper bound in viscosity experimentally related to the torque limit of the viscometer. The induction time, \(t_0\), corresponds to time required for viscosity to rise halfway between \(\eta_0\) and \(\eta_\infty\) on a log scale. The other kinetic parameter, \(\Delta t\), correlates to the inverse of the slope of the viscosity rise. Increasing temperature results in a faster response in dynamic viscosity due to cure conversion and can be observed by the changes mostly in the time constants of the model. Theoretically, the sigmoidal model would predict an initial induction period of nearly constant viscosity followed by a transient period the slope of which is related to the reaction dynamics as advancement occurs. Both the induction period and the rate of slope rise in viscosity could be accommodated by adjusting the time constants. The model does not predict a viscosity reduction due to the initial cure exotherm but it successfully has tracked viscosity changes of several advancing resins including epoxies, polyurethanes, and acrylamides.

We compared all of these other models re-evaluating prior published results from Sangwai et al., which could be extracted for reanalysis. The results follow.

**EXPERIMENTAL**

Previously published reaction conversion results for free radical bulk polymerization of methyl methacrylate (MMA) were identified using a near isothermal polymerization process and comparing the dynamic effect of conversion on viscosity and growing molecular weight were collected for reanalysis. Briefly, those experiments determined conversion, \(x_m(t)\), \(M_d(t)\), and \(\eta(t)\) for near-isothermal (NI) experiments using a Haake® viscometer (M5 osc, Haake® Mess-Technik GmbH, Germany) modified to function as a cup and bob reactor/viscometer. NI polymerization was one in which temperature is increased rapidly from a preheated condition of 43°C to a temperature ranging from 50–80°C and fixed thereafter. There is a short time excursion (probably less than 1 min) to reach this isothermal end-point temperature after which isothermal polymerization occurs.

MMA was polymerized in the presence of 2,2'-azoisobutyronitrile (AIBN; SAS Chemicals, Mumbai, India) with initiator concentrations of 15.48 mol/m³ using an initial shear rate 10 s⁻¹ and reduced to 0.01 s⁻¹ with increasing conversion. The tabulated results of dynamic viscosity were exported into Origin 7.0 for reanalysis.

The datasets from the original manuscripts were extracted for \(\eta(t)\) and analyzed with the power law, first-order isothermal, microgel, and Boltzmann sigmoidal models described above for comparison and reported on in Table 1.
viscosity of the crosslinked network, \((\log \eta_\infty = 7.3)\) were fixed. The limitation on \(\log \eta_\infty\) is purely a torque constraint from the viscometer used and not a property of the polymer. Figure 3 compares all four different mathematical models for \(\eta(t)\) described for the MMA dataset polymerized only at 70°C.

The comparison of the sigmoidal model using the datasets with the power law model led to some obvious differences. First, it was necessary to link several regimes of rheology with different power law exponents to force different zones of polymerization to mesh together on one dynamic viscosity curve as shown for resins polymerized at \(T = 70\) and 80°C in Figure 2. The sigmoidal model more accurately describes a wider dynamic range of reaction-induced viscosity changes. Also, the determination of \(\eta(t)\) at both the initial stages and at higher conversion was not captured. There are rheometer torque limitations in the high shear regime and at high conversion. More experiments at higher conversion are needed to validate the accuracy of each model. At the low end, \(\eta_0\) for the simulated models should more closely represent that of the monomer mixture before polymerization. Activation energies regulating monomer viscosity and reaction kinetics would suggest lower initial viscosity and higher reactivity with higher polymerization temperature.

Figure 2 clearly shows the trend of reactivity, but the low threshold of the measured viscosity range is much higher than the initial monomer viscosity estimated to be 0.6 cP (\(6 \times 10^{-4}\) Pa s) at 20°C. Huets et al. reported that initial methacrylate viscosity drops to 0.45 cP (\(4.5 \times 10^{-4}\) Pa s) at 40°C and as low as 0.33 cP (\(3.3 \times 10^{-4}\) Pa s) at 70°C with a reported activation energy of \(-9\) kJ/mol. Part of the discrepancy is the lag time needed to initiate each experiment. This problem is magnified at elevated temperature as the fixed time needed to place the monomer leads to less sampling with higher reaction rates. It is also reasoned that the parallel plate shear mode is less accurate. Better characterization of the initial viscosity could clearly yield a more accurate model overall.

The kinetic parameters \(\Delta t\) and \(t_0\) from the two-parameter sigmoidal models fixing \(\eta_0\) and \(\eta_\infty\) (not

<table>
<thead>
<tr>
<th>Near-isothermal 70°C</th>
<th>First-order isothermal model</th>
<th>Microgelation model $\log \eta = \log A' + b \log (1 + t)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R^2)</td>
<td>0.993</td>
<td>–</td>
</tr>
<tr>
<td>(\log \eta_0) (Pa s)</td>
<td>0</td>
<td>(A)</td>
</tr>
<tr>
<td>(\log \eta_\infty) (Pa s)</td>
<td>7.3</td>
<td>(\tau)</td>
</tr>
<tr>
<td>(t_0) (Pa s)</td>
<td>60.79 min</td>
<td>–</td>
</tr>
<tr>
<td>(\Delta t)</td>
<td>3.94 min</td>
<td>–</td>
</tr>
</tbody>
</table>
allowing them to be part of the variable fit) are correlated as a function of $1/T$ in Figures 4(a,b). Both parameters have a $1/T$ Arrhenius dependence sug-

suggesting an activation energy barrier exists to poly-
merize MMA. Neither parameter is linear over the
30°C differential in temperature in an Arrhenius
analysis.

Removing the fixed constraints associated with $\eta_0$
(allowing it to vary as opposed to fixed parameter in
the Sigmoidal Model) leads a counterintuitive tem-
perature dependence on initial viscosity. Lower tem-
perature cure corresponds to measurements of lower
initial viscosity, which does not follow the Arrhenius
trend noted by Huets at the monomer stage.$^{33,34}$ The
increased reactivity at higher temperature coupled
with the gap in viscosity measurements at earlier
times in the cure profile may have led to early resin
advancement and increased the uncertainty with
resolving $\eta_0(T)$. If more data at the early stages of
cure were available, that would help. Efforts to raise
the accuracy of dynamic viscosity measurements
offer the strongest chance to yield the most accurate
picture of $\eta(t)$. Perhaps even more important is
the need to link the new sigmoidal model to a reac-
tion kinetics analysis model, so that $\eta(t)$ can be
linked with regimes of polymerization. The rheome-
ter seemed best suited for in situ tracking of instan-
taneous viscosity with conversion and might be less
accurate at either end of the $\eta(t)$ spectrum. It is also
appropriate to consider how the structure of the
growing polymer affected its rheology, similar to
work by Scorah et al. who varied initiator type and
observed differences in the resulting branch
structure.$^{35}$

**CONCLUSIONS**

Published data on MMA polymerization where $\eta(t)$
was measured in situ and previously analyzed using
the power model were reanalyzed using three other
mathematical models. The Boltzmann sigmoidal analysis yielded three fits at each polymerization temperature, with 2, 3, and 4 fitting parameters. These were also compared with the microgel and the first-order isothermal models for polymerization. The sigmoidal analysis represented a wider range of dynamic viscosity. The other models represent a significant fraction of the dynamic viscosity during polymerization, but the nonlinearities are less fully captured. The future use of the sigmoidal model is tied to link the kinetic parameters to functional molecular models of resin advancement with more accurate viscosity measurements at all degrees of conversion. This alternative representation offers stronger hope that a more accurate model to describe thermal runaway during polymerization can be developed.

S. K. Gupta and J. S. Sangwai are graciously acknowledged for providing the raw data for the reanalysis and S. K. Gupta for his insights on the initial analyses. F. Teyssandier also acknowledges fellowship support from Univ LYON 1.

References