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DYNAMIC MECHANICAL AND THERMOGRAVIMETRIC ANALYSES OF THE EFFECT OF FERRIC OXIDE ON THE THERMALOXIDATIVE DEGRADATION OF SILICONE RUBBER *

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ABSTRACT

The thermaloxidative degradation of hydrosilation formed dimethylsiloxane rubber networks containing ferric oxide in amounts of 0 to 60% (w/w) was investigated by dynamic mechanical analysis (DMA) and thermogravimetry (TG). Scanning work showed that the key weight loss event from TG and the key stiffening event on DMA correlated, showing maximum temperatures at 40% ferric oxide content. Isothermal work showed TG and DMA to be of a very complementary nature. Under isothermal decomposition three chemistry regions were identified—one dominated by thermal decomposition, one dominated by oxidative crosslinking, and a transition region. From Arrhenius kinetics, apparent activation energies, pre-exponential factors, and rate constants were calculated.

INTRODUCTION

Silicone rubbers have long been used in high temperatures applications owing to their excellent resistance to thermaloxidative degradation [12]. Continuous use temperatures of 200 °C with peak temperatures above 300 °C are not uncommon [2]. Although the siloxane bonds which make up the backbone of silicone rubbers are intrinsically resistive to heterolytic bond cleavage [3], the methyl side groups attached to the silicon atom of typical silicone rubbers are prone to thermaloxidative degradation leading to the formation of siloxane crosslinks [1]. Therefore, silicone rubber used in high temperature applications in the presence of air typically fails due to embrittlement beyond a point which can be tolerated.

Stabilization of silicone rubbers against thermaloxidative degradation is most frequently accomplished by compounding with ferric oxide [14]. Other iron containing compounds such as iron octoate [5], iron tris(acetyla-

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cetonate) [6], and various ferrocenes [7] have also been reported as effective in retarding thermaloxidative degradation. The mechanism by which iron retards thermaloxidative degradation of silicone rubbers has been speculated to be a result of radical elimination by both iron(II) reduction and iron complex formation [4,5].

We recently reported the use of dynamic mechanical analysis (DMA) for the continuous monitoring of the mechanical changes occurring in silicone rubbers owing to thermal and thermaloxidative degradation [8]. It was shown that this technique was very useful in both the isothermal and continuous heating rate mode to observe the mechanical stiffening occurring during thermaloxidative degradation of the rubbers. It was further shown that these initial results mirrored results obtained by traditional thermogravimetric (TG) analysis, with the added advantage of describing a generally more important property—mechanical changes as opposed to changes in weight. In this paper we show how DMA and TG complement each other in the investigation of the effect of ferric oxide content on the thermal and thermaloxidative stability of a hydrosilation cured dimethylsilicone rubber. After a brief review of the constant heating rate results, we will describe our most recent isothermal TG and DMA results. Using an Arrhenius kinetics treatment, apparent activation energies, pre-exponential factors, and apparent rate constants were determined for the thermaloxidative degradation of silicone rubbers with ferric oxide contents ranging from 0 to 60% (w/w). The complementary nature of TG and DMA in studying this process, and the particular advantages and disadvantages of our DMA technique will be discussed.

EXPERIMENTAL

Materials

All siloxane materials were prepared by mixing ferric oxide in Dow-Corning Sylgard 182 silicone resin. A total of 9% (w/w) curing agent was added and all composites were identically cured in the mold for 30 min at 170 °C followed by a 1.5 h postbake at 170 °C.

Measurements

Scanning TG was carried out on a Perkin-Elmer TGS-2 as previously described [8]. Isothermal TG was carried out using a Perkin-Elmer TGS-7, using identically shaped 10 mg samples in an air atmosphere. All samples were heated at a rate of 10 °C min^{-1} to the desired isothermal decomposition temperature. The rate of the decomposition was read from the derivative of the weight loss curve.

A Du Pont 982 with 1090 controller was used for the dynamic mechanical analyses. Scanning DMA was performed at a heating rate of 1.3° C min^{-1} in the horizontal mode in the desired atmosphere. Isothermal runs were carried out in the vertical mode with 2 mm long × 14 mm wide × 2 mm thick samples. After heating at a rate of 10° C min^{-1} to the desired temperature, the samples were allowed to degrade isothermally for the required time in either air on inert atmosphere.

RESULTS AND DISCUSSION

Scanning DMA and TG

Our initial evaluation of the thermaloxidative stability of silicone rubbers involved the use of constant heating rate TG. Silicone rubbers with a ferric oxide content varying from 0 to 50% by weight were identically prepared and run at a constant heating rate of 1.25° C min^{-1} in an ambient air flow. As can be seen from Fig. 1, the point at which the first major weight loss event occurs is labelled T_{k1}.

Scanning DMA was performed in an ambient air flow on samples cut from the same materials used for our TG analysis. The results are shown in Fig. 1. We identify a point labeled T_s as that point at which the material starts to stiffen. This presumably is the point at which the crosslinking reactions occur more quickly than the main-chain scission reactions, resulting in an overall increase in the crosslink density of the material. As is apparent in Fig. 1, T_{k1} from the TG experiments and T_s from the DMA

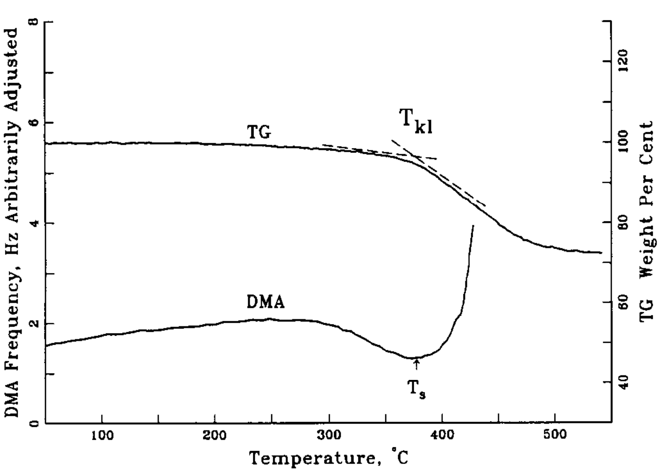

Fig. 1. Comparison of scanning TG and scanning DMA curves in air: polysiloxane 182 + 50% ferric oxide.

experiments occur at very similar temperatures. As reported previously [8], the temperature of the key events increases with increasing iron oxide content up to 40% and then decreases at 50% (w/w) ferric oxide content in the rubber. However it is important to note that, in addition to telling at what temperature key thermaloxidative events occur, the DMA results also indicate that the result of the event is stiffening of the material.

Isothermal DMA and TG

To gain information about the degradation kinetics of the siloxane rubbers during thermaloxidation, both isothermal DMA and TG experiments at various temperatures were performed. Figures 2 and 3 show typical TG and DMA isothermal results respectively. Upon close inspection, particularly of the DMA curves, one can identify three distinct regions versus time that we will call chemistry I, II, and III. In DMA the three regions express themselves as an initial region dominated by a loss of modulus owing to main chain scission, a region of initial stiffening marked by a low slope, and a final region of constant high slope. In TG, the initial regions shows rapid weight loss, the third region is one of very slow weight loss, and the second region is a transition region between that of early weight loss and that of slow weight loss. S-shaped TG decomposition curves have been reported in the literature and identified as representing two distinct processes–thermal decomposition and thermal oxidation [9]. Inspection of the many TG and DMA runs from our work shows that the time for transition from chemistry I to II to III (i.e. the transition from thermal decomposition to oxidative crosslinking dominated zones) correlate well

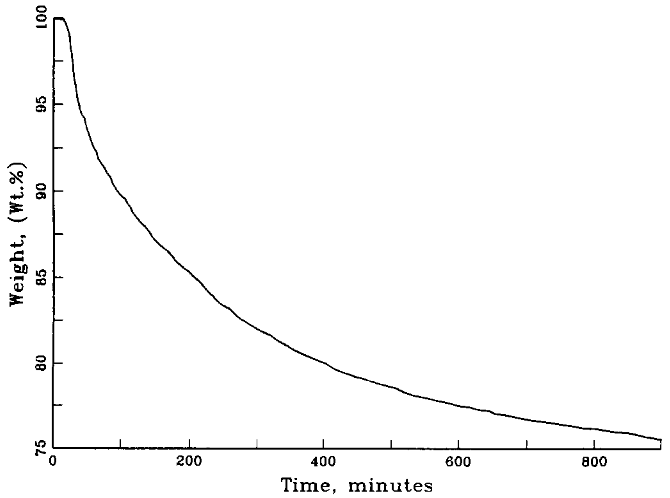

Fig. 2. Isothermal TG in air: polysiloxane 182+40% ferric oxide.

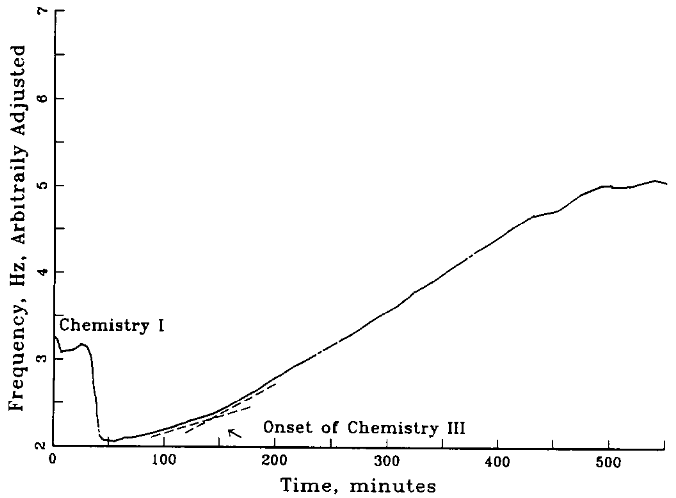

Fig. 3. Isothermal DMA in air: polysiloxane 182+40% ferric oxide.

between TG and DMA, and that the onset of chemistry III, the area dominated by oxidation, is delayed by decreased decomposition temperatures and increased iron oxide contents. Similarly, an increased isothermal TG temperature sometimes results in less weight loss at 900 min. At first, this seems illogical since the higher the temperature, the higher the expected weight loss. However, since higher temperatures encourage increased rates of oxidation, a weight gaining process, the actual net weight loss can be less with higher temperatures. As can be seen from Figs. 2 and 3, the chemistry III region in DMA is the region of highest reaction rate; while in TG it is the most static area. This complementary nature of TG and DMA greatly clarifies the complex processes occurring during the thermaloxidation of our silicone rubbers.

Figures 4–6 give apparent rate constant versus ferric oxide content from our TG and DMA results respectively. The apparent rate constants were calculated based on the energy of activation and preexponential factors gathered from Arrhenius plots of the ln Rate (i.e. the slope of the TG or DMA curves) versus reciprocal temperature as described previously [8]. Tables 1 and 2 show all of the activation energy and preexponential results attained for chemistry regions, I, II, and III for both TG and DMA respectively. As can be seen, the table is not complete. No chemistry I data is available for DMA since chemistry I in DMA is a softening process. During this softening, spikes in the frequency curve were frequently encountered. Some preliminary work on the new 983 DuPont DMA, which has a fixed frequency mode, has lessened this problem. Further, data for the chemistry II region, the transition zone between thermal decomposition and oxidation, is not complete since at high temperatures and low iron oxide concentrations this region is very small. Additionally, since this is hypothe-

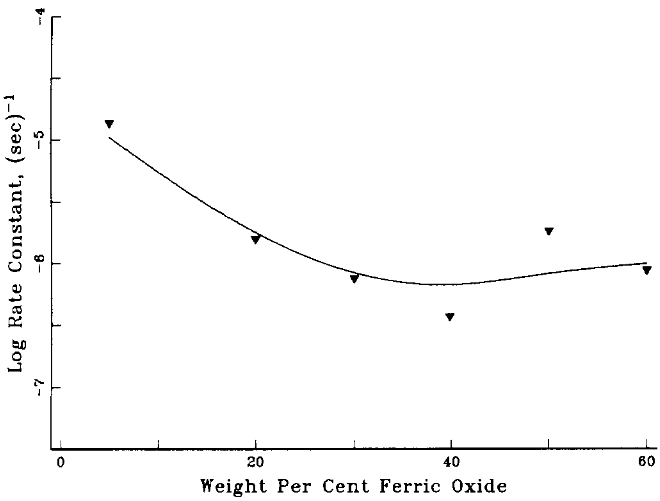

Fig. 4. Apparent rate constant at 300 ° C for chemistry I region, calculated from TG data for polysiloxane 182 + ferric oxide.

sized as a region of transition in the decomposition process, satisfactory Arrhenius plots were not always attainable.

The TG kinetic data for chemistry region I, the area of rapid weight loss, indicates a rate dependence on the ferric oxide content. The pre-exponential factors are relatively constant versus ferric oxide content, however, there is a clear increase in the activation energy with increasing ferric oxide up to the maximum at 40% weight content. Thus Fig. 4 shows a minimum in the rate constant versus iron oxide content at 40%. This is similar to the results

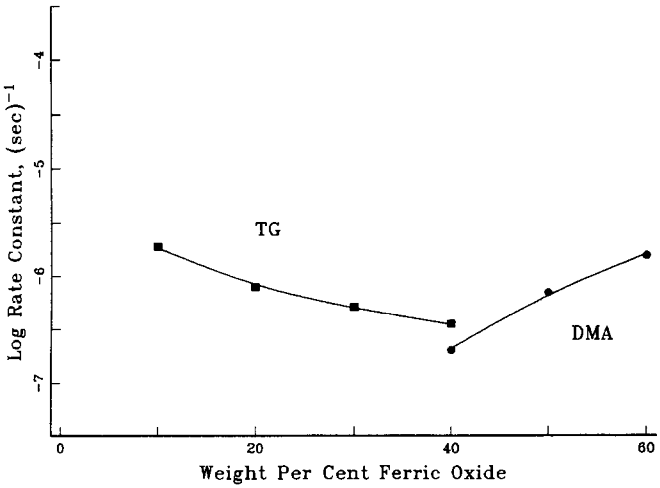

Fig. 5. Apparent rate constant at 300 ° C for chemistry II region, calculated from both TG and DMA data for polysiloxane 182 + ferric oxide.

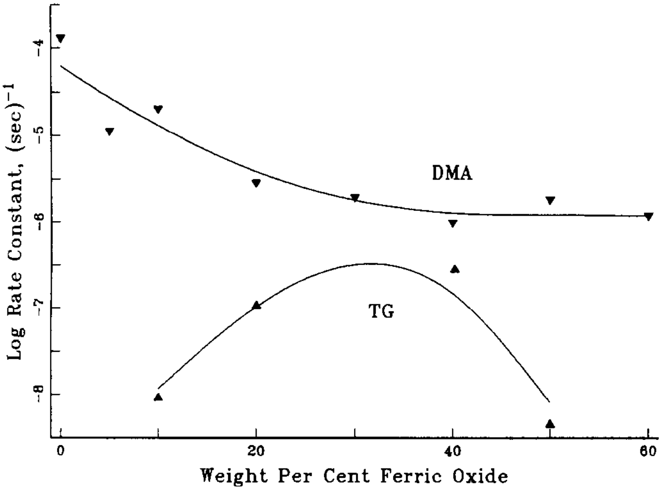

Fig. 6. Apparent rate constant at 300 °C for chemistry III region, calculated from both TG and DMA data for polysiloxane 182 + ferric oxide.

previously reported in our constant heating rate experiments [8]. In chemistry region II, the transition zone from thermal decomposition to oxidative dominance, both TG and DMA show the lowest apparent rate constant at 40%. However, as mentioned previously, this data set is incomplete. Both the TG and DMA data show a general decrease in activation energy and pre-exponential factor with increasing iron oxide content in this region.

The chemistry III region, the zone of oxidation dominance, is where the complementary nature of TG and DMA is most evident. As shown in Fig. 6, one sees a maximum in the rate constant near 40% ferric oxide content in TG, and a minimum in rate constant near 40% ferric oxide content in DMA.

TABLE 1

Values calculated from isothermal TG curves

%Fe_2O_3	Chemistry I		Chemistry II		Chemistry III	
	E_a (s^{-1})	A (kJ mol^{-1})	E_a (s^{-1})	A (kJ mol^{-1})	E_a (s^{-1})	A (kJ mol^{-1})
0	–	–	–	–	–	–
2.5	–	–	–	–	–	–
5	104	4.6×10^4	–	–	–	–
10	–	–	134	3.2×10^6	213	2.4×10^{11}
20	115	5.1×10^4	81	2.0×10^1	124	2.0×10^4
30	124	1.4×10^5	80	1.0×10^1	–	–
40	130	2.5×10^5	92	9.1×10^1	64	0.2×10^{-1}
50	116	6.4×10^4	–	–	226	1.9×10^{12}
60	111	1.2×10^4	–	–	–	–

TABLE 2

Values calculated from isothermal DMA curves

%Fe_2O_3	Chemistry I		Chemistry II		Chemistry III	
	E_a (s^{-1})	A (kJ mol^{-1})	E_a (s^{-1})	A (kJ mol^{-1})	E_a (s^{-1})	A (kJ mol^{-1})
0	–	–	–	–	148	4.1×10^9
2.5	–	–	–	–	–	–
5	–	–	–	–	84	4.8×10^2
10	–	–	–	–	54	1.9×10^0
20	–	–	–	–	111	3.4×10^4
30	–	–	–	–	122	2.4×10^5
40	–	–	184	1.4×10^{10}	147	2.6×10^7
50	–	–	147	1.9×10^7	130	1.2×10^6
60	–	–	144	2.6×10^6	170	3.7×10^9

At first this appears to be a contradiction, however, when one takes into account that TG is looking at rate of weight loss while DMA is looking at rate of oxidative crosslinking, the contradiction disappears. Up to 40% ferric oxide content in the silicone rubbers, the rate of oxidative crosslinking is suppressed, as shown by DMA, and thus the weight losing process of siloxane bond breakage and ring formation is relatively enhanced. That is why that, with decreased temperature and increased iron oxide content, more rather than less weight loss is sometimes observed. The TG data show a minimum in the activation energy and pre-exponential factor near 40%, suggesting that at this point a low energy of activation, yet sterically hindered, reaction is dominant. The DMA data for this region show a maximum in the energy of activation near 40% weight content, suggesting that lower activation energy processes are hindered at this ferric oxide content. The reason for increased rates of thermal decomposition and oxidation above 40% ferric oxide content is not clear at this time, however, one might speculate that this is a result of enhanced diffusion of oxygen into and decomposition products out of the silicone rubber owing to the presence of voids in the rubber. Voids in the rubber would occur when insufficient rubber exists to fully wet all of the iron oxide.

CONCLUSIONS

In conclusion, the complementary nature of the use of DMA and TG to investigate the thermaloxidative degradation of silicone rubber has been shown. Both results are consistent with chemical decomposition zones showing that ferric oxide inhibits both thermal decomposition and, more effectively, oxidative crosslinking. The kinetics data described in this paper along with future planned TG/MS work is aimed at gaining a greater understanding of the mechanistic effect of ferric oxide stabilization of silicone rubbers against thermaloxidative degradation.

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