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Advances in Thermogravimetric Analyses of Elastomer Systems

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ABSTRACT

Practical rubber formulations are complex mixtures of polymer(s), fillers, plasticizers, curatives, and processing aids. Classical methods exist for determining many of the components of these systems but are too time consuming for routine use in quality control or problem solving activities. Thus a need has existed for more rapid procedures. Previous studies of gum, compounded, and cured elastomers showed that thermogravimetry (TG) can provide information regarding the polymer, oil, carbon black, mineral filler, and ash content of vulcanizates. The present study extends this approach to multicomponent polymer and carbon black systems to determine whether components of similar thermal characteristics can be effectively analyzed. Vulcanizates containing binary (natural rubber (NR)/ethylene propylene terpolymer (EPDM) or ternary (NR/EPDM/styrene-butadiene rubber) blends were successfully analyzed by the standard, dynamic TG method. Isothermal TG was shown to have significant potential for

analyzing blends of FEF and SRF carbon blacks (CB) in a standard formulation. Two additional approaches, derivative TG (DTG) and normal probability analysis are examined for potential applicability in these analyses. The former has apparent value for polymer blend analysis; the latter, based on preliminary data, may have value in the analysis of some CB blends.

RESULTS AND DISCUSSION

Analysis of Polymer Blends in Vulcanizates

Evaluation of polymer decomposition characteristics has potential for quantitative analyses of polymer blends. The degree to which this can be achieved in a given elastomer system will depend on a variety of factors including the overall composition of the rubber formulation as well as the relative inherent characteristics of the particular polymers. The general problem to be considered is the possible overlap of the thermal decomposition or volatilization characteristics of the components of the formulation. When this occurs due to nonpolymeric components, it can often be compensated for by extraction of the sample prior to thermogravimetry by a correction procedure for a "standard" system, or by manipulation of the TG conditions to selectively remove volatile, nonpolymeric components prior to decomposition of the polymers [1]. The following discussion is concerned, however, with another type of overlap problem, i.e., that due to the polymer components in a blend.

Two-Component Blends

Assuming no interaction between the polymeric components, quantitative analysis via TG should be feasible for many elastomer blends if the components differ to a high degree in thermal stability. The present case deals with a more difficult system wherein 1) one of the components (natural rubber, NR) has a more complex decomposition pattern than the other (ethylene propylene terpolymer, EPDM), and 2) the systems overlap to a moderate degree. Figure 1 compares the individual systems and a 50/50 blend of the two polymers. Initial inspection of the shape of the TG curve for the latter system does not suggest a major difference vs that of the 100 NR system. However, it will be shown that careful examination of both the position and the detailed shape of the TG curve can provide an effective basis for quantitative analysis of polymer composition in these blend systems.

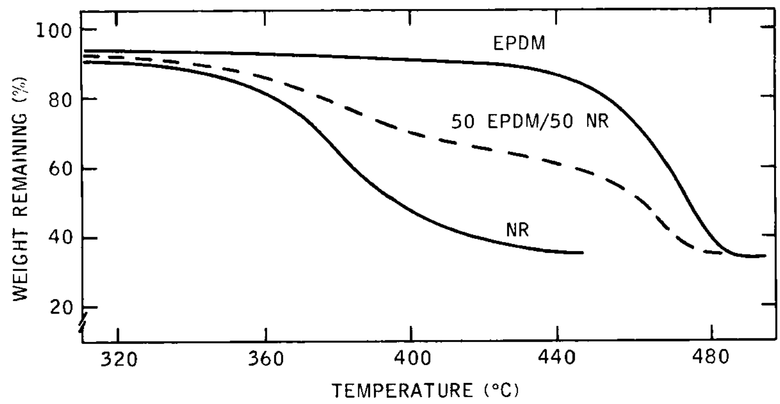

FIG. 1. TG analysis of EPDM/natural rubber systems.

The first method by which such analysis can be accomplished takes advantage of the fact that most of the NR decomposition occurs at a lower temperature than that of the EPDM system. Thus it is possible to locate a temperature above which most of the polymer weight loss is due to EPDM. A graph of the data in Table 1 reveals a highly linear relationship. This system also presents an opportunity for evaluating the derivative of the TG curve as a means to amplify small, but significant differences in the detailed shape of primary TG curves such as those shown in Fig. 1. Notice, for example, that the derivative thermogravimetry (DTG) curves (Fig. 2) make it much easier to distinguish between these systems. Table 1 compares the peak heights of such

TABLE 1. TG Analysis of Vulcanized Natural Rubber/EPDM Blends

Composition wt% EPDM	Wt% remaining (410°C)	DTG Peak (in.) (NR)
0	8.5	2.95
20	26.3	2.20
50	48.8	1.30
80	63.3	0.78
100	84.7	-

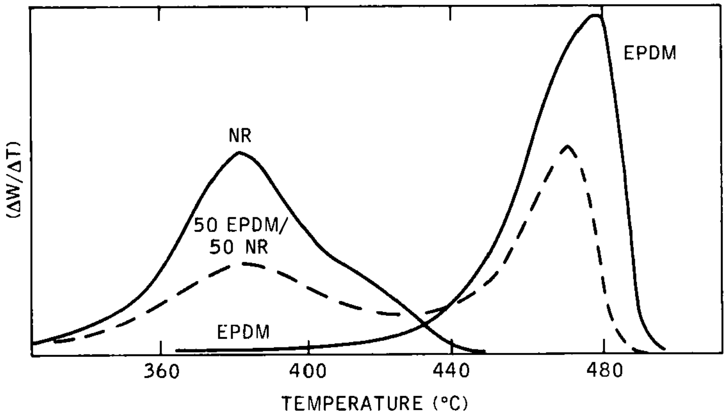

FIG. 2. Derivative TG of EPDM/NR systems.

curves to blend compositions; a graph of these data indicates that this approach, properly calibrated, should be feasible. An interesting aspect of this type of system is that there are at least two measures of polymer composition to provide a cross-check of polymer content in the blend.

Three-Component Blends

The success of the methods outlined above for the two component systems prompted examination of their applicability to an even more complex system, in this case, ternary blends of NR, styrene-butadiene rubber (SBR), and EPDM. The particular blends under examination had a fixed EPDM content of 20 phr; NR and SBR contents ranged from zero to 80 phr. Figures 3 and 4, which present representative TG and DTG data for these systems, reveal basic characteristics generally similar to those of the NR/EPDM system. Plots of the weight loss and peak height data of Table 2 indicate that quantitative analysis via TG techniques is feasible even for these complex systems.

Due particulary to the complexity of the systems described throughout this paper, it is essential that the basic TG experiment be conducted in a standardized, highly controlled manner [1, 2]. It has previously been established that meaningful analyses of vulcanizate composition can be conducted if reproducible operating conditions are established, monitored, and maintained. Although the methods outlined in this presentation have been developed for specific vulcanizates, it is reasonable to anticipate that other compositions may be analyzed in similar fashion. Because of the wide variety of practical formulations which may be encountered, however, each system must be treated as a

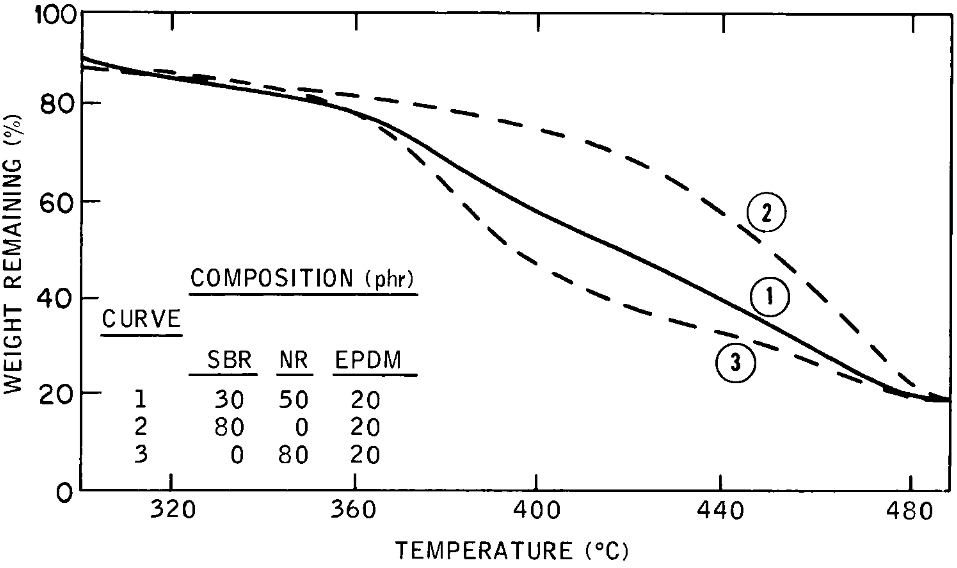

FIG. 3. TG analysis of SBR/NR/EPDM systems.

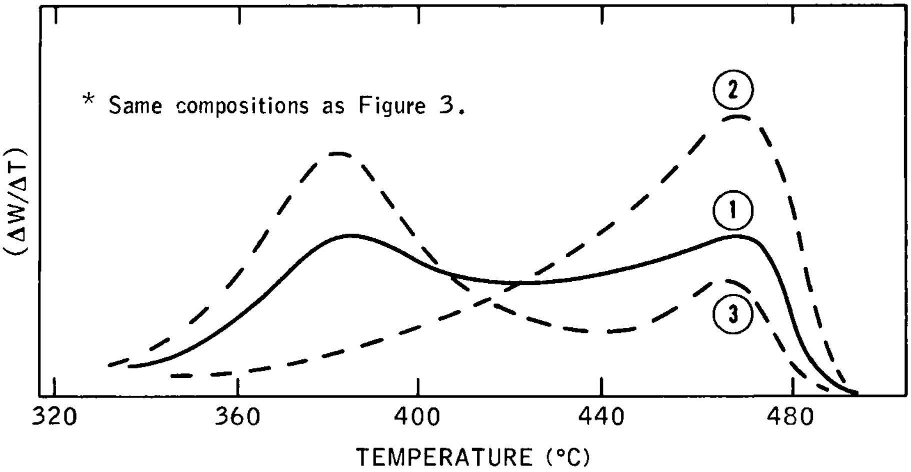

FIG. 4. Derivative TG of SBR/NR/EPDM systems.

TABLE 2. TG Analysis of Vulcanized EPDM/NR/SBR Blends

Composition (phr)			Weight % remaining (400° C)	DTG peak (in.)	
EPDM	NR	SBR		NR	SBR
20	80	0	40.5	2.81	1.35
20	50	30	58.0	1.85	1.85
20	30	50	66.5	1.28	2.35
20	0	80	80.0	0.60	3.25

new case until the feasibility of these methods have been established for the particular formulation of interest.

Analysis of Carbon Black Blends in Vulcanizates

Practical rubber compounds frequently contain blends of carbon blacks (CB) of various particle size, surface area, and/or "structure" chosen to yield the proper balance of compound cost and product properties. It has previously been shown that single carbon blacks of different surface area could be statistically differentiated in a standard vulcanizate via their oxidation characteristics during controlled TG experiments. The potential for analyzing CB blends whose components had large differences in surface area was also indicated. The present treatment will examine the applicability of such techniques to blends of similar surface area. Before proceeding into a detailed analysis of one of these systems, mention should be made of the fact that previous work indicated that both physical and chemical factors associated with the complete formulation can influence the decomposition of carbon blacks during this type of analysis [2]. The present case will involve only factors associated with the carbon blacks since all of the compounds are in a fixed formulation except for CB blend ratio.

Analysis of FEF/SRF Blends

A series of blends was analyzed in the vulcanized, unextracted state as indicated in the Experimental Procedures. Figure 5 presents the average data for four determinations of each system. It is apparent that major variations in the CB blend composition of this formulation should be readily detected by the TG procedure. Small variations, especially in blends rich in one component, appear directionally more difficult to

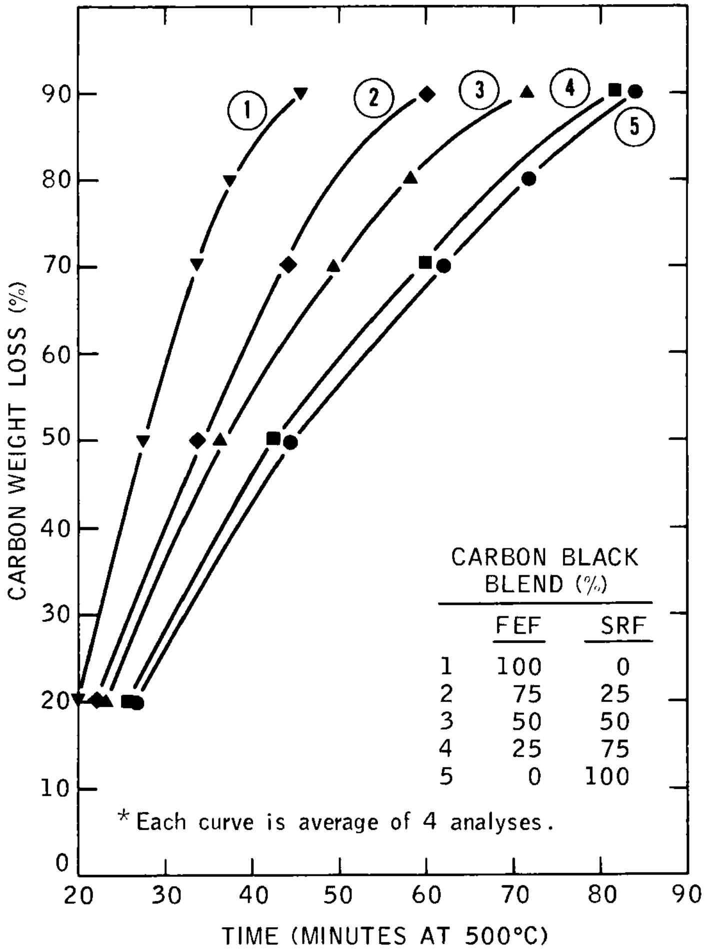

FIG. 5. Analysis of SRF/FEF blends in vulcanizate residues.

detect. Replicate determinations will probably be required for successful analyses of such systems. The times to reach various percentages of total carbon black weight loss have been shown for each system to illustrate the fact than an improved analysis will probably result from the use of times to reach a high degree of weight loss. Presumably this is due to the fact that the residue in this region is primarily some of the SRF black. Thus, despite their similarity in surface area, these blacks are, in effect, "separated" during the TG experiment.

Graphical Treatment of CB Oxidation Data

The oxidation characteristics (weight loss vs time) of FEF in this vulcanizate residue suggest an additional, perhaps novel approach to CB blend analysis. In particular it was noted (Fig. 6) that the weight loss curve for this system displayed a high degree of symmetry. Because of this, it was expected that this curve could be transformed to linear form via normal probability analysis. A successful test of this assumption is shown for the FEF system in Fig. 7. In making this type of plot it is necessary to have values for the initial and final weights of the material which was subjected to the oxidation treatment. The initial values of these quantities were read directly from the TG chart. Minor adjustment of the value of the final weight was then made to improve the linearity of the probability plot. The linearity of this plot suggests that graphical or computer analysis of carbon black bend composition may be possible for carbon blacks whose individual oxidation characteristics resemble that of FEF (Fig. 7). This follows from consideration of the characteristics of normal distributions and bimodal blends of such systems. In brief, one would expect that for two CB's which display the FEF type of oxidation characteristics, the individual components may appear as two different lines on a normal probability plot; whereas a blend of these blacks would fall between, and asymptote, these lines.

The SRF data in Fig. 7 show an interesting result, i.e., this 100% SRF system yields a normal probability plot which resembles that anticipated for a bimodal blend of normal distribution. Several possibilities follow from this observation. First, SRF/FEF blends cannot be simply analyzed by the normal probability approach, but modification of the method may be useful for a well-calibrated system. Second, SRF oxidation characteristics follow a much different form than those of FEF. Third, SRF behaves like a blend of materials, and this graphical approach may provide a means of estimating the relative proportion of these components in a given sample. The latter possibility warrants further consideration since CB oxidation via a dynamic TG method also suggested that the SRF oxidation pattern was inherently more complex than that of several other carbon black types [3].

Additional examination of this approach will consist of 1) attempting to identify another carbon black which resembles the behavior of FEF, 2) examining blends of these blacks to determine whether the normal probability analysis route offers any advantages for CB blend analysis, and 3) some further consideration of the significance of the SRF behavior depicted in Fig. 7.

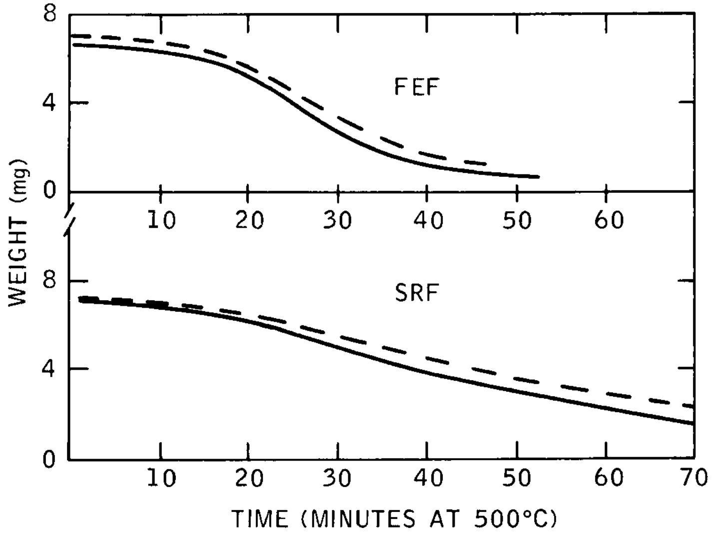

FIG. 6. Oxidation of CB residues from vulcanizates (reproducibility).

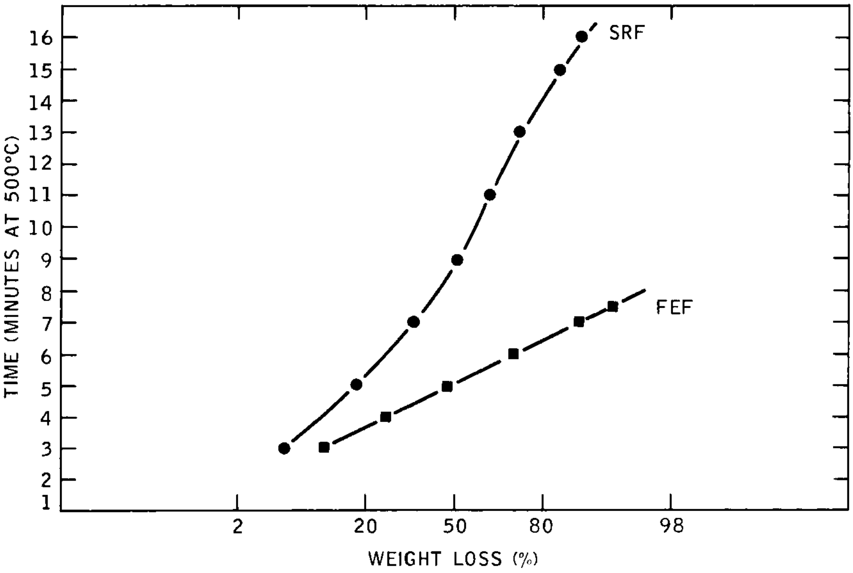

FIG. 7. Decomposition of carbon blacks from vulcanizates: probability plot.

EXPERIMENTAL PROCEDURES

Carbon Black Blends

Formulation. Butyl rubber, 200; carbon black, 100 [FEF (Philblack "A") and/or SRF (Pelletex NS)]; Stearic acid, 4.0; ZnO, 10.0.

Acceleration. 50 g of above formulation plus 0.40 g sulfur, 0.48 g TMTDS, 0.32 g MBT. Cure: 40 min at 320°F.

TGA conditions. 950 TGA plus Du Pont 900 DTA system. Unit initially purged with N_2 for 15 min. Sample size: 20.2 mg. Remove polymers, etc. by heating to ~550°C in nitrogen; set unit at 500°C (isothermal); switch to air atmosphere; and record weight loss vs time.

Polymer Blends

TGA conditions: Du Pont 950 TGA plus 990 DTA system. Sample size: 6.5 ± 0.3 mg. Nitrogen atmosphere. Heat 10°C/min, dy [(mg/min)/in.] = 0.2. TGA: 1.0 mg/in. Time constant: 1.0. Suppression: 0

EPDM/NR/SBR blends. Composition (phr): Oil (Flexon 580), 10; HAF (Philblack 0), 40; stearic acid, 1.0; ZnO, 5.0; MBT (Captax), 1.5; DPG, 0.75; sulfur, 2. Cure: 30 min at 307°F.

EPDM/NR blends. Composition: Polymer (100); MT, 60; LSF, 20, ZnO, 5; HSt, 2; Santowhite 127, 3; Flexon 840, 10; Altax, 1.5; Tuads, 0.2; sulfur, 1.2. Cure: 15 to 30 min at 307°F.

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