Thermogravimetric Analysis of Methyl Methacrylate-Graft-Natural Rubber

ZHENG PENG, SI-DONG LI, MAO-FANG HUANG, KUI XU, CHEN WANG, PU-WANG LI, XIAO-GUANG CHEN

Agriculture Ministry Key Laboratory of Natural Rubber Processing, South China Tropical Agricultural Product Processing Research Institute, P. O. Box 318 Zhanjiang 524001, People's Republic of China

Received 20 July 2001; accepted 14 January 2002

ABSTRACT: The thermal degradations of methyl methacrylate-graft-natural rubber (MG) at different heating rates (B) in nitrogen were studied by thermogravimetric analysis. The results indicate that the thermal degradation of MG in nitrogen is a one-step reaction. The degradation temperatures increase along with the increment of heating rates. The temperature of initial degradation (T_0) is $0.448B + 362.4$°C, the temperature at maximum degradation rate, that is, the peak temperature on a differential thermogravimetric curve (T_p) is $0.545B + 380.7$°C, and the temperature of final degradation (T_f) is $0.476B + 409.4$°C. The degradation rate at T_p is not affected by B, and its average value is 48.9%; the degradation rate at T_f is not affected by B either, and its average value is 99.3%. The reaction order (n) is 2.1 and is not affected by B. The reaction activation energy (E) and the frequency factor (A) increase along with B, and the apparent reaction activation energy (E_0) is 254.6 kJ/mol. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2952–2955, 2002

Key words: natural rubber; grafting; thermal degradation, reaction kinetic; thermal stability; thermogravimetric analysis

INTRODUCTION

The grafted copolymerization of ethylene monomers onto natural rubber is an effective method of improving the properties and extending the application of natural rubber. Products with different purposes are available through grafting modification by various monomers. Research are focused at present on the methyl methacrylate-graft-natural rubber (MG) prepared by the grafting copolymerization of methyl methacrylate onto natural rubber. Grafted with methyl methacrylate (MMA), the properties of natural rubber, such as cohesive strength, adhesion bond, resistance to dynamic fatigue, wear resistance, oil resistance, and aging properties, are improved; therefore, the application scopes of NR are greatly extended. The previous research on MG mainly focused on the preparation of MG,[1–3] while in recent decades, more and more importance has been attached to the application of MG. Reports on the blend,[4] reinforcement,[5] and toughening,[6,7] of MG were published in addition to those on the application of MG in adhesive. Other researchers have studied the structures and properties of MG by means of Fourier transform infrared spectroscopy,[8] nuclear magnetic resonance, dynamic mechanical analysis,[8,9] and so on, but there are few reports on the thermal degradation of MG. In this article, the thermal degradations of MG at different heating rates (B) in nitrogen were studied by thermogravimetric analysis. The effects of heating rate on degradation temperature and degradation rate were discussed, and the kinetic parameters such as reaction order (n), reaction activation energy (E), and frequency factor (A) were calculated.

Correspondence to: S. D. Li (lisidong@pub.zhanjiang. gd.cn).

Journal of Applied Polymer Science, Vol. 85, 2952–2955 (2002)

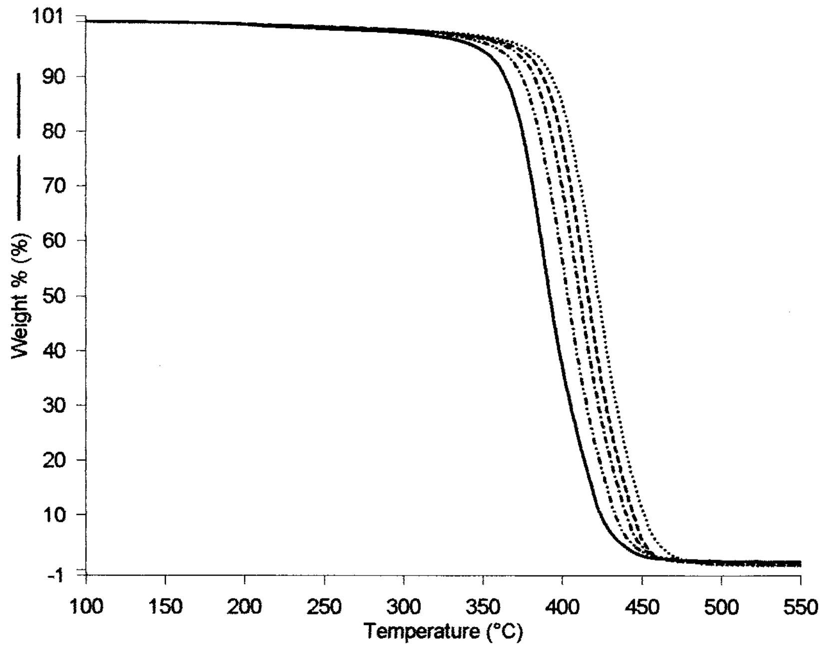

Figure 1 Thermogravimetric curves of thermal degradation of methyl methacrylate-graft-natural rubber: (—) B = 10°C/min; (– · · –) B = 20°C/min; (– · – ·) B = 30°C/min; (–––) B = 40°C/min; (· · ·) B = 50°C/min.

EXPERIMENTAL

Material

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

Thermogravimetric Analysis

The thermogravimetric analyses were carried out with a Perkin Elmer TGA-7 thermogravimetric analyzer. The mass of each sample was 5~6 mg, the carrier gas was nitrogen, with a flow rate of 50 mL min^{-1}. The samples were heated from 50° to 550°C at heating rates of 10°C min^{-1}, 20°C min^{-1}, 30°C min^{-1}, 40°C min^{-1}, and 50°C min^{-1} to record the thermogravimetric (TG) and differential thermogravimetric (DTG) curves.

Data Processing

The reaction kinetic factors were obtained by the processing of TG data through the Coats-Redfern method.[10] Integrating the reaction kinetic equation

$$d\alpha/dt = k(1-\alpha)^n \quad (1)$$

and using the Arrhenius equation

$$k = Ae^{-E/RT} \quad (2)$$

the following equations can be obtained:

$$\ln\{[1-(1-\alpha)^{1-n}]/[T^2(1-n)]\} = \ln[(1-2RT/E)AR/BE] - E/RT \quad (n \neq 1) \quad (3)$$

and

$$\ln[-\ln(1-\alpha)/T^2] = \ln[(1-2RT/E)AR/BE] - E/RT \quad (n = 1) \quad (4)$$

in which n is the reaction order, α is the reaction degree, T is the absolute temperature, B is the heating rate, E is the reaction activation energy, R is the gas constant, and A is the frequency factor. Where $n \neq 1$, a line can be obtained from the plot of $\ln\{[1-(1-\alpha)^{1-n}]/[T^2(1-n)]\}$ versus $1/T$, of which the slope is $-E/R$ and the intercept is $\ln[(1-2RT/E)AR/BE]$. Where $n = 1$, a line can be obtained from the plot of $\ln[-\ln(1-\alpha)/T^2]$ versus $1/T$, of which the slope is $-E/R$ and the intercept is $\ln[(1-2RT/E)AR/BE]$. Adopting the least squares fitting method with different n, the n with the maximum correlated coefficient (r) is

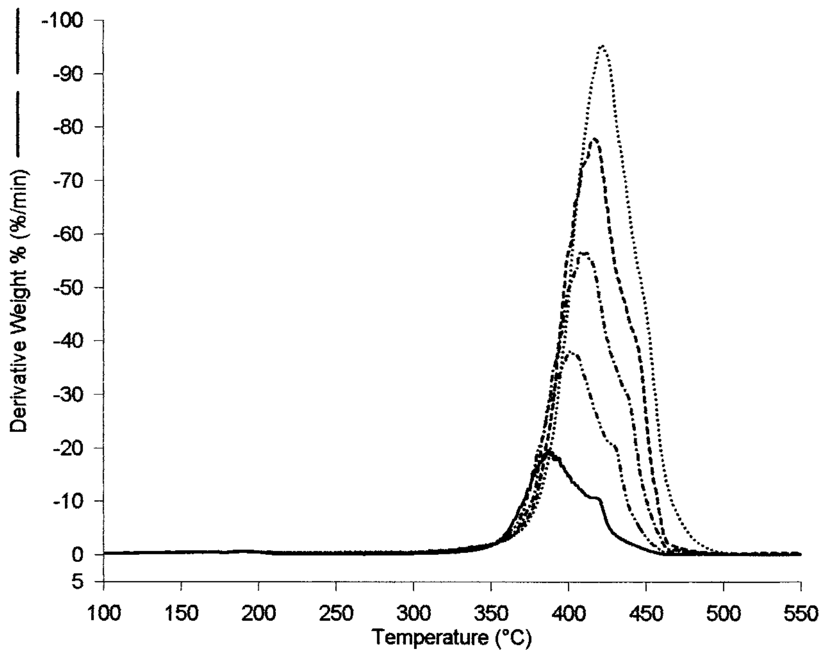

Figure 2 Differential thermogravimetric curves of thermal degradation of methyl methacrylate-graft-natural rubber: (—) B = 10°C/min; (– · · –) B = 20°C/min; (– · – ·) B = 30°C/min; (–––) B = 40°C/min; (· · ·) B = 50°C/min.

the apparent reaction order, and the corresponding E is the activation energy.

RESULTS AND DISCUSSION

Effect of Heating Rate on the Process of Thermal Degradation

Figure 1 and Figure 2 are the TG and DTG curves of thermal degradation of MG in nitrogen at five different heating rates. It can be seen that the TG curve is a smooth curve with one turn and that there is only one obvious peak on the DTG curve, indicating that the thermal degradation of MG in nitrogen is simple and is a one-step reaction. Both TG and DTG curves shift toward high temperatures along with the rising of the heating rate. The features seen in the TG and DTG curves at five different heating rates are similar.

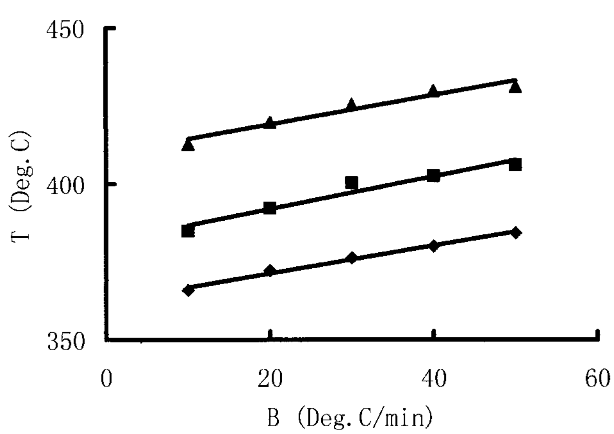

Figure 3 Relation between heating rate (B) and thermal degradation temperature (T) of methyl methacrylate-graft-natural rubber: (▲) T_f; (■) T_p; (◆) T_0.

Relation between Heating Rate and Thermal Degradation Temperature

Figure 3 shows the relation between the heating rates and the thermal degradation temperature (T). 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 the T_p is the temperature at maximum weight loss rate. The peak widths of DTG curves

Table I Relation Between B and C

B (°C/min)	10	20	30	40	50
C_p (%)	48.3	49.3	50.4	48.5	47.9
C_f (%)	99.3	99.1	99.5	99.3	99.2

Table II Kinetic Parameters of Thermal Degradation of Methyl Methacrylate-graft-natural rubber

B (°C/min)	10	20	30	40	50
n	2.1	2.1	2.1	2.1	2.1
E (kJ/mol)	261.1	276.4	284.7	295.8	299.5
A ($\times 10^{19}$)	0.19	0.26	10.00	67.31	96.08
r	0.9991	0.9999	0.9999	0.9999	0.9994

are expressed in $T_f - T_0$. It can be seen that all the degradation temperatures increase linearly with the increasing of B, indicating that the degradation temperatures are mainly affected by B. The relations between B and T are as follows:

$$T_0 = 0.448B + 362.4 \qquad T_p = 0.545B + 380.7°C$$
$$T_f = 0.476B + 409.4°C$$

The linear increment of thermal degradation temperatures along with the increasing of B is a result of the heat hysteresis. To eliminate the heat hysteresis, the thermal degradation temperatures should be expressed in equilibrium thermal degradation temperatures (T^0, the temperatures when B approaches 0). The equilibrium temperatures of MG are as follows:

$$T_0^0 = 362.4°C \qquad T_p^0 = 380.7°C \qquad T_f^0 = 409.4°C$$

The peak width of DTG curve, which is expressed in $T_f - T_0 = 47°C + 0.097\,B$, increases with the increasing of B.

Effect of *B* on Thermal Degradation Rate

Table I shows the relations between B and thermal degradation rate (C), in which C_p and C_f are the thermal degradation rates corresponding to T_p and T_f. It can be seen that the effects of B on C_p and C_f are not obvious. The average value of C_p is 48.9% and that of C_f is 99.3%.

Kinetics of Thermal Degradation

The kinetic parameters obtained by the Coats-Redfern equation are shown in Table II. It can be seen that the reaction order (n) of the thermal degradation of MG is 2.1 and is not affected by B. The frequency factor (A) rises along with B. The reaction activation energy (E) increases linearly with B.

By regressing the values of E in Table II linearly by the least square method, it can be calculated that the apparent reaction activation energy (E_0) at $B = 0$°C/min is 254.6 kJ/mol.

CONCLUSION

The thermal degradation of MG in nitrogen was a one-step reaction. The degradation temperatures increase along with the increment of heating rate. $T_0 = 0.448\,B + 362.4$, $T_p = 0.545\,B + 380.7$, $T_f = 0.476\,B + 409.4$. The peak width of the DTG curve increases with the increasing of B. The degradation rates are not affected obviously by B, and the average values of C_p and C_f are 48.9% and 99.3%, respectively. The reaction order (n) is 2.1, the reaction activation energy (E) and the frequency factor (A) increase along with the increment of B, and the apparent reaction activation energy (E_0) is 254.6 kJ/mol.

REFERENCES

1. Cooper, W.; Vangham, G.; Miller, S. J Polym Sci 1959, 34, 651.
2. Lenka, S.; Mayak, P. L.; Das, A. P. Angew Makromol Chem 1984, 126, 107.
3. Lenka, S.; Nayak, P. L.; Das, A. P. J Appl Polym Sci 1985, 30, 429.
4. Seriver, R. M. Eur Pat Appl EP 514 910, 1992.
5. Gorton, A. D. NR Technol 1984, 15, 7.
6. Schneider, M.; Pith, T.; Lambla, M. Polym Adv Technol 1995, 6, 326.
7. Schneider, M.; Pith, T.; Lambla, M. J Mater Sci 1997, 32, 6343.
8. Oommen, Z.; Thomas, S. J Appl Polym Sci 1997, 65, 1245.
9. Perera, M. C. S. J Polym Sci 1999, 37, 1141.
10. Coats, A. W.; Redfern, J. P. Nature 1964, 201, 8.