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The influences of elastomer ratio and preparation mode on the degradation behavior of NR/BR Natural rubber and polybutadiene rubber blends were investigated by using non-isothermal thermogravimetric analysis (TGA). The activation energy for the degradation process was determined by using both the Ozawa and the Kissinger methods, none of them requiring the knowledge of the reaction mechanism. TGA shows that degradation of NR/BR blends takes place in two steps.

Keywords: polymer blend, thermal degradation, thermogravimetric analysis

INTRODUCTION

In recent years, polymers have been increasingly utilized in quite widespread applications. Along with the enhanced usage, though, incidences of polymeric materials loss of performance due to thermal, chemical, or mechanical degradation are more and more likely to occur. In order to prevent catastrophic failures of polymeric components, it is

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necessary to fully understand the service environmental history of a polymeric device and its effect on material properties.

One element of this history, as mentioned earlier, may be thermal degradation. If the rates of degradation can be accurately measured, then it becomes possible to predict material properties as they relate to the specific thermal environment [1].

Blending of existing polymers is an important way of getting new commercially useful materials having desired properties. The thermal stability of an individual polymer can be manipulated to a great extent by blending with other polymers [2].

The study of thermal degradation of polymers is of major interest because it can, in many cases, determine the upper limit temperature of use for a material. Also, considerable attention has been directed toward the exploitation of thermogravimetric data for the determination of kinetic parameters. For this purpose, the thermogravimetric analysis (TGA) is a technique widely used because of its simplicity and the information afforded from a simple thermogram. Thermogravimetric analysis cannot be used to elucidate a clear mechanism of thermal degradation. Nevertheless, dynamic thermogravimetric analysis has been frequently used to study the overall thermal degradation kinetics of polymers because it gives reliable information on the frequency factor, the activation energy and the overall reaction order [3–8].

There are many proposed methods to calculate kinetic parameters and the reported values depend not only on experimental conditions but also on the mathematical treatment of data [3,6].

This work is concerned with the degradation behavior of NR/BR blends (prepared according to four different preparation modes) using non-isothermal thermogravimetric analysis.

EXPERIMENTAL

The composites were prepared according to the following formulation (in phr): zinc oxide (3.0), stearic acid (2.5), aminox (2.0), PVI, n-cyclohexylthiophthalimide (2.0), sulfur (2.5), TBBS, t-butyl-2-benzothiazol-sulfenamide (0.6). Rubber contents are presented in Table 1.

TABLE 1 Rubber Contents (in phr)

phr	NR	BR	N1, N2, N3, N4	M1, M2, M3, M4	B1, B2, B3, B4
NR	100	0	75	50	25
BR	0	100	25	50	75

The blends were prepared in a Berstoff two roll mill, according to four different preparation modes:

N1, M1, B1 → all additives, except the accelerator, were incorporated into natural rubber and, after homogenizing, polybutadiene was added. To the resulting mixture the accelerator was added;

N2, M2, B2 → all additives, except the accelerator, were incorporated into polybutadiene and, after homogenizing, natural rubber was added. To the resulting mixture the accelerator was added;

N3, M3, B3 → The rubbers were mixed and after homogenization all additives were introduced into the mixture;

N4, M4, B4 → Half the content of each additive was introduced into BR and the other half added to NR. The obtained compositions were mixed and after complete homogenization the accelerator was incorporated.

The kinetics of thermal degradation of NB/BR blends under non-isothermal conditions has been investigated thermogravimetrically. The thermogravimetric analysis was performed on a TA Instruments, model TGA2050. Samples were placed in an open platinum pan and the experiments were conducted in N₂. The temperature was calibrated with indium. Runs were conducted at 2.5, 5, 10, and 20°C/min heating rates. The activation energies were determined using two different methods, neither of which required the knowledge of the reaction mechanism. The methods used are presented in the following sections.

Kissinger Method [3]

The Kissinger method has been reported in the literature in the determination of the activation energy of solid state reactions, without a precise knowledge of the reaction mechanism, by using the following equation:

$$\ln \frac{\beta_2}{T_p} = \ln \frac{AR}{E_a} + \ln [n(1 - \alpha_p)^{n-1}] - \frac{E_a}{RT_p}$$

where β is the heating rate, T_p and α_p are the absolute temperature and weight loss at the maximum weight-loss rate $(d\alpha/dt)_p$, respectively. R is the gas constant, A is the pre-exponential factor, and n is the reaction order.

From a plot of $\ln \frac{\beta_2}{T_p}$ versus $\frac{1}{T_p}$, and fitting to a straight line, the activation energy E_a can be calculated from the slope.

Flynn-Wall-Ozawa [1,3,9]

A popular “isoconversional” method was developed first by Flynn and Wall and then extended by Ozawa. This is one of the integral methods that can determine the activation energy without knowledge of reaction

order. It is used to determine the activation energy based on the equation:

$$\log \beta = \log \frac{A E_a}{g(\alpha)R} - 2.315 - \frac{0.457E_a}{RT}$$

where β , A , E_a , and T have the known meanings.

Thus, for fixed values of conversion, α (10 and 80%), the activation energy E_a is obtained from the slope of the plot of $\log \beta$ versus $1/T$.

In a rubber compound, most ingredients are used in very small quantities, compared with the rubber content, so, in order to check for lack of homogeneity, thermogravimetric analyses was carried out on samples taken from different areas of the vulcanized sheet. The results were quite similar.

RESULTS AND DISCUSSION

Figure 1 shows the thermal degradation curves of 75/25 NR/BR blends, corresponding to dynamic experiments carried out at 5°C/min. It is possible to see from this figure that the thermal degradation behavior is not affected by the different preparation modes. Moreover, similar behavior was observed independently of formulation or

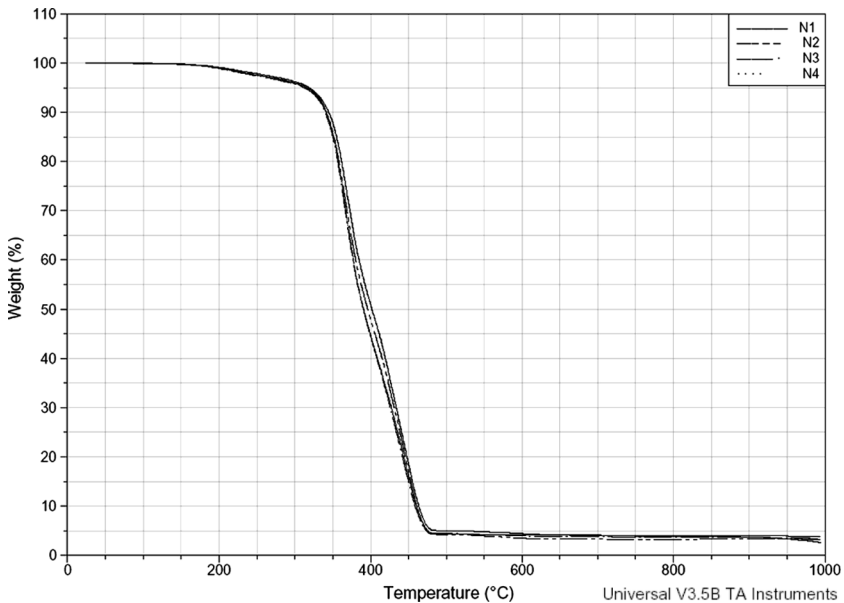


FIGURE 1 TG curves of 75/25 NR/BR blends; heating rate 5°C/min.

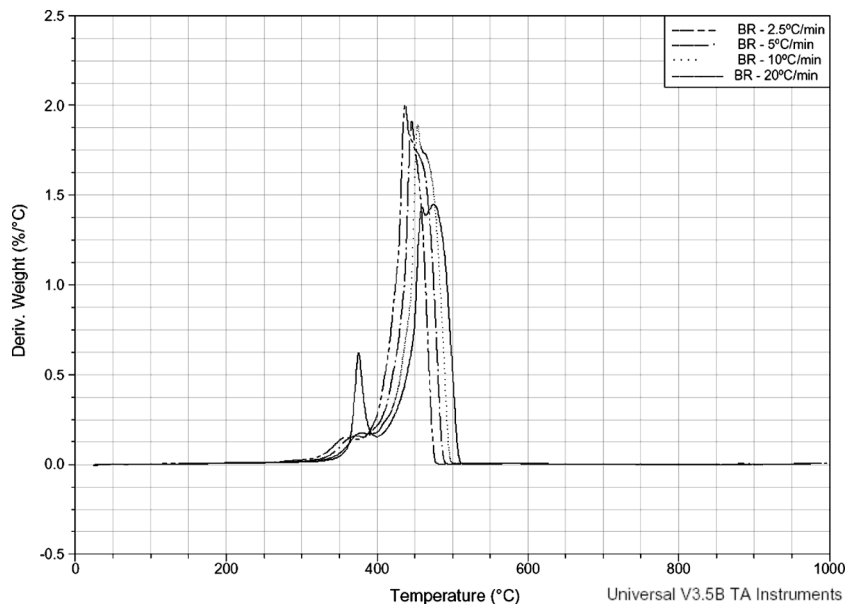


FIGURE 2 DTG curves of BR at heating rates 2.5, 5, 10, and 20°C min.

heating rate. In relation to the dependence on heating rate, as expected, the degradation temperature rises as heating rates increase.

The variation of DTG rate of weight loss with temperature for the four heating rates is shown in Figure 2 for pure BR. It is noted that two peaks can be identified. This may suggest that two major reactions take place during temperature scan. The first reaction may be attributed to the thermal formation of volatiles, which are likely to occur at low temperature and result from the depolymerization of BR (butadiene and vinylcyclohexane are produced). The second reaction, which occurs at a higher temperature is related to the decomposition of the cyclized and crosslinked polymer residue [10–12]. It is observed that the shape and the intensity of both peaks are affected by the heating rate. Some researchers showed that the depolymerization rate increases as the heating rate is increased [12].

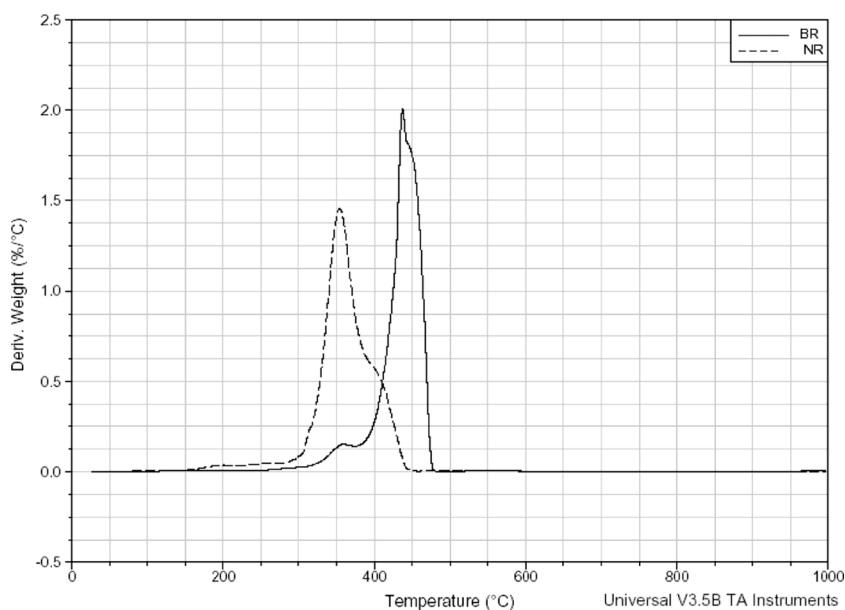
The activation energies calculated by the Ozawa and Kissinger methods are presented in Table 2. Although a good correlation coefficient is verified, the results from these methods show different tendencies. Nevertheless, in both cases the influences of preparation mode and rubber ratios are easily noticed.

Figure 3 shows an overlapping of DTG curves for pure NR and BR obtained at 2.5°C/min. As can be observed, the first step of BR

TABLE 2 Activation Energies by Ozawa and Kissinger Methods

	Ozawa				Kissinger			
	NR phase		BR phase		NR phase		BR phase	
	E_a	$r^2(^*)$	E_a	r^2	E_a	r^2	E_a	r^2
N1	222.2	1	331.6	1	254.8	0.99	312.3	0.99
N2	232	1	299.9	0.99	253.2	0.99	332.3	0.99
N3	208.2	0.99	290.1	0.99	208.7	0.99	308.6	0.99
N4	225.3	0.99	351.7	0.99	230.8	0.99	278.8	0.99
M1	211.7	1	343.2	1	261.4	0.99	277.5	0.99
M2	380.2	0.99	263.1	1	326.8	0.99	301.5	0.99
M3	233.3	1	305.4	0.99	285.1	0.99	318.6	0.99
M4	232.2	1	313.6	1	273.5	0.99	263.1	0.99
B1	219	0.99	276.4	1	233.8	0.99	209.4	0.99
B2	244.3	0.99	291.03	1	286.7	0.99	272.4	0.99
B3	250.7	1	309.6	1	250.8	0.99	214.8	0.99
B4	318.8	0.99	307	0.99	380.8	0.99	278.2	1
NR	219.5	1	—	—	213.3	0.99	—	—
BR	—	—	350.8	1	—	—	328.2	0.99

(*) r^2 is the correlation coefficient.

**FIGURE 3** DTG curves of NR and BR gums; heating rate: 2.5°C/min.

degradation occurs in the same region of NR, so for this rubber the value of weight loss at 10% conversion was chosen in an attempt to minimize BR influence. As for BR, the value at 80% conversion was taken to minimize NR interference. However, the difference found when comparing data from the two methods suggests that this approach was not valid.

The Kissinger method was considered more adequate for the analysis of the results in this work as, at the peak temperature in the DTG curves, the influence of polybutadiene on NR degradation is not significant, particularly at low heating rates. So, according to the Kissinger method, and considering the NR phase, it can be seen from Table 2 that the system N3 is more vulnerable and somehow B4 protects NR from degradation. In relation to BR phase, B1 and N2 show the worst and the best results, respectively. In these two mixtures, the scarce possibility of finding significant amounts of additives in BR, in addition to the large content of BR (B1), and the strong presence of additives in BR and the lowest content of this rubber (N2), seem to be decisive in imparting these performances.

CONCLUSION

The preparation of NR/BR blends according to four different preparation modes did not show detectable differences with respect to thermal degradation. The results of activation energy calculated by the Ozawa and Kissinger methods were not in good agreement, probably due to the influence of the first step of BR degradation on NR degradation. The degradation behavior of NR phase in the blend is not very clear but as for BR phase, the presence of additives in this phase and the lowest content of this rubber (N2) seem to give some protection to the NR phase.

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