Synergistic Thermal Stabilization Effect of Polyamide/Melamine on Polyoxymethylene

Youliang Hu, Xin Zheng, Lin Ye

The State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, People's Republic of China

ABSTRACT: The synergistic thermal stabilization effect of polyamide (PA) and melamine (MA) on polyoxymethylene (POM) was studied by isothermal weight loss analysis and nonisothermal thermogravimetric analysis, which showed that the complex stabilizer PA/MA was more efficient than the single-use formaldehyde absorbents MA or PA in improving the thermal stability of POM. The nonisothermal degradation kinetics study further demonstrated the synergistic thermal stabilization effect of PA/MA on POM. The mechanical property investigation showed that the addition of a proper amount of PA or the proper reduction of MA content improved the impact strength of POM. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 2387–2391, 2005

Key words: polyamides; stabilization; thermal properties

INTRODUCTION

Polyoxymethylene (POM) is an engineering plastic with excellent mechanical properties, and it has a wide range of applications in industry.[1,2] The main chain of the copolymer-type POM is composed of —CH_2—O— bonds with a few —CH_2CH_2—O— segments. The methyl oxide bonds are easy to break under heat and oxygen; this breakage results in a continuous deformaldehyde reaction. The formaldehyde and formic acid from the oxidized formaldehyde can accelerate such a reaction.[3–6] Therefore, study of the thermal stabilization of POM is substantially important.[7–11] For the thermal stabilization system of POM, low-molecular-weight compounds such as melamine (MA) and dicyandiamide are often used as the main formaldehyde absorbents in this industry due to their high thermostabilizing efficiencies. However, they are easily volatilized during high-temperature melting processes, which results in the loss of the compounds, a reduction of the thermostabilizing efficiency, and the formation of mold deposits. Excessive use of such compounds even leads to a decrease in the mechanical properties of POM. In this study, MA was used as the main formaldehyde absorbent of POM. Polyamide (PA) with high molecular weight displayed a compara-tively high processing thermal stability and was used to assist the formaldehyde absorbent of POM through the addition reaction of the active hydrogen from the amine group of the PA molecule to the formaldehyde produced by the POM decomposition.[12] The synergistic thermal stabilization effect of the complex stabilizer PA/MA on POM was studied.

EXPERIMENTAL

Materials

The POM used in this study was a commercial-grade powder without any additives and was supplied by Yuntianhua Co., Ltd. (Yunnan, China). The POM was a copolymer type with a melt flow index of 9.0 g/l0 min (M90). Both PA and MA were commercial-grade products, and MA was purchased from the Kelong Chemical Reagent Factory of Chengdu (Chengdu, China). Other processing aids were used without further purification.

Preparation of the modified POM

POM powder, PA, MA, and other processing aids were compounded at appropriate proportions in a high-speed mixer and were then extruded by a TSSJ-25/03 twin-screw extruder at a rotational speed of 45 rpm. The temperature of the barrel was in the range 180–220°C. The extrudate was pelletized and dried.
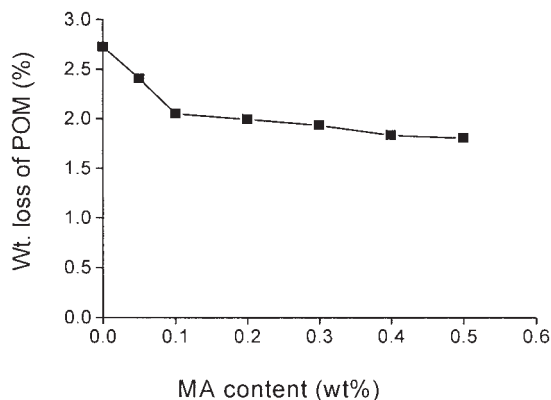
Figure 1 Effect of MA content on $W\%$ of POM (in the absence of PA).

Thermal stability analysis

Isothermal weight loss measurement

The isothermal weight loss measurements were carried out in a heating oven at 220°C for 1 h, and the samples were in the granulated state. The thermal weight loss ($W\%$) was calculated by the following equation:

$$W\% = \frac{W_0 - W_1}{W_0} \times 100\% \tag{1}$$

where W_0 is the original weight of the samples and W_1 is the weight of the samples after thermal degradation for 1 h.

Thermogravimetric analysis (TGA)

TGA was performed with a TA2950 thermobalance from TA Instruments (New Castle, DE) with a flow rate of 50 mL/min under an air atmosphere. The granulated samples (ca. 10 mg) were heated from ambient temperature to approximately 400°C at a rate of 10°C/min. All samples were dried in the heating oven at 80°C for 2 h before the test.

Nonisothermal degradation kinetics

The nonisothermal decomposition of a solid-state material can be expressed with eq. (2), from which the Coats–Redfern equations[13] [eqs. (3) and (4)] are deduced, and the nonisothermal degradation kinetics can be evaluated as

$$d\alpha/dT = \frac{1}{\beta} A \exp\left(-E/RT\right) f(\alpha) \tag{2}$$

$$\ln\left[\frac{1 - (1 - \alpha)^{1-n}}{T^2(1 - n)}\right]$$
$$= \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \qquad (n \neq 1) \quad (3)$$

$$\ln\left[\frac{-\ln(1 - \alpha)}{T^2}\right]$$
$$= \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \qquad (n=1) \quad (4)$$

where α is the decomposed fraction, T is the absolute temperature, A is the frequency factor, β is the heating rate, E is the activation energy, R is the gas constant, n is the order of the reaction, and $f(\alpha)$ is the differential expression of kinetics function.

For most of the reaction temperature ranges and E values, $E/RT \gg 1$ and $(1 - 2RT/E) \approx 1$. Therefore, the first item of the right side of eq. (3) or eq. (4), $\ln[AR/\beta E(1 - 2RT/E)]$, can be considered a constant. If one plots $\ln[-\ln(1 - \alpha)/T^2]$ versus $1/T$ at $n = 1$ or $\ln\{[1 - (1 - \alpha)^{1-n}]/[T^2(1 - n)]\}$ versus $1/T$ at $n \neq 1$, a linear curve can be obtained, and the parameters E and A can be estimated from the plots.

Mechanical property measurements

The tensile strengths of the samples were measured with a model 4302 material testing machine from Instron Co. (Norwood, MA), according to ISO527/1-1993 (E). The test speed was 50 mm/min, and the sample length between bench marks was 50 ± 0.5 mm.
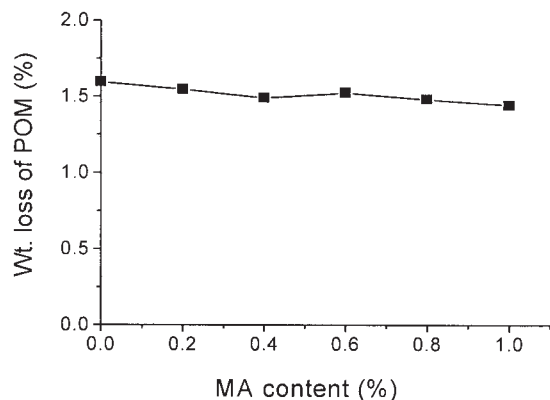
The impact strength of the samples was measured with ZBC-4B impact testing machine from Xinsansi Co. (Shenzhen, China) according to ISO179-1993 (E).
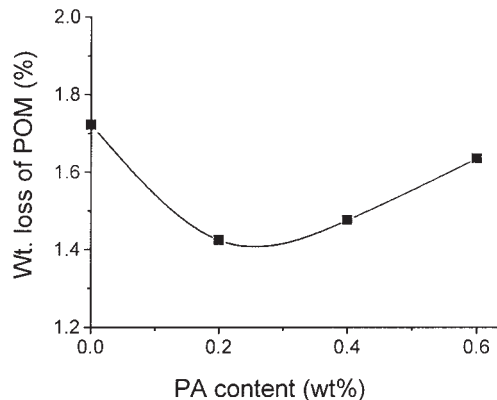
Differential scanning calorimetry (DSC)

The miscibility study of the POM/PA system was performed with a Netzsch 204 Phoenix (Germany)
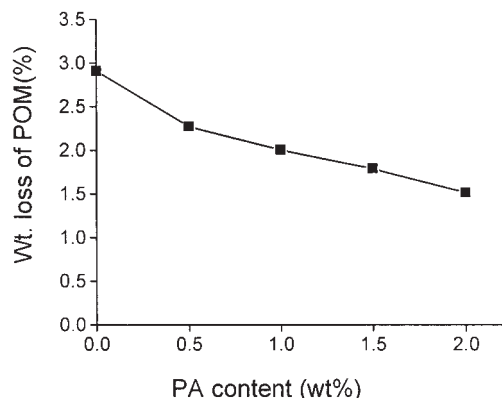
Figure 2 Effect of PA content on $W\%$ of POM (in the absence of MA).

Figure 3 Effect of MA content on $W\%$ of POM (0.6 wt % PA).

Figure 4 Synergistic effect of PA/MA on the thermal stability of POM.

differential scanning calorimeter. The temperature scale of DSC was calibrated with indium. The granulated samples (ca. 10 mg) were heated from ambient temperature to 200°C at a constant rate of 10 K/min under a nitrogen atmosphere. All samples were dried in a heating oven at 80°C for 2 h before the test.

RESULTS AND DISCUSSION

Effect of MA content on $W\%$ of POM

The thermal stability effect of the single-use formaldehyde absorbent MA on POM was first investigated. Figure 1 shows $W\%$ of POM with different contents of MA (in the absence of PA) after thermal degradation in the heating oven at 220°C for 1 h. $W\%$ of POM decreased with increasing MA content. When the MA content was lower than 0.1 wt %, $W\%$ of POM declined sharply with the addition of MA from 2.71 to 1.96 wt %, which indicated that MA absorbed the formaldehyde produced by the thermal degradation efficiently and restrained the depolymerization of POM. When the MA content was higher than 0.1 wt %, $W\%$ of POM decreased slowly. Therefore, 0.1 wt % MA was a critical concentration and enough to enhance the thermal stability of POM.

TABLE I
Composition of the Complex Stabilizer MA/PA

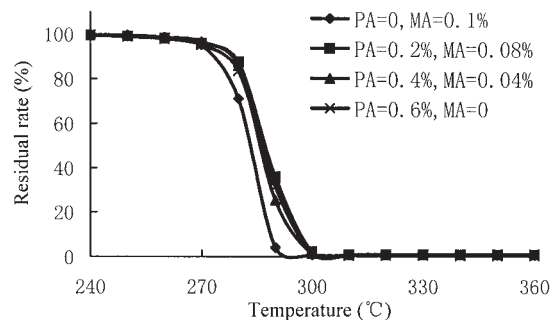| MA content (wt %)	PA content (wt %)	MA/PA
0.1	0	0.1 wt % MA
0.08	0.2	Equivalent to 0.1 wt % MA
0.04	0.4	Equivalent to 0.1 wt % MA
0	0.6	Equivalent to 0.1 wt % MA

Effect of PA content on $W\%$ of POM

Figure 2 shows $W\%$ of POM with different contents of PA (in the absence of MA) after thermal degradation in the heating oven at 220°C for 1 h. $W\%$ of POM decreased with the addition of the single-use formaldehyde absorbent PA. When the PA content was lower than 0.6 wt %, $W\%$ of POM decreased quickly with the addition of PA. When the PA content was higher than 0.6 wt %, $W\%$ of POM decreased slowly.

Effect of MA content on $W\%$ of POM (in the presence of PA)

With the PA content maintained at 0.6 wt %, the effect of MA content on the thermal stability of POM was studied.

Figure 3 shows $W\%$ of POM with different contents of MA (0.6 wt % PA) after thermal degradation in the heating oven at 220°C for 1 h. There were very small changes in $W\%$ of POM with increasing MA content when the POM contained 0.6 wt % PA. This indicated that this content of PA was enough to improve the thermal stability of POM, and any further addition of
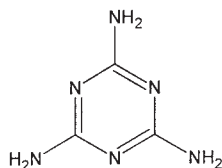

Figure 5 TGA curves of POM with different PA/MA contents (in air at 10°C/min).

TABLE II
TGA Parameters of POM with Different PA/MA Contents (in Air)

PA content (wt %)	MA content (wt %)	T_{onset} (°C)	T_{peak} (°C)	T_{end} (°C)	$T_{5\%}$ (°C)	$T_{20\%}$ (°C)	$T_{50\%}$ (°C)	V_{max} (%/°C)
0	0.1	276.73	284.13	289.62	271.6	279.7	283.0	5.75
0.2	0.08	280.81	287.33	294.43	272.3	283.1	287.0	5.1
0.4	0.04	280.88	288.56	293.01	274.8	282.8	287.0	5.5
0.6	0	279.97	289.69	294.67	270.2	282.9	287.0	5.0

formaldehyde absorbent was not favorable for the reduction of $W\%$.

This study showed that for MA or PA used alone, the thermal stabilization efficiency for POM with 0.6 wt % PA was equivalent to that with 0.1 wt % MA.

The molecular weight of MA is 126, which is approximately that of the PA molecule segment. There are six active hydrogen atoms for one MA molecule, which could be used as the high-efficient formaldehyde absorbent. PA with a high molecular weight can also be used as a formaldehyde absorbent, but there is only one active hydrogen atom for one PA molecule segment. Therefore, for PA, about six times the weight of MA is required to achieve the same thermostabilizing efficiency, which is coincident with the evidence described previously. Moreover, the formula design could be varied to study the synergistic effect of PA/MA on the thermal stability of POM, in which the total amount of the formaldehyde absorbent used was equivalent to 0.1 wt % MA, as shown in Table I.
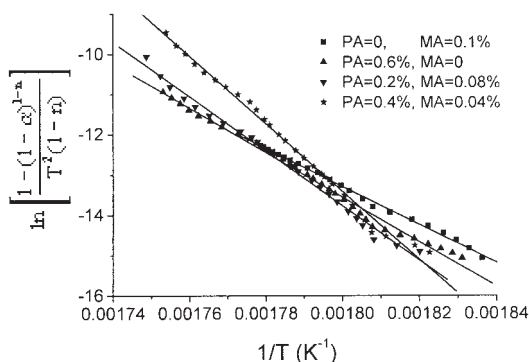
Synergistic thermal stabilization effect of PA/MA on POM

The molecular formulas of MA and PA are as follows:

$$-[\,NH-(CH_2)_m-CO\,]_n-$$

PA

Figure 4 shows $W\%$ of POM for the compositions of Table I after thermal degradation in the heating oven at 220°C for 1 h. $W\%$ of POM by the addition of the complex stabilizer PA/MA was much lower than that by the addition of the single-use PA or MA with equal contents. This higher stabilizing effect indicated that PA and MA had synergistic effects on the thermal stability of POM.

TGA is an important method for the study of the thermal stability of materials.[14] The thermal degradation characteristic temperatures T_{onset} and T_{end} represent the temperatures at the intersection point of the tangent line at the fastest $W\%$ rate with the extension line at the start and end of the degradation, respectively. V_{max} and T_{peak} are the maximal thermal degradation rate and the temperature at this point, respectively. $T_{5\%}$, $T_{20\%}$, and $T_{50\%}$ are the temperatures of the samples with weight losses of 5, 20, and 50 wt %, respectively.

Figure 6 Kinetics of POM thermal degradation.

TABLE III
Thermal Degradation Kinetic Parameters of POM with the Coats–Redfern Equation

PA content (wt %)	MA content (wt %)	n	E (kJ/mol)	A (s^{-1})
0	0.1	0.6	390.8	4.47×10^{36}
0.2	0.08	2	561.7	4.64×10^{52}
0.4	0.04	2.5	698.9	6.5×10^{65}
0.6	0	1.7	459.2	1.08×10^{43}

TABLE IV
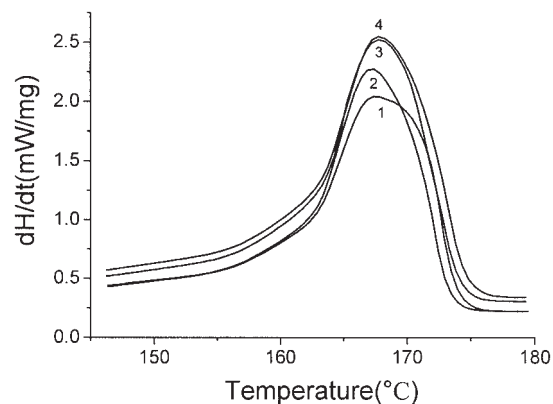**Effect of PA/MA Content on the Mechanical Properties of POM**

PA content (wt %)	MA content (wt %)	Tensile strength (MPa)	Elongation at break (%)	Charpy notched impact strength (kJ/m²)
0	0.1	59.07	41.59	5.87
0.2	0.08	58.65	48.71	7.15
0.4	0.04	57.93	54.65	6.99
0.6	0	57.63	46.68	7.29

Figure 7 DSC curves of virgin POM and POM with different contents of PA with a β value of 10 K/min. The PA contents of samples 1–4 were 0, 0.2, 0.4, and 0.6 wt %, respectively. H = melt enthalpy.

As shown in Figure 5, the TGA curves of the samples presented simple inverse *S*-shape correlations, which indicated that the decomposition process of POM had only one stage. Table II lists the TGA characteristic temperatures of POM. As shown, the thermal degradation characteristic temperatures T_{onset}, T_{peak}, T_{end}, $T_{5\%}$, $T_{20\%}$, and $T_{50\%}$ for POM with the complex stabilizer PA/MA were much higher than those with single-use MA and a little higher than those with single-use PA. The complex stabilizer PA/MA was more efficient for the thermal stability of POM because of the synergistic effect of PA and MA. On the other hand, the single-use MA was easily volatilized during the high-temperature melting process, which led to loss of the compounds and the reduction of the thermostabilizing efficiency. The curves in Figure 5 also provide information for evaluating the kinetics of degradation by the Coats–Redfern method. Theoretically, a linear line can be obtained with a proper *n*, as shown in Figure 6. These curves are fitted by the method of least squares, *E* is determined from the slope, and *A* is determined from the intercept at $1/T = 0$, as presented in Table III.

E represents the energy to destroy the molecular structure of polymers, and *A* is the frequency factor of the molecular movement at this time. *E* and *A* reflect the thermal stability of POM. The higher *E* and *A* are, the more stable POM is at high temperatures. As shown in Table III, the *E* and *A* values of POM with the single-use

formaldehyde absorbents MA or PA were far lower than those of the complex stabilizer PA/MA, which further demonstrated that the synergistic effect of PA/MA on POM improved the thermal stability of POM.

The mechanical properties of POM with an equal total amount of formaldehyde absorbent used are shown in Table IV. As shown, the elongation at break and charpy notched impact strength improved with increasing PA content, whereas the tensile strength dropped. As shown in Table V, for the same PA content, a proper reduction in the amount of MA improved the impact strength of POM. In summary, the partial replacement of MA with PA improved the thermal stability and mechanical properties of POM.

As shown in Figure 7, the DSC curves of POM with different contents of PA/MA had only one melting peak, which indicated the very nice miscibility of POM with PA resulting from the interaction of hydrogen bonds, coincident with the improvement in the mechanical properties of POM with the addition of PA.

TABLE V
Comparison of the Mechanical Properties of POM with Different PA/MA Contents

PA content (wt %)	MA content (wt %)	Elongation at break (%)	Charpy notched impact strength (kJ/m²)
0.2	0.1	50.99	7.07
0.2	0.08	48.71	7.15
0.4	0.1	49.16	6.83
0.4	0.04	54.65	6.99
0.6	0.1	49.90	7.01
0.6	0	46.68	7.29

References

1. Hasegawa, S.; Takeshita, H.; Yoshii, F.; Sasaki, T.; Makuuchi, K.; Nishimoto, S. Polymer 2000, 41, 111.
2. Hisakatsu, H.; Kohji, T. Polymer 2003, 44, 3107.
3. Merrill; O'Brien, N.; Frank, M. B. U.S. Pat. 3,444,265 (1969).
4. Kohan, M. I. U.S. Pat. 3,960,984 (1976).
5. Showaib, E. A.; Wyzgoski, M. G. J Mater Sci 2002, 37, 1895.
6. Pearson, A. W. N.; Groves, G. W. J Polym Sci: Polym Phys Ed 1976, 14, 903.
7. Wunderlich, B.; Robb, R. Chemie 1971, 147, 79.
8. Mucha, M. Colloid Polym Sci 1984, 262, 851.
9. Pecorini, T. J.; Manson, J. A.; Hertzherg, R. M. J Mater Sci 1990, 25, 3388.
10. Showaib, E. A.; Sehanobish, K.; Moet, A. Polym Eng Sci 1995, 35, 786.
11. Seidler, S.; Sczerba, T.; Zelenka, R. Kunstst Plast Eur 2001, 92, 40.
12. Kumar, G.; Mahesh, L.; Neelakantan, N. R.; Subramanisn, N. Polym Int 1993, 31, 289.
13. Coats, A. W.; Redfern, J. P. Nature 1964, 201, 68.
14. Li, Y. Thermal Analysis; Beijing: Tsinghua University Press, 1987; p 12.