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Water-soluble binder with high flexural modulus for powder injection molding

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A new binder system, containing ternary polymer blends of poly(methyl methacrylate) (PMMA), cellulose acetate butyrate (CAB) and polyethylene glycol (PEG), was introduced for the powder injection molding of stainless steel powders. The weight fraction of PEG in the binder was maintained to be 0.65. When the weight fraction of PMMA in the binder was 0.1–0.25 (thus the weight fraction of CAB was 0.1–0.25), the feedstocks with 56 vol% of steel powders were successfully injection molded without showing any jetting. Furthermore, the feedstocks have much higher flexural modulus compared with those prepared by a binder consisting only 35/65 (wt/wt) CAB/PEG blend. Three binary blends, PMMA/CAB, PMMA/PEG, and CAB/PEG, were completely miscible at an injection molding temperature of 130°C. The extraction process employed in this study becomes environmentally favorable due to the major component (PEG) of the binder which is easily extracted by a solvent of water or ethanol. Also, the shape maintenance during the solvent extraction was excellent, and final sintered parts had excellent dimensional stability. Due to high flexural modulus of feedstocks, this binder system can be employed for preparing large sized injection-mold articles.

1. Introduction

Powder injection molding (PIM) processing of metals or ceramics has been employed to develop tiny and sophisticated metal or ceramic parts, and it is a very economic process compared with a casting and a machining [1, 2]. Among the many steps in the PIM, the suitable choice of a binder becomes crucial to determine the mechanical properties of the final product. Wax-based binders containing a backbone material of polyethylene or a poly(ethylene-*ran*-vinyl acetate) have been widely used in the powder injection molding industries [3, 4]. However, organic solvent such as hexane and heptane, which is not an environmentally favorable solvent, should be used to extract the wax.

To avoid using hexane or heptane during the extraction, efforts have been focused on finding new types of binders that would be removed by an environmentally favored solvent such as water [5–11]. Davies and coworkers [7, 8] introduced a poly(methyl methacrylate)/poly(ethylene glycol) [PMMA/PEG] binder system for stainless steel powders. Although a very high molecular weight (∼1,000,000) of PMMA was used, the binder was mixed with steel powder in the presence of water, because water is a solvent of lower molecular weight (<1500) PEG and an emulsion medium of PMMA. However, without using emulsion containing water for PMMA particles, a binder consisting of PMMA and PEG might not be mixed effectively with steel powders.

Previously, we introduced a water-soluble binder consisting of cellulose acetate butyrate (CAB) and various molecular weights of PEG. We found that the crystallization of PEG depending upon the molecular weight affected profoundly the shape maintenance during solvent extraction [12, 13]. Namely, when the molecular weight of PEG was larger than 3400, cracks were found in green parts after the solvent extraction. Although binders of CAB/PEG with molecular weight less than 2000 could be injection molded, jetting resulting from low viscosity of PEG was sometimes observed. Also, mechanical properties such as flexural strength of green parts are poor, which restricts one to making large sized injection-molded articles.

In order to overcome these disadvantages, we added PMMA to CAB as the backbone material. The rational behind choosing PMMA is that (i) PMMA is miscible with both CAB and PEG at a processing

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temperature of 130°C; (ii) it shows good adhesion with metal powder due to having a polar group, which prevents binder separation during injection molding; and (iii) it provides good mechanical properties of green parts. We could use higher molecular weight of PEG up to 8,000 when PMMA was employed. A binder consisting of PMMA/CAB/PEG ternary blends exhibited higher flexural modulus and suitable rheological properties for injection molding; thus a large sized injection-molded article was successfully prepared. Also, we observed that the shape maintenance during the extraction was excellent, and final sintered parts had excellent dimensional stability.

2. Experimental

2.1. Materials

PMMA was also kindly supplied by LG MMA Co, and the molecular weight and polydispersity of PMMA were determined by using gel permeation chromatography (Waters Co.) with PMMA standards. CAB with 54 mol% butyrate side group was purchased from Acros Co. and PEG with different molecular weights was kindly supplied by Korea Polyol Co. (Korea). The molecular characteristics of these materials are given in Table I. CAB and PMMA are amorphous materials with a glass transition temperature of 94°C and 100°C, respectively, measured by DSC (Perkin-Elmer DSC7 series) at a heating rate of 20°C/min. The metallic powder was stainless steel (17-4PH, Mitsubishi Steel MFG Co.) having irregular shape and a median particle size of 8.86 μm.

2.2. Sample preparation and rheological properties

The feedstock, a mixture of the binder and metallic powder, was first prepared by mixing at 130°C for 1 h by using the Kneading Blade Type Mixer (IKAVISC Co.); then it was shaped into a rectangular bar 70.22 × 7.12 × 3.57 mm ($L \times W \times T$) by using a 180 ton precision injection-molding machine (Sodick Plustech Co.; Japan) at 130°C and mold temperature of 25°C. An Advanced Rheometrics Expansion System (ARES) using the dynamic oscillatory mode with parallel plate fixture (25 mm diameter) was used to measure the viscosity of the binder itself. The strain amplitude was 5%, which lies in linear viscoelasticity range.

TABLE I Molecular characteristics of blend components employed in this study

	M_n	Polydispersity index	T_g or T_m (°C)
PMMA	63.000	1.47	$T_g = 100$
CAB	11,000	2.3	$T_g = 94$
PEG-1	1,500	1.15	$T_m = 43$
PEG-2	2,000	1.10	$T_m = 50$
PEG-3	3,350	1.14	$T_m = 54$
PEG-8	8,000	1.16	$T_m = 56$

2.3. Turbidity experiment of PMMA/CAB blend

Various blend compositions of PMMA and CAB for turbidity temperature (T_b) measurement were prepared by dissolving a predetermined amount of the mixture in toluene (10 wt%) and slowly evaporating the solvent over 8 h at room temperature. The sample thickness was 10 μm. Each specimen was annealed in the homogeneous state (~120°C) for 4 h. The T_b of each composition was measured from the sudden increase in light scattering intensity at a scattering angle of 30° upon heating the mixture from 120°C at a rate of 0.1°C/min. Once the T_b of a specimen was estimated, the exact T_b was determined by the naked eye upon a temperature increment by 0.5°C near the temperature of interest. The specimen was held at each temperature for 1 h. The maximum error in the values of T_b determined was ±0.5°C.

2.4. Debinding and sintering

Two steps of debinding of green parts were conducted. The first step was to extract PEG out of green parts by distilled water at room temperature for 24 h. The second step was referred to as the thermal debinding, where the backbones composed of PMMA and CAB were completely removed and pre-sintering of metal powders occurred. Finally the sintering of metal powders was carried out. Thermal debinding and sintering were carried out in a tube-type furnace (Lenton Thermal Design Ltd.) under hydrogen atmosphere by using the same thermal history as ref. [12].

3. Results and discussion

3.1. Miscibility between binder components

The binder employed in PIM has a multi-component system: (a) a backbone polymer that provides shape maintenance during solvent extraction; (b) an extractable polymer that is removed during the first step of the debinding process, and (c) a surfactant to bridge between the binder and powder [1]. It is necessary that all components should be miscible at processing temperatures. Otherwise, the binder components become macrophase-separated. Previously, we showed that a binary blend of CAB/PEG having a molecular weight (M) of 35000 showed lower critical solution temperature (LCST) of 168°C [13]. Since M of PEG employed in this study is less than 8000, we found that the CAB/PEG mixture does not become phase-separated up to 250°C. The PMMA/PEG blend becomes completely miscible at temperatures greater than the melting temperature of PEG [14].

Fig. 1 gives the phase behavior of the PMMA/CAB blend, from which the LCST was 142°C at 20/80 (w/w) PMMA/CAB composition. Thus, we conclude that macrophase-separation among all three binary blends (PMMA/PEG, CAB/PEG, and PMMA/CAB blends) does not occur at a processing temperature of 130°C, which is the mixing and injection molding temperatures. Also, when the amount of PMMA was changed

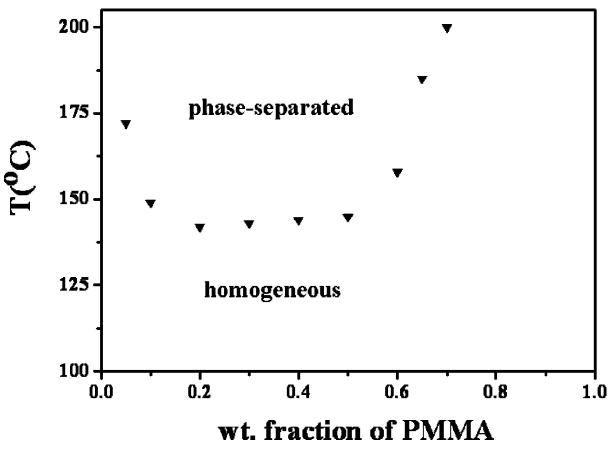

Figure 1 Phase diagrams of PMMA/CAB blend.

from 15 to 25 wt% at a fixed amount of PEG (65 wt%), no turbidity was detected up to 200°C.

3.2. Rheological properties

It is known that feedstocks should have a low enough viscosity to be processed by injection molding. However, when the viscosity becomes too small, jetting occurs during the injection molding process; thus the exact shape of molded article is impossible. Fig. 2 gives the complex viscosity (η^*) as a function of frequency for the binders composed of various compositions of PMMA/CAB/PEGs with two different molecular weights of PEGs. It shows that as the content of PMMA and M of PEG increase, the viscosity becomes larger. When the binders do not contain CAB, a binder consisting of 35/65 (wt/wt) PMMA/PEG has zero-shear viscosity (η_0) of 100 Pa·s, regardless of molecular weights of PEG. It is known that when η_0 of a binder is larger than ~20 Pa·s, the feedstocks including high volume of powders could not be molded by injection molding [1]. Therefore, it is considered that feedstocks consisting of 15/20/65 and 25/10/65 (wt/wt/wt) PMMA/CAB/PEG-8 binder and 56 vol% of steel powders could be injection molded.

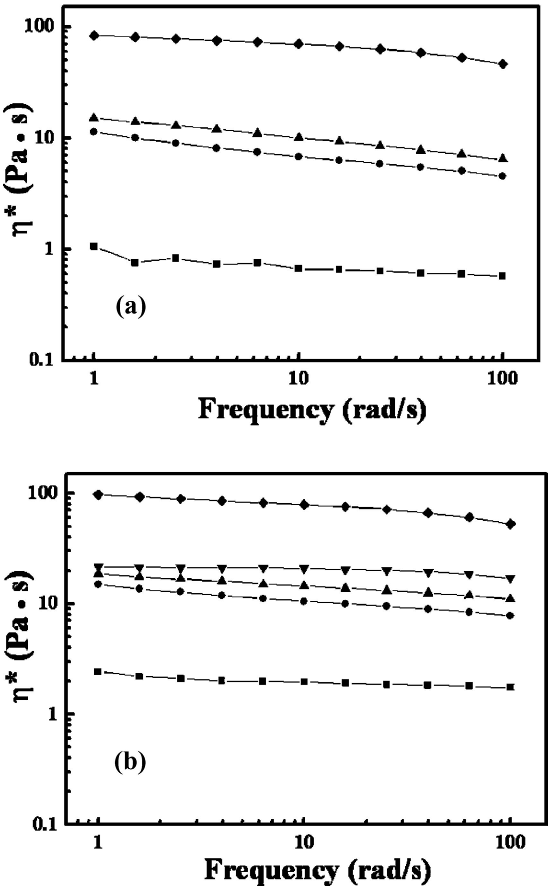

Figure 2 The complex viscosities as a function of frequency at 130°C for various compositions (wt/wt/wt) in PMMA/CAB/PEG with two different molecular weights: (a) PEG-3 and (b) PEG-8. The weight percents in PMMA/CAB/PEG blends are: (■) (0/35/65); (●) (15/20/65); (▲) (20/15/65); (▼) (25/10/65), and (♦) (35/0/65).

3.3. Injection molding and extraction process

Previously, we showed that green parts consisting of 35/65 (wt/wt) CAB/PEG blend with M of PEG greater than 3,350, failed to maintain their shapes during the solvent extraction [12]. When PMMA was added to CAB/PEG-8 binder system, we found that there were no cracks and deformation at the green parts during solvent extraction.

The injection molding process was performed for two different feedstocks whose blend compositions are shown in Table II. The temperatures at the injection molding machine and inside the molder were 130 and 25°C, respectively. The injection molding cycle time for these two feedstocks could be performed within ~1 min. We found that none of the feedstocks showed any jetting during the injection molding.

The flexural modulus of the green parts was measured with the 3-point flexural test using a universal test machine (UTM, Instron 3302, Canton, MA). At least five specimens were employed to minimize the error in determining the flexural modulus and averaged. The crosshead speed of the feedstock is 1.17 mm/min. Table III gives the flexural strength of green parts prepared by feedstocks 1 and 2, as well as green parts

TABLE II Feedstocks consisting 17-4PH powder and PMMA/CAB/PEG binder systems

	Binder type and composition (wt percent)	17-PH powder loading (vol%)
Feedstock 1	PMMA/CAB/PEG-8 (15/25/65)	56
Feedstock 2	PMMA/CAB/PEG-8 (25/10/65)	56

TABLE III The flexural moduli of green parts prepared by various binders at a powder loading of 56 vol%

(wt/wt/wt)	Flexural modulus (MPa)
CAB/PEG-1 (35/65)	2038 ± 97
CAB/PEG-2 (35/65)	7062 ± 312
CAB/PEG-3 (35/65)	7847 ± 248
PMMA/CAB/PEG-8 (15/20/65)	11607 ± 144
PMMA/CAB/PEG-8 (25/10/65)	13560 ± 135

prepared by binary blends of CAB/PEG. Since the feedstocks 1 and 2 contain PEG-8 as a major component, the flexible strength of green part prepared by feedstocks 1 and 2 is much higher than that prepared by feedstock consisting only binary blend of CAB/PEG. Feedstock 2 has higher flexural strength than feedstock 1 due to the larger portion of PMMA.

The PEG in the injection-molded articles (green parts) prepared by all feedstocks were extracted by distilled water at room temperature for 24 h. After solvent extraction, more than 85% PEG-8 was removed, and no cracks were found. The better shape maintenance is due to the good mechanical property of PMMA even though a higher molecular weight of PEG was employed compared with a previous study [12].

3.4. Thermal debinding and sintering

Fig. 3 gives the weight loss with temperature for PMMA, CAB, and PEG-8 in the nitrogen and air environments. It is seen that PMMA and PEG-8 did not have any residue at temperatures higher than 420°C. But, CAB was not completely pyrolyzed even at 600°C under nitrogen atmosphere, while this completely disappeared at 600°C under air environment, which implied that PMMA/CAB/PEG binder can be completely removed under air atmosphere. However, the use of air atmosphere is not good for metal powder due to oxidization of metal. Thus, hydrogen atmosphere was employed for the thermal debinding of green parts with metal powders. The carbon residues after thermal debinding of two feedstocks are 0.11 wt%, as shown in Table IV. Since the carbon residue of the steel powder (17-4PH) itself is 0.07% [12], the increase in the carbon residue due to the binder is not large. Also, we found that the oxidation of metal did not occur. Even though a small increase in the carbon after thermal debinding was observed, this residue carbon was further reduced during the sintering process.

The dimensions and densities of the sintered parts are given in Table IV. Five specimens were employed to determine the dimensional stability and the final density. Final density of products prepared by two feedstocks was 99%. Also, the standard deviation of the dimensions was less than ±0.3%, which is a commercially allowed tolerance. It is seen in Table IV that the standard deviation (~0.25%) for the thickness direction is much larger that that for the length (or the width) direction (~0.1%). Because the thickness of a specimen during the sintering inside the furnace was largely affected by its gravity compared with the length (or width), the decrease in the specimen was not uniform [1]. Thus, we consider that the anisotropic decrease in the specimen was not due to an improper injection molding condition, but to the sintering the specimen in the furnace. The final sintered part and green part prepared from feedstock 2 are shown in Fig. 4. It is seen that the sintered part was reduced uniformly from the original size of green part and shows a typical metal gloss.

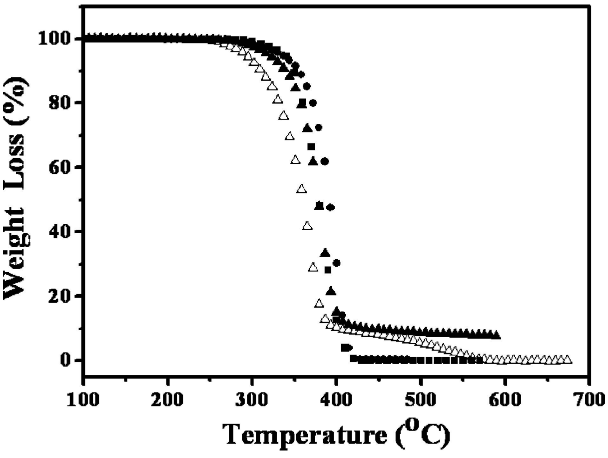

Figure 3 TGA thermograms of PMMA (■), CAB (▲), and PEG (●) at a heating rate of 20°C/min under nitrogen atmosphere. TGA thermogram of CAB (△) under air environment is added.

TABLE IV Dimensions and densities of final parts fabricated by the feedstocks 1 and 2

	Dimension	Standard deviation (%)	Sintered density[a]	Carbon contents[b]
Feedstock 1				
L	58.47 ± 0.02	±0.034	99%	0.11 wt%
W	5.84 ± 0.005	±0.080		
T	2.922 ± 0.007	±0.23		
Feedstock 2				
L	58.07 ± 0.03	±0.052	99%	0.11 wt%
W	5.80 ± 0.008	±0.137		
T	2.93 ± 0.008	±0.27		

[a] Sintered density: measured density divided by the density of 17-4PH metal (7.7 g/cm^3).

[b] Residual carbon content after thermal debinding.

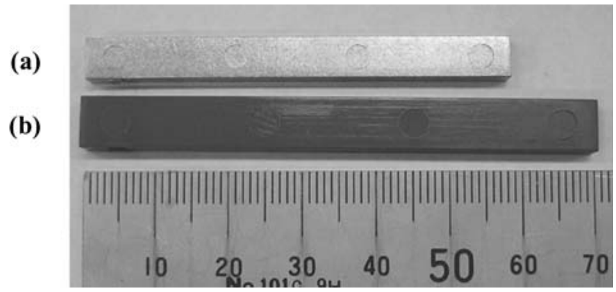

Figure 4 The shapes of (a) the final article after sintering and (b) green part prepared by feedstock 2 in Table II.

4. Conclusion

We introduced a ternary binder system, composed of PMMA, CAB and PEG, to improve the mechanical strength of green parts and shape maintenance. The binders of CAB/PEG-2 and CAB/PEG-3 blends were easily processed by injection molding due to low viscosity, but jetting was observed. On the other hand, CAB/PEG-8 binder exhibited cracks and deformation during the solvent extraction. When the PMMA was added to CAB/PEG binder, the feedstocks could be injection molded. Also, the injection-molded articles prepared by the ternary blend showed significantly improved mechanical properties such as flexural modulus of the feedstocks compared with a binder consisting of only CAB/PEG blend. Thus, this binder system could be employed for preparing large sized injection-molded articles.

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