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Effect of solvent debinding variables on the shape maintenance of green molded bodies

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In order to study the effect of solvent extraction debinding variables on the shape maintenance of green molded bodies, powder compression molded bodies (the feed) were debound in various organic solvents such as *n*-hexane, *n*-heptane and isooctane at various extraction temperatures ranging from 30 to 60°C. The solvent to feed ratio of dilution was studied in the range of 7:1 to 15:1 by weight. Finally the effect of extraction time on the amount of binder extracted and diffusion coefficient of paraffin wax was studied in the range of 1 to 5 h. Thermo gravimetric analysis (TGA) was used to confirm the extraction of the major binder and stearic acid constituents completely from the binder mixture. Scanning electron microscopy (SEM) was used to see the pores in the green bodies created after solvent extraction process which allowing the degraded products (minor binder) to diffuse to the surface easily. © *2004 Kluwer Academic Publishers*

1. Introduction

The powder injection molding (PIM) process is used widely for the production of metal parts with complex shapes [1]. It consists of the preparation of a feedstock by mixing of a binder and metal powders, injection molding of the feedstock into a mold, removal of the binder from the feedstock (solvent and thermal debinding), and sintering of the metal or ceramic powders [2].

The removal of organic binder is a procedure (usually termed debinding) that is known to be critical in obtaining a green compact with desired microstructure [3]. Debinding is a key problem with PIM because the time for binder removal depends on the section thickness. Consequently, various manufactures have set upper limits on section thickness ranging from 10 to 50 mm. Thus, the goal in debinding is to remove the binder in the shortest time with the least impact on the compact [4]. There are several debinding techniques consisting of solvent and thermal methods in PIM process. Solvent debinding takes advantage of the high solubility of low molecular weight constituents (major binder) in organic solvents. The leaching or extraction of one binder component creates porosity in green bodies. A large amount of open porosity, after solvent debinding, allows the degraded products (minor binder) to diffuse to the surface easily. Therefore, the thermal removal of insoluble binder components will be finished in a much shorter period without endangering the integrity of the green piece. Consequently the combination of solvent debinding and thermal debinding can be time saving [5, 6].

Many authors studied different variables affecting the solvent debinding process but they keep the solvent to feed ratio constant. White and German [6] found that a high powder loading needed a long solvent debinding time to remove the wax from the binder. They attributed the long debinding time to the difficulties of diffusion through smaller pores. Lin and German [7] studied the debinding of PIM parts by the condensed C7 solvent at 95°C and used a diffusion model to describe the wax removal process. Nanjo *et al.* [5] reported the rate controlling step in the solvent debinding process by using different organic solvent vapors when using two kinds of binders. They stated that, selection of organic solvents of lower viscosity such as hexane is most important to enhance the debinding rate. In addition, they investigated whether a liquid component involved in binders such as dispersant can enhance the debinding rate in order to shorten the debinding times. Tsai and Chen [6] studied the effect of C_6, C_7 and C_8 leaching solvents at different high temperatures (50, 60 and 80°C) on the kinetics of solvent immersion debinding process. They used very large amounts of solvents in the leaching operations.

Thus, the objective of the present study is to investigate the effects of different organic solvents at different extraction temperatures (30, 40, 50 and 60°C) by varying the solvent to feed ratios (S/F) and extraction times on the amount of binder extracted, diffusion coefficient of paraffin wax and the shape maintenance of green molded bodies.

2. Experimental

2.1. Materials and preparation of green molded bodies

The metallic powder used in this study was water-atomized 17-4PH stainless steel (STS, Mitsubishi Steel

TABLE I Chemical composition of water-atomized 17-4PH stainless steel powder

17-4PH	C	Cr	Ni	Si	Mn	Cu	Nb	P	S	O
wt%	0.07	15.99	4.15	0.71	0.28	3.88	0.35	0.004	0.006	0.49

MFG Co.) having irregular shape with average particle diameter of 8 μm and tap density of 3.96 g/cm^3. The chemical composition and particle size distribution analysis of the metallic powder are given in Tables I and II respectively.

The binder system employed is well known [8] and was prepared with a mechanical stirrer at 150°C for 30 min. It consisted of 35 wt% poly(ethylene-ran-vinyl acetate) (EVA), 62 wt% of paraffin wax and 3 wt% of stearic acid which enhances the wetting between the binder and metallic powder. EVA having vinyl acetate content of 9.5 wt% was kindly supplied by Hanwha Chemical Co. (Taejon, South Korea) and the paraffin wax purchased from Oxford Co. (St. Louis, MO). The role and characteristics of each component as well as the composition of the mixture are summarized in Table III. The weight-average molecular weights of the EVA and paraffin wax were determined using high temperature gel permeation chromatography (GPC-150C, Waters Co., Milford, MA) [9].

The feedstock for molding is prepared by mixing a suitable ratio of powder and binder. It is important that the mixture is homogeneous, free of agglomeration and contains no porosity. Some of the mixing parameters that could affect the homogeneity of the feedstock are: the type of the mixer and mixer blades, the mixing speed and the temperature, the mixing time and the sequence. The binder and powder characteristics will affect homogeneity [10]. Thus, in this experimental work the feedstock which is a mixture of the binder and metallic powders (44/56 by volume) [4], was first prepared by melt mixing at 150°C and 50 rpm for 1 h using Kneading Blade Type Mixer (IKAVISC Co.). The powder were added in stages and the homogeneity of the mixture was found experimentally better.

For studying the effect of solvent extraction debinding process on the shape maintenance of green bodies, the samples were formed by molding the mixture using compression molding machine (CARVER Laboratory Equipment—USA) at 130°C under pressure of 60 MPa for 10 min and mold temperature of 20°C. The compression molded samples were rectangular bars with dimensions of $50 \times 13 \times 3.0$ mm ($L \times W \times T$), batch size of 1.95 cm^3 and final bar density of 4.713 g/cm^3.

2.2. Solvent extraction

Solvent extraction operations were carried out by using different organic solvents (n-hexane, n-heptane and isooctane) at different extraction temperatures (ranging from 30 to 60°C). Another extraction variables studied were solvent feed ratios (S/F) of dilution (ranging from 7:1 to 15:1 by weight) and time (ranging from 1 to 5 h).

Bar samples were placed at the center of a 250 ml beaker which contained the solvent. The beaker was kept at constant temperatures by shaking thermostat. The solvent was stirred during debinding to remove the dissolved wax and stearic acid quickly from the surface of the sample. The debinded sample after a predetermined interval was vacuum-dried at room temperature to evaporate the solvent and its weight was measured. The debinding ratio (Wd) was measured according to the following equation [5] :

$$Wd(\%) = (Wi - W)/Wi \times 100$$

where Wi is the initial weight of compressed bodies and W is the weight after solvent debinding. The amount of binder extracted was calculated by dividing Wd by the total binder content (wt%) in the feedstock. The diffusion coefficient of paraffin wax in compressed bodies was measured according to the following equation [5, 11]:

$$(Ca - Co)/(Ci - Co) = 8/\pi \exp(-\pi/h^2 Dt)$$

where Ca is the average concentration of binder remaining in compressed body, Ci is the initial concentration of binder, Co is the boundary condition and zero, t is the debinding time, D is the diffusion coefficient of paraffin wax and h is the thickness of compressed body.

TABLE II Particle size distribution of water-atomized 17-4PH stainless steel powder

Particle size (μm)	−3.9	3.9/5.5	5.5/7.8	7.8/11	11/16	16/22	22/31	31/44	44/62
Weight fraction (%)	7.5	12.7	18.2	23.2	23.1	11.9	3.3	0.1	–

TABLE III The Characteristics and compositions of the raw materials

Raw materials	Role	Melting point T_m(°C)	M_w	Density (g/cm^3)	Composition of compression-molded bodies (wt%)
17-4PH	Metallic powder	–	–	7.7	91.50
Paraffin wax	Major binder	55	560	0.900	5.27
EVA	Minor binder	95	74,800	0.930	2.98
Stearic acid	Surfactant	68	–	0.900	0.25

M_w = Weight-average molecular weight.

2.3. Thermal analysis and scanning electron microscopy observations

Thermo gravimetric analysis (TGA) was conducted on a Perkin-Elmer TGA model 7. The pyrolysis of the binder system in the green molded body was conducted in the temperature range of 30 to 600°C, under a dynamic nitrogen gas. The heating rate used was 15°C/min.

The cavities created in the green molded bodies after solvent extraction of the major binder constituent from the binder mixture have been shown by using Scanning electron microscopy (SEM; Hitachi S-4200).

3. Results and discussion

Among many steps in the powder injection or compression molding, the solvent extraction debinding process is considered the most important step. Whereas, the dissolution of binders in suitable solvent is frequently used as a means of accelerating the removal of the major constituents of the binder system while leaving the minor constituent to support the structure. This minor constituent is removed later by a thermal treatment which, because of the porosity network created by the solvent extraction step, can performed rapidly [12].

3.1. Choice of the extraction variables

3.1.1. Extraction temperature

The temperature is one of the important variables in the solvent extraction process. Figs 1 and 2 show the effect of extraction temperature on the amount of binder extracted and the diffusion coefficient of paraffin wax by using different organic solvents at fixed solvent to feed ratio of dilution (S/F = 7:1) [13] and extraction time of 1 h. As the extraction temperature increases, the amount of binder extracted and the diffusion coefficient of paraffin wax increase. This means that, the diffusion coefficient decreases in the following order: $60 > 50 > 40 > 30$°C. This attributed to that, the penetration rate at 60°C is relatively the fastest and the diffusion coefficient becomes the rate-limiting step. Although the highest temperature leads to the highest extraction rate and the debinding operation appears to be more efficient at the high extraction temperature of 60°C, this temperature is too high and can form cracks in the green molded body after extraction as shown in Fig. 3b. These cracks are assumed to be associated with the swelling effect of solvent (i.e., the solvent diffuses into the minor binder) which increases with temperature. Wherefore, temperature control is important to successful debinding [4], thus, 50°C was chosen as a suitable extraction temperature for extracting the major constituent of the binder system.

Also, it can be noticed from Figs 1 and 2 that the amount of binder extracted and the diffusion coefficient of paraffin wax are increased with decreasing the carbon number of the solvent. This is attributed to the fact that, the solubility of paraffin wax in the solvent increases with decreasing the carbon number of the solvent as a result of decreasing the solvent viscosity [14]. Thus, the high solubility of the solvent enhances the debinding rate and the diffusion coefficient.

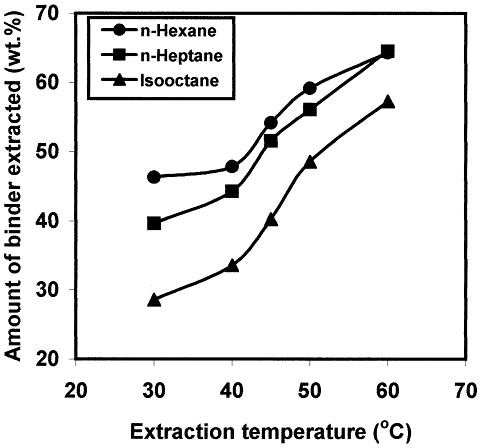

Figure 1 Effect of extraction temperature on the amount of binder extracted by using different organic solvents at S/F = 7:1 and time of 1 h.

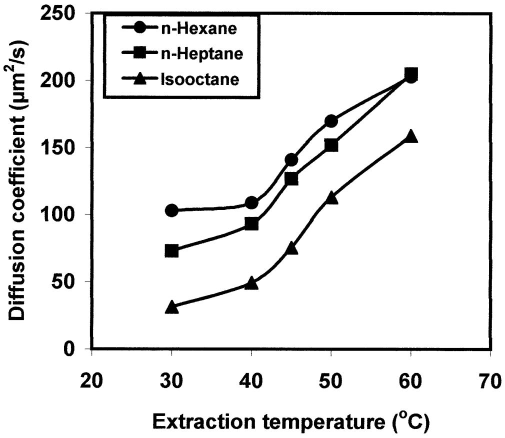

Figure 2 Effect of extraction temperature on the diffusion coefficient of paraffin wax by using different organic solvents at S/F = 7:1 and time of 1 h.

From the above findings, it can be concluded that n-hexane is the most suitable solvent for extracting the soluble binder constituents from the binder mixture.

3.1.2. Solvent feed ratio

The cost of an extraction process is related directly to the quantity of solvent required for a given feedstock. Study of solvent to feed ratio is performed by using n-hexane solvent, extraction temperature of 50°C, solvent to feed ratio ranging from 7:1 to 15:1 by weight and the extraction time of one hour was kept fixed.

Fig. 4 shows the effect of solvent to feed ratio on the amount of binder extracted and the diffusion coefficient of paraffin wax. Increasing the solvent to feed ratio from 7:1 to 15:1 leads to a very slight increase in the amount of binder extracted (approximately from 59 to 61 wt%) and the diffusion coefficient of paraffin wax (from 170 to 181 $\mu m^2/s$). Thus, from economic point of view, the solvent to feed ratio of 7:1 is chosen as the most suitable ratio for extracting the major binder constituent from the binder mixture.

3.1.3. Extraction time

The time is considered the most important problem in powder injection or compression molding process.

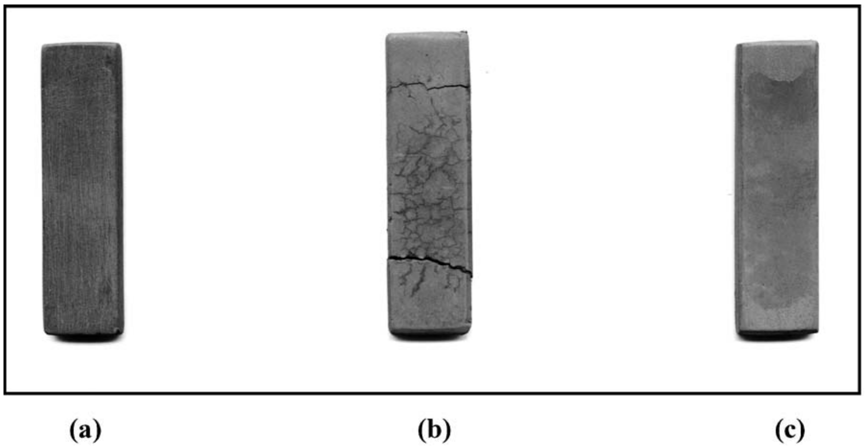

Figure 3 Photographs of green molded bodies before extraction (a), after extraction with n-hexane at 60°C, 1 h and $S/F = 7{:}1$ (b) and at the suitable extraction conditions (c).

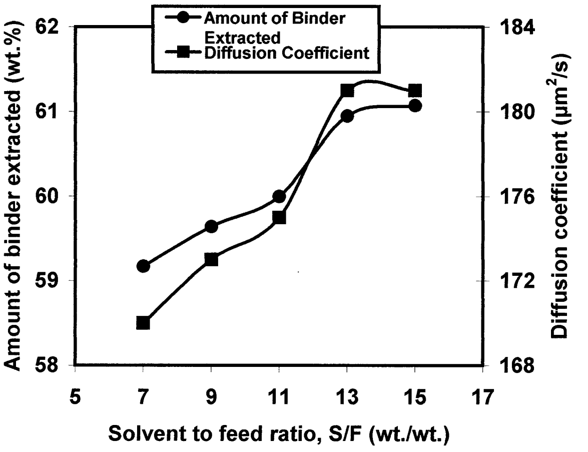

Figure 4 Effect of solvent to feed ratio on the amount of binder extracted and the diffusion coefficient of paraffin wax by using n-hexane at 50°C and 1 h.

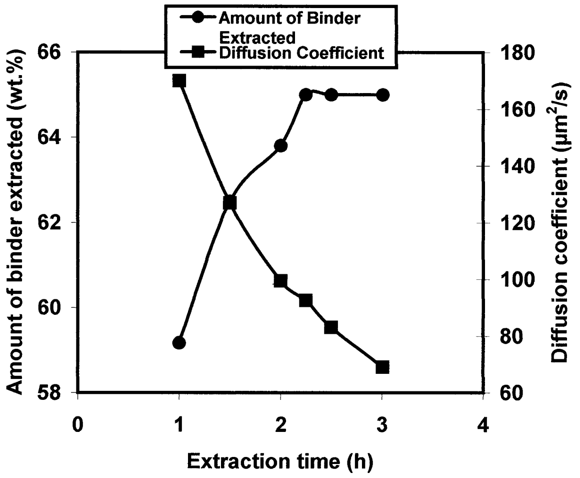

Figure 5 Effect of extraction time on the amount of binder extracted and the diffusion coefficient of paraffin wax by using n-hexane at 50°C and $S/F = 7{:}1$.

Therefore, this study was aimed to remove the major binder and stearic acid constituents in a short time with the least impact on the green molded bodies. Study of extraction time is performed by using n-hexane solvent, extraction temperature of 50°C, solvent to feed ratio of 7:1 and the extraction time ranging from 1 to 3 h.

Fig. 5 shows the effect of extraction time on the amount of binder extracted and the diffusion coefficient of paraffin wax. As the extraction time increases from 1 to 2.25 h, the amount of binder extracted increases approximately from 59 to 65 wt% and the diffusion coefficient of paraffin wax decreases from 170 to about 93 μm^2/s. At the time ranging from 2.25 to 3 h, the amount of binder extracted not changed and the diffusion coefficient of paraffin wax still decreases. It can be noticed that the amount of binder extracted approaches the limit of 65 wt% at a short time of 2.25 h. This limit corresponding to all the paraffin wax and stearic acid contents in the binder mixture. Thus, the extraction time of 2.25 h is chosen as the enough time for extracting the major binder and stearic acid constituents completely from the binder mixture.

In an attempt for saving some energy, the extraction temperature of 45°C was studied at various extraction times ranging from 2.25 to 5 h by using n-hexane solvent and solvent to feed ratio of 7:1. As the extraction time increases from 2.25 to 5 h, the diffusion coefficient of paraffin wax decreases from about 86 to 40 μm^2/s and the amount of binder extracted increases slightly from about 63 to 64 wt% as shown in Fig. 6. The amount

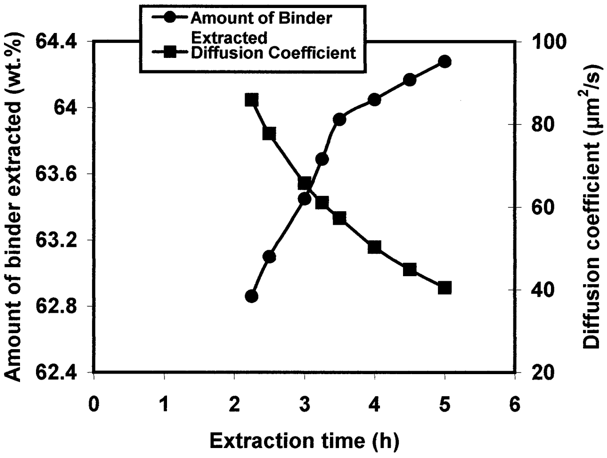

Figure 6 Effect of extraction time on the amount of binder extracted and the diffusion coefficient of paraffin wax by using n-hexane at 45°C and $S/F = 7{:}1$.

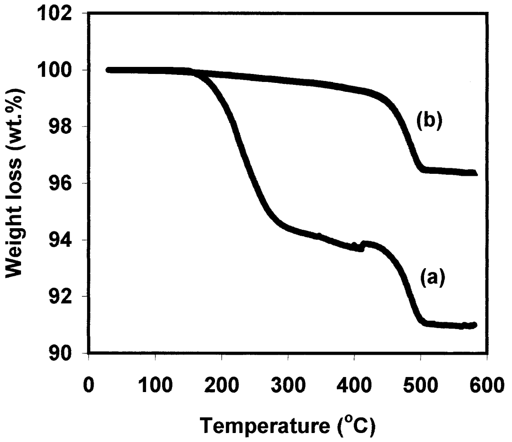

Figure 7 TGA thermograms of green molded bodies before (a) and after (b) extraction with n-hexane at 50°C, 2.25 h and $S/F = 7{:}1$.

of binder extracted after 5 h is less than the limit of all paraffin wax and stearic acid contents in the binder mixture (Fig. 6). This means that, 5 h is not enough time for extracting all the major binder and stearic acid constituents completely at the extraction temperature of 45°C. This may be attributed to the fact that stearic acid is not completely soluble in n-hexane solvent at 45°C and solvent feed ratio of 7:1 due to the higher solubility parameter of stearic acid ($\delta = 7.5$) than that of n-hexane solvent ($\delta = 7.3$) at 25°C [15].

Finally, it can be concluded that the most suitable extraction conditions under study for extracting the major binder and stearic acid constituents completely from the binder mixture without affecting on the shape maintenance of green molded bodies as shown in Fig. 3c are:

1. Solvent is n-hexane
2. Extraction temperature is 50°C
3. Solvent to feed ratio is 7:1 by weight
4. Extraction time is 2.25 h.

3.2. TGA analysis

The binder concentration in the green molded body at each position is determined by TGA. Fig. 7a shows the TGA thermogram of the binder components in the green molded body before solvent debinding process. It can be seen that, the binder starts to degrade at about 180°C and completes the degradation at about 500°C through three weight loss stages and overall weight loss of the binder components is 8.5 wt%. The first weight loss stage (about 5.3 wt% which is equivalent to the paraffin wax content in the green molded body) in the

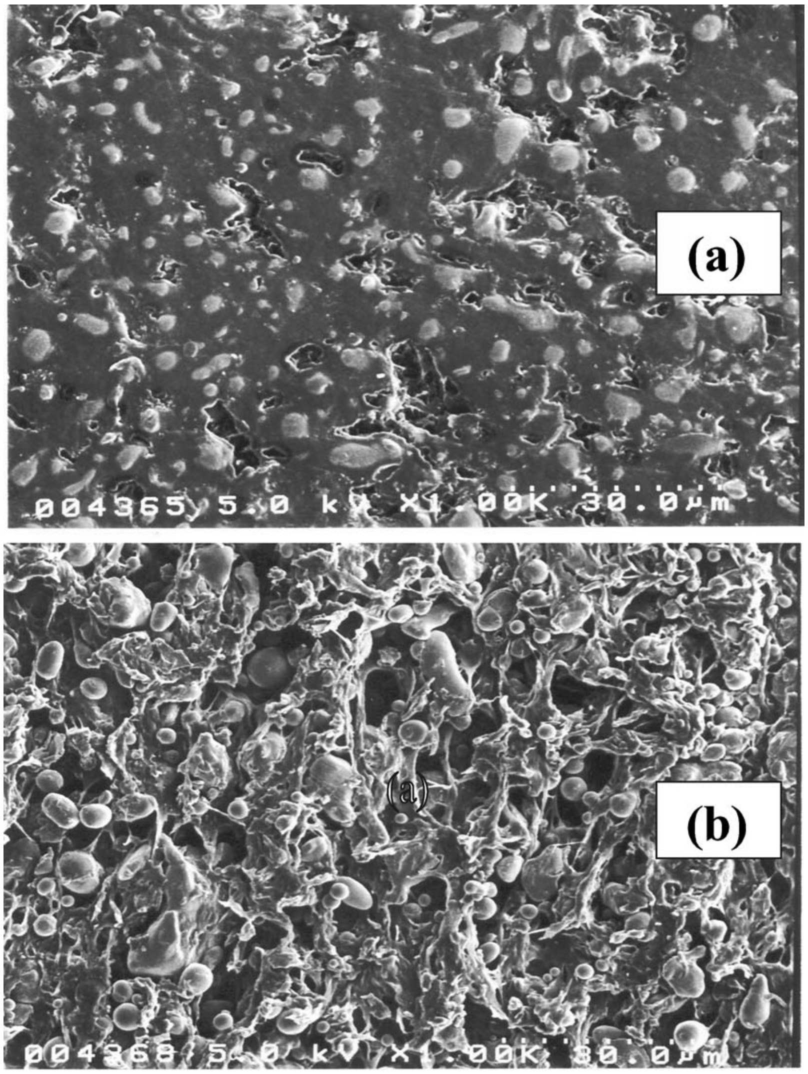

Figure 8 SEM photographs of green molded bodies before (a) and after (b) extraction with n-hexane at 50°C, 2.25 h and $S/F = 7{:}1$.

temperature range of 180 to 300°C is due to the degradation of paraffin wax in the binder system. The second weight loss stage (about 0.3 wt% which is equivalent to the stearic acid content in the green molded body) from 300 to 400°C is due to the degradation of stearic acid in the binder system. The third weight loss stage (about 3.0 wt% which is equivalent to the EVA content in the green molded body) above 400°C is reflect to the degradation of the minor binder component (EVA).

Fig. 7b shows the TGA thermogram of the binder in the green molded body after solvent debinding process. It can be observed only a degradation at about 400°C, which represents the weight loss curve of the minor binder component (EVA). This indicates that, all the major binder (paraffin wax) and stearic acid constituents in the green molded body are completely extracted which is in line with the above findings.

3.3. SEM observations

SEM photographs of the green parts before and after extraction are shown in Fig. 8a and b respectively. It can be observed that, the green molded bodies have a large amount of open pores after extraction (Fig. 8b). This indicates the success of *n*-hexane as a solvent for debinding of the major binder and stearic acid constituents. These pores allow the degraded products produced after thermal treatment to diffuse to the surface easily. Therefore, the thermal removal of insoluble binder component (minor binder) will be finished in a much shorter period without endangering the integrity of green body [6].

4. Conclusions

Powder compression molded bodies consisting of EVA—paraffin wax—stearic acid based binders were debound through solvent extraction with *n*-hexane, *n*-heptane and isooctane. Selection of organic solvent of higher solubility such as *n*-hexane is most important to enhance the debinding rate. The extraction temperature of 50°C, solvent to feed ratio of 7:1 by weight and extraction time of 2.25 h are the most suitable conditions for extracting all the major binder and stearic acid constituents completely from the binder mixture without affecting on the shape maintenance of green molded bodies. Thermo gravimetric analysis (TGA) showed also, all the paraffin wax and stearic acid constituents are completely extracted from the binder mixture which confirmed the above findings. SEM observations show the creation of a large amount of pores after solvent debinding which facilitate the subsequent thermal debinding without endangering the integrity of green body.

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