A Differential Thermal Analysis Study of Fluoroelastomer Vulcanization

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Received: 13 December 1994; accepted 21 August 1995

ABSTRACT

The reaction taking place during the cure of a rubber compound are often complex and not easily understood. Also, the curing temperature of a compound is often determined in an empirical manner. This paper discusses the differential thermal analysis (DTA) method which has been used to determine the curing temperature range of a fluoroelastomer compound. The results were used to determine the postcuring temperature of fluoroelastomer vulcanizates. The DTA results were used to prepare vulcanizates which were found to possess good tensile properties; however, the results were not sufficient to propose a mechanism of crosslink formation.

Key Words: fluoroelastomer, differential thermal analysis, curing, postcuring, physical properties

INTRODUCTION

Differential thermal analysis (DTA) is a powerful method that can be used to study the thermal behaviour of polymer materials and the reactions they undergo. The detailed theories of the DTA method has been presented in many excellent reviews [1-3] and will not be included here.

Since vulcanization of elastomers is exothermic, it should be an obvious reaction for study by DTA. Paciorek and coworkers [4] have studied the DTA of some fluoroelastomer systems and concluded that crosslinking occurs between 140 °C to 200 °C. Fluoroelastomer are especially important because they possess outstanding resistance to heat, flame, chemicals and solvents; consequently, they are used in many application fields such as automotive, aerospace, oil well and other industries where such harsh environments exclusively require the high performance of fluoroelastomers. Kruger and McGill [5-12] used DSC studies to investigate the interaction of various curatives and used their results to throw more light on the chemistry of diene rubber vulcanization.

Thus, the aims of this paper are:

-To determine the curing temperature region of fluoroelastomer compounds by the examination of the thermal changes taking place in the uncured compound during cure.
- To determine the postcuring temperature by the examination of the thermal changes taking place when the non-postcured vulcanizate is postcured to various degrees.
- To determine the possibility of using the DTA information to propose a mechanism of cross-linking.

MATERIALS AND METHODS

DTA Equipment
The DTA equipment used was Dupont 990 thermal analyzer and it was calibrated by obtaining the melting point of a known pure substance (indium: melting point = 156.4 °C). The value obtained from the equipment agreed with the value quoted in the literature [13]. Heating rate was at 10 °C/min and an empty sample pan was used as the reference material. Both the rubber compound samples and reference material were heated in a nitrogen atmosphere to prevent any extraneous reaction from occurring.

Materials
Viton GF fluoroclastomer was obtained from Dupont (U.K.) Ltd. Viton GF is a tradename of E.I. duPont de Nemours and Company, U.S.A. and has the following structure:

\[
\text{CF}_3 \quad \text{(CH}_2\text{-CF}_2)_x - (\text{CF}_2\text{-CF})_y - (\text{CF}_2\text{-CF})_z \quad \text{Br}
\]

Rubber-grade calcium oxide and calcium hydroxide were obtained from John and E. Sturge Ltd., U.K. Hexamethylene-N,N’-bis (tertiary butyl peroxy-carbamate) (HBTBP) was prepared as described in the literature [14]. Dry nitrogen was obtained from British Gas Ltd.

Table 1. Compound formulations for thermal analysis study.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>X</th>
<th>Y</th>
</tr>
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<tbody>
<tr>
<td>Viton GF</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>CaO</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Ca(OH)\textsubscript{2}</td>
<td>6.0</td>
<td>6.0</td>
</tr>
<tr>
<td>HBTBP</td>
<td>-</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Sample Preparation
The formulations for fluoroclastomer compounds shown in Table 1 were mixed on a two roll mill according to the guidelines set by BS 1674: 1976. This involved shearing the rubber on the two roll mill and adding the compounding ingredients evenly across the mill at a uniform rate. In addition, cold water was passed into the roll mills to keep the mill temperature below 25 °C so as to prevent scorching. Samples from the fluoroclastomer compounds were used in DTA studies. Based on the information obtained from DTA results, the curing characteristics of the compounds were obtained with a Monsanto Oscillating Disc Rheometer (ODR) and consequently, vulcanizates were prepared by press curing techniques.

RESULTS AND DISCUSSION

Thermal Analysis of Uncured Compounds
The DTA traces (thermograms) for the uncured compounds X and Y are shown in Figure 1a. Examination of the thermograms for compound X (which serves as a control formulation) shows that there is no thermal change of state or any indication of chemical reaction up to a temperature of 260 °C; this proves that calcium oxide and calcium hydroxide cannot bring about the curing of Viton GF. Likewise, it can be said that there is no interaction between calcium oxide and calcium hydroxide. Also, the ODR cure trace of compound X obtained at 170 °C, in Figure 2 shows no sign of crosslink formation and this further
Figure 1a. Differential thermal analysis of Viton GF compounds X and Y of Table 1.

Figure 1b. Differential thermal analysis of hexamethylene-N,N' bis(tertiary butyl peroxycarbamate).

confirms the results of thermal analysis. Indeed, a sample of compound X heated in a press at 170 °C for 15 minutes did not crosslink and the sample dissolved completely in methyl ethyl ketone; another evidence that no crosslinks were formed in the heated compound X.

However, the DTA trace of compound Y (Figure 1a) shows a melting endotherm at 93 °C which is attributed to the melting of the HBTBP curing agent. The DTA plot of HBTBP alone (Figure 1b) shows that it melts at 93 °C while it decomposes at about 140 °C. Further inspection of the thermogram of compound Y shows an exotherm with a maximum at 166 °C; this exotherm is attributed to the crosslinking reaction that occurs between Viton GF and HBTBP. A re-scan of the
cooled samples produced thermograms without a thermal event. Consequently, a temperature of 170°C was chosen for investigating the curing characteristics of compound Y (this was due to the ease with which the Monsanto ODR could be adjusted). The ODR cure trace of compound Y is also shown in Figure 2 and a reasonable crosslink formation is observed from the difference between the minimum and maximum torque reading. Thus, the crosslinking of the fluoroelastomer by HBTBP, as observed on DTA thermograms correlate well with the results of Monsanto ODR.

**Thermal Analysis of Postcured and Non-Postcured Vulcanizates**

It has been found that the ultimate physical properties of press-cured fluoroelastomer vulcanizates are not fully developed until they are postcured in air oven at elevated temperature [15,16]. The reason for postcuring is attributed to volatilization of low molecular weight vulcanization reaction products and the formation of new, thermally stable crosslinks [16]. Thus, DTA was used to determine the postcuring temperature of non-postcured vulcanizates. The thermograms of both the postcured and non-postcured vulcanizate are shown in Figure 3. On the thermogram for the non-postcured vulcanizates, a trough is obtained at about 140°C which is probably due to the volatilization of low molecular weight product (e.g., moisture was found to be present in the vapour from a simulated postcuring operation which was condensed, and the refractive index of the condensate was 1.33). The thermogram for the non-postcured vulcanizate also shows the beginning of an exotherm at 200°C which indicates further crosslinking reaction(s) to be occurring; this is probably due to Diels-Alder type aromatization reaction [17] which is said to be responsible for the development of new, thermally stable crosslinks. A re-scan of the cooled samples produced thermograms without a thermal event.
Having now obtained 200 °C as the postcuring temperature and following an earlier method [15], a press-cured vulcanizate was postcured for 24 hours in air oven at 200 °C and the thermogram of the postcured vulcanizate was obtained which is also shown in Figure 3. The thermogram for the postcured vulcanizate shows no thermal change up to 280 °C and this indicates that it does not undergo any DTA-sensitive thermal changes within the range of temperature investigated. This is also a proof of the thermal stability of the fluoroelastomer vulcanizate which is a two stage process and the stages are very distinct, i.e., they cannot be combined into one. Consequently, the thermal events of the different stages are different.

**Mechanism of Crosslink Formation**

The information provided by DTA studies are not sufficient to postulate a mechanism of crosslink formation. However, previous studies [18,19] have proposed the mechanism of crosslink formation in bisperoxycarbamate systems to occur through a free radical process.

**Ultimate Physical Properties**

The curing and postcuring temperature obtained from DTA studies was applied to the preparation of carbon black-filled vulcanizates (carbon black is normally used as a filler in commercial recipes).

The physical properties of the compound both in the postcured and non-postcured states were obtained and shown in Table 2. Better physical properties were obtained for postcured vulcanizates; improvement of physical properties on postcuring is expected and normal for fluoroelastomer vulcanizates [20].

**Table 2. Physical properties of postcured and non-postcured Viton GF vulcanizates.**

<table>
<thead>
<tr>
<th>Properties</th>
<th>No Postcuring</th>
<th>Air-oven Postcured at 200 °C for 24 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength</td>
<td>11.11 (MPa)</td>
<td>13.26</td>
</tr>
<tr>
<td>Elongation-at-break</td>
<td>275 (%)</td>
<td>200</td>
</tr>
<tr>
<td>100% Modulus</td>
<td>4.07 (MPa)</td>
<td>8.52</td>
</tr>
</tbody>
</table>

**Formulation** - Viton GF: 100, medium thermal black: 25, CaO: 4, Ca(OH)₂: 8, HHTBP: 5
Cure conditions: 15 minutes at 170 °C.
CONCLUSION

On the basis of the results of differential thermal analysis studies, it can be concluded that a press or 'set' curing temperature of 170 °C is found to be appropriate for Viton GF/HBTBP compound while a suitable postcuring temperature is indicated to be from 200 °C and above. It is also considered that the DTA data implies that volatilization of low molecular weight products can occur between 138 °C and 145 °C in non-postcured vulcanizates. Furthermore, the DTA study of fluoroelastomer compounds also suggests that HBTBP is the agent responsible for bringing about the curing of Viton GF while postcured fluoroelastomer vulcanizate is thermally stable as judged from its thermogram. Also, the application of DTA results to a practical compound gave vulcanizates with good physical properties. It is worth pointing out that since curing reactions are generally exothermic, the DTA principle applied to fluoroelastomer compounds can be used to determine the curing temperature for other elastomer systems.

REFERENCES

6. Ibid. p 2651.
7. Ibid. p 2661.
8. Ibid. p 2669.
10. Ibid. p 587.
12. Ibid. p 573.