On amine treated polyoxymethylene (POM) blends with low formaldehyde emission for metal injection moulding (MIM)

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ABSTRACT

When polyoxymethylene (POM)—a common polymer used in metal injection moulding feedstock—is exposed to heat and oxygen during compounding, it can be easily decomposed, releasing undesired gaseous formaldehyde products. In order to reduce the formaldehyde emission from POM, amine treatment was performed. The effectiveness of propylamine at different concentrations and its role as a formaldehyde scavenger was studied via the UV–vis Spectrophotometry, Fourier Transform Infra-red, Thermogravimetric Analysis, Scanning Electron Microscopy, and melt flow index. The results proved that a simple amine, such as propylamine, is a promising candidate for scavenging formaldehyde in POM. It is also demonstrated that the best concentration of propylamine is 2 wt.% (POM-PA2) with a minimum formaldehyde emission of 1.44 mg/L. Further, when used in formulating metal injection moulding feedstock (MIM), the POM-PA2 reveals good rheological properties and high green strength. These advantages make the modified polyoxymethylene (POM-PA2) a promising binder system for MIM feedstock.

Introduction

Metal injection moulding (MIM) is a manufacturing process for producing precise, intricate metal parts in large quantities. It combines the versatility and high productivity of the (plastics) injection moulding with the powder metallurgy technique of sintering \cite{1,2}. Since obtaining the compacted powder through sintering and injection moulding is a similar process, the greatest challenge in MIM is to mould the metal powder particles together and retain the shape of the
moulded part prior to sintering. By mixing metal powders with binders (thermoplastic polymers), it allows the powder-binder mixture to form a paste (called a feedstock) that can provide the necessary flow at high temperature and becomes solid at room temperature. The binder eases the feedstock flow during injection moulding and retains the shape of the part until the initial stage of sintering [3–7]. Hence, the binder used in the feedstock is the core of metal injection moulding.

The emergence of the polyoxymethylene (POM) binder system is one of the hot topics in the powder injection moulding industry for metals and ceramics [4, 8]. Owing to its excellent properties, such as high dimensional stability, high rigidity, good warm strength, and fast debinding time, POM is one of the preferred binders for MIM feedstocks [3, 9, 10]. However, upon exposure to heat and high shear stresses during compounding and moulding, POM degrades into formaldehyde [9]. Notably, the vapours of formaldehyde are known to be irritants and have been regarded as a potential human carcinogen that could lead to serious health issues [11, 12]. According to the Occupational Safety and Health Administration (OSHA) Formaldehyde Standard 29 CFR 1910.1048, the permissible exposure limit to formaldehyde is 0.75 ppm for an 8-h time-weighted average (TWA) and the airborne concentration of formaldehyde should not exceed 2 ppm on a short-term exposure limit [13].

Moreover, binder systems based on POM required expensive capital equipment to manage the decomposition of the formaldehyde oligomers [14]. Therefore, it is believed that by reducing the production of formaldehyde in POM, a safer working environment can be realised. Secondly, this will lower the operational cost of disposing of the formaldehyde emission originating from POM.

In the literature, different types of formaldehyde scavengers have been reported. For the leather substrates, the use of plant extracts (for instance, gallic acid, pyrogallol and ethylene urea) have been studied to reduce the formaldehyde content [15]. For wood substrates, addition of formaldehyde scavengers such as tannins, phenolic compounds, sodium metabisulphite, and amines have shown successful results in reducing the formaldehyde emission [16, 17]. Nonetheless, the best functional reacting group for formaldehyde absorption is the amine group [16]. For polymer substrates, Sun et al. demonstrated that the addition of hexamethylenediamine (HA) and triethanolamine (TEA) help reduced the formaldehyde emission in POM [18, 19]. It has been suggested that the addition of an amine group serves three functions during melt treatment of POM; (1) absorbing the formaldehyde by an addition reaction, (2) neutralising the formic acid from the oxidised formaldehyde, and (3) promoting the hydrolytic degradation of the unstable end groups of POM into stable groups [18, 19]. Mantaranon et al. [20] investigated a simple reactive blending of POM with bisphenol-A and aniline [20]. They found that by in situ mixing of the blends, benzoxazines were formed via a Mannich reaction and could effectively consume the formaldehyde generated from POM and retard the thermal degradation of POM. Interestingly, Xu et al. [21] reported that not all organic amines have the ability to remove formaldehyde. The results showed that amines with two -NH groups could not effectively remove formaldehyde, as compared to those with one -NH group.

Nonetheless, these approaches use a complex amine group, which can significantly change the structure of the POM backbone and its mechanical properties. Herein, we used a simple amine group, propylamine, to modify POM. Besides, the use of propylamine to modify POM for MIM has not yet been reported in the literature. Therefore, this study aims to understand the decomposition mechanism of POM and how it can be modified to minimise the release of formaldehyde while maintaining its good rheological properties for MIM. A comparison between the commercial POM and modified POM (i.e., POM-PA2 in this study) on the MIM feedstock was studied in terms of formaldehyde emission, rheological properties and green strength.

Materials and methods

Materials

A commercial POM copolymer (Duracon M90-44) with a melt flow rate of 9 g/10 min was purchased from Polyplastics Company. Propylamine and aluminium oxide (~ 50–150 μm particle size) were purchased from Sigma-Aldrich. Gas atomised spherical commercially pure titanium powder was supplied by TLS Technik Spezialpulver, Germany, with a nominal size of 45 μm. The impurity contents
are 0.122 wt.% O, 0.003 wt.% C, and 0.008 wt.% N. Other chemicals for preparing metal feedstock included isotactic polyethylene (PP, Sigma-Aldrich), poly(ethylene-co-methyl acrylate-co-glycidyl methacrylate) (EMA-GMA, Sigma-Aldrich) and stearic acid (SA, Sigma-Aldrich). All chemicals were reagent grade and used as received.

Methods

To study the effectiveness of propylamine (PA) in reducing the formaldehyde emission of POM, we blended POM and PA using a ThermoHaake Brabender (Germany) mixer at 190 °C for 10 min with a rotor speed of 50 rpm. 0.2 wt.% aluminium oxide was added to the blends as a formic acid absorber to prevent any aggravated degradation of POM during melt blending [22]. The formulations of POM blends are presented in Table 1. Compression moulding was conducted at 200 °C under a pressure of 10 MPa. The preheating, compression moulding and cooling times were 3 min., 2 min., and 2 min., respectively. Samples with 120 μm and 3 mm thickness were used for characterisation. Solid density was measured using a helium micro-pycnometer Accu-Pyc 1200e (Micromeritics, Unterschleißheim, Germany), with a relative standard deviation of 0.005%. The reported value was the average of 10 determinations in a single run.

Next, the preparation of Ti-MIM feedstock was performed using a Thermo Haake Brabender mixer (Germany) at 180 °C, with a rotor speed of 50 rpm for 40 min. A formulation of 63 vol% powder loading of titanium powder was used for investigation. The binder system is composed of commercial polyoxymethylene (POM) or the best-modified polyoxymethylene as the major component (80 wt.%), polypropylene (PP) as the backbone polymer (15 wt.%), poly(ethylene-co-methyl acrylate-co-glycidyl methacrylate) (EMA-GMA) as a compatibiliser (2 wt.%), and stearic acid (SA) as a surfactant (3 wt.%). It is noted that, after mixing titanium powder with the modified POM, the amount of aluminium oxide present in the formulated feedstock is only 0.03 wt.%, which does not cause defects in the final product.

Characterisation of POM and POM-PA blends

Fourier transform infrared (FTIR) spectra of POM and POM-PA blends were analysed using the PerkinElmer Spectrum 100 series spectrophotometer (Shelton, Connecticut, USA) equipped with attenuated total reflectance mode (ATR) on a diamond crystal. All measurements were performed in the range of 4000–400 cm⁻¹ with 4 cm⁻¹ scanning resolution. A total of 16 background scans were performed under a constant pressure for each sample.

The formaldehyde emission was measured using the standard test method VDA 275 (German Automakers Association recommendation No. 275) with slight modifications. In brief, two test specimens having dimensions of 67 × 57 × 3 (mm) were hooked on a copper metal in a 1 L glass bottle above 100 ml of distilled water. The glass bottle containing test specimens was heated in an air-circulating oven at 60 °C for three hours. After that, the test specimens were removed from the glass bottle, and 5 ml of the distilled water (known as sample solution) was extracted and transferred into a test tube. The sample solution was heated at 95 °C for 10 min. Then, 5 ml of acetylacetone reagent were added to the test tube. A blank solution was prepared without any test specimens. Formaldehyde absorbance was measured photometrically at 412 nm wavelength using a UV–vis Spectrophotometer (Shimadzu UV-2550, Japan). The concentration of formaldehyde was determined using the following Eq. (1) [23]:

| Code | Compositions (wt.%) | Density (g/cm³) |
|------|--------------------|----------------|
| POM  | 100                | 1.427          |
| POM-PA1 | 98.8 1           | 1.426          |
| POM-PA2 | 97.8 2           | 1.424          |
| POM-PA3 | 96.8 3           | 1.425          |
| POM-PA4 | 95.8 4           | 1.426          |
| POM-PA5 | 94.8 5           | 1.425          |
\[ G = f \times (A_d - A_b) \times 100 \times \frac{1}{S} \]  

where \( G \) is the concentration of formaldehyde (mg L\(^{-1}\)), \( A_b \) is the absorbance of a blank solution, \( A_d \) denotes the absorbance of the sample solution, \( f \) is the gradient of calibration curve for the standard formaldehyde solution (which is 2.466), and \( S \) is the total surface area of the samples (cm\(^2\)).

Thermal gravimetric analysis (TGA) was carried out on an SDT Q600 thermogravimetric analyser at a heating rate of 10 °C/ min under an argon atmosphere to evaluate the thermal debinding behaviour of the polymers for Ti-MIM process. The temperature range was 25 to 500 °C. The decomposition temperatures at initial weight loss (\( T_{\text{onset}} \)) and the maximum weight loss (\( T_d \)) were determined from the TGA graph. The maximum decomposition temperature (\( T_{\text{max}} \)) was obtained from the derivative thermogravimetric (DTG) curves.

The melt flow index (MFI) values of POM and POM-PA blends were measured using a Dynisco melt flow indexer with a weight of 2.16 kg at 190 °C, as specified in ASTM D 1238 standard [24]. The results are expressed in grams per 10 min.

Scanning electron microscopy (SEM) micrographs of the gold-coated fractured surfaces (broken in the liquid nitrogen) of POM and POM-PA blends were analysed using a Hitachi SU-70 Scanning Electron Microscope.

Rheological experiments were carried out using a capillary rheometer (Shimadzu, CFT-500D) in the temperature range of 180 °C to 200 °C. Different pressure values and die sets with different length/ radius (L/R) ratios (\( D_1 = 1 \text{ mm}, \ L_1 = 1 \text{ mm}; \ D_2 = 1 \text{ mm}, \ L_2 = 2 \text{ mm} \)) were used for calculations based on the Bagley & Rabinowitsch corrections [25–28].

The green strength of the unsintered Ti-MIM compacts was evaluated using the transverse rupture strength test. Rectangle-shaped specimens with dimensions of \( 12.7 \times 31.75 \times 6.35 \text{ mm} \) (length x wide x thickness) were prepared, as specified in the ASTM B 312 [29]. The reported values were the average of six bars.

Results and discussion

Reaction mechanism of POM and propylamine (PA)

The previous literature has found that the oxidative scission reaction of POM starts at approximately 160 °C [30]. Our melt-blending process was carried out at 180 and 190 °C; thus, the oxidative scission reaction is expected. During melt blending, in the presence of heat and oxygen, an intermediate product containing hydroperoxide groups is produced from POM. As shown in Fig. 1a, the hydroperoxides on the methylene groups can induce a \( \beta \)-scission reaction, followed by the formation of formaldehyde, which later oxidises into formic acid, causing aci-dolysis of the polymer and further accelerating degradation [30–32].

However, when propylamine is added, a different reaction route is expected. During the \( \beta \) scission, formaldehyde gas generated from POM will react with propylamine to form an imine (N=C) group [33]. Since imine is unstable, it undergoes an addition reaction with the POM to form a new and stable mixture of POM polymer containing nitrogen functional group (Fig. 1b). However, if basicity is continuously increased (with an increased pH) by adding excessive propylamine and at lower formaldehyde concentrations, the formation of imine will not occur. Instead, the excessive amine will react with formaldehyde and form protonation of hydroxymethyl amine that would reversibly convert back to its free base form and formaldehyde gas (Fig. 1c) [34]. Besides, a certain degree of polymeri-sation is necessary for the propylamine to be stable during the processing of POM.

FTIR analysis

Figure 2 demonstrates the typical stretching vibrations of POM, propylamine (PA), and POM-PA blends. Figures 3 and 4 elucidate the interaction between POM and PA at different concentrations. As shown in Fig. 2, the stretching mode of POM C–O–C bonds can be observed at 1088 and 891 cm\(^{-1}\).
Meanwhile, the moderate bands at 2920, 1237, and 630 cm\(^{-1}\) are attributed to the stretching of CH\(_2\) [30, 35]. As for the propylamine (PA), a twin peak can be observed at 3364 cm\(^{-1}\) and 3289 cm\(^{-1}\), corresponding to primary amines –NH stretching vibration. On the other hand, the characteristic absorption peak at 1070 cm\(^{-1}\) belongs to the C–N stretching vibrations of propylamine.

After adding propylamine, it is notable that POM-PA blends demonstrate a single weak band at 3297 cm\(^{-1}\) (Fig. 3). This is well attributed to the stretching vibrations of –NH groups (secondary amine), suggesting the successful incorporation of propylamine within the POM main chain. Furthermore, from Fig. 4, it is noticeable that the peak of POM-PA blends at 1088 cm\(^{-1}\) (C–O–C absorption bands) becomes sharper and slightly shifted to a lower wavenumber (1087 cm\(^{-1}\)) after modification. This shift towards a lower wavenumber proves an interaction between POM and propylamine, feasibly
forming a stronger C–N bond within the C–O–C bond. Interestingly, the addition of 2 wt.% propylamine reveals the highest intensity increase. The strong intensity at 2 wt.% propylamine corresponds to a maximum amount of molecular bonding between POM and propylamine. However, beyond 2 wt.% propylamine, the intensity at the C–O–C and CH₂ absorption bands slightly decrease. We suggest that the degradation of POM and propylamine generates a stable product (as proposed in Fig. 1).

**UV–vis Spectrophotometer**

The formaldehyde emission values of POM and POM-PA blends are shown in Fig. 5. All POM-PA blends demonstrate a lower formaldehyde emission than un-modified POM. Besides, a comparison between POM and POM-Al₂O₃ has been made (with constant wt.% of aluminium oxide), and the results show that the reduction in formaldehyde emission is not significant without propylamine. This suggests that the addition of propylamine (PA) is necessary to absorb or react with the formaldehyde produced from the decomposition of POM through an addition reaction (Fig. 1b). Besides, it has been reported that the mixture of polyoxymethylene with amine functional groups produces a synergistic effect in reducing formaldehyde [19, 36]. As can be seen, at a low concentration of propylamine (1 and 2 wt.%), the formaldehyde emission of the POM-PA blends decreases. At 2 wt.% concentration, the formaldehyde emission is reduced by 35% compared to unmodified POM (2.04 mg/L). This reveals that propylamine, with its basic properties, could remove the unstable ends groups of POM and replace them with a relatively stable -NH group. However, beyond 2 wt.% concentration, the formaldehyde emission level increases again. It is stipulated that the reaction proceeds rapidly at a higher propylamine concentration, leading to the formation of hydroxymethyl (R-OH) groups (Fig. 1c). As a result, this creates product molecules with less content of the remaining active hydrogen group. These observations agree with the study by Sun et al. [18], who reported that the produced molecules with a lack of active hydrogen atoms are the reason for the poor scavenging efficiency of formaldehyde. It is also noteworthy to mention that the addition of a simple amine, propylamine, to the POM matrix is able to achieve much lower emissions than the latest commercial low-emission POM grades—Duracon Low Volatile POM. The low level of formaldehyde emission of POM-PA2 allows compliance with the current and future more formidable emissions industry norms [37].

**TGA Analysis**

Figure 6 shows the thermal decomposition of the unmodified POM and modified POM-PA blends, while Table 2 tabulates the T onset, T d, T max, and MFI values of POM and its blends. MFI value is an inverse function of viscosity and can be used to estimate the interaction between the phases in polymer mixtures [38].

As presented in Fig. 6, the POM and POM-PA blends display a single-step degradation behaviour at 500 °C. The thermal degradation of POM is due to the randomly initiated bond cleavage in the carbon-
The influence of increasing propylamine concentration on POM can be analysed by the decomposition temperature. From Table 2, the thermal degradation characteristic temperature for all POM-PA blends is higher than that of pure POM. This indicates that propylamine can hinder the tendency of molecular degradation of POM during processing. However, it appears that the addition of propylamine increases the thermal stability of POM in a manner dependent on amine concentration. By increasing the concentration of propylamine, the degradation temperature increases, and beyond a certain concentration, it shifts towards a lower temperature. Besides, when comparing the MFI value, we found that thermal stability increases at a lower MFI value. The maximum decrease in MFI value at 2 wt.% propylamine demonstrates higher viscosity due to the formation of a higher molecular weight chain mechanism that effectively retard the thermal degradation of POM. Therefore, the relationship between high thermal stability and low MFI value of the POM-PA matrix are important factors in reducing formaldehyde emission, as it inhibits the tendency of molecular degradation of POM. Furthermore, it is worth noting that at 589 °C, neither POM-PA 1 nor POM-PA2 produce any residues. However, for the blends of POM, POM-PA3, POM-PA4, and POM-PA5, the residues were 0.32, 0.59, 0.69, and 1.60%, respectively. The residue of pure POM detected less than 1% is mainly attributed to the thermally degraded processing aid and stabilising compound [32]. In the case of high PA contents (such as POM-PA 3 to POM-PA 5), we assume that the structures produced differ from those formed in POM-PA1 and POM-PA2.

**SEM observations**

As shown in Fig. 7a, the fracture surface of the unmodified POM reveals a smooth, wave-like structure, indicating the characteristic of a brittle fracture behaviour [40, 41]. However, after adding propylamine, the fractured surface of the polymer blends (POM-PA) becomes craggy. The craggy fracture surface can be ascribed to the good interaction of the dispersed phase within the continuous matrix [42]. Figure 7a and b reveal that no aggregation or formation of voids is observed when propylamine concentrations are low. Besides, it is most evident in the blends of POM-PA2, where the fracture surface is the craggiest. This reveals that the addition of 2 wt.% of propylamine could generate the most substantial interaction between propylamine and POM. Nonetheless, at higher propylamine concentrations (3 wt.% and above), the fractured surface of the polymer blends exhibits some micro-cracks (Fig. 7d, e and f). This phenomenon is not well understood. However, we speculate that possible degradation of POM within the blends during melt blending may contribute to the formation of these cracks. This is reflected in the MFI value. When too much amine is added, the MFI value increases, suggesting the presence of lower molecular weight within the polymer blends.

**Table 2** Thermal decomposition and MFI value of POM and POM-PA blends

| Material designation | T\_onset (°C) | T\_d (°C) | T\_max (°C) | MFI (g/10 min) |
|----------------------|--------------|-----------|-------------|----------------|
| POM                  | 275.59       | 350.74    | 326.84      | 9.84 ± 0.19    |
| POM-PA1              | 285.83       | 372.74    | 330.25      | 9.82 ± 0.13    |
| POM-PA2              | 294.72       | 387.21    | 358.39      | 9.73 ± 0.17    |
| POM-PA3              | 302.27       | 406.38    | 365.95      | 9.77 ± 0.24    |
| POM-PA4              | 301.48       | 399.70    | 362.98      | 9.95 ± 0.13    |
| POM-PA5              | 284.09       | 386.97    | 354.18      | 9.98 ± 0.04    |

**Rheological properties**

Based on the above results, POM-PA2 with the lowest formaldehyde emission was used to formulate the metal injection moulding (MIM) feedstock. For comparison purposes, a feedstock using commercial POM was also prepared. Figure 8 shows the rheological behaviour of two feedstocks containing POM and POM-PA2 as the primary binder component. Both feedstocks display pseudoplastic behaviour. Notably, the feedstock containing POM-PA2 demonstrates a slightly lower viscosity than the feedstock containing unmodified POM. This might be due to the better interaction between the modified polymeric binder (POM-PA2) and titanium powder attributed to the increased hydrogen bonds on the POM molecular chains. Nonetheless, it is discernable
that both feedstocks show reasonably good viscosity in the entire shear rate range of $10^2$ to $10^5 \text{ s}^{-1}$, where the upper viscosity limit has been set at 1000 Pa·s [26].

Other important factors that must be considered during MIM feedstock design are the shear sensitivity ($n$) and temperature sensitivity ($E_a$). A suitable MIM feedstock should have a low $n$ value and low $E_a$. However, if the $n$ value is too low, it may cause problems such as flashing or jetting during moulding [26, 43, 44]. As shown in Table 3, the difference in shear sensitivity ($n$) values between feedstocks containing POM and POM-PA2 at each temperature does not differ significantly. Moreover, the change in the thermal sensitivity of both feedstocks is considered negligible (with a difference of

| Properties          | Feedstock | POM   | POM-PA2 |
|---------------------|-----------|-------|---------|
| Flow behaviour index ($n$) | 180 °C: 0.58 | 180 °C: 0.60 |
|                      | 190 °C: 0.53 | 190 °C: 0.50 |
|                      | 200 °C: 0.54 | 200 °C: 0.57 |
| Activation energy ($E_a$) | 9.45 J/mol | 9.78 J/mol |
| Mouldability index ($a_{stv}$) | $52.4 \times 10^{-4}$ | $58.1 \times 10^{-4}$ |
only 0.3 J/mol). Therefore, we further consider the general mouldability index to determine the final decision for the best selection of titanium feedstock. A high value of the mouldability index is desirable for the MIM process since it indicates that the feedstocks will possess a better ability to be moulded during the injection moulding process. We observe that the feedstock containing POM-PA2 has a higher mouldability index than the feedstock containing POM, with values of 0.0058 and 0.0052, respectively (see Table 3). Nevertheless, the overall rheological properties of the feedstock containing POM-PA2 are almost similar to that containing POM. This fulfils our main objective, which is to retain the excellent properties of POM after modification with propylamine.

Green Strength of the MIM Parts

The high green strength of the moulded parts is necessary for subsequent handling. The green strength is usually dependent on the binder constituents. From Table 4, the highest mean flexural strength is observed in the feedstock containing POM-PA2, with a value of 20.3 MPa. This is 7.3% higher than feedstock containing POM (18.8 MPa). It is suggested that the higher flexural strength is due to the additional polar group in the modified POM binder constituent, attributing to the more interaction between binder and titanium powder.

Conclusions

This study focuses on preparing low formaldehyde-poloxymethylene (POM) binder for metal injection moulding (MIM). The following conclusions can be drawn:

- the addition of propylamine in poloxymethylene (POM) can significantly reduce formaldehyde emission. However, the concentration of propylamine should be carefully decided.
- At low propylamine concentration (typically 2 wt.%), formaldehyde emissions have been effectively reduced by 35%. When amine concentration is low, the unstable terminal groups of POM are easily removed via the addition reaction. However, a different reaction occurs at a high amine concentration, reversibly converting the molecule back to its free base form and formaldehyde gas.
- The feedstock formulated from the modified POM-PA2 binder displays almost identical characteristics to the feedstock containing POM.
- Overall, POM-PA2 is a better alternative than POM as a binder for MIM due to its significantly reduced formaldehyde emission and excellent mechanical properties.

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| Feedstock | Flexure load (N) | Flexural strength (MPa) | Standard deviation (MPa) |
|-----------|-----------------|-------------------------|--------------------------|
| POM       | 6.03            | 18.79                   | ± 1.02                   |
| POM-PA2   | 7.56            | 20.27                   | ± 1.11                   |

Table 4 The green strength of POM and POM-PA2 feedstock
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