Thermooxidative Degradation of Methyl Methacrylate-*graft*-Natural Rubber

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ABSTRACT: The thermooxidative degradation of methyl methacrylate-*graft*-natural rubber (MG) at different heating rates (B) has been studied with thermogravimetric analysis in an air environment. The results indicate that the thermooxidative degradation of MG in air is a one-step reaction. The degradation temperatures increase with B. The initial degradation temperature (T_o) is $0.697B + 350.7$; the temperature at the maximum degradation rate, that is, the peak temperature on a differential thermogravimetry curve (T_p), is $0.755B + 368.8$; and the final degradation temperature (T_f) is $1.016B + 497.4$. The degradation rates at T_p and T_f are not affected by B, and their average values are 46.7 and 99.7%, respectively. The maximum thermooxidative degradation reaction rate, that is, the peak height on a differential thermogravimetry curve (R_p), increases with B. The relationship between B and R_p is $R_p = 2.12B + 7.28$. The thermooxidative degradation kinetic parameters are calculated with the Doyle model. The reaction energy (E) and frequency factor (A) change with an increasing reaction degree, and the variational trends of the two kinetic parameters are similar. The values of E and A increase remarkably during the initial stage of the reaction, then keep relevantly steady, and finally reach a peak during the last stage. The velocity constants of the thermooxidative degradation vary with the reaction degree and increase with the reaction temperature. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1227–1232, 2003

Key words: rubber; natural rubber; thermogravimetric analysis (TGA); grafting

INTRODUCTION

One effective method for improving the properties and extending the applications of natural rubber (NR) is grafting and copolymerizing ethylene monomers onto NR. Products for different purposes are available through grafting modifications by various monomers. Research is currently focused on methyl methacrylate-*graft*-natural rubber (MG) prepared by the grafting or copolymerization of methyl methacrylate (MMA) onto NR. By such grafting, the properties of NR, such as the cohesive strength, adhesion bond, resistance to dynamic fatigue, wear resistance, oil resistance, and aging properties, are improved remarkably, and the applications of NR are, therefore, greatly extended. Earlier attempts were mainly focused on the preparation of MG,[1–3] whereas in recent decades, more and more importance has been attached to the applications of MG. Reports on the blending,[4–8] reinforcement,[9] and toughening[10,11] of MG have been published in addition to reports on the applications of MG in adhesives. With the improvement of modern analytical equipment, some researchers have promoted fruitful discussions on the structures and properties of MG by using Fourier transform infrared spectroscopy,[12] nuclear magnetic resonance,[13–15] dynamic mechanical analysis,[13,15] differential scanning calorimetry,[16] and so forth. As is well known, the thermal properties of a polymer are very important, but there are, unfortunately, few reports on the thermooxidative degradation of MG. In this study, the thermooxidative degradations of MG at different heating rates (B) in an air environment have been examined with thermogravimetric analysis, and the effects of B on the thermooxidative degradation and thermooxidative degradation kinetic parameters are discussed.

EXPERIMENTAL

Material

MG with a grafted MMA content of 49 wt % was obtained from Chemical Industrial Co. through the South China Tropical Agricultural Product Processing Research Institute (Zhanjiang, China).

Thermogravimetric analysis

Thermogravimetric analysis was performed with a PerkinElmer TGA-7 thermogravimetric analyzer (Norwalk, CT). The mass of each sample was 5–6 mg. The carrier gas was air at a flow rate of 50 mL min^{-1}. The samples were heated from 50 to 650°C at $B = 10$°C
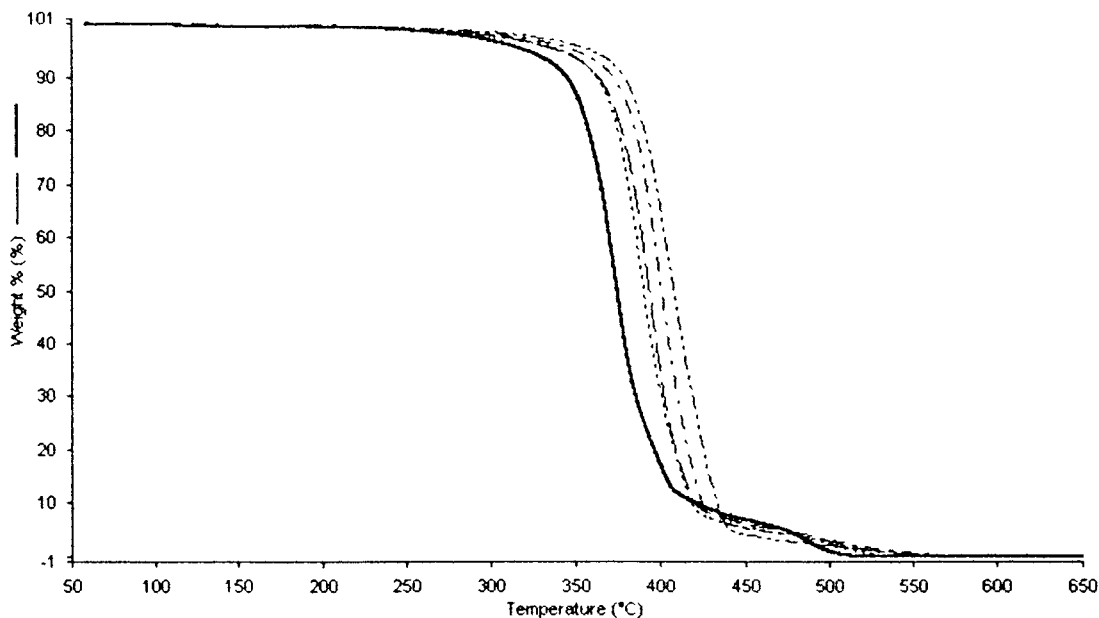
Figure 1 TG curves of the thermooxidative degradation of MG: B = (—) 10, ($\cdots$) 20, (–) 30, (- $\cdot$ -) 40, and (- $\cdot\cdot$ -) 50°C min^{-1}.

min^{-1}, B = 20°C min^{-1}, B = 30°C min^{-1}, B = 40°C min^{-1}, and B = 50°C min^{-1} for the recording of the thermogravimetry (TG) and differential thermogravimetry (DTG) curves

Data processing

The reaction kinetic factors were obtained by the processing of TG data through the Doyle kinetic model.[17] Integrating the reaction kinetic equation

$$d\alpha/dt = k(1-\alpha)^n \tag{1}$$

and using the Arrhenius equation

$$k = Ae^{-E/RT} \tag{2}$$

we obtained the following equation:

$$\log B = \log\{AE/[RF(\alpha)]\} - 2.315 - 0.4567E/RT$$
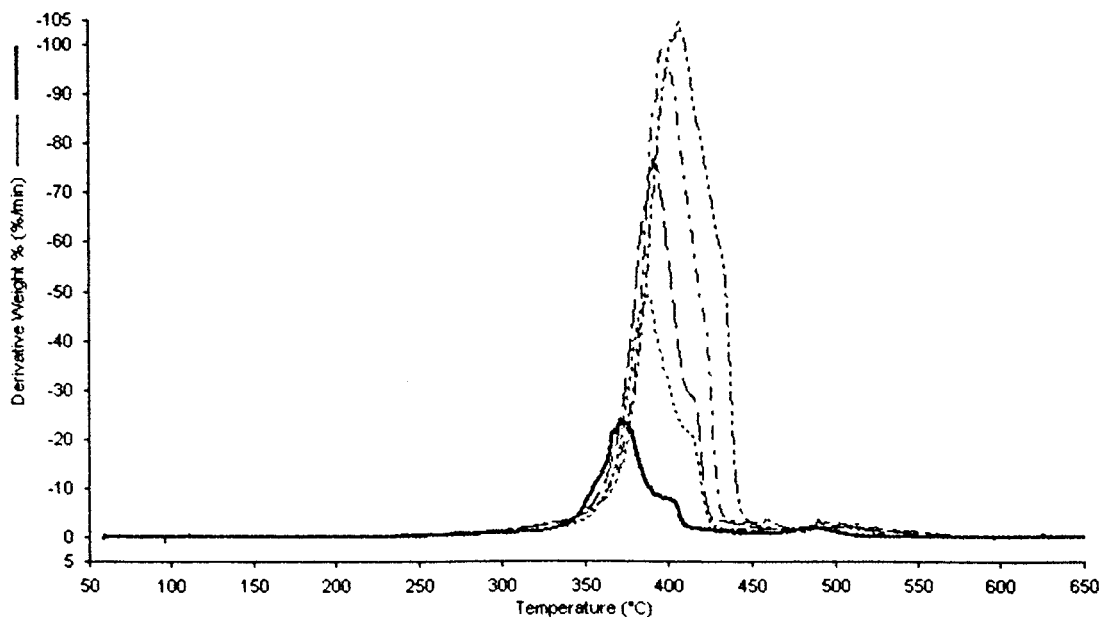
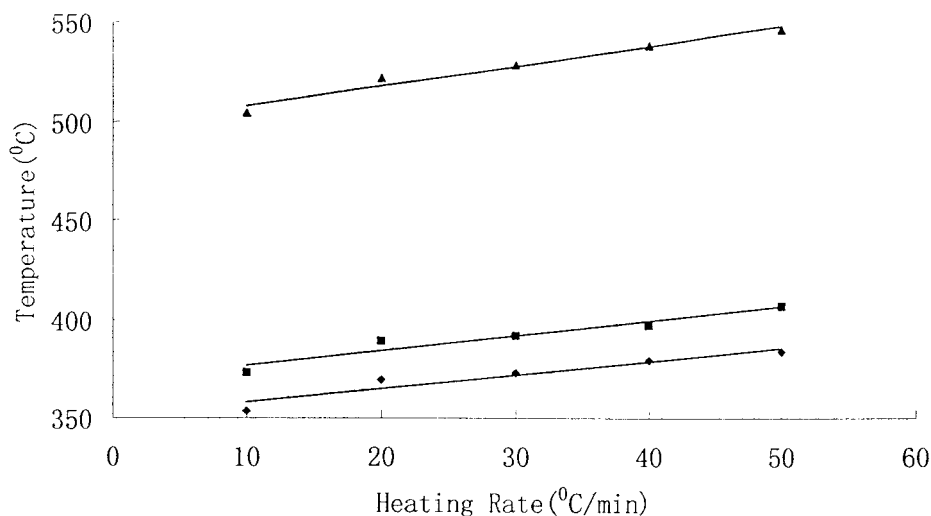**Figure 2** DTG curves of the thermooxidative degradation of MG: B = (—) 10, ($\cdots$) 20, (–) 30, (- $\cdot$ -) 40, and (- $\cdot\cdot$ -) 50°C min^{-1}.

Figure 3 Relationship between B and the thermal degradation temperatures of MG: ($\blacklozenge$) T_0, ($\blacksquare$) T_p, and ($\blacktriangle$) T_f.

where k is the reaction velocity constant of thermooxidative degradation, T is the absolute temperature, E is the reaction activation energy, R is the gas constant, $F(\alpha)$ is the reaction degree, and A is the frequency factor. A line can be obtained from a plot of log B versus $1/T$, the slope and intercept of which are $-0.4567E/R$ and $\log\{AE/[RF(\alpha)]\} - 2.315$, respectively. E, A, and k are, therefore, available.

RESULTS AND DISCUSSION

Effect of B on the process of thermooxidative degradation

Figures 1 and 2 present the TG and DTG curves, respectively, of the thermooxidative degradation of MG in air at five different values of B. There is an obvious turn in the TG curve. The DTG curve shows one corresponding weight-loss peak. Although the main peak of the DTG curve is accompanied by a faint side peak at a lower value of B, with an increase in B, the side peak disappears gradually. Therefore, the thermooxidative degradation of MG in air can be regarded as a one-step reaction. Both the TG and DTG curves shift toward a high temperature with B. The features shown in the TG and DTG curves at five B values are similar.

Relationship between B and the thermooxidative degradation temperature

The relationship between B and the thermooxidative degradation temperature is illustrated in Figure 3. The initial temperature of weight loss (T_0) and the final temperature of weight loss (T_f) are calculated by a bitangent method from TG curves, and T_p is the temperature at the maximum weight-loss rate. The peak widths of DTG curves are expressed as $T_f - T_0$. All the degradation temperatures increase linearly with in-
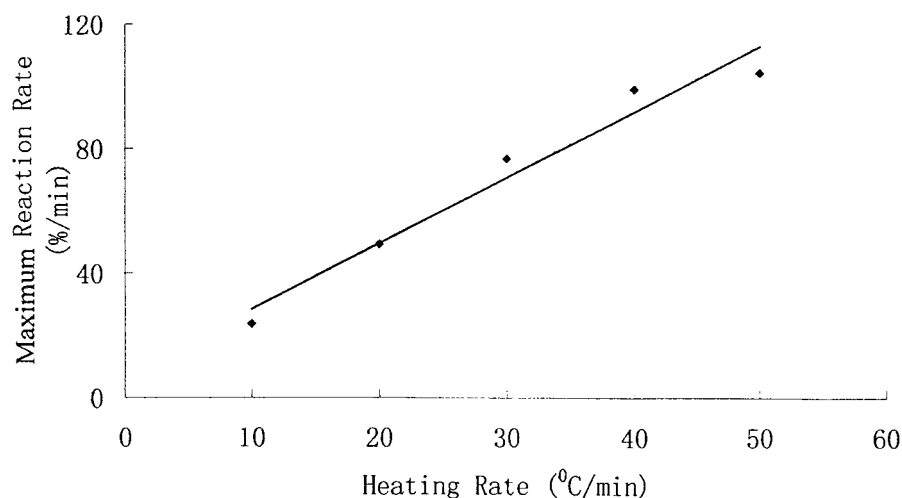

Figure 4 Relationship between B and R_p for MG.

TABLE I
Relation Between B and C

B (°C/min)	10	20	30	40	50
C_p (%)	43.7	46.8	47.3	47.6	48.2
C_f (%)	99.6	99.8	99.7	99.6	99.8

creasing B, and this indicates that the degradation temperatures are mainly affected by B. The relationships between B and the thermooxidative degradation temperature are as follows:

$$T_0 = 0.697B + 350.7 \qquad T_p = 0.755B + 368.8$$

$$T_f = 1.016B + 497.4$$

The linear increments of the thermooxidative degradation temperatures with increasing B result from the heat hysteresis. For the elimination of the heating hysteresis, the thermooxidative degradation temperatures should be expressed as equilibrium thermooxidative degradation temperatures (T^0; i.e., the temperatures at which B approaches 0). The equilibrium temperatures of MG are as follows:

$$T_0^0 = 350.7 \qquad T_p^0 = 368.8 \qquad T_f^0 = 497.4$$

The peak width of the DTG curve, which is expressed as $T_f - T_0 = 146.7 + 0.319B$, increases with increasing B. The peak height of the DTG curve, that is, the maximum reaction rate of thermooxidative degradation (R_p), increases with B, as shown in Figure 4. The relationship between B and R_p is as follows:

$$R_p = 2.12B + 7.28$$

Effect of B on the thermooxidative degradation rate

Table I shows the relationships between B and the thermooxidative degradation rate (C), in which C_p and C_f are the thermooxidative degradation rates corresponding to T_p and T_f. The effects of B on C_p and C_f are not obvious. The average value of C_p is 46.7%, and that of C_f is 99.7%.

Kinetics of thermooxidative degradation

The kinetic parameters calculated with the Doyle model are shown in Table II. Figure 5 demonstrates that E of MG varies with $F(\alpha)$ during the thermooxidative degradation process, which can be divided into three weight-loss phases: 0.5–5%, 5–70%, and 70–100%, respectively. At the first stage, E increases sharply (30–125 kJ/mol); this is due to the volatilization of low-molecular-weight materials. After that, E remains relatively steady (155–187 kJ/mol), and this is mainly caused by the thermooxidative degradation stage of MG. During the last stage, when the weight loss reaches 70%, E begins to increase with increasing weight loss and reaches a peak (282 kJ/mol) at a 90% weight loss. This is mainly due to the oxidative reaction of residual carbon becoming dominant. The variational tendency of A is similar to that of E (Fig. 6). Figure 7 shows the relationship of k at different values of $F(\alpha)$ and the temperatures. There are different k values at different values of $F(\alpha)$, and k increases with the reaction temperatures.

TABLE II
Reaction Kinetic Parameters of Thermooxidative Degradation

| Weight loss (%)	Heating rate (°C/min)	Weight loss temperature (°C)					Reaction energy (kJ/mol)	lg A
		10	20	30	40	50		
0.5		151.1	166.2	182.0	216.5	234.6	29.7	4.4
1.0		238.4	249.3	256.1	269.6	275.8	91.5	10.2
1.5		261.0	274.7	280.5	290.3	300.2	101.3	10.9
2.0		277.2	296.3	292.4	305.1	316.4	104.3	11.0
5.0		320.6	342.3	339.5	349.7	359.0	125.3	12.4
10.0		345.9	362.3	364.0	372.5	379.6	155.8	14.9
15.0		353.2	371.6	373.6	380.9	386.5	160.2	15.2
20.0		358.1	375.5	378.6	386.4	391.4	163.4	15.5
30.0		366.2	381.5	385.6	392.3	398.6	175.0	16.5
40.0		370.2	386.5	390.3	394.6	403.6	176.1	16.6
50.0		375.3	390.4	394.6	401.2	408.6	176.1	16.6
60.0		379.5	395.0	398.3	405.7	413.8	174.0	16.4
70.0		386.8	401.2	403.5	410.5	419.6	186.8	17.4
80.0		396.5	408.3	409.5	416.5	425.3	214.2	19.4
85.0		403.7	413.2	414.5	420.1	429.8	237.3	21.1
90.0		420.0	418.5	420.3	424.6	434.2	281.6	24.4
92.0		430.0	423.6	428.5	429.5	435.5	263.3	22.8
98.0		491.1	503.2	510.3	517.6	522.3	245.5	19.5
99.0		501.3	515.6	530.2	539.4	545.2	177.6	19.7
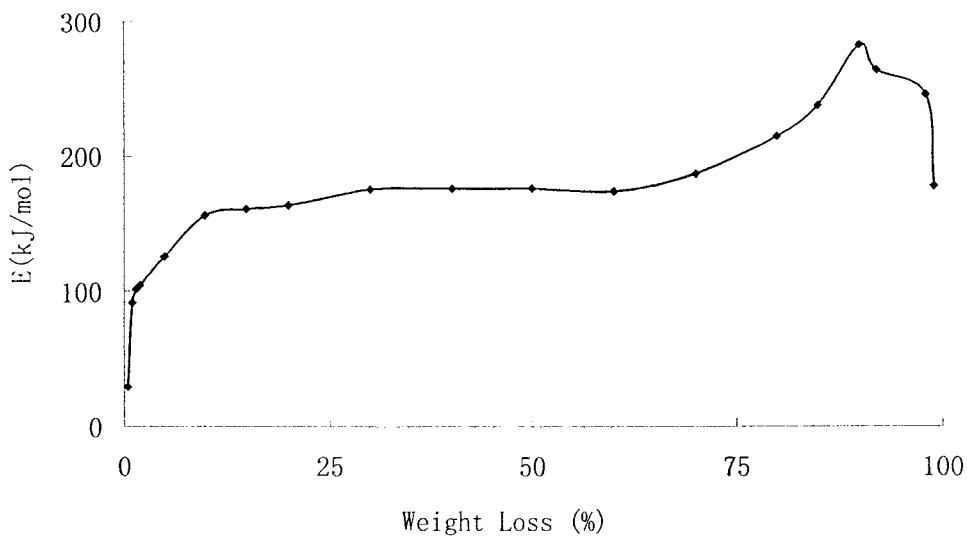
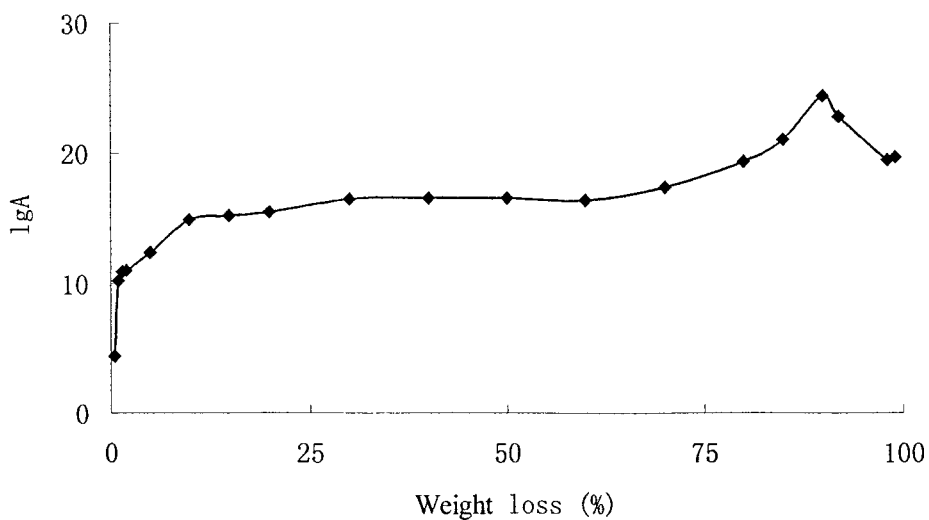**Figure 5** Relationship between E and $F(\alpha)$.

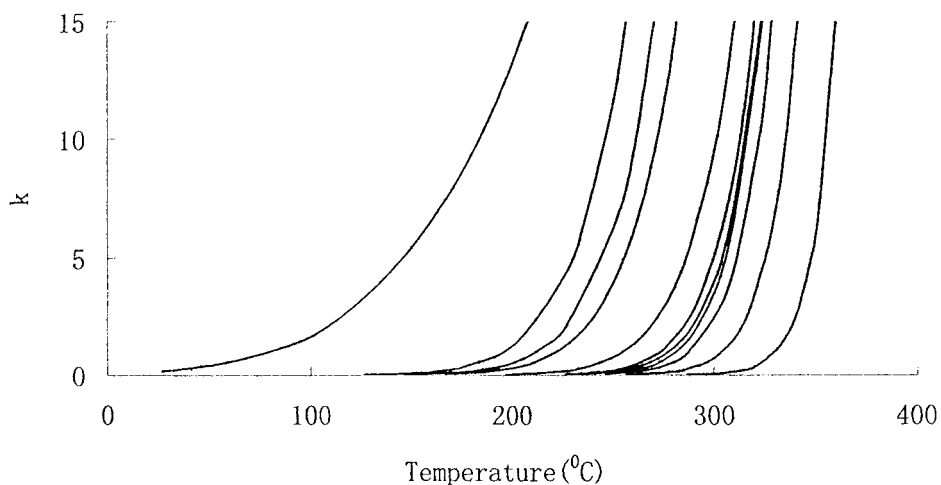**Figure 6** Relationship between A and $F(\alpha)$.

Figure 7 Relationship between k at different values of $F(\alpha)$ and the temperature: $\alpha =$ (1) 0.5, (2) 1.0, (3) 1.5, (4) 2.0, (5) 5.0, (6) 10, (7) 20, (8) 40, (9) 70, (10) 80, and (11) 90% (from left to right).

CONCLUSIONS

The thermooxidative degradation of MG in an air environment is a one-step reaction. The degradation temperatures increase with B: $T_0 = 0.697B + 350.7$, $T_p = 0.755B + 368.8$, and $T_f = 1.016B + 497.4$. The peak width of the DTG curve increases with increasing B. R_p increases with B: $R_p = 2.12B + 7.28$. The degradation rates are not affected obviously by B, and the average values of C_p and C_f are 46.7 and 99.7%, respectively. E and A vary with the increase in $F(\alpha)$ and can be divided into three phases corresponding to the volatilization of low-molecular-weight materials, the thermooxidative degradation of MG, and the oxidative reaction of residual carbon. k varies with $F(\alpha)$ and increases with the reaction temperatures.

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