

Model-free Kinetics Analysis of Thermal Degradation of Polysiloxane Lubricant

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Original scientific paper

Received: March 16, 2009

Accepted: October 1, 2009

Dedicated to the memory of Professor Dr. Valentin Koloini

The object of this study was to investigate the thermal stability and degradation kinetics of polysiloxane material used as lubricant in the die casting process of aluminium alloys. The degradation of dried polysiloxane emulsion was studied by thermal gravimetric analysis (TGA) using nitrogen atmosphere. Several non-isothermal experiments at different heating rates and isothermal experiments were performed. The isoconversional kinetic analysis using the integral procedure was applied to the non-isothermal TGA results. The apparent activation energy was calculated by the Flynn-Wall-Ozawa method as a reliable way of determining the kinetics parameters. Based on the determined apparent activation energy isothermal degradation behavior of the lubricant at different temperatures was predicted. The efficiency of the predictions was verified and confirmed by isothermal TGA experiments.

Key words:

Polysiloxanes, thermogravimetric analysis, isoconversional methods, model-free kinetics

Introduction

Due to superior thermal stability, polysiloxanes are widely applied in various aspects, such as lubricants, coating and adhesives for elevated temperatures. Researches show that polysiloxane is of higher thermal stability due to the higher energy of the Si–O bond (about 460.5 kJ mol⁻¹) relative to the C–O bond (358.0 kJ mol⁻¹) and C–C bond (304.0 kJ mol⁻¹).¹

Die-casting is the process of forcing molten metal under high pressure and temperature into mold cavities. To protect the die from wear and soldering, to help release the formed component, and to provide the adequate boundary conditions for the flow of material, the die casting industries use lubricants. Often, such lubricants are polysiloxanes, which are applied as water emulsion. In a die casting cycle, the emulsion is sprayed over the hot dies, where the liquid carrier evaporates, leaving behind a thin and uniform layer of solid lubricant. Afterwards, when the molten metal of temperature above 600 °C is transferred into the die, the polymer is exposed to extremely high heating rates and temperatures, and therefore degrades thermally.² The behaviors and mechanisms of the thermal degradation of different polysiloxanes used in several applications under different conditions have been studied.^{1,3–11}

The overall kinetics of thermal degradation processes is usually studied by using TGA. The overall kinetics is complex as it includes information on several simultaneous multiple steps. Disentangling overall kinetics represents a challenge that can only be met with computational methods that allow detecting and treating multi-step processes. Isoconversional methods are among a few methods that are up to this challenge.^{12–20} These methods yield the values of apparent activation energy as a function of conversion. Model-free isoconversional methods are among the most reliable for determining apparent activation energies of thermally stimulated complex processes. The most popular methods are represented by the differential method of Friedman (FR)¹⁵ and by the integral methods proposed by Ozawa-Flynn-Wall (OFW)^{16,19} or Kissinger-Akahira-Sunose (KAS).^{17,18} These methods enable isothermal simulations derived from nonisothermal data and allow the computation of complete conversion-time curves at a given temperature with no assumption on the reaction mechanism.

The object of this study was to investigate the thermal stability and degradation kinetics of polysiloxane material used as lubricant in the die-casting process of aluminium alloys. The experiments were performed by dynamic thermogravimetric analysis (TGA). For prediction of isothermal degradation behavior, the isoconversional method was used. The results were verified by isothermal TGA experiments.

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Experimental

Materials

Commercial polysiloxane emulsion (Safety Lube 2382, Chem Trend, Germany) used for high-pressure die casting industry of aluminium alloy.

Methods

Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/DSC1 instrument. About 20 mg samples of dried lubricant were placed in a 70 μL Al_2O_3 crucible. All the experiments were conducted in a nitrogen atmosphere with a flow rate of 30 mL min^{-1} and for all measurements the baseline was subtracted. By the dynamic experiments, the samples were heated from 50 to 800 $^\circ\text{C}$ using heating rates of 10, 15, and 20 K min^{-1} . The isothermal experiments were performed at temperatures 400, 440, 460 and 500 $^\circ\text{C}$.

Results and discussion

The thermogravimetric (TGA) curves obtained at heating rates of 10, 15, and 20 K min^{-1} representing residual mass versus temperatures are shown in Fig. 1. In the figure, it may be seen that the sample degraded between 350 $^\circ\text{C}$ and 550 $^\circ\text{C}$.

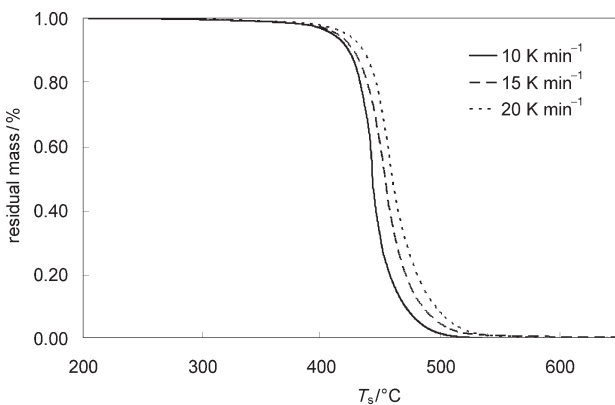


Fig. 1 – TGA curves for lubricant obtained at 10, 15 and 20 K min^{-1} heating rates under nitrogen atmosphere

The results presented in Fig. 1 were used for the isoconversional analysis by model-free method as described below.

All kinetic studies assume that the isothermal rate of conversion $d\alpha/dt$, is a linear function of the temperature-dependent rate constant, $k(T)$, and a temperature-independent function of the conversion, $f(\alpha)$, that is

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where t represents time, α is the extent of reaction, which can be determined from TGA runs as a fractional mass loss, T is the temperature, $k(T)$ is the temperature-dependent rate constant and $f(\alpha)$ is a function that represents the reaction model.^{12–14} According to Arrhenius's equation, the temperature-dependent rate constant, $k(T)$ is defined as

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (2)$$

where A is the pre-exponential factor independent of temperature, E is the activation energy and R is the gas constant. Moreover, taking into account that under non-isothermal conditions the heating rate $\beta = dT/dt$, by combining eqs. 1 and 2, it results

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt} \frac{dt}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (3)$$

Most of the methods that describe the kinetics of reactions in solids use eq. 3 as well as several approximations of its integral form

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT \quad (4)$$

where

$$g(\alpha) = \int_0^\alpha (f(\alpha))^{-1} d\alpha \quad (5)$$

is the integral form of the model function. The integral part of eq. 4 does not depend on the heating rate used.

The isoconversional methods take their origin in the single-step kinetic equation eq. 1 and make use of the isoconversional principle which states that at a constant extent of conversion, the reaction rate is a function only of the temperature, so that

$$\left[\frac{d \ln (d\alpha/dt)}{dT^{-1}} \right]_\alpha = -\frac{E_\alpha}{R} \quad (6)$$

A series of experiments at different temperature programs must be performed, because this is the only way to obtain data on varying rates at a constant extent of reaction. The isoconversional methods describe kinetics of the process by using multiple single-step kinetic equations, each of which is associated with a certain extent of conversion in the temperature region related to this conversion. Therefore, they allow complex processes to be detected via variation of E_α with α .

For a given extent of reaction, the direct use of the logarithm form of eq. 3. eq. 7 produces a set of

linear relationships between the \ln of reaction rate versus $1/T$.

$$\ln\left(\beta \frac{d\alpha}{dT}\right)_\alpha = \ln[A_\alpha f(\alpha)] - \frac{E_\alpha}{RT} \quad (7)$$

By using the integral isoconversional method, the problems of numerical differentiation are avoided.^{12–14} For nonisothermal conditions, for a given extent of reaction, the analytical integration of eq. 3 can be expressed as eq. 8 that does not have an analytical solution and it can be solved either by numerical integration or approximations.

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E_\alpha}{RT}\right) dT \quad (8)$$

One of the simplest approximations is given to the eq. 9, which is used in the most popular isoconversional methods of Flynn and Wall and Ozawa.^{12–14}

$$\ln(\beta)_\alpha = \ln\left[\frac{A_\alpha E_\alpha}{R}\right] - \ln g(\alpha) - 5.3305 - 1.052 \frac{E_\alpha}{RT_\alpha} \quad (9)$$

By the use of eq. 9, for a constant α , the plot $\ln \beta$ versus $1/T$, obtained from experiments recorded at several β , should be a straight line with slope E_α .

The linear relationship between $\ln \beta$ and $1/T$ obtained for our experiments is presented in Fig. 2. The E_α values, which were determined from slope of lines in Fig. 2, in dependence of α are shown in Fig. 3.

On the basis of apparent activation energy dependence on the extent of the reaction, the curves representing conversion of lubricant at isothermal conditions were obtained by the use of eq. 10, which is by Vyazovkin:¹³

$$t_\alpha = \frac{\frac{1}{\beta} \int_0^{T_\alpha} \exp\left(\frac{-E_\alpha}{RT}\right) dT}{\exp\left(\frac{-E_\alpha}{RT_0}\right)} \quad (10)$$

In eq. 10, t_α is the time to reach the extent of conversion α at a given temperature, T_0 , under isothermal conditions. The predictions of the isothermal decomposition kinetics of lubricants are shown in Fig. 4.

To verify the obtained results, which gave the predictions of kinetics of lubricant degradation at isothermal conditions, isothermal TGA experiments were carried out. The results obtained by isothermal analysis and results of predictions, obtained by model-free kinetics analysis, are compared in Fig. 5. In the figure, it may be seen, that the results are in agreement.

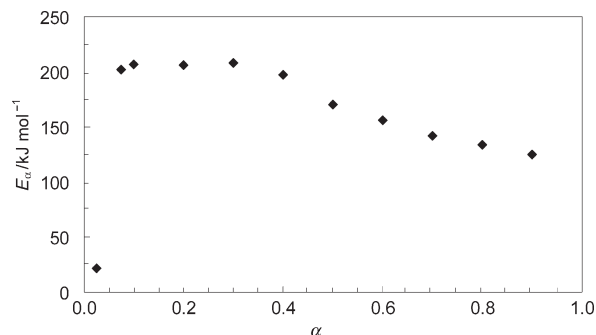


Fig. 2 – Linear fits of the logarithms of heating rate versus the reciprocal absolute temperature for different extents of conversion

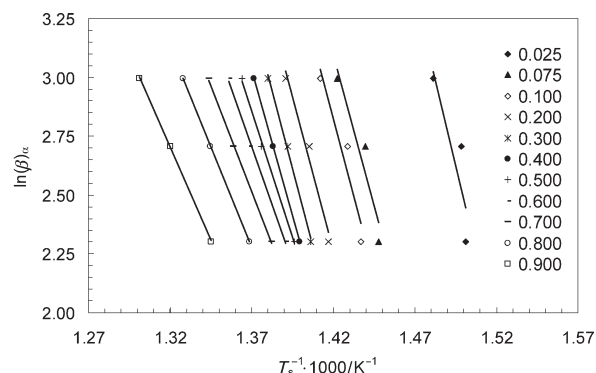


Fig. 3 – Dependency of the apparent activation energy on extent of conversion

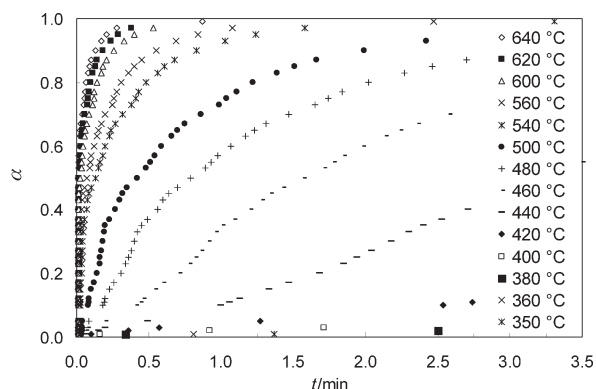


Fig. 4 – Prediction of model-free analysis: Extent of conversion for lubricant decomposition under isothermal conditions at different temperatures

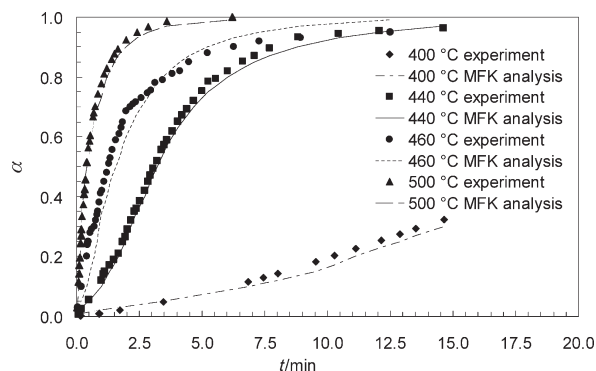


Fig. 5 – Extent of conversion versus time under isothermal conditions: Comparison of predictions of model-free analysis results and results obtained by isothermal TGA experiments

Conclusion

The decomposition kinetics of the die lubricant under nitrogen atmosphere was investigated using thermogravimetric analysis. The TGA data obtained from dynamic measurements showed that the lubricant degraded between 350 °C and 550 °C. On the basis of TGA dynamic experiments at different heating rates, the dependence of apparent activation energy on the extent of the reaction was determined, with the help of the model-free isoconversional method. Furthermore, once the apparent activation energy dependency on the extent of the reaction was known, the isothermal decomposition behavior of the lubricant under investigation was predicted. The predictions were in excellent agreement with results of the actual isothermal measurements. Therefore, it can be concluded that dynamic thermogravimetric analysis and the model-free isoconversional method are a useful tool for the investigation of thermal stability of polysiloxane lubricants. Dynamic experiments require less time, and the problems with fast reaching high experiment start temperature are omitted. Moreover, once the apparent activation energy dependency on the extent of the reaction is known, the isothermal decomposition behavior at arbitrary temperature can be predicted.

ACKNOWLEDGEMENTS

Operation part financed by the European Union, European Social Fund. Operation implemented in the framework of the Operational Programme for Human Resources Development for the Period 2007-2013, Priority axis 1: Promoting entrepreneurship and adaptability, Main type of activity 1.1.: Experts and researchers for competitive enterprises.

List of symbols

- A – pre-exponential factor, s^{-1}
 A_{α} – pre-exponential factor at α , s^{-1}
 E – activation energy, $kJ\ mol^{-1}$
 E_{α} – apparent activation energy at α , $kJ\ mol^{-1}$

- $f(\alpha)$ – the reaction model, a function of the conversion
 $g(\alpha)$ – integral form of the reaction model
 $k(T)$ – rate constant
 R – gas constant, $kJ\ mol^{-1}\ K^{-1}$
 T – temperature, K
 T_{α} – temperature at α , K
 T_0 – temperature, isothermal conditions, K
 t – time, min
 t_{α} – time to reach α at a given temperature, min
 α – extent of conversion, /
 $d\alpha/dt$ – isothermal rate of conversion, s^{-1}
 β – heating rate, $K\ min^{-1}$

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