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Synthesis of the melamine–formaldehyde polycondensate and its thermal stabilization effect on polyoxymethylene☆

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Abstract

Melamine (MA) was polymeric modified by condensation reacting with formaldehyde (FA) to form the melamine formaldehyde polycondensate (abbreviation: MF) with high molecule-weight and comparatively high processing thermo-stability. The effect of the reacting molar ratio of MA and FA, and the types and concentrations of the dispersion agents on the structure and properties of MF were discussed, and the finely divided, cross-linked, and thermo-stable MF polycondensates were obtained. The thermal stabilization effect of MF on POM was studied by the isothermal weight loss analysis at 220 °C, isothermal weight loss rate analysis at 222 °C, thermal gravity analysis (TGA) and balance torque analysis, which showed that MF has almost the equal thermal stabilization on POM to MA. The multiple processing and long-term thermal stability at high temperature measurements indicated that MF showed even higher thermal stabilization on POM than MA. Moreover, the impact strength was improved after five times of extrusion, due to the better dispersion of MF in POM matrix and better nucleation effect of MF on POM.

Keywords: Polyoxymethylene (POM); Melamine formaldehyde polycondensate (MF); Thermal stabilization

1. Introduction

Polyoxymethylene (POM) has a wide range of applications in industry due to its high mechanical strength, excellent abrasion resistance, fatigue resistance, moldability, and the like, for example, in electrical and electronic applications, automotive applications, and precision machine applications [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, and the continuous deformaldehyde reaction occurs. The formaldehyde and formic acid from the oxidized formaldehyde will accelerate the deformaldehyde reaction [3–7]. Therefore, POM displays very poor thermo-stability. For the thermal stabilization system of POM, low-molecular weight compounds such as melamine (MA) and dicyandiamide are often used as the main formaldehyde-absorbent in the present industry due to their high thermo-stabilizing efficiency. But they are easy to volatilize during high-temperature melting process resulting in the loss of the compounds, reduction of the thermo-stabilizing efficiency and formation of mould deposit. Excessive use of such compounds even leads to a decrease of the mechanical properties of POM. In this paper, MA was polymeric modified by condensation reacting with formaldehyde (FA) to form the melamine formaldehyde polycondensate (abbreviation: MF) with high molecule-weight and comparatively high processing thermo-stability, which acts as the formaldehyde-absorbent by the addition reaction of the hydrogen on the amine groups of it's molecules with formaldehyde produced by the decomposition of POM. MF has been widely studied and used as the paper reinforcing agents, surface coating materials, adhesives and polymer synthesis additives, and few literature reports about the application as the formaldehyde absorbent. This research focused on the synthesis of MF and its stabilization effect on POM.

2. Experimental

2.1. Materials

The POM used in this study is a commercial grade powder without any additives and supplied by Yuntianhua Co., Ltd (Yunnan, China), which is a copolymer type with a melt flow

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index value of 9.0 g/10 min (M90). Melamine (MA) with the chemical purity, formaldehyde (FA), ethanolamine, gelatin and sodium carboxylmethyl cellulose with the analytical purity were all purchased from Kelong Chemical Factory of Chengdu, China. Polyvinyl alcohol with analytic purity was purchased from Beipei Chemical Factory of Chongqing, China. Other processing aids and chemical agents are all commercial grade products and used without further purification.

2.2. Synthesis of the melamine–formaldehyde polycondensate (MF)

A certain amount of melamine (MA) and the formaldehyde (FA) aqueous solution were added to the three-necked bottle with the molar ratio of MA/FA 1:1.33, 4.They were heated to 75 °C. Then the dispersion agent was added and the pH value was adjusted to weak acidic. When the reaction system became white cloudy, the temperature was raised to 90–95 °C, and the reaction lasted for 1.5 h. The pH value was adjusted to 7–8, and the reaction was terminated. The cross-linked polycondensate was precipitated and washed with water, dried, and stored at low temperature.

2.3. Preparation of the modified POM

POM powder, MA or MF and other processing aids were compounded with appropriate proportion in a high-speed mixer, and 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 of 180–220 °C. The extrudate was pelletized and dried.

2.4. Measurements

2.4.1. Isothermal weight loss measurement

The isothermal weight loss measurement is carried out in the heating oven at 220 °C for 1 h. The thermal weight loss ($W\%$) can be calculated as follows:

$$W\% = \frac{W_0 - W_t}{W_0} 100\%$$

where W_0 is the original weight of the sample and W_t is the weight of the samples after thermal degradation for the time t.

After the unstable part of POM sample decomposed rapidly, the degradation rate can be obtained by plotting the denary logarithm of the residual weight percentage (R) of the remained sample against heating time (t). The samples underwent thermal degradation in the heating oven at 222 °C, and then were taken out for the measurement of R per 20 min, respectively.

2.4.2. Thermogravimetric analysis (TGA)

TGA was performed by a TA2950 thermobalance from TA Co. (USA) with the flow rate of 50 ml/min under air atmosphere. The granulated samples of about 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 measurement.

2.4.3. 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 and the thermal stability of the polymer [10].

The balance torque analysis was performed with HC-90 HAAKE torque rheometer. The granulated sample weight was 74 g, and the measurement temperature and time were 230 °C and 30 min, respectively.

2.4.4. Yellow index measurement

The yellow index (YI) was measured with DC-P3 full automatic chromatic aberration meter from Xingguang instrument Co. (China). The samples were reprocessed by extrusion up to five times and then pressed to a flake which thickness was 1.5 mm. According to GB 2409–80 of China, a few points on the flake were selected and the relevant stimulus values X, Y, Z were measured. Then YI can be calculated as the following formula:

$$\mathrm{YI} = \frac{100(1.28X - 1.06Z)}{Y}$$

The YI of the samples was the average value of YI for all the points on the flake samples.

2.4.5. Melt index measurement

The melt index (MI) was measured with CS-127C melt index meter from Subsidiary of Atlas Electric Devices Co. (USA). The measurement temperature was 190 °C, and the load was 2.16 kg.

2.4.6. Non-isothermal crystallization analysis

The non-isothermal crystallization was performed with Netzsch 204 Phoenix DSC of Germany. The temperature scale of DSC was calibrated with indium. The granulated samples of about 10 mg were heated from ambient temperature to 200 °C at a constant rate of 10 K/min under nitrogen atmosphere. After keeping for 5 min to eliminate the effect of the previous thermal history, the samples were cooled to 80 °C at the same constant rate. All samples were dried in the heating oven at 80 °C for 2 h before the test. The absorbed quantity of heat during melt of the polymer is substantively the quantity of heat for destroying the crystal structure. The higher the crystallinity (X_c), the more the melting heat. X_c can be calculated by the following equation

$$X_c = \frac{\Delta H_m}{\Delta H_0} 100\% \tag{1}$$

where ΔH_m is the melting heat of the samples and ΔH_0 is the equilibrium melting heat, i.e. the melting heat of 100% crystallizing polymer, which is 190 J/g.

2.4.7. Scanning electron microscopy measurement (SEM)

The surfaces morphology analysis of the tensile fractured samples and the particle size and distribution of the MF-polycondensate were performed with JEOL JSM-5900LV scanning electron microscopy (SEM) of Japan. The operating voltage was 20 KV.

2.4.8. Particle size measurement

The particle size and distribution measurement of the MF-polycondensate was performed with Jl-1155 laser diffraction particle size analyzer. The sample was prepared by being dispersed in distilled water, and further ultrasonic-dispersing for 5 min.

2.4.9. FTIR analysis

The FTIR analysis of the MF composition was conducted with Nicolet-560 infrared spectrometer of USA.

2.4.10. Mechanical property measurement

The tensile strength of the samples was measured with 4302 material testing machine from Instron Co. (USA) 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 Notched charpy impact strength of the samples was measured with ZBC-4B impact testing machine from Xinsansi Co. (Shenzhen of China) according to ISO179-1993 (E).

3. Results and discussion

3.1. The synthesis of the melamine–formaldehyde polycondensate (MF)

3.1.1. The effect of the reactants ratio on the molecular structure of MF

The reaction of MA and FA mainly includes two steps, the addition reaction resulting in the production of hydroxymethyl precondensate, and the condensation reaction resulting in the production of cross-linking polycondensate [8–9]. The molar ratio of MA/FA has significantly effect on the molecular structure and property of the polycondensate product. The higher amount of FA led to much more amount of hydroxylmethyl and higher degree of cross-linking MF product with less content of the remained active hydrogen atoms on the product molecules, which are not suitable for use as the formaldehyde absorbent anymore. On the other hand, low amount of FA led to the low cross-linking degree and low thermo-stability for the product. So it's substantially important to determine the suitable molar ratio of MA/FA to ensure a certain degree of crosslinking and high thermo-stability of the product, and in the meantime to remain the unreacted hydrogen on MF molecules as much as possible to play the role as the formaldehyde absorbent. The molar ratio of MA/FA 1:1.33, 1:1.6, 1:2 and 1:4 were used to prepare MF-polycondensate.

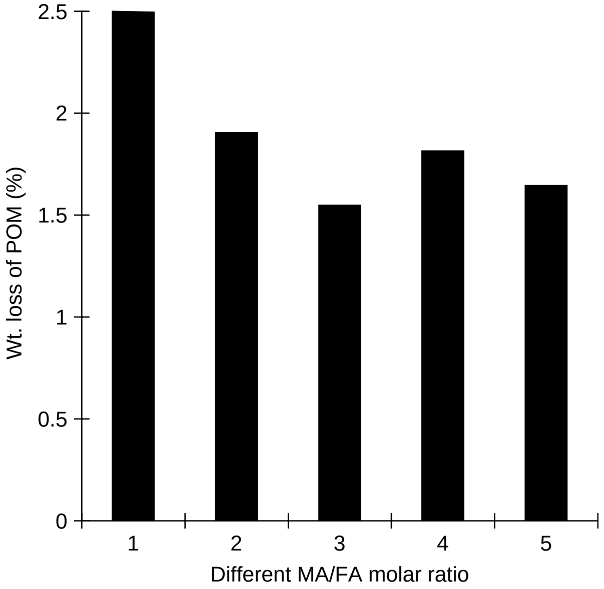


Fig. 1. Effect of MF with different MA/FA molar ratio on the isothermal weight loss of POM. The sample 1 is virgin POM in absence of FA absorbent. The MA/FA molar ratio of the samples 2–5 are 1:1.33, 1:1.6, 1:2 and 1:4, respectively.

Fig. 1 showed the thermal weight loss of POM in absence or in presence of MF with the amount of 1 wt% under 220 °C for 1 h. For POM in absence of MF, the thermal weight loss was remarkable high. For MF with the molar ratio MA:FA = 1:1.6, POM had the smallest thermal weight loss. For lower amount of FA (MA:FA = 1:1.33), the lower cross-linking degree of MF polycondensate was produced, which was unstable and decomposed during the process of the thermal weight loss measurement under high temperature. But for too high amount of FA, the unreacted hydrogen on the MF molecules was not remained enough for application as the formaldehyde absorbent, and its thermal stabilization effect on POM was reduced.

Fig. 2 showed the FTIR of MA and MF with different MA/FA molar ratio. For MA molecule, the absorbance peak at 3134–3470 and 1652 cm^{-1} attributed to the stretching vibration and bending vibration of primary amine group H–N–H, respectively. But for MF, the above absorbance peaks all disappeared, and the stretching vibration peak of secondary amine group N–H appeared at 3382 cm^{-1}, the methylene group C–H stretching vibration peak appeared at 2960 cm^{-1}, the C–N stretching vibration peak of the secondary and tertiary amines appeared at 1339 cm^{-1}, and the ether bond C–O stretching vibration peak appeared at 1157 cm^{-1}.

According to the reaction conditions and the above composition analysis of the synthesized MF product, the molecule structure of MF can be proposed as shown in Fig. 3.

3.1.2. The effect of dispersants on MF

Polyvinyl alcohol (PVA), sodium carboxylmethyl cellulose (CMC) and gelatin (GEL) are the commonly used polymer dispersants. Both PVA and CMC have very good dispersion

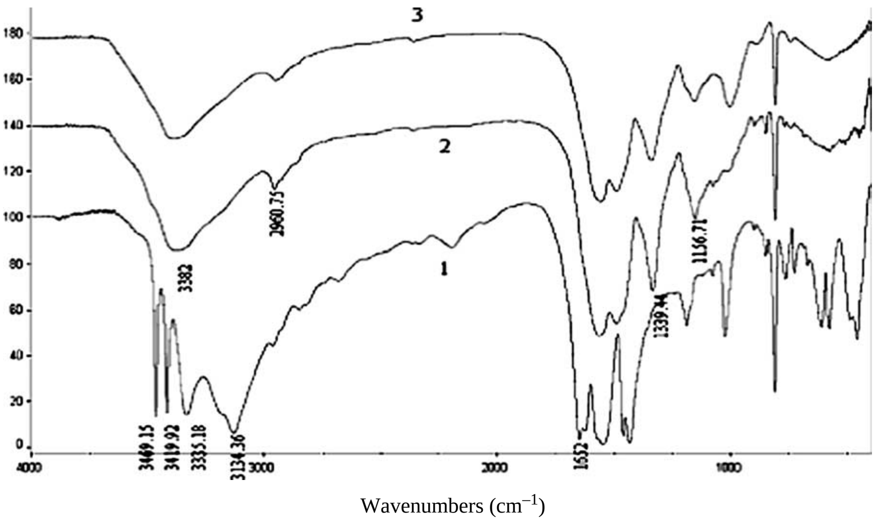


Fig. 2. FTIR of MA or MF with different MA/FA molar ratio. 1: MA 2: MF (MA:FA = 1:1.6) 3: MF (MA:FA = 1:4).

effect, but their gel-keeping capability is poor. On the contrary, GEL has very poor dispersion effect and high gel-keeping capability [8]. The complex dispersants of gelatin/polyvinyl alcohol (GEL/PVA), and gelatin/sodium carboxylmethyl cellulose (GEL/CMC) were applied in the reaction system with both high dispersibility and gel-keeping capability for the synthesis of MF.

Fig. 4 and Table 1 displayed the particle size and its distribution of MF prepared with different dispersants under the reactants ratio MA:FA = 1:1.6 for the reaction system. The dispersant of 1$^{\#}$, 2$^{\#}$ and 3$^{\#}$ reaction system was GEL/CMC with one, two, and three parts of weight, and 4# system was GEL/PVA with one part of weight. The particle size for the particle number of 10, 30, 50, 90 and 97% can be presented as D10, D30,

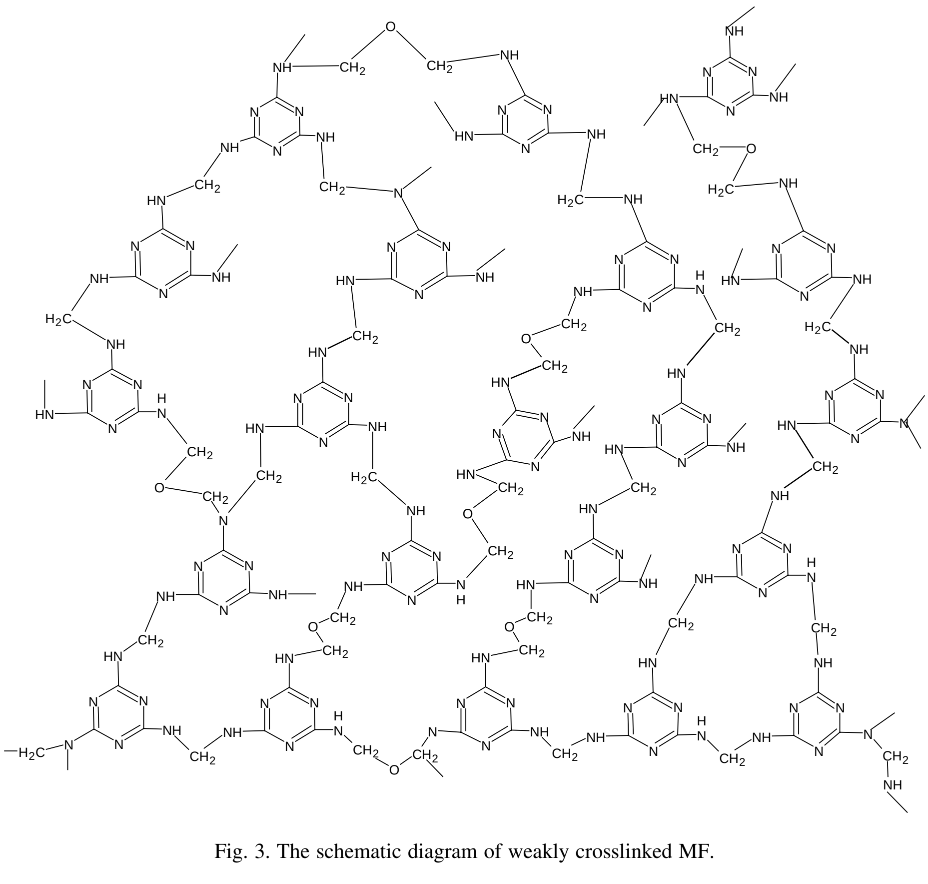


Fig. 3. The schematic diagram of weakly crosslinked MF.

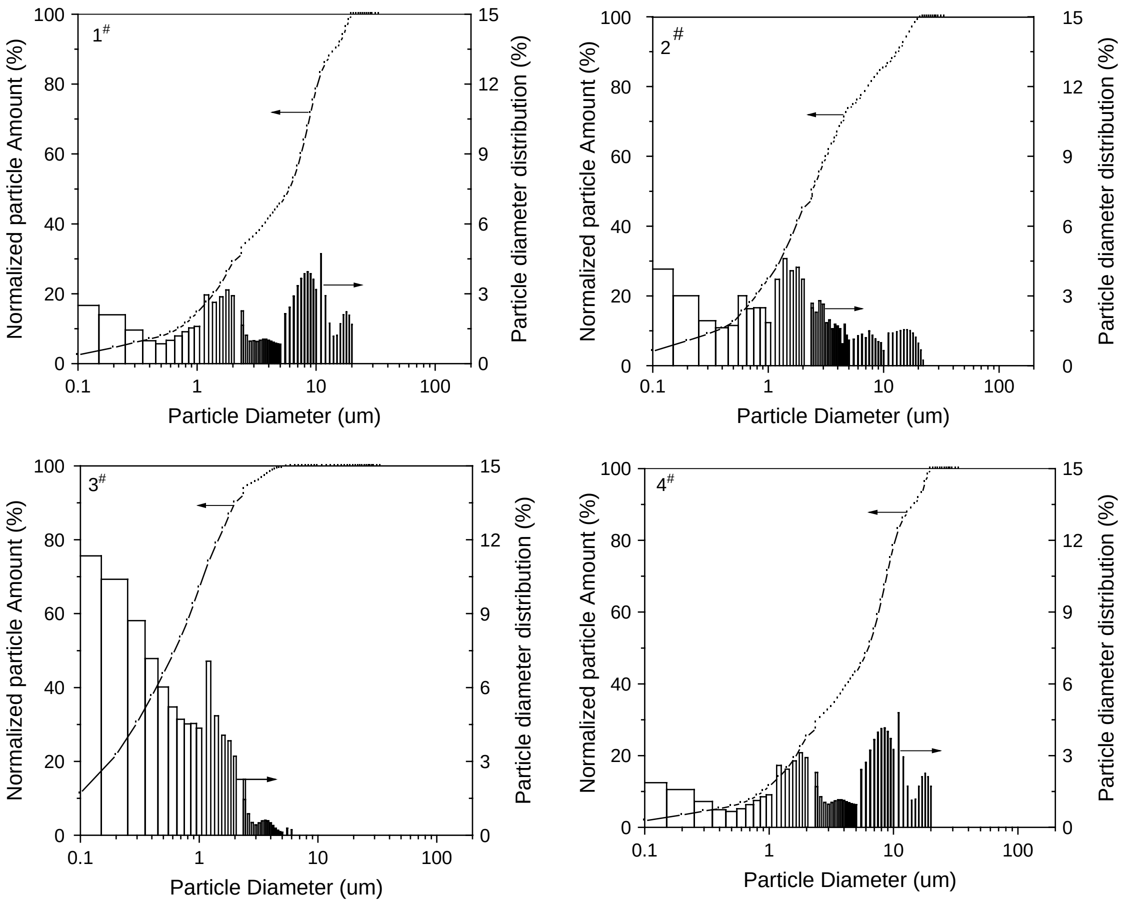


Fig. 4. The particle size and distribution of MF with different dispersant. The dispersant of sample 1–4$^{\#}$ is: 1×(GEL/CMC), 2×(GEL/CMC), 3×(GEL/CMC), 1×(GEL/PVA), respectively.

D50, D90 and D97%. All the particle sizes and distribution for MF with 1# and 4# reaction system were similar with each other, which indicated that the dispersion effect of PVA and CMC for MF synthesis system were equivalent. The D50% of MF with 1–3$^{\#}$system was 6.0, 2.3 and 0.6 μm, respectively. The D10, D30, D50, D90 and D97% decreased with the increase of the amount of GEL/CMC, and the distribution also moved to the small particle size, which was also demonstrated by SEM analysis result, as shown in Fig. 5.

The SEM images also indicated that MF with 1$^{\#}$ and 2$^{\#}$ had good dispersion effect, and the particles for 3$^{\#}$ and 4$^{\#}$ were easy to agglomerate with poor dispersion.

Fig. 6 showed the effect of MF with the above four dispersants on the Notched charpy impact strength of POM. The MF amount was all 1 wt%. The impact strength of POM for MF with GEL/PVA was lower than that of GEL/CMC, and MF with two parts of weight of GEL/CMC was higher than that with one and three parts of weight of GEL/CMC, which indicated that POM for MF with two parts of weight of GEL/CMC showed the best impact toughness.

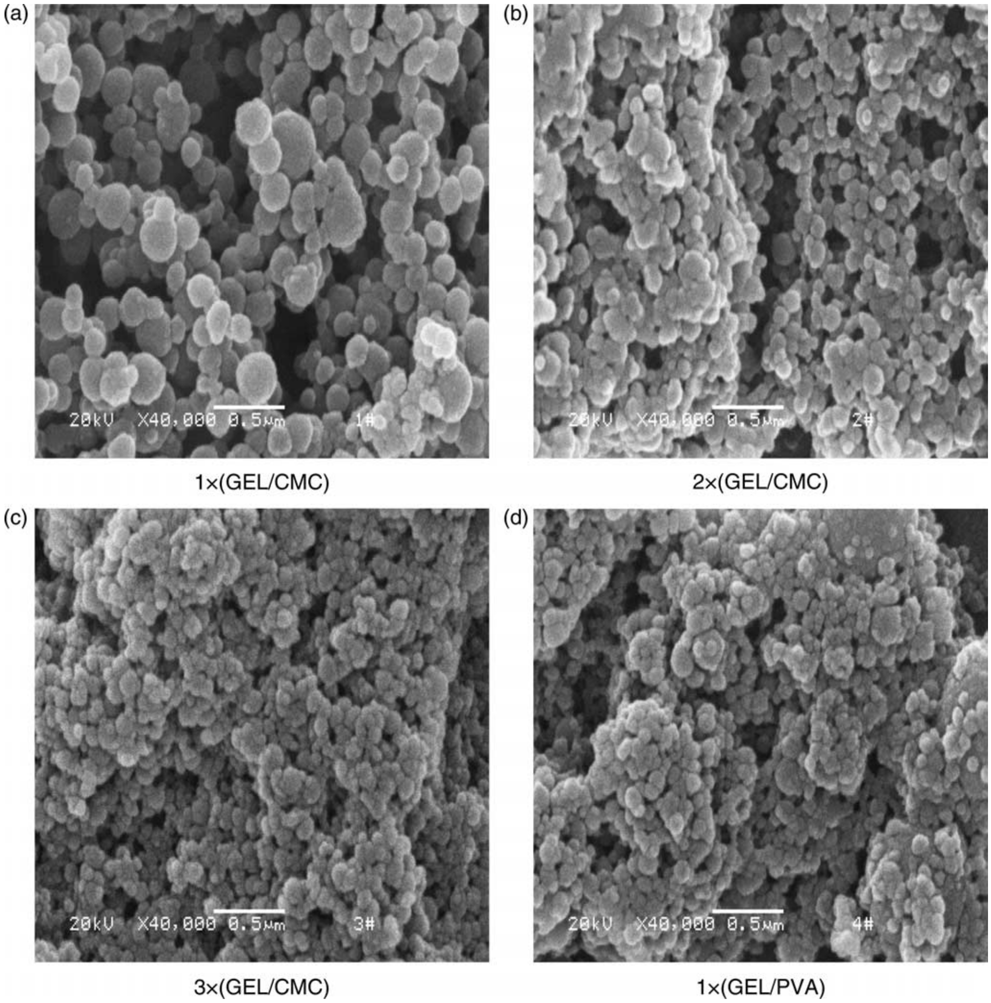
Based on the above research, MF with suitable crosslinking degree, stable structure and high stabilization effect, and micro-size was prepared under the reactants molar ratio MA:FA = 1:1.6 and two parts of weight of the complex dispersant GEL/CMC, which can be applied as the formaldehyde absorbent of POM, and the effect of MF on the thermo-stability of POM was investigated.

3.2. The thermo-stabilization of MF on POM

For POM with MA as the formaldehyde absorbent, a part of MA escaped during high temperature processing, resulting in the 'bloomings' occurring on moulded articles, and white

Table 1
The particle diameter of MF with different dispersants

Particle diameter (μm)	Sample			
	1$^{\#}$	2$^{\#}$	3$^{\#}$	4$^{\#}$
D10%	0.7	0.39	0.1	0.9
D30%	2.2	1.3	0.3	2.5
D50%	6.0	2.3	0.62	6.3
D90%	14.9	13.4	2	14.9
D97%	18.4	18.1	3.5	18.4
Average	6.5	4.5	0.9	6.7



1×(GEL/CMC) 2×(GEL/CMC)

3×(GEL/CMC) 1×(GEL/PVA)

Fig. 5. SEM images of MF with different dispersants.

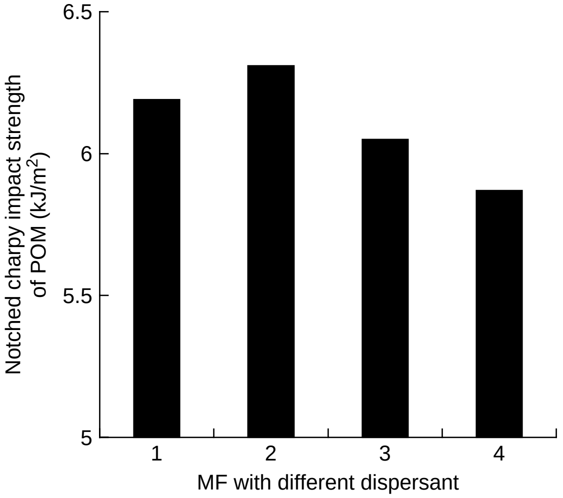


Fig. 6. The effect of dispersants on the Notched charpy impact strength of POM. The dispersant of the sample 1–4 is: 1×(GEL/CMC), 2×(GEL/CMC), 3×(GEL/CMC), 1×(GEL/PVA), respectively.

coatings occurring on processing equipment. While there was no such phenomenon for POM with MF, which overcame the above problem existing in POM industry for long time.

3.2.1. The effect of MF content on the isothermal weight loss of POM

The effect of MF content on the isothermal weight loss of POM was shown in Fig. 7. By addition of 0.1 wt% MF, the thermal weight loss of POM decreased sharply by about 14% in comparison with the virgin POM (in the absence of FA absorbent), indicating that very small amount of MF can show thermo-stabilization effect on POM. With the increase of MF content, the thermal weight loss of the samples decreased continuously, while above 0.7 wt% of MF content, the decrease trend became slowly, and at 1 wt% of MF, the thermo-weight loss of POM decreased by about 35% in comparison with the virgin one, indicating that MF can improve the thermo-stability of POM remarkably.

Fig. 8 displayed the relationship between denary logarithm of the residual weight percentage (R) and heating time (t). It can be seen that the R of all samples decreased with the heating

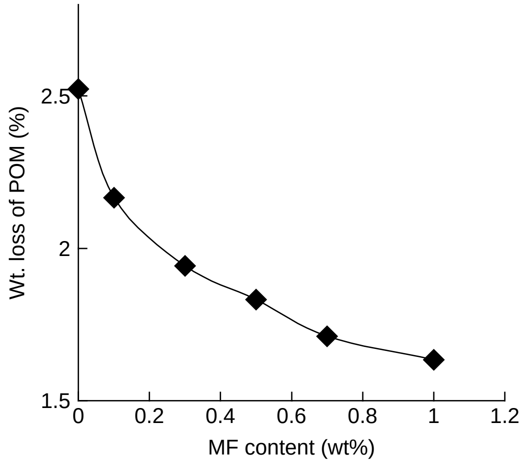


Fig. 7. Effect of MF content on the isothermal weight loss of POM.

time, and it does much more slowly by addition of 0.1 wt% MA or 1 wt% MF than the virgin POM. The thermal weight loss rate of POM with MA was close to that of MF, indicating that the addition of MF can inhibit the molecular degradation of POM, and the thermo-stabilization of 1 wt% MF was equivalent with 0.1 wt% MA.

MF was prepared by the condensation reaction of MA and FA. The hydrogens on amine groups of MA was depleted and MF contains much less primary and secondary amine groups than MA, which play the role as formaldehyde-absorbent to absorb the formaldehyde produced by the decomposition of POM under oxygen and heat. So the same stabilization effect can be achieved by using much more MF than MA.

3.2.2. The balance torque of POM

As shown in Fig. 9, 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 MF than MA, which value was 1.9 and 1.6 N m, respectively, indicating that MF had higher thermo-stabilization effect on POM than MA during the processing of POM.

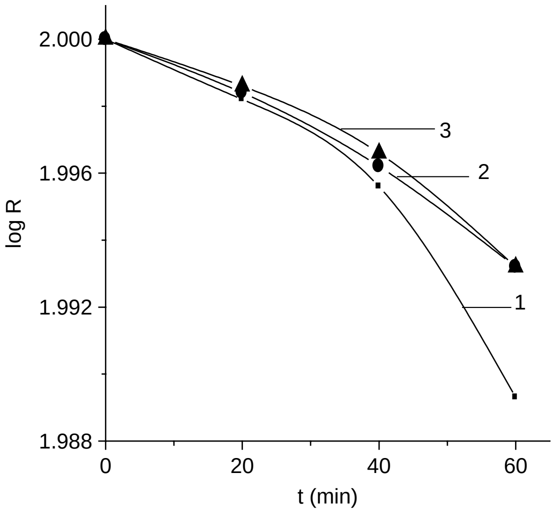


Fig. 8. Degradation rate curves of POM with different FA absorbent 1: no FA absorent, 2: 0.1 wt% MA, 3: 1 wt% MF.

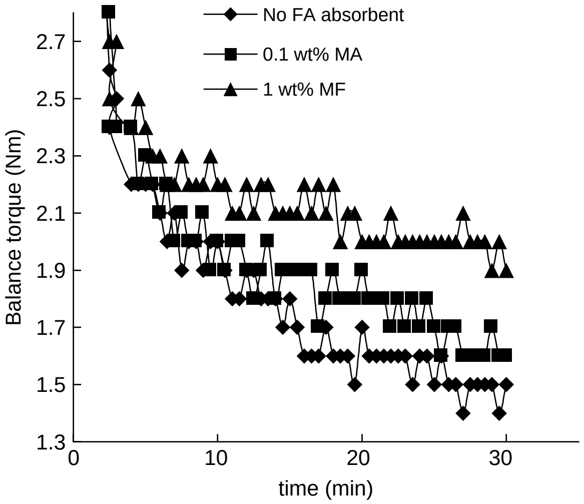


Fig. 9. Effect of FA absorbent on the balance torque of POM.

3.2.3. The non-isothermal degradation

TGA is an important method for the study on the thermostability of POM [11,12]. Thermal degradation characteristic temperatures such as T_{onset}, T_{end}, respectively, represent the temperature at the intersection point of the tangent line at the fastest thermal weight loss rate with the extension line at the start and end of the degradation. $V_{\max}$ and T_{peak} are, respectively, the maximal thermal degradation rate and the temperature at this point. $T_{5\%}$, $T_{20\%}$ and $T_{50\%}$ are the temperatures of the samples with the weight loss of 5, 10, and 50%, respectively, (Table 2).

As shown in Fig. 10, the TG curves of the samples presented simple inverse ‘S’ shape correlation, which indicated that the degradation process of POM had only one stage [13]. The TG curves and the thermal degradation characteristic temperatures of POM with MF was close to that with MA, as listed in Table 1, which $V_{\max}$ was, respectively, 3.4 and 3.7%/°C, being also similar to each other, indicating that the thermo-stabilization effect of 1 wt% MF was equivalent with 0.1 wt% MA.

3.2.4. The multiple-processing performance of POM

The multiple-processing performance can also be used to characterize the processing stability and recycle capability of polymers [14]. Figs. 11 and 12 showed the YI and MI change with the number of extrusion times for POM with MA and MF. It can be seen that both YI and MI increased when the samples were reprocessed, indicating that some thermal degradation occurred during melting processing [7]. The primary value of YI for POM with MF was a little higher than that of POM with MA. However, with the increase of extrusion times, the increase extent of YI and MI of POM with MF was lower than that of POM with MA. After five times of extrusion, the increase percent rate of YI value of POM with MF and MA was

Table 2
TGA characteristic parameters of POM with different FA absorbent (in air)

FA absorbent	T_{onset} (°C)	T_{peak} (°C)	T_{end} (°C)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{20\%}$ (°C)	$T_{50\%}$ (°C)	V_{max} (%/°C)
MA	309.9	326	338.1	294.3	302.8	311.8	323.4	3.7
MF	310.4	325.5	334.5	294.2	303.7	311.7	323.6	3.4

34.5 and 50.5%, respectively, and MI was 15.5 and 27.3%, respectively, indicating that replace of MA with MF as the FA absorbent can reduce the tendency of POM toward molecular-weight degradation and yellowing under the application of the combined effect of high mechanical shearing and high temperature during melt processing, and MF showed better stabilization effect on POM than MA [7].

The average molecular weight (M_w) of POM at each time of extrusion can be calculated by the following equation and listed in Table 3.

$$\mathrm{MI} = 1.3 \times 10^{18} M_w^{-3.55}$$

The mechanical properties of POM with MA and MF by multiple-processing were shown in Figs. 13–15. There was a little change for their tensile strength during the five times of extrusion, and the charpy Notched impact strength and the elongation at break decreased for POM with MA, perhaps due to the molecular degradation and drop of the molecular weight of POM.

But for POM with MF, both the charpy Notched impact strength and elongation at break increased with the increase of extrusion times, perhaps resulting from the low volatilization of MF, keeping high thermo-stabilization effect on POM during the multiple-processing, and inhibiting the molecular degradation and molecular weight drop of POM. On the other hand, the miscibility of POM with MF was improved during the multiple-processing, as shown in Fig. 16. The interface bonding of POM/MF was poor for the first time of extrusion, and was enhanced with the increase of extrusion times. There was no obvious gap at the interface of POM/MF at three and five extrusion times.

The non-isothermal DSC measurement showed that T_p and X_c increased and ΔW decreased with the increase of extrusion times, as listed in Table 4, perhaps due to the size reduction and enhanced dispersion of MF particle agglomeration in POM matrix, resulting in the improvement of the crystallization

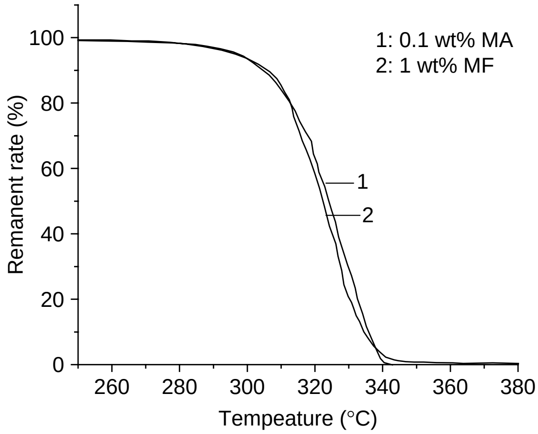


Fig. 10. TG curves of POM with different FA absorbents (in air).

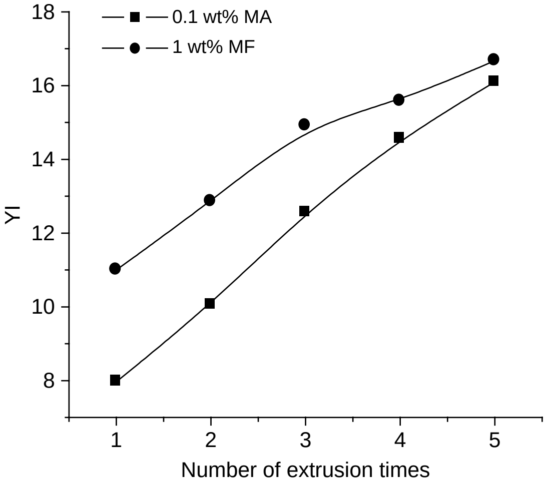


Fig. 11. YI versus number of extrusion times.

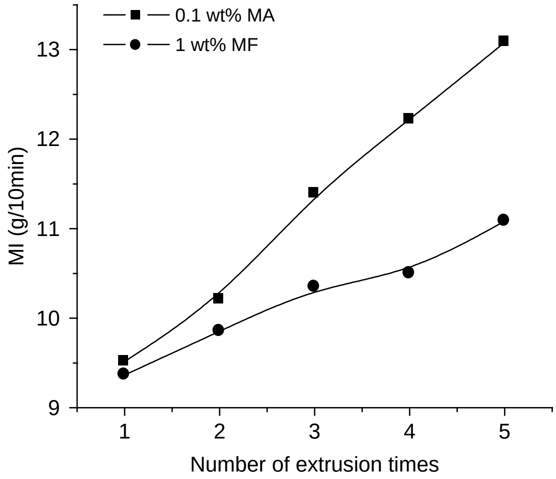


Fig. 12. MI versus number of extrusion times.

Table 3
Effect of number of extrusion times on M_w of POM

Extrusion times	M_w	
	POM/MA	POM/MF
1	67127	67426
2	65811	66474
3	63808	65564
4	62564	65292
5	61372	64306

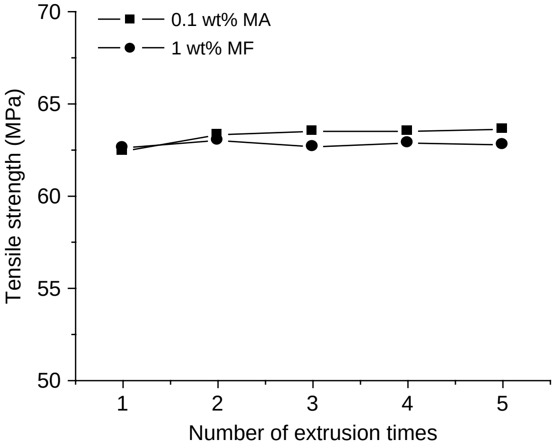


Fig. 13. Effect of number of extrusion times on the tensile strength of POM.

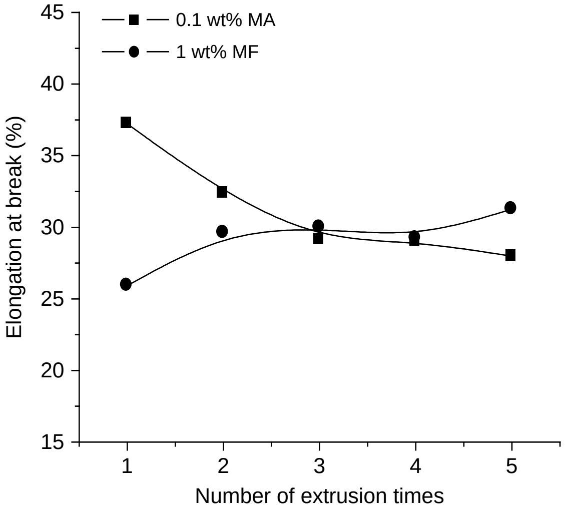


Fig. 14. Effect of number of extrusion times on the elongation at break of POM.

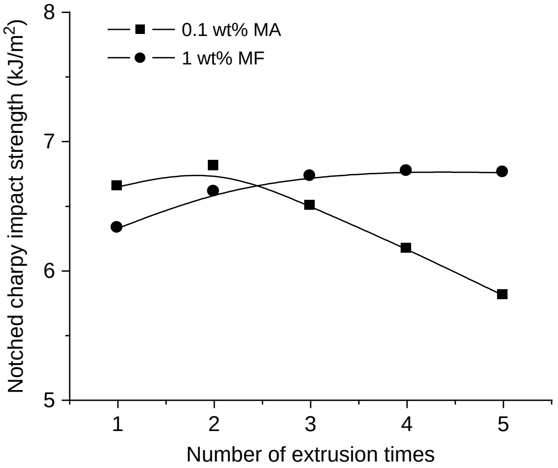


Fig. 15. Effect of number of extrusion times on the Notched charpy impact strength of POM.

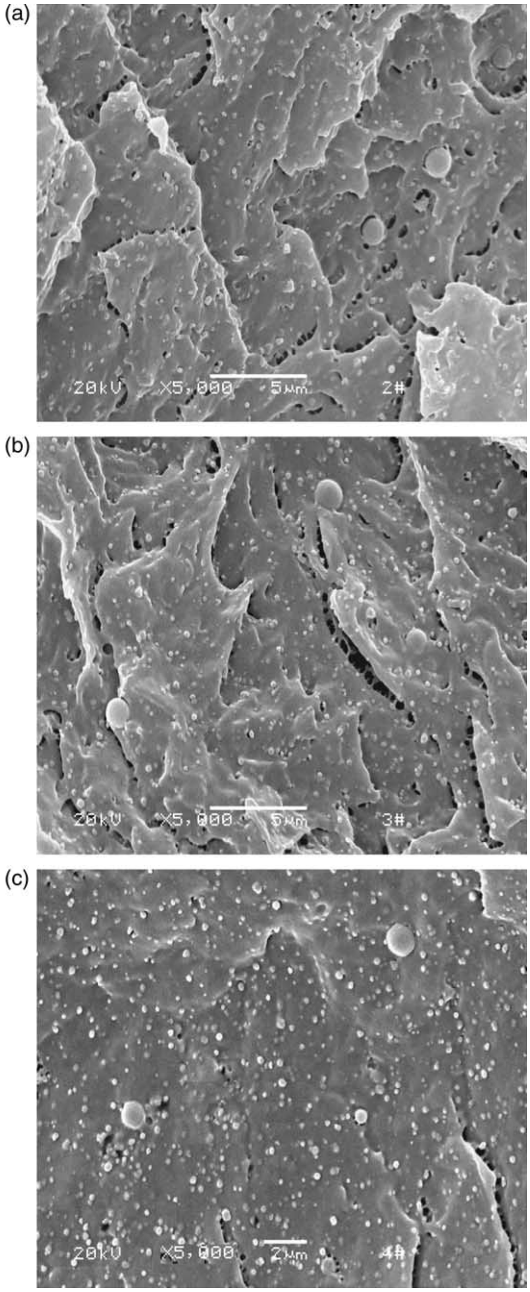


Fig. 16. SEM images of POM/MF with different extrusion times. (a) One time of extrusion (b) three times of extrusion (c) five times of extrusion.

growth rate, crystallinity and the nucleation effect, as well as the mechanical properties, especially the impact toughness.

3.2.5. The long-term thermo-stability of POM

As shown in Figs. 17 and 18, the values of YI and MI increased with the aging time at 140 °C for POM with MA and MF due to the thermo-oxidation degradation of POM, and the increase extent of YI and MI for POM/MF was lower than that of POM/MA. After 15 days' aging, the increase percent rate of YI for POM with MF and MA was 57.5 and 76.4%, respectively, and MI was 20.1 and 27.2%, respectively, indicating that MF can reduce the degree of molecule

Table 4
Effect of extrusion time on the crystallization parameters of POM

Extrusion time	T_{onset} (°C)	T_{p} (°C)	ΔH_{m} (J g^{-1})	X_{c} (%)	ΔW (°C)
1	147.9	143.6	147.2	77.5	10.2
2	147.8	144.8	149.9	78.9	9.6
3	147.8	144.0	150.3	79.1	10.2
4	147.9	144.2	150.7	79.3	8.6
5	147.9	144.1	151.3	79.6	9.4

Notes: T_{onset}, the onset crystallization temperature; T_{p}, the crystallization peak temperature; ΔH_{m}, the melting heat; X_{c}, the crystallinity; ΔW, the crystalline half-peak width.

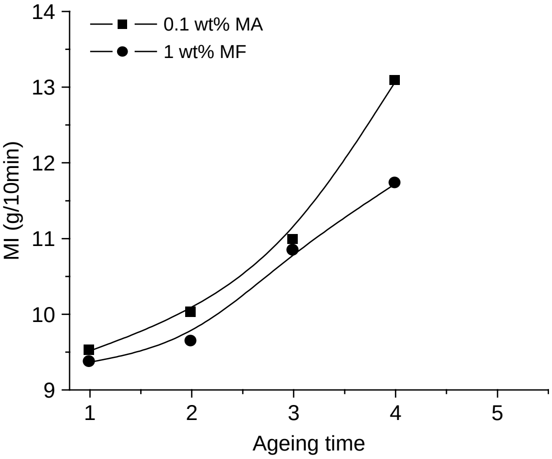


Fig. 17. MI versus ageing time.

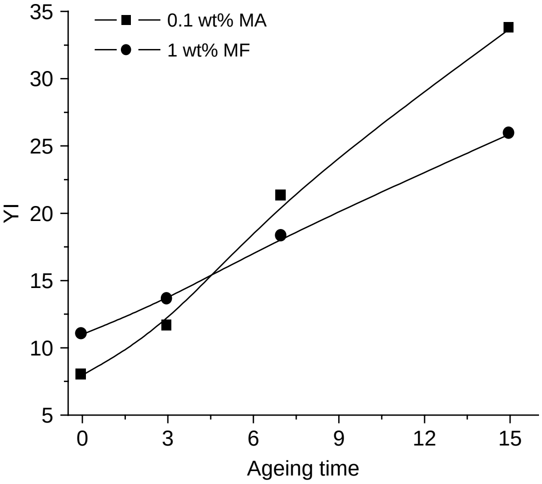


Fig. 18. YI versus ageing time.

Table 5
Effect of ageing time on M_{w} of POM

Ageing time (day)	M_{w}	
	POM/MA	POM/MF
0	67127	67426
3	66162	66887
7	64482	64712
15	61376	63296

degradation and yellowing of POM during the long-term aging under heat and oxygen.

The average molecular weight (M_{w}) of POM can be calculated and listed in Table 5.

Figs. 19–21 displayed the mechanical properties of POM/MA and POM/MF during the long time aging, which increased after three days' aging, perhaps due to the more perfect crystallization of POM induced by heat. With further increase of aging time, the tensile strength and elongation at break

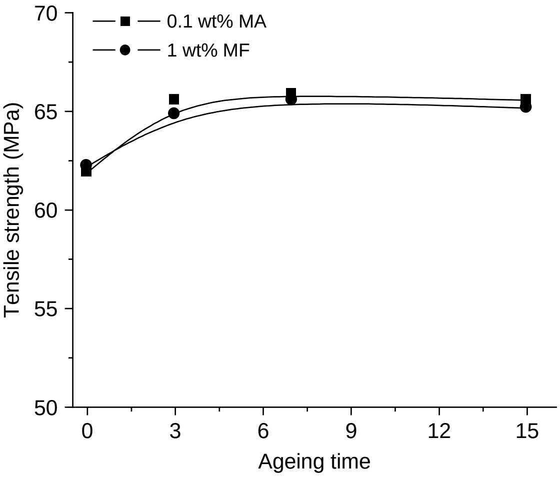


Fig. 19. Effect of ageing time on the tensile strength of POM.

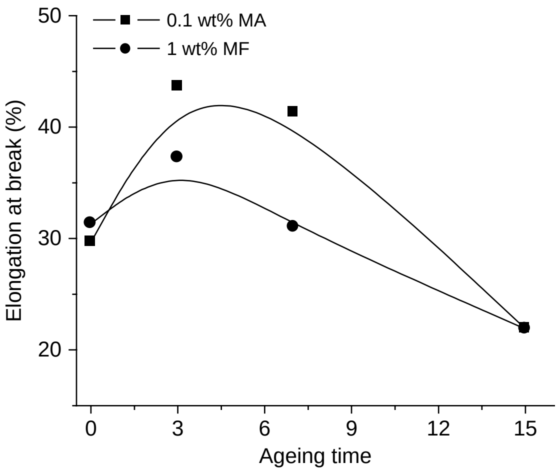


Fig. 20. Effect of ageing time on the elongation at break of POM.

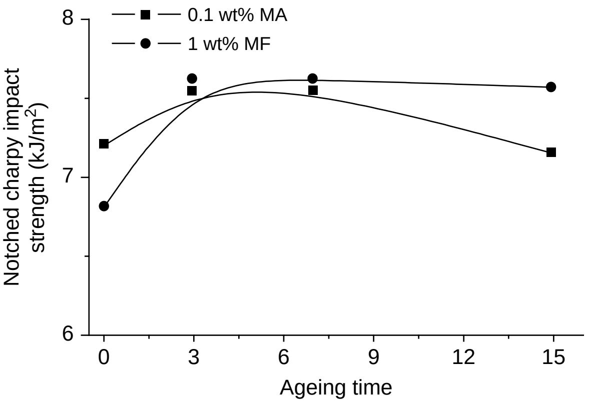


Fig. 21. Effect of ageing time on the Notched charpy impact strength of POM.

decreased for both samples, and the impact strength decreased for the sample POM/MA resulting from the molecule degradation and drop of the molecular weight of POM, while for POM/MF, there was no obvious decrease of impact strength.

4. Conclusion

MA was polymeric modified by condensation reacting with FA to form the melamine formaldehyde polycondensate (MF) with high molecule-weight and comparatively high processing thermo-stability. The balance between the cross-linkage degree of MF and the remaining content of active hydrogen atoms on MF molecules, which can react with formaldehyde produced by POM decomposition as the formaldehyde absorbent of POM, can be determined by the reacting molar ratio of MA and FA. The thermal stabilization effect of MF on POM was studied comprehensively by the measurements of isothermal weight loss at 220 °C, isothermal weight loss rate at 222 °C, TGA, balance torque, the multiple processing and long-term thermo-stability at high temperature, which showed that MF had significantly high thermal stabilization effect on POM in comparison with MA. The particle size of the MF product can be controlled by the types and concentrations of the dispersion agents, which was substantially important for the mechanical properties, especially the impact toughness of POM, and the finely divided, cross-linked, and thermo-stable MF polycondensates were obtained. Moreover, the impact strength of POM was improved after five times of extrusion, due to the better dispersion of MF in POM matrix and better nucleation effect of MF on POM, which was demonstrated by the SEM and DSC analysis.

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