

The Effect of Heat History on Thermal Degradation of Elastomers Containing Butadiene Units

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ABSTRACT: The aim of this research is to develop a new method for studying thermal degradation behavior of elastomers containing butadiene units by isothermal and anisothermal analysis. Accelerated aging such as isothermal thermogravimetry analysis shows that when BR, SBR and NBR elastomers are subjected to specific time and temperature condition in nitrogen atmosphere, an inter-chain reaction occurs. Experimental observations also show that thermal degradation mechanism of these elastomers

depends on heating rate and time–temperature history. For these types of elastomers, the effect of time is similar to temperature and time–temperature superposition principle can be employed for studying the thermal degradation mechanism of elastomer containing butadiene units. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3896–3900, 2009

Key words: thermogravimetric analysis; thermal degradation; elastomer

INTRODUCTION

Polymer degradation is one of the most important fields of polymer chemistry in both scientific and technological respects. There are various schemes to classify polymer degradation. Some of the most probable phenomena that take place through this process are as follows: random chain scission, depolymerization, crosslinking, side group elimination, substitution, and reaction of side groups among themselves.

As mentioned above, the method of polymer degradation investigation depends on the actual mode of degradation. Among the various techniques, thermal analysis is widely used in studying polymer degradation that includes thermogravimetry (TG), differential thermal analysis, differential scanning calorimetry (DSC), thermal volatilization analysis, thermomechanical analysis, and dynamic mechanical analysis.

Thermal analysis may be simply defined as detection of variation of material properties as a function of temperature. TG is the measurement of the change, or weight loss, of a substance whose temperature is raised in a controlled manner. By means of two methods of thermogravimetric analysis (TGA; iso- and anisothermal methods), the kinetics of degradation processes can be studied. In isothermal TG,

the weight loss of a sample is measured continuously as a function of time at a constant temperature. In the nonisothermal method, the derivative of the mass loss with time is measured as a function of temperature at a constant heating rate. By means of TGA, the mechanism of thermal degradation of elastomers containing butadiene units has been studied.^{1,2} It has been shown that, when these elastomers are thermally degraded in an inert atmosphere, a variety of thermograms can be obtained corresponding to heating rate of elastomers. It is important to know that, at a higher heating rate, elastomers with butadiene units lose their mass in two stages; whereas at a lower heating rate, one stage for weight loss is observed. On the other hand, the degradation mechanism of elastomers containing butadiene units differs at low and high heating rates.^{1,2} The evaluation of the kinetics of the degradation process can be accomplished by using the DSC technique. Sircar and Lamond used DSC for characterizing the polymer degradation mechanism in nitrogen atmosphere.³ Sircar and Lamond^{4,5} and Brazier and Nickel⁶ also described the use of DSC and differential TG (DTG) for distinguishing vulcanized natural rubber and isoprene rubber.

Estimation of butadiene content of vulcanized styrene butadiene rubber (SBR) and butadiene rubber (BR) by DSC has been proposed by Sircar and Lamond.⁷ This method is based on evaluation of a DSC exothermic peak at about 380°C in nitrogen atmosphere, which seems to be unaffected by vulcanization or compounding ingredients.

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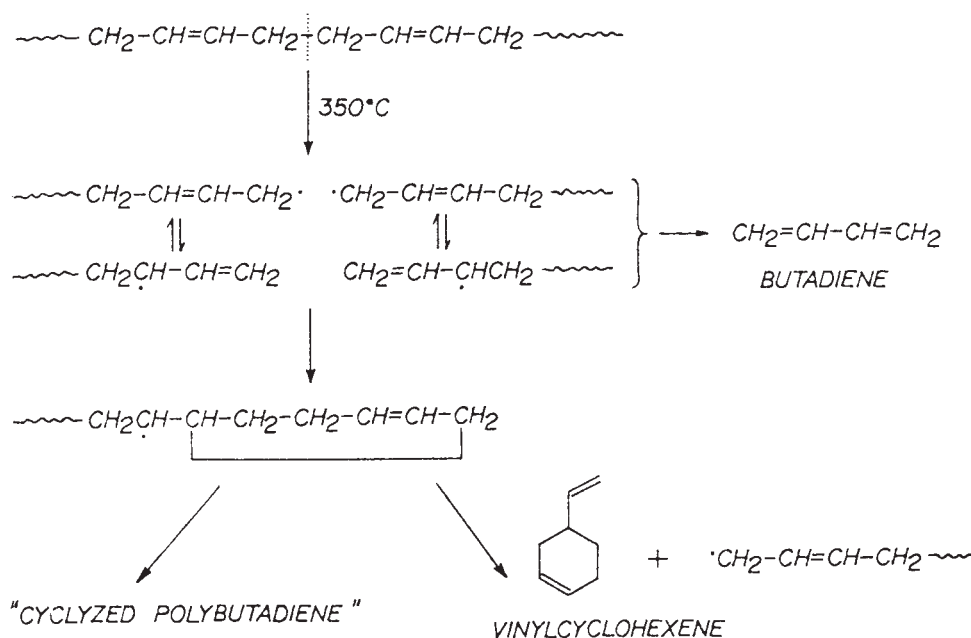


Figure 1 Polybutadiene degradation mechanism.

Schwartz and Brazier⁸ studied the effect of heating rate on the BR degradation process. It has been noted that BR degradation takes place in two distinct steps. The first is said to be almost exclusively due to volatile depolymerized products, and the second is attributed to degradation of a residue due to cyclized and crosslinked BR. McCreedy and Keskula^{9,10} Showed that the degradation mechanism of BR differs substantially for static and dynamic heating. It was further shown that polymers that do not thermally cyclize or crosslink, such as polystyrene, degrade similarly in both static and dynamic heating.

One of the mechanisms that has been suggested by Golub and Gargiulo is shown in Figure 1. It can be seen that, when the sample is heated at 50°C/min, the main structure of gathered volatile fractions at the maximum degradation rate in the first stage will be butadiene. Also, there is dimmer of 4-vinyl-

cyclohexene with a minor amount of the other hydrocarbons. At the start of the second stage, a significant amount of butadiene is still observed, whereas the 4-vinylcyclohexene content is very low. Fractions gathered at the maximum rate of the second stage have little butadiene or vinylcyclohexene content.⁸

EXPERIMENTAL

The recipe used for the vulcanization is given in Table I. The formulation was prepared in a lab internal mixer. Then, 8 g of the final compound were cured

TABLE I
Formulation

Components	PHR
Rubber	100
Carbon black	40
Aromatic processing oil	10
6 PPD	1
Paraffin wax	2
Stearic acid	2
Zinc oxide	3
Sulfur	1.5
TBBS	1.3
TMTM	0.2

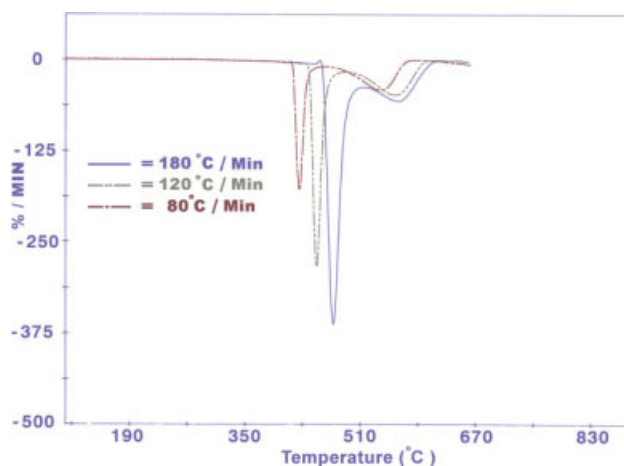


Figure 2 The effect of heating rate on DTG curves of polybutadiene compound containing 50 PHR carbon black. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Thermal Degradation of Polybutadiene-Vulcanized Compound Containing 50 PHR Carbon Black: Effect of Heating Rate on First- and Second-Stage Contribution

Heating rate (°C/min)	Peak height from DTG thermogram		% Contribution		T_{\max}^a
	h1	h2	1st stage	2nd stage	
20	–	–	–	–	–
40	31.25	30.38	26.84	73.16	407.40
60	103.75	37.35	40.85	59.42	416.32
80	178.22	41.66	48.82	51.18	425.69
100	253.13	43.79	55.03	44.97	436.67
120	283.37	48.12	58.55	41.45	450.29
140	320.52	54.52	62.51	37.49	457.12
160	341.54	54.79	64.22	35.78	463.74
180	360	56.39	68.55	31.45	473.17

^a Temperature at maximum degradation rate of first stage.

in a rheometer (Monsanto ODR-2000, Belgium) for 15 min at 160°C. The cured samples were taken for TGA. A Perkin Elmer TGA 7 (USA) was used to obtain the isothermal and nonisothermal curves. In the isothermal experiments, the samples were heated

in isothermal temperature in nitrogen environment for 10 min. In the nonisothermal method, the samples were heated in nitrogen atmosphere to 550°C. At this point, the purge atmosphere was changed to air and heating continued until a constant weight was achieved. For the evaluation of heat history effects, initially the samples were subjected to the isothermal temperature, and then they were exposed to nonisothermal experiments.

RESULTS AND DISCUSSION

The effect of heating rate on the thermal degradation mechanism of polybutadiene compound is shown in Figure 2. With increasing heating rate, the height of first-stage peak increases, whereas the intensity of second-stage peak decreases. The first- and second-stage thermal degradation contributions at different heating rates are shown in Table II. Experimental observation by TGA technique shows that, when these elastomers are initially subjected to different isothermal temperatures at constant time in nitrogen atmosphere, and thereafter passing TGA experiment, the first- and second-stage contributions are changed (Fig. 3). It can be observed that increasing the

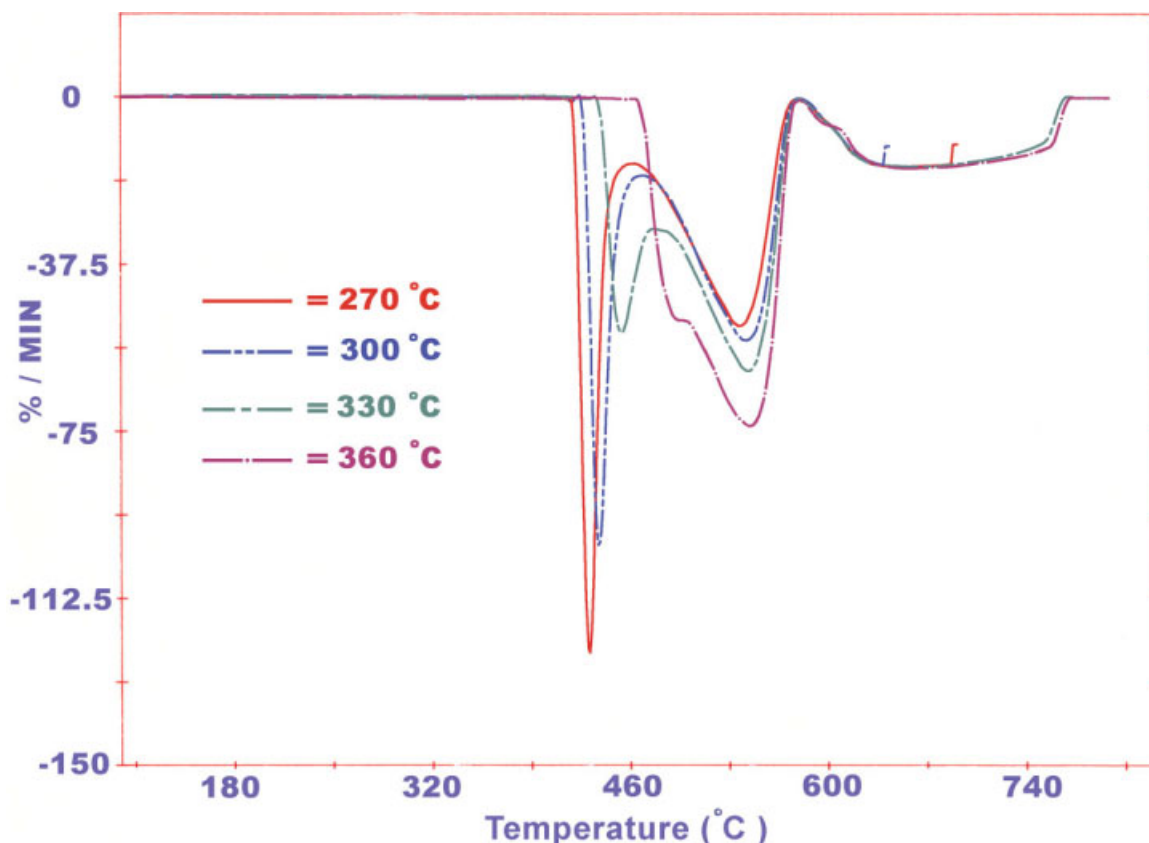


Figure 3 DTG curves of 60/40 BR/SBR compound containing 40 PHR carbon black. The samples first experience isothermal step for 10 min at four indicated temperatures, and then run a dynamic scan at heating rate 80°C/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

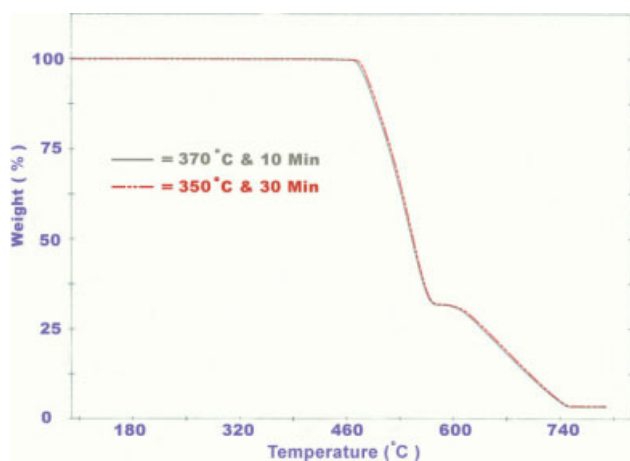


Figure 4 TGA curves of 60/40 BR/SBR compound containing 40 PHR carbon black. The samples first experience isothermal temperatures of 350°C for 30 min and 370°C for 10 min, and then run a dynamic scan at heating rate of 80°C/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

isothermal temperature causes a decrease in first-stage and increase in second-stage contribution in TGA experiment.

Experimental results also show that, when the samples are initially exposed to different isothermal conditions and then subjected to TGA, it can be concluded that the effect of time is similar to temperature. As indicated in Figure 4, the thermogram of SBR/BR compound that was initially exposed to isothermal temperature of 370°C for 10 min is almost the same as the thermogram of the sample that was subjected to isothermal temperature of 350°C for 30 min.

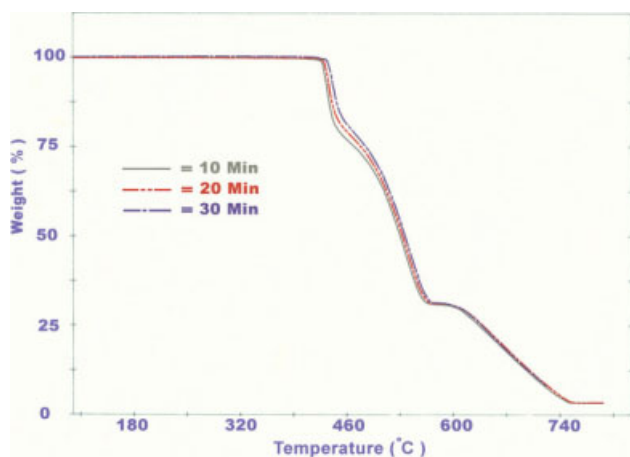


Figure 5 TGA curves of 60/40 BR/SBR compound containing 40 PHR carbon black. The samples first experience isothermal temperature of 300°C at three indicated times, then run a dynamic scan at heating rate of 80°C/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

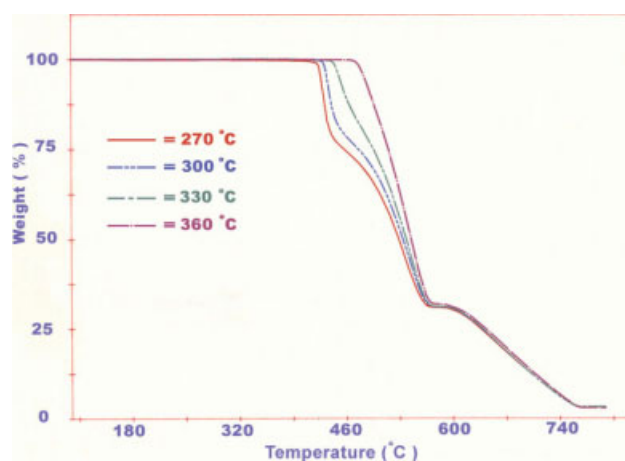


Figure 6 TGA curves of 60/40 BR/SBR compound containing 40 PHR carbon black. The samples first experience isothermal steps for 10 min at four indicated temperatures, then run a dynamic scan at a heating rate of 80°C/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

For better understanding of the effect of time and temperature on thermal degradation mechanism and development of interchain reactions, a series of experiments was carried out. In the first experiment, the sample was initially exposed to constant isothermal temperature at different times, and then nonisothermal experiments were carried out (Fig. 5). In the other experiment, the sample was initially subjected to different isothermal temperatures for a constant time, and then the nonisothermal experiments were done (Fig. 6). Comparison of Figures 5 and 6 shows that the effect of time increasing is the same as the effect of temperature increasing. On the other hand, the mechanism of thermal degradation of elastomers containing butadiene units has time–temperature dependency. Then, the superposition of time and

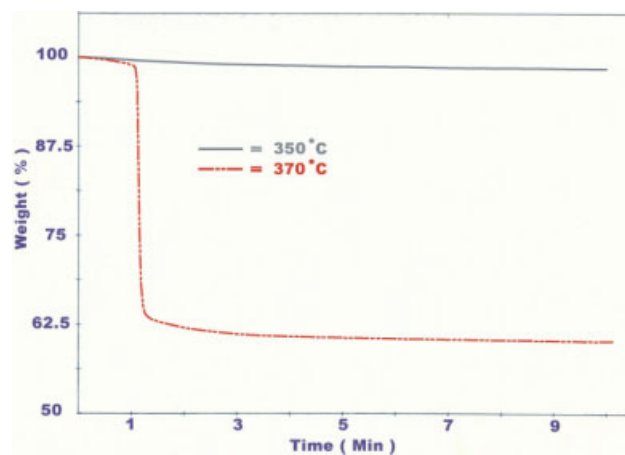


Figure 7 Isothermal curves of polybutadiene elastomer. The effect of isothermal temperature on thermal degradation mechanism. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

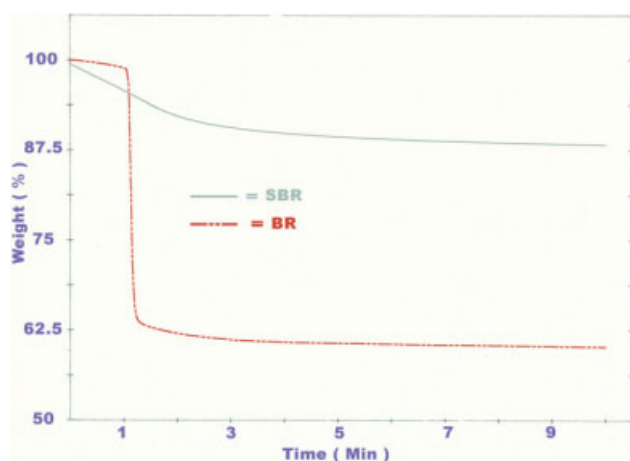


Figure 8 Isothermal curves of SBR and BR elastomers. Thermal degradation behavior in 370°C for 10 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

temperature creates a heat history for the sample. So, for this kind of elastomer, the mechanism of thermal degradation will be dependent on the heat history.

The effect of different isothermal temperature on thermal degradation mechanism of polybutadiene elastomers is indicated in Figure 7. As it is observed, for the isothermal temperatures of 350 and 370°C, the weight loss of samples after 10 min are 2 and 40%, respectively. Comparison of polybutadiene degradation at two different isothermal temperatures indicates that, for isothermal temperature of 350°C, an interchain reaction occurred, but for the isothermal temperature of 370°C, the first-stage reaction takes place and causes depolymerization.

Thermal degradation mechanism of SBR and BR elastomers in isothermal temperature of 370°C is shown in Figure 8. As it can be seen, the weight losses of SBR and BR elastomers after 10 min are approximately 13 and 40%, respectively.

CONCLUSIONS

Thermal degradation mechanisms of elastomers containing butadiene units depend on heating rate. Increasing the heating rate increases the contribution of first-stage (depolymerization) and decreases the second-stage interchain reaction (cyclized and cross-linked polybutadiene).

In addition, it was shown that the mechanisms of thermal degradation of mentioned elastomers have a time–temperature dependency. The combination of time and temperature creates a heat history in the sample. For these types of elastomers, the mechanism of thermal degradation is very dependent on the heat history of elastomers.

Experimental observation also shows that, at interchain reactions, the effect of time is similar to temperature, and time–temperature superposition principle can be employed for studying the thermal degradation mechanism of elastomers containing butadiene units.

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