Effect of interaction from the reaction of carboxyl/epoxy hyperbranched polyesters on properties of feedstocks for metal injection molding

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Abstract
The purpose of this study is to improve the properties of the feedstocks and shape retention of debinded parts by the reaction between 17-4PH stainless steel powders. Carboxyl-terminated hyperbranched polyester (CTHP) and epoxy-terminated hyperbranched polyester (ETHP) were used to treat the powders, and termed as CTHP-m and ETHP-m with carboxyl and epoxy group, respectively. Comparing with pristine, CTHP-m and ETHP-m, feedstock prepared from equal amount of CTHP-m and ETHP-m (CTHP-m/ETHP-m) possessed more excellent properties. The experimental results showed that the critical solids loading, flexural modulus, density and melt flow index of CTHP-m/ETHP-m feedstock were 63.8 vol.%, 2800 Mpa, 5.06 g cm$^{-3}$ and 62 g/10 min, respectively, which were obviously higher than that of others. Also, the shape retention of CTHP-m/ETHP-m debinded parts was the best of all the samples. The improved properties of CTHP-m/ETHP-m feedstock were attributed to the powder interaction between CTHP-m and ETHP-m formed by the chemical reaction between epoxy and carboxyl group.

Abbreviations
CTHP carboxyl-terminated hyperbranched polyester;
ETHP epoxy-terminated hyperbranched polyester;
CTHP-m 17-4PH stainless steel powders modified by carboxyl-terminated hyperbranched polyester;
ETHP-m 17-4PH stainless steel powders modified by epoxy-terminated hyperbranched polyester;
CTHP-m/ETHP-m 17-4PH stainless steel powders modified by equal amount of CTHP-m and ETHP-m.

1. Introduction
Metal injection molding (MIM) integrates the advantages of conventional plastic injection molding and powder metallurgy. This is a good way to produce parts with complicated shapes and high dimensional accuracy [1]. Metal injection molding process was used in various application fields, e.g., automotive technology, medical devices and consumer markets for many years [2]. Better homogeneity and rheological property of feedstocks [3], higher critical powder solids loading [4], mixing of appropriate types of powder [5], the stronger interfacial bonding strength between powder and binder [6] and the enhanced mechanical properties such as hardness and tensile strength [7] were all helpful to improve the shape retention of debinded parts and dimensional accuracy of sintered parts.
To obtain excellent shape retention of debinded parts and a high dimensional accuracy of sintered parts, high critical solids loading is a basic requirement in MIM. Many researchers found different influencing factors, which can increase powder loading. Ma et al. [8] investigated the influences of ball milling technique on the characteristics of the carbonyl iron and carbonyl nickel mixed powders and the powder injection molding procession. They found that the homogeneity and dispersion of the mixed powders had improved after ball milling treatment, the critical powder solids loading of the feedstock was increased from 52% to 62%. Mukund et al. [9] researched the effect of particle size and shape differences of water atomized 17-4PH stainless steel powder on the critical solids loading of PIM parts. The results indicated that the increment in the population of finer particle fraction accompanied with relatively more regular shape improved the powder loading. Hausnerova et al. [10] revealed that for coarser 17-4PH powder particles, the critical solids loading was better in case of gas atomized powders, but water atomized powders showed better performance for finer powders. Choi et al. [11] designed a trimodal powder feedstock using Fe micro-powder and nano-powder agglomerates consisting of a bimodal particle distribution and the powder solids loading was increased to 72 vol%.

The mechanical property of green bodies and sintered parts are strongly influenced by different backbone polymers and powder compositions, and it was necessary to know the injection-molding behavior at different powder-binder compositions [12–14]. The higher strength is critical for producing MIM products with excellent dimensional accuracy. Huang et al. [15] compared the influences of different types of backbone polymers on the mechanical performance of 316 L stainless steel PIM green compacts and sintered parts. They found that the bending strength of the PIM compacts using high-density polyethylene as the backbone polymer in binder was stronger than that of low-density polyethylene, and the dimensional accuracy of sintered parts was better than the latter. Oh et al. [16] researched the effects of nanoparticles in bimodal powder that contains both nanoparticles and microparticles on the strength of powder injection molding parts. The results showed that the powder loading and homogeneity of the feedstock decreased slightly owing to the existence of nanoparticles, but greatly enhanced the mechanical strength including Vickers hardness, the tensile strength and the flexural strength and strain of the PIM parts.

The surface treatment agents including surfactant and coupling agent are usually used as additives when mixing powder and binder to improve the interfacial strength and compatibility, which can also make the powder evenly disperse into binder and increase the flowability of feedstock. Wen et al. [17] modified the surface of the zirconia powders by adding a small amount of oleic acid (OA), and the polarity of powder surface was changed from hydrophilic to hydrophobic when mixing the binder and powders, the surface modification could improve the compatibility between binder/powder to obtained the sintered part with excellent properties. Wongpanit et al. [18] studied the influence of acrylic-acid grafted HDPE (AAHDPE), which acted as one portion of HDPE-based binder on the properties of the MIM parts. The results showed that the mechanical property, ductility of the green bodies and the distortion of the debinded parts had been enhanced, which indicated that AAHDPE used as compatibilizer in the binder improved the compatibility and packing stability between binder and powder. Liu et al. [19] modified zirconia powder by titanate coupling agent, which interacted with the powder surface by a chemical bonding and used them for ceramic injection molding. The results revealed that the powder modification was beneficial to improve the homogeneity and dispersity between powder and organic binders, and improved the performance including the flowability of feedstock, mechanical strength of sintered parts, densification and grain refinement of the water-based binders ceramic injection molding system. Deng et al. [20] treated ZrO2 ceramic powders by silane coupling agent (A151) and investigated the injection molding and debinding procession. The results revealed that the melt flow rate (MFR) of the ZrO2 feedstocks increased, the bending strength of the green bodies enhanced, and the weight removal ratio of soluble binders and the rate of the solvent debinding were both increased after using the method of powder modification by the addition of A151. Lindqvist et al. [21] modified the silicon nitride powder by silane coupling agent and titanate coupling agent, and applied them in powder injection molding. Glycidoxytrimethoxysilane was used in conjunction with tetrabutyl titanate and successfully decreased the viscosity of feedstock drastically in the process of injection molding. Qi et al. [22] used the coupling agent of vinyltrimethoxysilane (VTMS) to modify the Ba(Mg1/3 Nb2/3)O3 (BMN) ceramic powders, and investigated the influence of powder modification on the compatibility between modified filler (BMN) and pure polytetrafluoroethylene (PTFE). The results indicated that the particle modification method was beneficial to improve the compactness and uniformity of the composites. Raji et al. [23] prepared polypropylene/clay nanocomposites in which the clay was modified by organosilanes namely 3-aminopropyltriethoxysilane (APTES) and vinyltrimethoxysilane (VTMS), and the results revealed that the process of silylation of clays had high efficiency to improve the proprieties of silane grafted clays nanocomposites, in terms of interfacial adhesion strength between the organoclay and the PP matrix, and greatly enlarged the spatial dispersion-distribution.

Hyperbranched polymer, which own high branching density with strong branching potential in each repeating unit [24], is one type of dendritic polymers different from common ones, and they have attracted comprehensive attention for their good solubility in different types of organic solvents, good dispersity as fillers,
relatively lower melt viscosity, multifunctionality of end active groups [25]. Hyperbranched polymers can be used as additives or matrix to treat organic polymer or inorganic filler to improve the compatibility of composite materials or dispersibility of inorganic filler. Shi et al [26] found that the covalent grafting of hydroxyl-terminated hyperbranched polymer (HTHBP) on the carbon fiber (CF) surface can significantly enhance the interfacial properties of composites. Jiang et al [27] used a high molecular weight, highly active terminal hydroxyl hyperbranched polymer based on an aromatic polyamide hyperbranched polymer (HPN202) as a modifier of POM-based binder and investigated the catalytic debinding process and properties of feedstock in MIM. They found that the flowability of feedstock, mechanical strength of the green parts and dimensional accuracy of sintered parts were all well improved.

In our previous work, silane coupling agent of KH550 and KH560 was used to modify the 17-4PH gas atomized stainless steel powders, respectively. The residual silicon in the green parts may affect the properties of the sintered parts. In our present study, terminated hyperbranched polyesters containing only carbon, hydrogen and oxygen elements are used as surface treatment agent for powder, and the carboxyl group and epoxy group were grafted onto the surface of 17-4PH stainless steel powders, respectively. The strong interaction among powders comes from the reaction as well as hydrogen bonding between carboxyl group and epoxy group. The influence of powders interaction on the properties of feedstocks in especial the shape retention of debinded parts after debinding was investigated.

2. Experimental and methods

2.1. Experimental raw materials

The 17-4PH stainless steel powders (atomization atmosphere: nitrogen, microscopic shape: spherical, density: 7.88 g cm$^{-3}$) was supplied by Sandvik Osprey Company of the United Kingdom. Table 1 showed the main chemical compositions of the powder which were received from the manufacturer’s data explanation sheets. Figure 1 showed the morphology of the powder. The size distribution of 17-4PH powders used in this experiment was analyzed by a particle size laser analyzer (MS-2000, Malvern, UK) and was shown in figure 2. Carboxyl-terminated hyperbranched polyester (CTHP) and epoxy-terminated hyperbranched polyester (ETHP) purchased from Wuhan Hyperbranched Polymer Resins Science & Technology Co. Ltd (China), and the characteristics of them are summarized in table 2. The binder was composed of high-density polyethylene (HDPE) and paraffin wax. The melt flow index of HDPE was 8.8 g/10 min determined by the condition of 190 °C and 2.16 kg, and was purchased from Petrochemical Commercial Co. (PCC) (Iran), and paraffin wax (melting point: 58 °C) was supported by Daqing Petrochemical Corporation (China). All purchased chemical reagents were used as obtained.
2.2. Powder surface modification
Firstly, CTHP (0.3 wt% by the weight of 17-4PH powders) was poured into a beaker containing acetone, then stirring repeatedly until CTHP fully dissolved. Added an appropriate weight of 17-4PH powders to a high-speed mixer with a rotation rate of 800 rpm. The dissolved CTHP solution and the catalyst of stannous octanoate (1 wt% based on the weight of CTHP) were both added gradually and uniformly to the high-speed mixer when the temperature of powders reached 135°C, the powders were stirred for 45 min. In order to eliminate the unreacted CTHP and extra solvent, the modified powder was firstly washed by acetone and filtered for three times, and then dried in a vacuum oven at 85°C for 6 h. Secondly, the ETHP (0.3 wt% by weight of 17-4PH powders), absolute ethanol and toluene (the molar ratio of absolute ethanol to toluene was 2:1) were added to a beaker and stirred till the ETHP fully dissolved. The 17-4PH powders were poured into the high-speed mixer (850 rpm). When the temperature of 17-4PH powders reached 140°C, the ETHP solution and the catalyst 2,4,6-tris-(dimethylaminomethyl) phenol (1.2 wt% by the weight of ETHP) were both added gradually and uniformly to the high-speed mixer and stirred for 1 h, then the modified powders were washed with absolute ethanol and toluene for three times, and then dried in a vacuum oven at 110°C for 10 h. Finally, surface modified 17-4PH powders with CTHP and ETHP were obtained, which were termed as CTHP-m and ETHP-m, respectively.

2.3. Feedstock preparation
A batch mixer (XSS-300, Shanghai Science and Technology Rubber Machinery Corporation, China) was used to fabricate the feedstocks. The chamber of mixer owned the capacity of 54 cm³ with in-built thermocouples to monitor a melt temperature during mixing. The rotor speed and temperature when mixing the powder/binder was set at 50 rpm and 160°C, respectively. The binder ingredients composed of HDPE and paraffin wax (the volume ratio was 7:3) were premixed in the mixing chamber, followed by the addition of 17-4PH powders and mixed for 30 min. Especially, the catalyst 2,4,6-tris(dimethylaminomethyl) phenol (0.5 wt% by the weight of binder) was also put into the chamber when mixing the feedstock that filled with CTHP-m/ETHP-m (the mass ratio was 1:1). The mixing torque development with time was recorded. When the modified powders were used, the organic treatment agent connected with the modified powders was calculated as part of the binder.

Table 2. Characteristics of two hyperbranched polyesters.

| Properties                        | CTHP       | ETHP       |
|-----------------------------------|------------|------------|
| Number of carboxyl groups/mol     | 12         |            |
| Acid value/mg KOH/g               | 250-280    |            |
| Hydroxyl value/mg KOH/g           | <15        |            |
| Molecular weight/g/mol            | 2600       | 3200-3600  |
| Epoxy value/mol/100 g             |            | 0.20 ± 0.05|

Figure 2. The particle size distribution of 17-4PH powders.
2.4. Thermal debinding
A dumbbell-shaped compression mold on an XLB-D400 × 400 × 2 machine (Shanghai Rubber Machinery No.1 Factory, China) were used to prepared green parts. When performing the compression process, the pressure and temperature of the machine was 12Mpa and 165 °C, respectively. Thermal debinding of green bodies is universally used to remove the binder components in MIM, and it was taken in vacuum atmosphere furnace (XL-GWL04, Luoyang Luke Kiln Co., Ltd, China) under argon, and the schedule of thermal debinding was determined by TG curves of binders (figure 3) as follows: (1) the green parts were heated at the uniform heating rate of 1.5 K min \(^{-1}\) from room temperature to 473 K, (2) the samples' holding time were 30 min at the temperature of 473 K, (3) the samples were heated at the uniform heating rate of 1 K min \(^{-1}\) from 473 K to 623 K, (4) the samples' holding time were 2 h at the temperature of 623 K, (5) the samples were heated at the uniform heating rate of 1.2 K min \(^{-1}\) from 623 K to 693 K, (6) the samples' holding time were 30 min at the temperature of 693 K, (7) the samples were heated at the uniform heating rate of 1 K min \(^{-1}\) from 693 K to 813 K, (8) the samples' holding time were 2 h at the temperature of 813 K, (9) the samples were cooled from 813 K to the room temperature naturally.

2.5. Instrument and equipment characterization
X-ray photoelectron spectrometer (AXIS ULTRA DLD, Kratos, UK) was used to analyze the powder surface of CTHP-m and ETHP-m. Field emission scanning electron microscope (S-4800, Hitachi, Japan) was taken to observe the morphology of the green parts and debinded parts. Thermogravimetric analysis (TG) was carried out on a TGA-8000 instrument (PE, U.S.) under argon at a heating rate of 5 °C min \(^{-1}\). Zeta potentiometer (NanoZS90, Malvern, UK) was used to determine the surface potential of the powders in ethanol solvent. The melt flow index of the feedstocks was obtained on a melt index instrument (XRL-400, Mts system Co., Ltd, China) at the temperature and load of 150 °C and 12.5 kg, respectively. The viscosity of feedstock was measured using a capillary rheometer (XLY-II, Scientific Instrument Factory, Jilin University, China). The flexural modulus was measured by a material electronic universal testing machine (AGX-V100KN, Shimadzu, Japan). The test method was based on the international standard (ISO178:2001). The crosshead speed and the length of the supported span was set at 0.4 mm min \(^{-1}\) and 64 mm, respectively.

3. Results and discussion
3.1. Powders modification
Many researchers investigated how to improve the compatibility and enhanced the interfacial interaction strength between inorganic fillers and organic substrates. Liu et al [28] used a prior ball milling treatment by adding some stearic acid (SA) to the ceramic powders before blending procession, and the SA can react with the powder surfaces demonstrated by the FTIR results. The strategy of prior ball milling treatment was helpful to improve the compatibility between powder/binder to prepared the feedstock with excellent properties. Yang et al [29] used L-lactide and L-lactic acid (LA) oligomer to modify the biphasic calcium phosphate powder.
(BCP), and the surface grafting can improve the interfacial compatibility of BCP biceramic with biopolymer-PLLA. In this study, the surface elements of powders were evaluated by XPS spectra and the results were summarized in Table 3. The surface of powders was mainly composed of C, O and negligible Si element. The content of carbon element increased greatly from 37.31% to 56.03% and 53.1% for CTHP-m and ETHP-m, respectively. Figure 4 showed the XPS wide-scan and C1s curve fit spectra of powders. The peaks for Si 2p, C 1s and O 1s were centralized at near 102 eV, 285 eV, and 530 eV, respectively. The C1s peak at 284.8 eV for the fit spectra C1s curve of pristine originated from the sp2 hybridized graphitic carbon [30], the C1s (2) at around 288.6 eV originated from a small amount of carbon on the ester group [31]. After surface modification, CTHP-m and ETHP-m appeared a new characteristic peak at 286.2 eV in C1s high resolution spectra, which was assigned to −C−O−(ether) and −C−O−(alcohol) [32]. The above results indicated that CTHP and ETHP had been successfully connected to the surface of 17-4PH powders, respectively.

Figure 5 showed the thermogravimetric analysis results of powders. The residual mass percent at 800 °C of pristine powders, CTHP-m and ETHP-m was 99.73%, 99.67% and 99.65%, respectively. The hydroxyl groups and little hyperbranched polyester residue on the surface of CTHP-m and ETHP-m were removed at 800 °C. The grafting ratio of hyperbranched polyester on the surface of 17-4PH powders could be calculated by the difference of residual mass percent between pristine powders and modified powders. Therefore, the organic residue for CTHP-m and ETHP-m were 0.06%, 0.08%, respectively, which indicated in the modified 17-4PH stainless steel powders, a chemical bonding is formed between the surface treatment agent CTHP or ETHP and the 17-4PH stainless steel powders. When preparing the feedstocks, the organic treatment agent connected with the modified 17-4PH powder was calculated as part of the binder.

| Powders     | Si   | C    | O    |
|-------------|------|------|------|
| Pristine    | 6.64 | 37.31| 56.05|
| CTHP-m      | 2.77 | 56.03| 41.20|
| ETHP-m      | 3.06 | 53.10| 43.83|

Figure 4. Wide-scan XPS spectra (a), C1s high-resolution XPS spectrum of (b) Pristine, (c) CTHP-m, (d) ETHP-m.
The values of zeta potential represent the potential state of the particle surface and indicate the degree of stability or dispersion of powder particles. Generally, the greater the absolute value, the more stable and better dispersion the system tends to be. Huo et al. [33] used long-chain surfactant sodium dodecyl sulfate (SDS) and cetyltrimethylammonium chloride (CTAC) to modify the colloidal particles and weak agglomerations formed which was beneficial for the stability of the colloidal suspension system. The results also showed that high absolute values of zeta potential (>40 mV) resulted in instability system due to the strong particle-particle repulsion force. Table 4 listed the zeta potential values of powders in ethanol solvent, the absolute zeta potential value of ETHP-m was relatively lower than that of pristine powders and CTHP-m, which indicated that there was a certain interaction among ETHP-m. It was worth noting that the zeta potential values of CTHP-m/ETHP-m decreased to −1.16 mV when equal amount of CTHP-m and ETHP-m were mixed in ethanol solvent, which indicated that the interaction in CTHP-m/ETHP-m was higher and the hydrogen bonding existed between carboxyl group and epoxy group in the surface of CTHP-m and ETHP-m, respectively.

### Table 4. The zeta potential of samples in ethanol solvent.

| Sample          | Pristine | CTHP-m | ETHP-m | CTHP-m/ETHP-m |
|-----------------|----------|--------|--------|---------------|
| Zeta potential (mV) | 7.2      | −12.3  | −2.49  | −1.16         |

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### 3.2. Feedstock properties

Higher critical powder solids loading is beneficial to improve the performance of feedstock and final parts. Hnatkova et al. [34] studied the influence of stearic acid (SA) as a part of organic binders on the critical solid loading (CSL) and corresponding flowability of aluminum oxide (Al₂O₃) feedstocks. It was found that apparent viscosities of the CIM feedstocks reduced by adding SA. Su et al. [35] investigated the effects of powder solids loading on the properties of ceramic parts by soft molding. The results revealed that the density of green and sintered parts increased with the increment of powder solids loading, while the linear shrinkage showed the opposite result.

Figure 6 showed the values of mixing torque of feedstock versus increasing powder solids loading. It can be seen from the figure that the mixing torque of feedstock performed by using CTHP-m or ETHP-m was higher than that of pristine powders. This might be because the organic hyperbranched polyester residue in the powder particle surface was regarded as a part of binder, and the viscosity of the organic residue was higher than the binder. It was worth emphasizing that the mixing torque values of feedstock obtained by adding equal amount of CTHP-m/ETHP-m was lower than that of others. The result might due to the reaction between the carboxyl group and epoxy group in CTHP-m and ETHP-m, respectively. Therefore, CTHP-m and ETHP-m was more tightly packed through reaction so that some binder between powders released as shown in figure 7, and the close combination of powders reduced the contact area between the powder and the binder [36], thereby reducing the flow friction of powders in binder, and the flowability of feedstock increased. In our previous study [37], the
interaction between powders improved the fluidity of the feedstock. However, the silicon element in the surface treatment agent may not be conducive to the sintering process of the products.

Shin et al [38] indicated that mixing torque increased with increasing added powders, and increased sharply at the point of critical solids loading. Therefore, the change of mixing torque of feedstocks prepared from CTHP-m/ETHP-m versus the increasement of powder volume loading was plotted in figure 8 and the values of critical solids loading of feedstocks were listed in table 5. The critical solids loading of feedstocks prepared by adding pristine powders, CTHP-m and ETHP-m was 62.7 vol%, 63.3 vol% and 63.2 vol%, respectively, while that of CTHP-m/ETHP-m feedstock was up to 63.8 vol%. This might due to the reaction between carboxyl group on the surface of CTHP-m and epoxy group on the surface of ETHP-m. Therefore, the interaction makes the powders connect more closely, what’s more, hyperbranched polyesters themselves had a lot of free volumes and spaces [26], and the powders could avoid a large extent of agglomeration, thus the flowability of feedstock and the loading capacity of powder was both increased. These results were consistent with figure 7.

In order to conveniently study the effects of powder reaction on the properties of feedstock, according to table 5, the optimal powder loading could be determined as 62 vol% which was little lower than the critical solids loading. The density and flexural modulus of as-prepared feedstocks were listed in table 6. Comparing with the feedstock fabricated from pristine powders, the density and flexural modulus of the feedstock prepared by CTHP-m or ETHP-m obviously increased. It could be concluded that the method of powder surface modification with CTHP or ETHP was helpful to improve the compatibility and enhanced the interfacial interaction strength between powder/binder. Especially, the green density and flexural modulus of CTHP-m/
ETHP-m feedstock was up to 5.06 g cm$^{-3}$ and 2800Mpa, respectively, the reaction between CTHP-m and ETHP-m increased the density and enhanced the mechanical strength of green parts.

As shown in figure 9, the melt flow index (MFI) of feedstock fabricated from CTHP-m and ETHP-m decreased compared to that of pristine powders. It was because the flowability of CTHP or ETHP residue in the modified powder particles surface was lower than that of selected binder when mixing the feedstocks.

**Table 5.** Powder critical solids loading of feedstocks.

| Feedstock prepared from | Pristine | CTHP-m | ETHP-m | CTHP-m/ETHP-m |
|-------------------------|----------|--------|--------|---------------|
| Critical solids loading (vol%) | 62.7     | 63.3   | 63.2   | 63.8          |

**Table 6.** Density and flexural modulus of as-prepared feedstocks.

| Feedstock prepared by | Pristine | CTHP-m | ETHP-m | CTHP-m/ETHP-m |
|-----------------------|----------|--------|--------|---------------|
| Density (g/cm$^3$)    | 4.82     | 4.94   | 4.97   | 5.06          |
| Flexural modulus (MPa)| 1746     | 2356   | 2466   | 2800          |

ETHP-m feedstock was up to 5.06 g cm$^{-3}$ and 2800Mpa, respectively, the reaction between CTHP-m and ETHP-m increased the density and enhanced the mechanical strength of green parts.

As shown in figure 9, the melt flow index (MFI) of feedstock fabricated from CTHP-m and ETHP-m decreased compared to that of pristine powders. It was because the flowability of CTHP or ETHP residue in the modified powder particles surface was lower than that of selected binder when mixing the feedstocks.
Particularly, the flowability of feedstock prepared by adding CTHP-m/ETHP-m was obviously higher than that of others, it was concluded that CTHP-m and ETHP-m were tightly packed when mixing the feedstock to release some binder as shown in figure 7 due to the reaction of CTHP-m/ETHP-m, thus the rheological property improved.

MIM feedstocks generally tend to exhibit pseudo-plastic behavior over the range of shear rates, and the shear thinning phenomenon is necessary to reduce the powder-binder segregation of feedstocks to be injected. Regarding the pseudo-plastic fluid, the general relationship between viscosity and shear rate at different temperatures can be described by equation (1) [7]:

\[ \eta = K\gamma^{n-1} \]  

where \( \eta \) is the viscosity of the feedstock, \( K \) is the material constant, \( \gamma \) is the shear rate, and \( n \) is the flow behavior index that is smaller than 1. The value of \( n \) or \( (n-1) \) indicated the degree of shear sensitivity for evaluating the rheological properties of feedstock. A relatively lower absolute value of \( n \) or a higher absolute value of \( (n-1) \) is desirable for injection molding of complex precision parts because the viscosity of feedstock shows higher dependency on the shear rate [17], which revealed stronger pseudo-plastic. Figure 10 shows the relationship between viscosity and shear rate at different temperatures can be described by equation (1) [7]:

![Figure 10. Plot of the double logarithm of feedstock viscosity versus the shear rate at four different temperatures: (a) Pristine, (b) CTHP-m, (c) ETHP-m, (d) CTHP-m/ETHP-m.](image-url)

where \( n \) is the viscosity of the feedstock, \( K \) is the material constant, \( \gamma \) is the shear rate, and \( n \) is the flow behavior index that is smaller than 1. The value of \( n \) or \( (n-1) \) indicated the degree of shear sensitivity for evaluating the rheological properties of feedstock. A relatively lower absolute value of \( n \) or a higher absolute value of \( (n-1) \) is desirable for injection molding of complex precision parts because the viscosity of feedstock shows higher dependency on the shear rate [17], which revealed stronger pseudo-plastic. Figure 10 shows the relationship between viscosity and shear rate at different temperatures from 140 °C to 170 °C. As seen in figure 10, with the increasement of shear rate, the viscosity of all feedstocks at different temperatures decreased rapidly, which showed pseudo-plastic fluid behavior, and the viscosity of each feedstock decreased linearly from the temperature of 140 °C to 170 °C, which indicated that higher temperature is more suitable for MIM. The values of flow behavior index \( n \) of each feedstock at different temperatures can be calculated from the slope of the \( \log(\eta) \) versus \( \log(\gamma) \) curve (value of \( n-1 \)) by the linear fitting and summarized in table 7. It can be seen from table 7 that all the flow behavior index \( n \) at the temperatures from 140 °C to 170 °C were lower than 1, which indicated that four feedstocks owned strong pseudoplastic behavior. And it was known that the lower value of \( n \) was important for producing complex MIM parts due to the higher shear sensitivity of feedstock, this fact can ensure better flowability and filling during molding process. Comparing with other feedstocks, the \( n \) values of CTHP-m/
ETHP-m feedstock was calculated to be 0.425, 0.431, 0.460 and 0.484 at the temperature of 140 °C, 150 °C, 160 °C and 170 °C, respectively, which were lower than feedstocks prepared from pristine, CTHP-m and ETHP-m. This experimental result might be caused by the strong interaction between CTHP-m and ETHP-m, and it could be expected to obtain higher quality parts with fewer defects.

In addition to the shear rate, the effect of temperature on the viscosity of feedstock is another significant factor for feedstock in MIM. Normally, the relationship between feedstock viscosity and temperature can be expressed by the Arrhenius equation shown in equation (2):

$$\eta(T) = B \exp \left(\frac{E}{RT}\right)$$

where $B$ is the reference viscosity, $E$ is the flow activation energy, $R$ is the gas constant, and $T$ is the absolute temperature. In Arrhenius equation, the $E$ value suggests the sensitivity of viscosity to the temperature variation of feedstock, which is an important influencing factor for the molding process in MIM. Lower value of $E$ indicates that the viscosity is not so sensitive to the change of temperature so that the feedstock could be flowed smoothly into the mold and broaden temperature ranges. If the value of $E$ is too large, it means that the viscosity is very sensitive to temperature, too large value of $E$ would lead to some problems during injection molding process, such as stress concentration which would result in cracks and distortions in the molded parts [39]. Therefore, weaker temperature dependence is critical to produce MIM parts with high quality. The relationship between feedstock viscosity and temperatures was shown in figure 11, the $E/R$ coefficient was obtained from the slop of the resulting linear fitting curve, and the $E$ values were listed in table 8. The calculated flow activation energy ($E$) of pristine, CTHP-m, ETHP-m and CTHP-m/ETHP-m was 37.4 kJ mol$^{-1}$, 34.83 kJ mol$^{-1}$, 41.24 kJ mol$^{-1}$ and 33.59 kJ mol$^{-1}$, respectively. As we know, the lower the activation energy of feedstock, the

![Figure 11. The relationship between the feedstock viscosity and temperature at a shear rate of 24.5 s$^{-1}$.](image)

| Feedstock | Temp (°C) | Pristine | CTHP-m | ETHP-m | CTHP-m/ETHP-m |
|-----------|-----------|----------|--------|--------|----------------|
| 140       | 0.444     | 0.430    | 0.437  | 0.425  |
| 150       | 0.493     | 0.460    | 0.450  | 0.431  |
| 160       | 0.514     | 0.482    | 0.470  | 0.460  |
| 170       | 0.525     | 0.486    | 0.502  | 0.484  |

| Feedstock | Pristine | CTHP-m | ETHP-m | CTHP-m/ETHP-m |
|-----------|----------|--------|--------|----------------|
| $E$(kJ/mol) | 37.41    | 34.83  | 41.24  | 33.59          |

Table 7. The values of flow behavior index (n) of each feedstock at different temperatures.

Table 8. Flow activation energy($E$) for each feedstock.
better the rheological property. Comparing with other feedstocks, the $E$ value of CTHP-m/ETHP-m is the lowest. This should be due to the interaction from the reaction of carboxyl/epoxy hyperbranched polyesters, which resulted in the closer connection of CTHP-m and ETHP-m in the feedstock, thus reducing the friction between powder and binder, increasing the fluidity of feedstock and decreasing the flow activation energy.

3.3. Microscopic morphology observation

Figure 12 showed SEM micrographs of the morphology of fractured surfaces of the green parts, as seen, the compatibility between the modified powders and the binder were better than that of pristine. Especially, the interparticle of CTHP-m/ETHP-m feedstock connected more tightly (figure 12(d)) than others (figures 12(a)–(c)), which was consistent with the results of the zeta potential values (table 4) and the flexural modulus and density of the green parts (table 6). What’s more, it could be observed that the number and size of holes circled in the images decreased from figures 12(a) to (d), that is, the fractured surfaces of the green parts of CTHP-m/ETHP-m has the least number of holes and the smallest holes diameter, which indicated that the method of powder modification and interaction from CTHP-m/ETHP-m can improve the compactness of the green parts and reduce defects. Figure 13 showed SEM micrographs of surface of the green parts. As shown in figure 13, there were more obvious holes on the surface of the green parts prepared by pristine, which indicated that the poor compatibility between the pristine and HDPE/paraffin wax binder. However, there were less holes on the surface of the green parts prepared by CTHP-m and ETHP-m, which revealed that the method of powder surface modification could improve the compatibility of powder and binder. Moreover, the surface of the green parts prepared by CTHP-m/ETHP-m was smoother than that of others, and there were no holes on the surface. The above results demonstrated that the strong interaction between CTHP-m and ETHP-m could not only promote the compatibility between the powder and binder, but also make the connection between the powder and binder more closely and easy to form uniform microstructure.

Figure 14 showed SEM pictures of the cross-sectional fractured surfaces of debinded parts, these images had little difference among the debinded parts, and the phenomenon indicated that powder modification did not affect the state of the powders. Compared with other debinded parts (figures 14(a)–(c)), the powders connected more closely and the surface of debinded part had fewer holes as seen in figure 14(d). The results demonstrated that the reaction between CTHP-m and ETHP-m was beneficial to improve the property of feedstock and reduced defects of debinded parts.

Figure 12. SEM micrographs of the morphology of fractured surfaces of the green parts: (a) pristine, (b) CTHP-m, (c) ETHP-m, (d) CTHP-m/ETHP-m.
3.4. Shape retention after thermal debinding

In the field of MIM, it is an important requirement for good shape retention for debinded or sintering parts to get final products with higher quality. Figure 15 was the front and side views of the debinded parts, and the
The change rate of the length of debinded parts was shown in Table 9. The length of green parts prepared by a compression mold was lower than that of corresponding debinded parts after thermal debinding, and the green components appeared the expansion after debinding, but the method of powder modification greatly decreased the extent of expansion, what’s more, the CTHP-m/ETHP-m green parts had the minimum length change rate after thermal debinding. The front view of all debinded parts had no significant bubbling and defects on the surface. However, the bulges and rough surface appeared in pristine and CTHP-m debinded parts, besides, the degree of distortion of pristine and CTHP-m debinded parts was higher than that of ETHP-m and CTHP-m/ETHP-m debinded parts. The slighter degree of deformation and distortion of ETHP-m debinded parts was the results of the better compatibility between modified powders and binder. Particularly, because the interaction of carboxyl/epoxy hyperbranched polyesters helps to make the modified powder closely connected, and then reduce the debinding deformation of CTHP-m/ETHP-m debinded parts, CTHP-m/ETHP-m debinded parts had the lowest length change rate, and this would be critical to improve the precision and quality of the final products.

4. Conclusion

The objective of this work presented herein is to analyze and compare the influence of interaction from the reaction of carboxyl/epoxy hyperbranched polyesters on properties of feedstocks which were prepared by pristine powders, CTHP-m, ETHP-m, and CTHP-m/ETHP-m. The XPS and TG results demonstrated that carboxyl group and epoxy group were successfully connected with the 17-4PH powders surface by CTHP and ETHP modification, respectively. Due to the reaction between CTHP-m and ETHP-m, the critical powder solids loading, flowability, green density, flexural modulus of feedstocks prepared by CTHP-m/ETHP-m were higher than that of pristine, CTHP-m and ETHP-m. Comparing with pristine, CTHP-m and ETHP-m, the feedstock prepared by CTHP-m/ETHP-m possessed the critical solids loading, flexural modulus and density and melt flow index of 63.8 vol.%, 2800 Mpa, 5.06 g cm$^{-3}$ and 62 g/10 min, respectively, which were higher than that of others. It is worth emphasizing that the shape retention of debinded parts prepared by CTHP-m/ETHP-m was the best of all, and this will help to improve the properties of MIM feedstocks and the precision and quality of the final products.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Declaration of competing interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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