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Investigation on thermo-stabilization effect and nonisothermal degradation kinetics of the new compound additives on polyoxymethylene

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Abstract An increase in the thermal stability of several new additives on polyoxymethylene (POM) was attempted via thermogravimetric analysis (TGA) (static state) and balance torque testing (dynamic state), which truly reflected the processing in practice. The thermal stability of POM was improved by adding some of additives actually, especially for the compound stabilizer with oxidized polyethylene wax (OPE), low molecular weight polyamide 6 (LMWPA6) and triphenyl phosphate (TPP) from the static and dynamic data. Furthermore, the kinetic parameters for compound stabilizers of POM degradation were calculated from thermogravimetry (TG) curves by Coats-Redfernd method. The results reveal that the degradation temperatures of POM can be obviously raised by compound stabilizers OPE/LMWPA6/TPP. The long-term thermo-stability test of POM shows that POM with stabilizing system above has no obvious decrease in impact strength after storage duration of 15 days in an oven at 140 °C.

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Introduction

Polyoxymethylene (POM) belongs to the group of engineering thermoplastics with high mechanical strength, excellent abrasion, fatigue resistance, moldability, etc., so it has a wide application in industry [1, 2]. Despite these apparent advantages, POM has a propensity to depolymerize (or "unzip") into formaldehyde (CH_2O) under specific circumstances (Fig. 1). Since 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 (FA) and formic acid from the oxidized FA can accelerate such a reaction, this is usually called zipper mechanism in academia [3, 4]. The stabalizers must be added into POM to prevent the attack of molecular oxygen to the methylene groups [5]. Searching heat stabilizers which is also called FA-absorbent is always an important study for the thermal stabilization system of POM. The effect of heat stabilizer is to consume the FA produced by POM decomposition through chemical reaction, inhibiting the continuous accelerated deterioration. An overview of commonly used additives, such as stabilizers against thermo- and photooxidative degradation, proton acceptors, nucleating agents, processing aids (Table 1), etc., for POM can be found in Ref. [6]. Thermogravimetry (TG) is a thermoanalytical technique where the weight of a sample is monitored during a linear heating program under a constant purge of inert gas or air [7]. As the degradation of POM mainly involves a zipper mechanism, thermogravimetric analysis (TGA) is a very adequate method to determine the relative stability of differently stabilized polyacetals [8]. With temperature increment, the weight of loss of POM resulted from randomly initiated chain scissions, this can be monitored by TGA exactly.

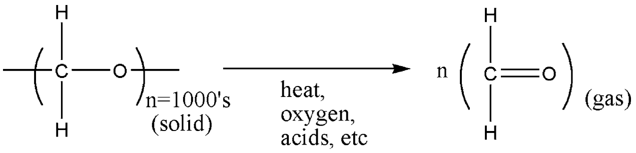


Fig. 1 Methods of degradation of pure POM

The initial studies for the thermal additives of POM focused on the compounds which contain nitrogen atom and then using polymer as thermal stabilizers gradually. Alsup [9] first reported that using polyamide synthesized by themselves as heat stabilizer for POM. Johnson [10] found carrier resin can make good dispersion for polyamide stabilizer. Hu and Ye [11] synthesized melamine-formaldehyde polycondensate (MF) as heat stabilizer for POM, and they found that MF made a significant increase in the thermal stability of POM in comparison with melamine. Thermal stability is not the only constraint on these materials, and processibility of these materials must also be considered. Polly, Wagman [12] investigated polyamide and polyurethane blending which had synergistic thermal stabilization effect on POM. This effect of polyamide/melamine on POM was also investigated by Hu et al. [13]. Furthermore, some studies [14] showed that compounds with hydroxyl and amine groups have better effect on the thermal stabilization for POM. It is because the active hydrogen atoms on these groups can react with FA produced by POM decomposition. However, the choice of new effective additives as stabilizers and compound stabilizers has hardly been reported. On the other hand, the effect of shearing stress on the decomposition of POM in processing was ignored in previous investigations. Thus the aim of the article was to study the thermo-stabilization effect of new additives on POM by means of thermogravimetric analysis (static state) and balance torque testing (dynamic state), which truly reflected processing in practice. Moreover, the mechanical property of the specimens in long-term thermal environment was also investigated.

Experimental

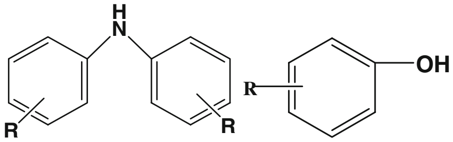
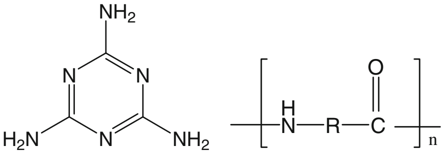
Materials

Polyoxymethylene which is a copolymer type with a melt flow index of 9.0 g/l0 min (M90), purchased from Yuntianhua Co., Ltd. (Yunnan, China), and was a commercial grade granule without any additives. Oxidized polyethylene wax (OPE), low molecular weight polyamide 6 (LMWPA6) were purchased from Shanghai Joule Wax Industry Co., Ltd. Triphenyl phosphate (TPP), Diethanolamine, Benzamide, and *β*-diketone were obtained from Shanghai Reagents Co. Other processing aids were used without further purification.

Preparation of the POM blends

Polyoxymethylene granule, LMWPA6, TPP, OPE, and other processing aids were compounded at appropriate proportions in a high-speed mixer and were then extruded by a twin-screw extruder at a rotational speed of 40 rpm. The temperature of the barrel was in the range of 180–220 °C. The extrudates were pelletized and dried.

Table 1 The types of additives used in POM processing

Types	Common additives	Structure
Antioxidant	Amine antioxidants, hindered phenol antioxidants	
Thermal stabilizer	Melamine, polyamides	
Nucleating agents	Zinc oxide, carboxylate nuclenting agent	ZnO, RCOOM
Photostabilizer	Hindered-amine, UV-absorber	
Processing aids	Fluoropolymer additive, acrylate copolymer	

Methods

Thermogravimetric analysis investigations: The thermogravimetric measurements were performed using a TGA Q50 (TA Instruments) under air and nitrogen atmosphere (sample purge gas flow 60 mL/min, balance purge gas flow (only nitrogen) 40 mL/min). The granulated samples (ca. 5 mg) were heated from ambient temperature to approximately 400 °C under air atmosphere and 500 °C under nitrogen atmosphere at a rate of 20 °C/min. In the following figures, the results of the TGA investigations were plotted as percentage of the remaining sample mass to the initial one (designated as TG) as a function of the temperature if not otherwise mentioned. All samples were dried in the heating oven at 80 °C for 2 h before the test.

Nonisothermal degradation kinetics: The nonisothermal degradation of a solid-state material can be expressed with Eq. 1, from which the Coats–Redfern equations (Eqs. 2 and 3) are deduced [15], and the nonisothermal degradation kinetics can be evaluated as follows:

$$\frac{d\alpha}{dt}=\frac{1}{\beta}A\exp(-E/RT)f(\alpha) \quad (1)$$

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

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

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 $(1\text{-}2RT/E) \approx 1$. Therefore, the first item of the right side of Eqs. 2 or 3, $\ln\,[AR/\beta E(1\text{-}2RT/E)]$, can be considered as a constant. If one plots $\ln\,[-\ln\,(1-\alpha)/T^2]$ versus $1/T$ at $n = 1$ or $\ln\,\{[1-(1-\alpha)^{1-\mathrm{n}}]/[T^2(1-n)]\}$ 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.

Balance torque analysis: The balance torque presents the melt viscosity of polymers. For the same polymer system, the higher the value of balance torque, the higher the value of the melt viscosity, the molecular weight (M_w) and the thermal stability of the polymer [16]. The balance torque analysis was performed with RM-200 HAPRO torque rheometer. The granulated sample weight was 40 g, the measurement temperature and time were 230 °C and 30 min, respectively.

Melt index measurement: The melt index (MI) was measured with XNR-400 melt index meter from Chengde Jinjian Testing Instrument Co., Ltd. The measurement temperature was 190 °C, and the load was 2.16 kg.

Mechanical property tests: The tensile strength of the samples was measured with RG 0-5 material testing machine from Shenzhen Reger Instrument Co., Ltd., according to GB/T 1040-90. The test speed was 50 mm/min, and the sample length between bench marks was 50 ± 0.5 mm. The Notched charpy impact strength of the samples was measured with XJU-22 impact testing machine from Chengde Jinjian Testing Instrument Co., Ltd., according to GB/T 1043–93.

Results and discussion

TGA investigations

As shown in Fig. 2, the TG curves of the samples presented simple inverse 'S' shape correlation, which indicated that the decomposition process of POM had only one stage [17], the onset degradation temperatures of these six single-use stabilizers by addition of 0.3 wt% on POM were almost improved. It is showed that diethanolamine, β-diketone, LMWPA6, TPP, especially LMWPA6 and TPP had better thermo-stabilization effect for POM. The onset degradation temperatures of POM with LMWPA6 and TPP are much higher than virgin POM, but the end degradation temperature of POM with LMWPA6 is much higher than that with TPP. Moreover, when the weight loss of 3 wt% for POM with LMWPA6 and TPP, their temperatures are almost improved more than 10 °C, respectively. Whereas, the thermal degradation characteristic temperatures of POM with Benzamide had no changes nearly in comparison with neat POM, and the thermal stability of other specimens was higher than that with Benzamide but lower than that with LMWPA6.

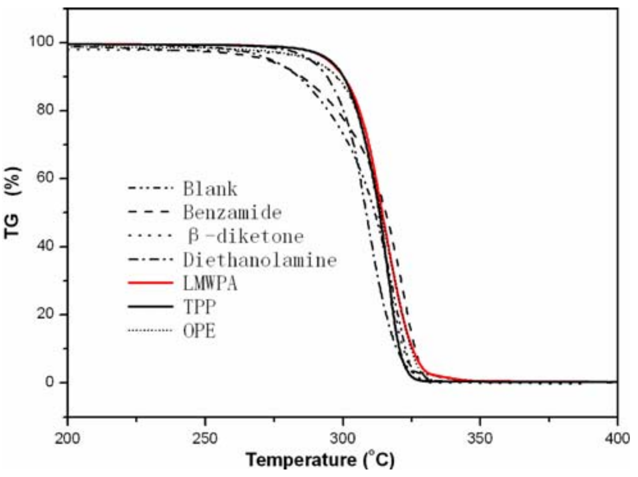


Fig. 2 TG curves of POM with different thermo-stabilizers (in air)

Polyamide with high M_w displayed a comparatively high processing thermal stability and was used to assist the FA-absorbent of POM through the addition reaction of the active hydrogen from the amine group of the polyamide molecule to the FA produced by the POM decomposition [18]. Despite these apparent merits, polyamide has much higher melting point than POM which make POM easier to degrade. LMWPA6 not only has these advantages, but also it has low melting point than polyamide due to its relative low M_w. Therefore, we chose LMWPA6 as additive and this analysis was testified by the result of experiment data.

Thermogravimetric analysis curves show that there was a first section with a low degradation rate followed by an accelerated degradation. In the section with the lower degradation rate, the stabilizers were systematically consumed and therefore retarded the degradation. After the complete depletion of the additives and the resulting random chain scissions, the thermal stability of the polymer no longer exists. In the following section, a more rapidly progressing degradation is going. Nevertheless, the accelerated degradation resulted not just from the lack of an efficient stabilizer, but mainly from the action of degradation products that induce the scission of POM, as reported in Refs. [19].

The lowering in the onset temperature in air is an indicator that the stabilizing system is consumed during thermooxidative degradation and that pre-damage (e.g., hydroperoxide substituents) in the molecular backbone happened [20]. The hydroperoxides on the backbone can induce chain scission and form FA, and hydroperoxides can also oxidize the FA to formic acid. Both the reactions are responsible for the acidolytic degradation of the polyacetal chain [21].

In every case, the onset temperatures and V_{max} (the maximal thermal degradation rate) were higher in nitrogen than in air (Fig. 3). As mentioned above the reaction POM with oxygen induces chain scissions and formation of compounds which accelerate the degradation. So as one can see on the TGA-results in Fig. 3, the presence of oxygen in combination with high temperature leads to an earlier breakdown of the POM-chain than only high temperatures in an inert atmosphere.

Most notably, it is observed that a decelerated degradation at about 5% residual mass in air. This effect is apparently not due to the decomposition of stabilizers, as suggested in Ref. [17]. The dynamic TGA of POM with addition of different content LMWPA6 shows that the presence of the stabilizer increased the thermal stability drastically in comparison with neat POM in nitrogen and air. In conclusion, the TG curves of POM with 0.5 wt% content LMWPA6 are shifted to higher temperatures than POM with other content LMWPA6 samples, in both air and nitrogen. Moreover, 0.5 wt% content of additives is the best content for effect of thermal stability on POM, which is also verified by a large number of tests.

Carrier resins have preferable dispersion as stabilizers for polymer [10]. OPE has very good dispersion effect and lubricating ability as a carrier resin. Furthermore, some hydroxyl groups on OPE can also be used as FA absorbent to improve thermo-stability of POM. In addition, TPP has absorbable effect for ultraviolet radiation. Therefore, we use OPE and TPP as the second and the third group of compound stabilizers with the same content of 0.5 wt%.

The TGA investigations reveal that the onset temperature increased by addition of the second and the third group, which showed OPE and TPP had the stabilizing ability for POM. As showed in Fig. 4, the onset and derivative TG_{max} (DTG_{max}) temperatures were higher with addition of the second group (OPE) on POM than virgin POM. From Figs. 4 and 5, we can find that TPP also made a big effect to improve thermal stability of POM

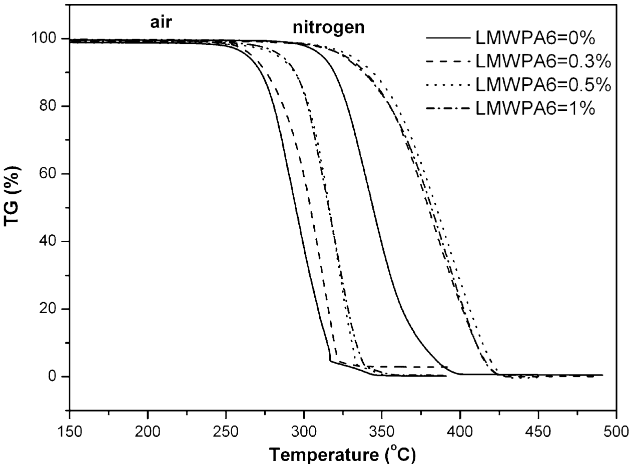


Fig. 3 TG curves of POM with different LMWPA6 contents in nitrogen and air

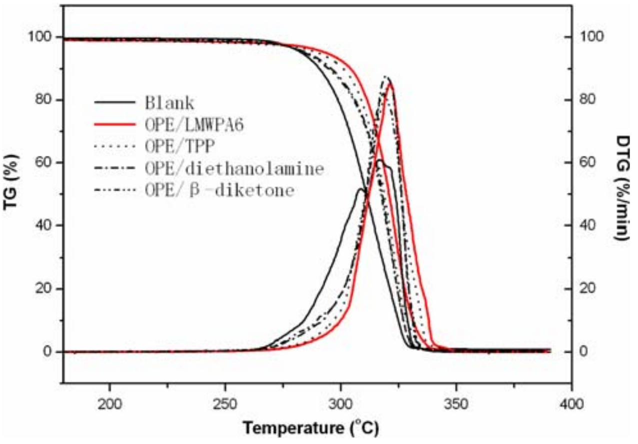


Fig. 4 TG and DTG curves of POM with addition of two groups of stabilizers in air

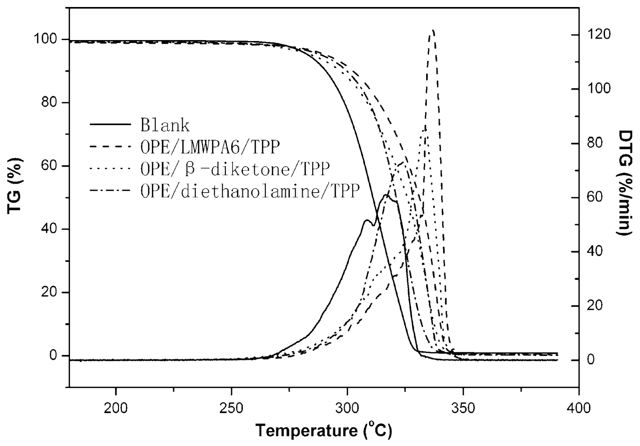


Fig. 5 TG and DTG curves of POM with addition of three groups of stabilizers in air

as the third group in compound stabilizer. Moreover, the characteristic temperatures of POM with the compound stabilizer OPE/LMWPA6/TPP increased notably. Also the corresponding degradation rate of POM with OPE/LMWPA6/TPP expressed by the DTG curves was remarkably higher than that with other compound stabilizers (Fig. 5). This higher heat stabilizing effect indicated that OPE, LMWPA6, and TPP had synergistic thermal stabilization effect on POM.

Nonisothermal degradation kinetics

The curves in Fig. 5 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 Fig. 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 2. *E* represents the energy to destroy the molecular structure of polymers, A and R are the frequency factor of the molecular movement and regression coefficient, respectively. *E* and *A* reflect the thermal stability of POM, besides, R shows us the reliability of this method. All the values of R are higher than 0.998, so the results through this method are creditable. The higher *E* and *A* are, the more stable POM is at high temperatures. As shown in Table 2, the *E* and *A* values of neat POM was far lower than those with the compound stabilizers, especially for POM with OPE/LMWPA6/TPP, which further demonstrated that the compound stabilizer OPE/LMWPA6/TPP on POM improved the thermal stability of POM greatly.

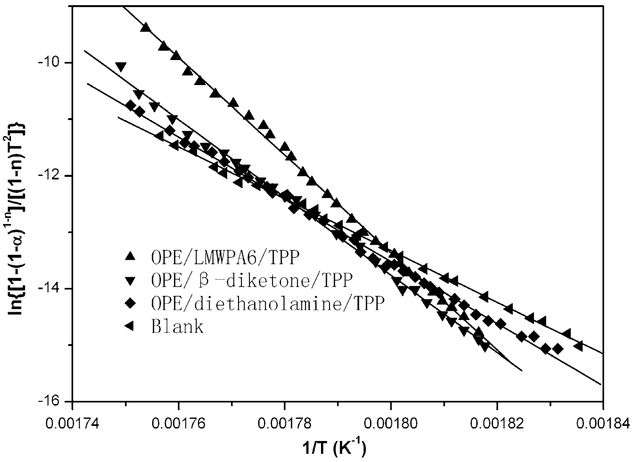


Fig. 6 Kinetics of POM thermal degradation

Table 2 Thermal degradation kinetic parameters of POM with the Coats–Redfern equation

Stabilizer	*n*	E (KJ/mol)	A (s^{-1})	R
Blank	1.3	381.03	9.98×10^{32}	0.99918
OPE/Diethanolamine/TPP	1.5	457.2	1.43×10^{40}	0.9986
OPE/LMWPA6/TPP	2	699.1	6.69×10^{63}	0.999
OPE/*β*-diketone/TPP	1.7	571.2	7.83×10^{50}	0.99867

The balance torque tests

The balance torque presents the melt viscosity of polymers. For the same polymer system, the higher the value of the balance torque, the higher the value of the melt viscosity, the M_w, and the thermal stability of the polymer. As shown in Fig. 7, the balance torque of POM decreased with mixing time, which was relatively low for the virgin POM, and dropped to 1.5 N m in 30 min, and can be improved remarkably by addition of FA absorbent. The decrease rate was obviously smaller for POM with OPE/LMWPA6/TPP than with OPE/Diethanolamine/TPP, the values were

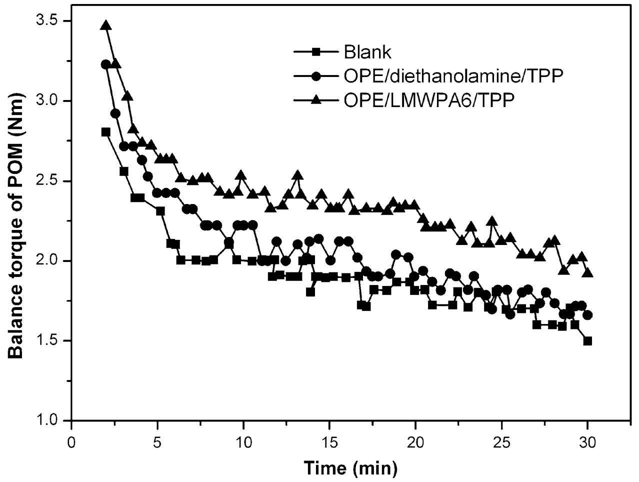


Fig. 7 Effect of different compound stabilizers on the balance torque of POM

1.92 N m and 1.66 N m, respectively, indicating that OPE/LMWPA6/TPP made an increase in the thermal stability of POM than OPE/Diethanolamine/TPP during the processing of POM. After the effect of heat, oxygen and shearing stress, the color of these products are different. The neat POM is becoming black, POM with OPE/Diethanolamine/TPP is yellowing, whereas the color of POM with OPE/LMWPA6/TPP is still keeping originally. This indicates that the three additives have some relationship for color retaining on POM.

The long-term thermo-stability

According to [6], 140 °C is a common critical temperature for long-term heat stability investigations. After the artificial aging, the visual aspect of the specimens shows changes in comparison to the initial condition. As reported in Ref. [6] the specimens are discolored as a result of the oven aging. Figure 8 shows that the weight loss of POM increased with the duration of the storage at 140 °C, and the increase extent of virgin POM was higher than POM with OPE/LMWPA6/TPP. The primary value of MI for POM with additives was almost the same as that of virgin POM as shown in Fig. 9. However, with an increase in aging time, the increase in MI for POM with the compound stabilizer was lower than that of POM without any additive, indicating that OPE/LMWPA6/TPP can reduce the degree of molecule degradation of POM during the long-term under heat and oxygen.

The average M_w of POM at aging time can be calculated by the following equation [22] and listed in Table 3.

$$MI = 1.3 \times 10^{18} M_w^{-3.55} \quad (4)$$

The mechanical properties of virgin POM and POM with OPE/LMWPA6/TPP after the long time aging are shown in Fig. 10a, c. After 3 days' aging, the values of mechanical properties for all samples increased, perhaps due to the more perfect crystallization of POM induced by heat. With further increment of time, the tensile strength and elongation at break decreased for both samples. Additionally, the impact strength decreased for the virgin POM, perhaps resulting from the molecule degradation and drop of the M_w of POM, while for POM with OPE/LMWPA6/TPP, there was no obvious decrease of impact strength.

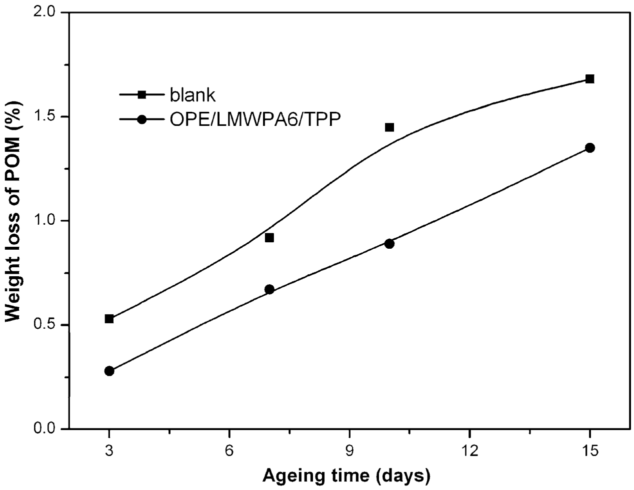


Fig. 8 Aging weight loss of POM with and without OPE/LMWPA6/TPP

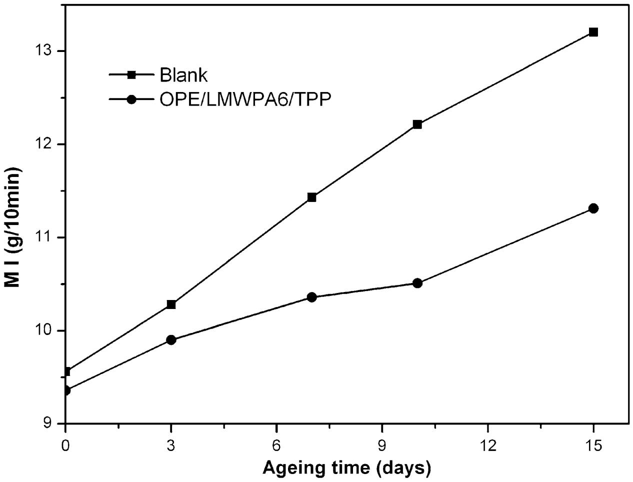


Fig. 9 Influence of aging time for POM with and without OPE/LMWPA6/TPP on melt index (MI)

Table 3 Effect of aging time on M_w of POM

Aging time (day)	M_w	
	Blank	OPE/LMWPA6/TPP
0	67034	67439
3	65678	66382
7	63748	65538
10	62564	65273
15	61206	63930

Conclusion

The present investigations revealed that the thermal stabilization of POM were improved by addition of new heat stabilizers selected on some conditions mentioned above. Furthermore, we found that OPE, LMWPA6, and TPP achieved very good thermal stability on POM through static and dynamic testing. The TGA investigations showed that the onset temperature increased with addition of the second and the third group. The nonisothermal degradation kinetics indicated that the activation energy of neat POM was far lower than those of the compound stabilizers,

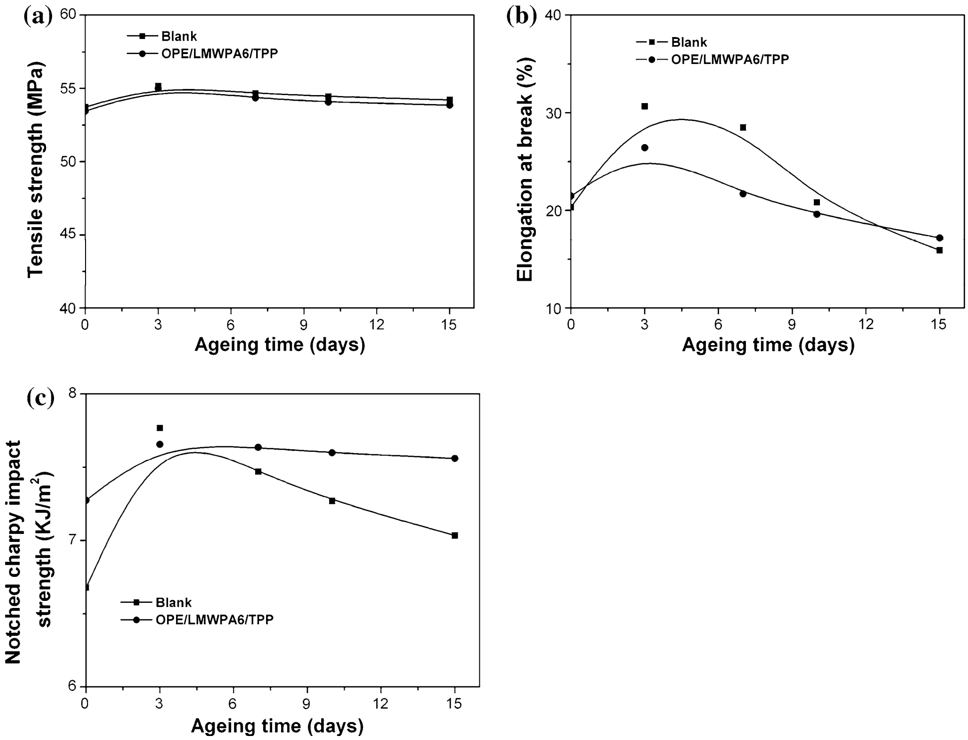


Fig. 10 Effect of aging time on the tensile strength (**a**), elongation at break (**b**), and Notched charpy impact strength (**c**) of POM

especially for POM with OPE/LMWPA6/TPP, which further demonstrated that the compound stabilizers on POM improved the thermal stability of POM greatly. After storage duration of 15 days in an oven at 140 °C, the specimens were discolored and the mechanical properties were decreased, while for POM with OPE/LMWPA6/TPP, there was no obvious decrease of impact strength. The condition mentioned in this article is similar to practice actually, so we believe that this study will have the value of potential application. Moreover, the detailed mechanism of the synergistic thermal stabilization effect of these compound stabilizers for POM is still under our research.

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References

1. Hasegawa S, Takeshita H, Yoshii F et al (2000) Polymer 41:111
2. Hisakatsu H, Kohji T (2003) Polymer 44:6973
3. Showaib EA, Wyzgoski MG (2002) J Mater Sci 37:1895. doi: 10.1023/A:1014971922547
4. Pearson AWN, Groves GW (1976) J Polym Sci: Polym Phys Ed 14:903
5. Lüftl S, Archodoulaki VM, Seidler S (2006) Polym Degrad Stab 91:464
6. Stohler FR, Berger K (1990) Angew Makromol Chem 176/177(3074):323
7. Moulinié P, Paroli RM, Wang ZY, Delgado AH (1996) Polym Test 15:75
8. Archodoulaki VM, Lüftl S, Seidler S (2008) Polym Test 27:236
9. Alsup et al (1961) United States Patent no. 2, 993, 025
10. Johnson R W (1978) United States Patent no. 4, 098, 843
11. Hu YL, Ye L (2006) Polymer 47:2649
12. Wagman M E et al (1987) United States Patent no. 4, 640, 949
13. Hu YL, Zheng X, Ye L (2005) J Appl Polym Sci 97:2387
14. Li X, Qu MJ (2007) Plastic Manuf (Chinese) 1/2(150):77
15. Coats AW, Redfern JP (1964) Nature 201(4914):68
16. Yu J (2001) Appl Eng Plast Chinese 29(4):28
17. Chang FC, Yang MY (1990) Polym Eng Sci 30:543
18. Kumar G, Mahesh L, Neelakantan NR, Subramanisn N (1993) Polym Int 31:289
19. Lüftl S, Archodoulaki VM, Koch T, Seidler S (2008) J Vinyl Addit Technol 10:21
20. Kern W (1967) Chemiker-Ztg/Chem Apparatur 91(8):255
21. Archodoulaki VM, Lüftl S, Seidler S (2004) Polym Degrad Stab 86(1):75
22. Youliang Hu, Lin Ye, Xiaowen Zhao (2006) Polymer 47:2656