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INTRODUCTION

In this report, the isoconversional method of thermal analysis was employed in conjunction with temperature programmed reaction (TPR) experiments to extract H_2O outgassing kinetics from TR55 and S5370. Moisture outgassing prediction models were then constructed for these silicones in a dry/vacuum environment at different temperatures. These outgassing prediction models are shown to follow the trend of isothermal outgassing data. The accuracy and limitation of the isoconversional analysis in predicting moisture outgassing from silica-filled polydimethylsiloxane (PDMS) family is also discussed.

EXPERIMENTS AND ANALYSIS

TR55 is composed of 70 wt. % polysiloxane gum formulation and 30 wt. % fumed silica filler pretreated with a silating agent. S5370 is composed of 15% diatomaceous silica filler, 60% high molecular weight polysiloxanediol, 12% low molecular weight polysiloxanediol, 5% diphenylmethylsilanol, 6% polymethylhydrogensiloxane, and 2% tetrapropoxysilane. Only very thin (a few hundred micrometers) TR55 and S5370 silicones were used in TPR experiments which has been described in details elsewhere.[1] After the TPR spectra were obtained, the kinetics of the reactions were extracted by analyzing the TPR spectra of similarly prepared samples at different heating rates in accordance with the Friedman isoconversional method of thermal analysis.[2,3] Kinetic predictions were also based on the Friedman isoconversional technique.[1,2,3]

RESULTS AND DISCUSSIONS

The moisture content in TR55 was measured to be on the order of 0.23 wt. % after 4 hours of vacuum pumping. Figure 1(a) shows mass 18 TPR spectra of three similar TR55 samples at heating rates of 0.15 K/s, 0.025 K/s and 0.004 K/s. A plot of the activation energy (*E)* versus the reacted fraction (α) established by the isoconversional technique using the TPR spectra in figure 1(a) is presented in figure 1(b).

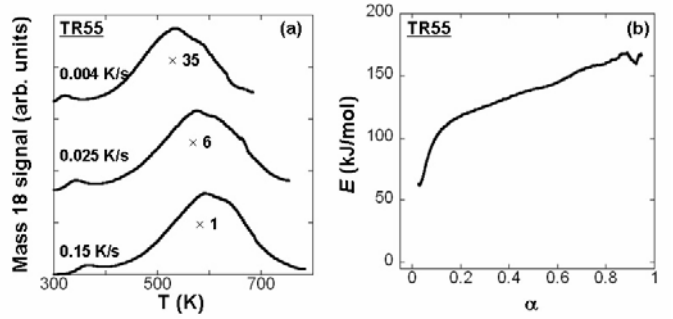

Figure 1. (a) Mass 18 TPR spectra of three similar TR55 samples at different heating rates; (b) *E* vs. α for the moisture outgassing process from TR55.

Similar experiments performed on S5370 yield a value of about 0.15 wt% for the total moisture released by TPR after 1 hour of vacuum pumping. The mass 18 TPR spectra of three similar S5370 samples at heating rates of 0.1 K/s, 0.01 K/s and 0.002 K/s are presented in figure 2(a). A plot of *E* versus α for the H_2O outgassing from S5370 obtained from the Friedman isoconversional method is presented in figure 2(b).

It is seen that the energy barrier for H_2O outgassing from TR55 and S5370 is an increasing function of the fractional H_2O release. Most of the physisorbed water (*E* < 63 kJ/mol), had been pumped off prior to the start of the TPR experiments. The increase in the value of *E* with α can be interpreted as the release of H_2O via the condensation of OH groups from the surfaces of the embedded silica particles according to:

$$SiOH + SiOH + heat \rightarrow Si_2O + H_2O(g) \quad (1)$$

As the chemical reaction (1) goes on, OH bonds have to diffuse from farther and farther distances before they can combine to give off H_2O, causing the activation energy barrier, *E*, to increase with increasing fractional H_2O release, α.

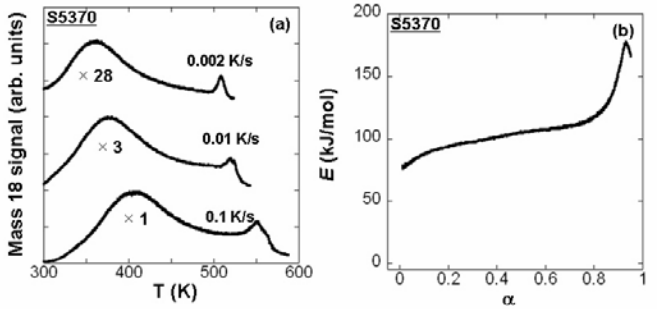

Figure 2. (a) Mass 18 TPR spectra of three similar S5370 samples at different heating rates; (b) *E* vs. α for the moisture outgassing process from S5370.

The comparisons between isoconversional kinetic predictions and isothermal long-term H_2O outgassing from TR55 and S5370 at various temperatures are presented in figures 3 and 4, respectively. In these figures, the dashed and solid lines represent kinetic predictions based on the measured kinetics by the Friedman method[1] and isothermal outgassing data, respectively. The light shaded areas are 35% error bands around the prediction lines. It is seen that, within an error band of 35%, there is agreement between isoconversional predictions and long-term isothermal outgassing.

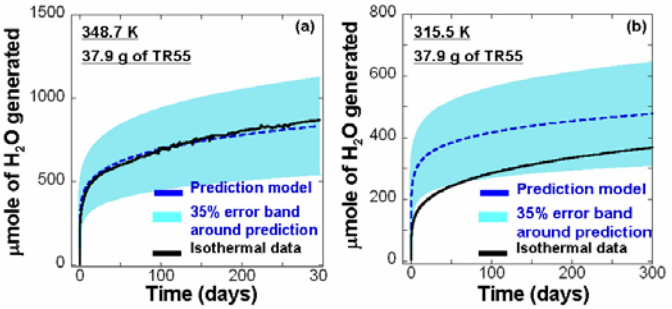

Figure 3. Comparison between moisture outgassing kinetic predictions and long term isothermal outgassing data for TR55.

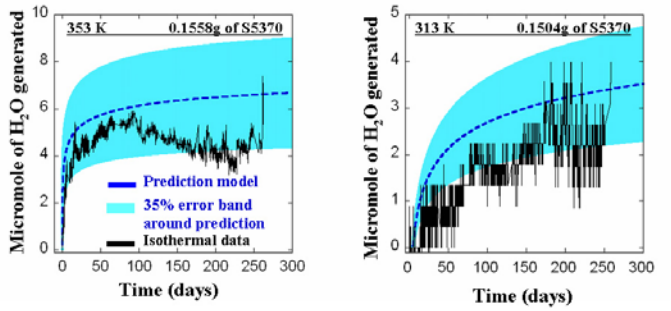

Fig. 4 Comparison between moisture outgassing kinetic predictions and long term isothermal outgassing data for S5370.

Given the unavoidable slight differences in preparation conditions and sample variations between TPR experiments and long term isothermal experiments, the prediction models do follow the trend of actual isothermal outgassing. The main advantages of the isoconversional technique are its ease of use (model-independent) and

its abilities to predict outgassing trend at any temperature within or a little bit below the temperature range studied from a set of short-time scale experiments at different heating rates. However, there is a possibility that some of the moisture producing reaction pathways captured in the TPR spectra at very high temperatures (such as the decomposition of the silicone matrix itself above 550K) may not necessarily happen at all at much lower temperatures. The end result is a somewhat over-predicted amount of moisture outgassing from silica-filled silicones at the lowest temperature (295K). More accurate outgassing predictions usually require exact mechanistic model fitting of the TPR spectra, a task which is very difficult if at all possible for TPR spectra that cover a very broad temperature range and involve multiple reaction pathways such as those described in this report. In such difficult situations, the isoconversional technique serves as a valuable tool to predict the trend of the outgassing process under study as long as the operator is aware of the potential weaknesses of the technique as described above.[4] In the above mentioned spirit, the long term moisture outgassing of TR55 and S5370 at room temperature (295K) is presented in figure 4.

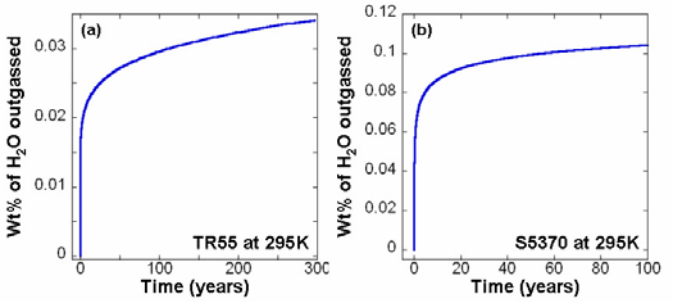

Figure 4. The kinetic predictions of moisture outgassing from TR55 (a) and S5370 (b) at 295K.

SUMMARY

The Friedman isoconversional thermal analysis technique has been employed in the kinetic extraction and prediction of H_2O outgassing from TR55 and S5370. The energy barriers for H_2O release from TR55 and S5370 increase with increasing fractional H_2O release. This can be interpreted as the release of H_2O from physisorbed water and then chemisorbed water with decreasing OH density from the surfaces of the embedded silica particles. As the temperature rises above 550 K, some of the recorded H_2O signal may be attributed to the decomposition of the silicones. Model-independent predictions of H_2O outgassing based on the measured kinetics agree do follow the trend of isothermal outgassing and suggest that much of the moisture outgassing from TR55 and S5370 occurs during the first few years of dry storage followed by much slower outgassing rates in the following decades. Within the context of accelerated aging studies, when the outgassing TPR spectra are very broad and involve mutiple reaction pathways such as in the case of H_2O outgassing from silica-filled PDMS, the isoconversional technique serves as a valuable tool to predict the outgassing trend.

ACKNOWLEDGEMENT

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REFERENCES

1. Dinh, L. N.; Burnham, A. K.; Schildbach, M. A; Maxwell, R. S.; Balazs, B.; McLean II, W. submitted to J. Vac. Sci. Technol. A.
2. Friedman, H. L. J. Polym. Sci. Part C **1963**, 6, 183.
3. Galwey, A. E; Brown, M. E. *Thermal Decomposition of Ionic Solids*; Elsevier: New York, 1999.
4. A. K. Burnham, L. N. Dinh, submitted to J. Thermal Analysis and Calorimetry.