Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Y. H. Kim[a]; K. -P. Yoo[a]; J. S. Lim[a]; Y. -W. Lee[b]
[a] Department of Chemical Engineering, Sogang University, Seoul, South Korea [b] School of Chemical Engineering and Institute of Chemical Processes, Seoul National University, Seoul, South Korea

To cite this Article Kim, Y. H. , Yoo, K. -P. , Lim, J. S. and Lee, Y. -W.(2005) 'Removal of Paraffin Wax Binder from Metal Injection Molded Part by Supercritical Fluids', Separation Science and Technology, 39: 8, 1967 — 1987
To link to this Article: DOI: 10.1081/SS-120030774
URL: http://dx.doi.org/10.1081/SS-120030774

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 39, No. 8, pp. 1967–1987, 2004

Removal of Paraffin Wax Binder from Metal Injection Molded Part by Supercritical Fluids

Y. H. Kim,[1] K.-P. Yoo,[1] J. S. Lim,[1,*] and Y.-W. Lee[2]

[1]Department of Chemical Engineering, Sogang University, Seoul,
South Korea
[2]School of Chemical Engineering and Institute of Chemical Processes,
Seoul National University, Shinlim, Kwanak, Seoul, South Korea

ABSTRACT

The metal injection mold (MIM) process is the most cost effective, highest quality means to produce complex shaped, high performance parts. In the MIM process, debinding is a key step for successful MIM. However, the conventional debinding processes, which are thermal debinding and solvent debinding, have disadvantages that include long product development times, and harm to the environment. Therefore, the study of supercritical CO_2 that can be used as solvent for debinding, a new debinding technology as substitute for a conventional technology, was considered. In this paper, we used two methods to investigate a method for reducing debinding time as well as lowering operation condition other than pure

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[*]Correspondence: J. S. Lim, Department of Chemical Engineering, Sogang University, C.P.O. Box 1142, Seoul, South Korea; E-mail: limjs@kist.re.kr.

DOI: 10.1081/SS-120030774
0149-6395 (Print); 1520-5754 (Online)

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supercritical CO_2 debinding: the first method was to add cosolvent in supercritical CO_2, the second method was to use the mixture of propane + CO_2, as the supercritical solvent. It was found that the addition of cosolvents and the use of binary mixture propane + CO_2 for supercritical solvent remarkably improved the binder removal rate, in comparison with using pure supercritical CO_2.

Key Words: Supercritical CO_2 debinding; Wicking debinding; Metal injection molding; Cosolvent; Propane.

INTRODUCTION

Metal injection molding (MIM), is a method for the production of real net-shaped parts from metallic powders.[1,2] Complex shapes produced using the MIM process can be formed inexpensively to nearly full-density through the use of a polymer–metal powder combination; therefore, any secondary machining processes are not necessary. One key component in the MIM process is the binder used to provide the powders with sufficient fluidity for injection molding.[3] But binder has to be removed prior to sintering. This process is called debinding; it is one of the most critical steps in the MIM process[4] because distortion or cracking of the surface of the molded part can take place during the debinding process. Therefore, debinding takes the major part of the processing time and is a serious drawback of the MIM technology. For these purposes, new debinding technology[5,6] has been studied in order to find an alternate way to remove the binder from the MIM parts as fast and environmentally friendly as possible. One of the new debinding technologies is supercritical CO_2 debinding and, recently, its study is very actively being investigated.[7–9] In general, because a supercritical fluid has a diffusion speed approaching that of gas, it has good penetrating and carrying properties, and because it has a strong solvency owing to its density, which is similar to that of liquid, it is very effective in extracting a binder from porous materials. In addition, because solvency is varied according to changes of temperature and pressure, it is possible to selectively extract a binder from other materials.

In this work, the mixture of a paraffin wax of a low molecular weight (MW), 300–400 MW, and low density poly ethylene (LDPE) were used as the major and minor binder, respectively. Among the binders, paraffin wax should be removed from a molded part in the debinding process, however, the LDPE should remain in the molded part after debinding, in order to combine metal powders with each other and maintain the shape of the molded part. In our investigation, first, the binder removal rates in supercritical CO_2 were measured at 333.15, 348.15, and 358.15 K in the pressure range from 20 to 28 MPa. In addition, we compared the debinding time of the supercritical CO_2 method with that of wicking debinding (one of the conventional debinding methods). Second, we used two methods in order to enhance the binder removal rate relative to the pure supercritical CO_2 debinding method. (1) We experimented with adding cosolvents in supercritical CO_2. One popular method of enhancing the solvent power of supercritical CO_2 is adding a small amount of organic cosolvent.[10,11] We used cosolvents such as *n*-hexane, dichloromethane, methanol, and 1-butanol, in this work. (2) We used a binary mixture of propane + CO_2, as supercritical solvent, because propane has a strong solubility for nonpolar organic materials. Propane has higher solvent power, but it is relatively expensive and flammable, on the other hand, CO_2 has lower solvent power than propane, but it is nonflammable and inexpensive. A binary mixture of the two compounds may have good potential as alternative supercritical solvent. In this work, the kinetic of supercritical debinding was explained using Fick's second law.

THEORY

Calculation of Critical Temperatures and Pressures of Propane + CO_2 Mixture

In order to use a binary mixture of propane + CO_2, as supercritical solvent, we had to calculate the critical point of propane + CO_2 mixtures first. In this work, we accepted an equation-of-state method[12–15] for calculating critical pressures using critical temperatures and volumes. By using the equation of Redlich and Kwong[13] together with the previously established correlation for critical temperatures and critical volumes, we calculated critical pressures and compared them with experimental data that are taken from Poettmann and Katz.[12] The results appear in Fig. 1, the average deviation for the critical pressure between calculated data and data of Poettmann was 6.5%. We could know through this figure conditions of this work, pressure ranging from 15 to 25 MPa at 348.15 K, satisfied the supercritical condition of binary mixtures.

Evaluation of Diffusivity

The diffusivity of a soluble wax through a porous injection molded part is evaluated by the Fick's diffusion-based model. We assumed that injection molded part is slab form with thickness *l*. We also assumed that diffusivity

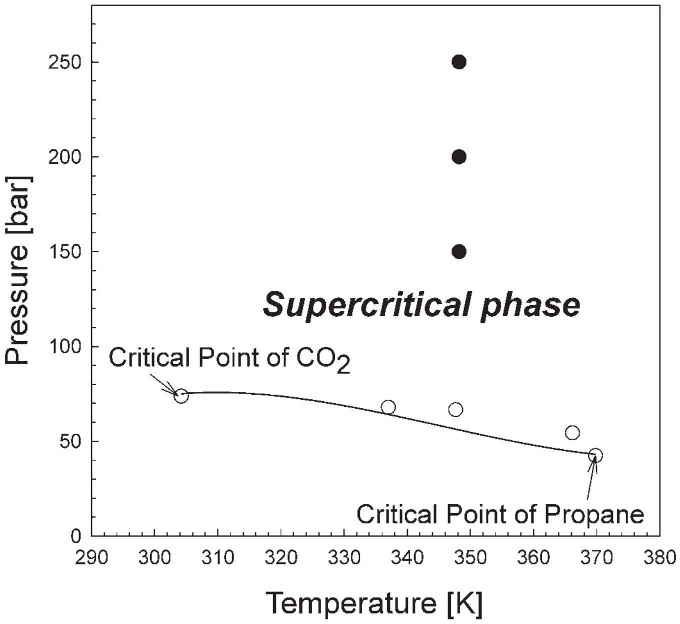

Figure 1. Critical locus of propane + CO_2 and experiment condition of this work. *Key:* ○, data of Ref. [12]; ● and —, predicted.

of solute is constant and diffusing solute comes out through the slab faces and a negligible amount through the edges. The diffusion of a solute can be described according to Crank[16] and Shewmon[17] by Eq. (1)

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{1}$$

where C is the solute concentration in a green part and D is the diffusivity of the solute. The boundary conditions to be assumed are

$$C = C_0 \quad \text{for } 0 < x < l, \quad \text{at } t = 0$$
$$C = 0 \quad \text{for } x = l \quad \text{and} \quad x = 0, \quad \text{at } t > 0$$

In the case of a slab, the local content of solute remaining in a green body after some time t of extraction can be expressed by

$$c(x,t) = \frac{4c_0}{\pi}\sum_{n=0}^{\infty}\frac{1}{2n+1}\exp\left\{\frac{-D(2n+1)^2\pi^2 t}{l^2}\right\}\sin\frac{(2n+1)\pi x}{l} \tag{2}$$

It is often difficult to determine the concentration at various depths, and what is experimentally determined is the quantity of solute, which has been removed, or the quantity remaining in an injection-molded part. For this purpose, the average concentration $\bar{c}$ is needed. This is obtained by integrating Eq. (2)

$$\bar{c}(t) = \frac{1}{l}\int_0^l c(x,t)dx = \frac{8c_0}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left\{\frac{-D(2n+1)^2\pi^2 t}{l^2}\right\} \tag{3}$$

$$\frac{\bar{c}}{c_0} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left\{\frac{-D(2n+1)^2\pi^2 t}{l^2}\right\} \tag{4}$$

for a long duration of supercritical debinding ($t \gg 0$), the first term in the right hand side of Eq. (4) shows much larger than the summation of the remaining terms, and hence, the fraction can be approximated by

$$\frac{\bar{c}}{c_0} = \frac{8}{\pi^2}\exp\left(\frac{-D\pi^2 t}{l^2}\right) \tag{5}$$

$$\ln\left(\frac{\bar{c}}{c_0}\right) = \ln\left(\frac{8}{\pi^2}\right) - \left(\frac{D\pi^2}{l^2}\right)t \tag{6}$$

A plot of $\ln(\bar{c}/c_0)$ vs. time, therefore, tends to become linear at longer times and this expression can be used to determine D values

EXPERIMENTAL APPARATUS AND PROCEDURE

The schematic diagram of the equipment used for supercritical debinding is shown in Fig. 2. This apparatus was designed to carry out supercritical debinding experiments in temperatures up to 373.15 K and pressure up to 30 MPa. The extraction vessel was made of 316 stainless steel and had an internal volume of approximately 300 cm^3. In the middle part of the cell, Pyrex glass windows of 18 mm thickness were placed to allow the visual observation of the debinding procedure. A duplex high-pressure pump (NP-D-321, Nihon Seimitsukagaku Co., Ltd., Japan; maximum flow rate of 17.4 mL/min) was used to feed CO_2 continuously from a liquid CO_2 cylinder, via a preheater, to the extraction vessel in which the metal sample (molded part) is loaded on a basket. In cases using a mixture of propane + CO_2, a mixed fluid of supercritical CO_2 and propane with an appropriate mixture ratio was put in a cylinder of the debinding apparatus, the weight ratio of propane ranged from 10 to 50 wt%. A simple thermostatic air bath was used to maintain the system temperature constant within ± 0.5 K. The temperature in the vessel was measured with a K-type thermocouple and a digital indicator (OMEGA Co.), which was calibrated by KRISS (Korea Institute of Standards and Science) with an uncertainty of

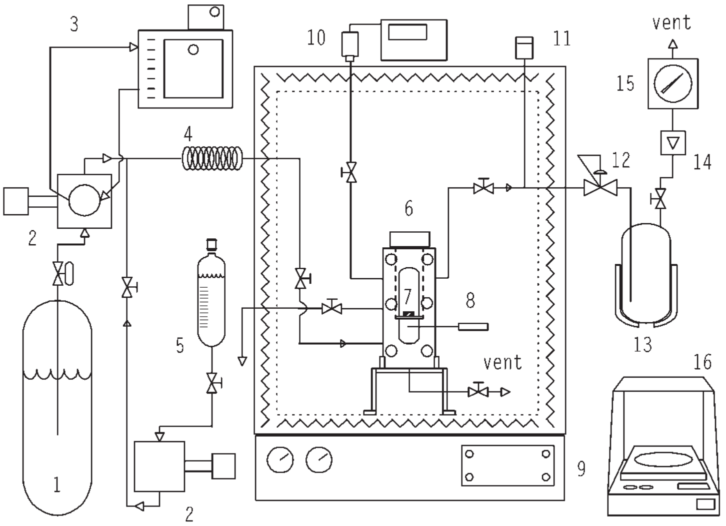

Figure 2. A schematic diagram of the experimental apparatus.

± 0.1 K. The pressure in the cell was measured by a pressure transducer (SENSOTEC model TJE/0743-06TJA) and digital indicator (SENSOTEC model L20000WM1), which were calibrated by a dead weight gauge (NAGANO KEIKI PD12) with the measuring accuracy of ± 0.005 MPa. The system pressure was regulated within ± 0.05 MPa by using a back-pressure regulator (TESCOM model 26-1722–24), which is located after the extraction vessel. The composition of binder materials is given in Table 1. The samples used in these binder removal experiments were injection molded metal part of 21 mm length, 10 mm width, and 3 mm thickness, the ratio of the area and thickness is 70 mm, used as a watchband (Fig. 3) and their average weights were about

Table 1. Characteristics of the binder system used.

Composition (wt%)	Density (g/cm^3)	Melting point (K)	MW
Paraffin wax[a] (71.3)	0.82–0.85	339.15–342.15	800–900
LDPE[b] (23.2)	0.90–0.94	371.15–388.15	50,000–100,000
Staric acid (5.5)	0.84	340.15–342.15	284

[a] Major binder: it should be removed in during debinding.
[b] Minor binder: it should remain after debinding.

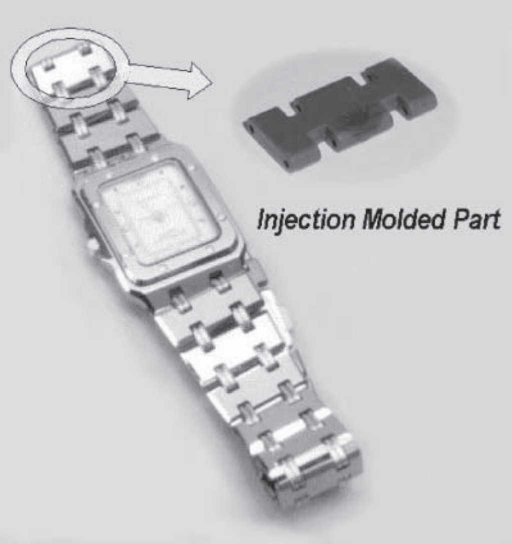

Figure 3. Injection molded part (watchband).

2.24 g. The green parts were composed of tungsten carbide (WC)–nickel (Ni) powder (TaeguTec Ltd., Korea), its particle size was 1.31 μm, and binder materials (5 wt% of the molded part), its weight was 0.112 ± 0.001 g. In the extraction vessel, a paraffin wax contained in the molded part was dissolved and extracted by the supercritical CO_2 (in cases using pure supercritical CO_2). Then the supercritical fluid containing a paraffin wax was expanded to an atmospheric pressure after passing through the back-pressure regulator to a separator. In the separator, the paraffin wax was separated from CO_2 gas and accumulated on the bottom. The amount of CO_2 consumed was determined by a dry gas meter. The flow rate of CO_2 gas during the experiments was fixed to 108 g/hr for all runs. In case of the experimental runs for investigating the cosolvent effects, *n*-hexane, dichloromethane, methanol, and 1-butanol were fed to the extraction vessel by means of a high-pressure pump (NP-S-321, Nihon Seimitsukagaku Co., Ltd., Japan; maximum flow rate of 8.7 mL/min). We used *n*-hexane, dichloromethane, methanol, and 1-butanol as cosolvents. The source and purity of the chemicals used in this study are listed in Table 2. In this work, we selected the binary mixture propane + CO_2 in order to use propane, which has strong solubility for nonpolar organic material (e.g., paraffin wax). The propane was purchased from MG Industry and its purity was 99.5%. The amount of binder removed was determined by measuring the weight of the debinded sample with a precision balance (Ohaus, model E04130).

Table 2. Source, purity, and solubility parameter of the chemicals used in this study.

Chemical	Source	Purity (%)	Solubility parameter[23] ($J^{1/2}/cm^{3/2}$)[a]
n-Hexane	MALLINCKRODT	99.8	7.24
Dichloromethane	MALLINCKRODT	99.9	9.93
Methanol	J. T. Baker	100	14.28
1-Butanol	KANTO	99.0	11.30

[a] At 298.15 K.

RESULTS AND DISCUSSION

Use of Supercritical CO_2 in Debinding Process

Comparison of Supercritical Debinding with Wicking Debinding

The supercritical CO_2 debinding was compared with the wicking debinding, which is one of the conventional debinding techniques, in Fig. 4. In Fig. 4, the experimental data of wicking debinding was supplied by Park[18] of the Ceramic Processing Center in KIST. As shown in Fig. 4, wicking debinding takes more than 15 hr at high temperatures up to 723 K. On the other hand, the supercritical CO_2 debinding needs only 2 hr for the same molded part at 348 K and 28 MPa. Despite supercritical debinding requiring an auxiliary process, which is carried out in a furnace to remove remaining polymer material in the injection molded part, it was found that the debinding time could be much more reduced compared to the wicking debinding process in KIST.

Effect of Temperature and Pressure on Supercritical Debinding

Figure 5 shows the effect of pressure in binder removal at the same temperature. At constant temperature, the increase in pressure enhances binder removal rate. Because an increase in pressure while holding temperature results in enhancing the density of supercritical CO_2, so the solubility of wax increases. For 1 hr extraction at 348.15 K under 20, 25, and 28 MPa, the amount of binder removal was 52, 60, and 63 wt%, respectively. Figure 6 shows the effect of temperature in binder removal at similar pressures. This figure shows that the supercritical fluids debinding should be performed at the temperature higher than the melting point of used wax (paraffin wax of the melting point about 340 K). It is important to recognize, if the supercritical fluids debinding temperature is lower than melting point, the solubility of paraffin wax decreases because paraffin

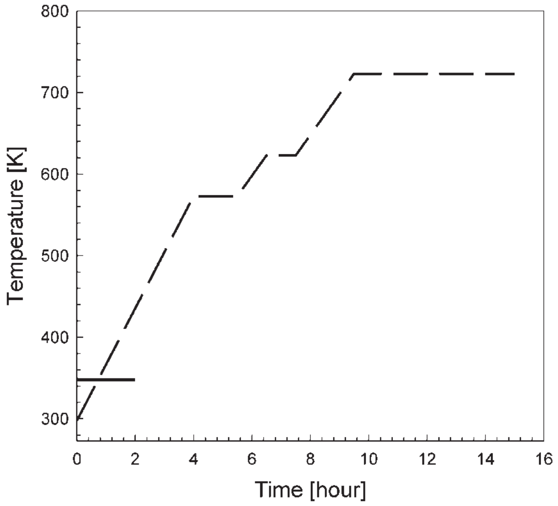

Figure 4. Comparison of the time consumed in debinding between supercritical debinding and wicking debinding: (—) supercritical debinding (28 MPa, 348.15 K), (---) wicking debinding.

wax is not in the liquid state. But, if the debinding temperature is higher than the melting point, as the temperature increases, binder removal rate will be affected simultaneously by decreasing density of the solvent and increasing volatility of the solute. As can be seen in Fig. 6, binder removal rate does not increase as the debinding temperature increased above 348.15 K. From this result, it was found that binder removal rate was affected by decreasing density of the solvent (supercritical CO_2) rather than increasing volatility of the wax. Figures 5 and 6 show that theoretical curves calculated with Eq. (4) are in good agreement with the measured data. In general, binder removal rate is affected by diffusivity of wax, because solute diffusion will probably govern the overall rate of mass transfer. Therefore, the diffusion of supercritical CO_2 might have relatively small effect on the rate of mass transfer.[19]

Use of Cosolvent in Supercritical CO_2 Debinding

Effect of Changing Cosolvent Identities in Supercritical CO_2 Debinding

In the supercritical state, the solvent power could be enhanced by adding cosolvent due to the modification of density and nature of the solvent. For this

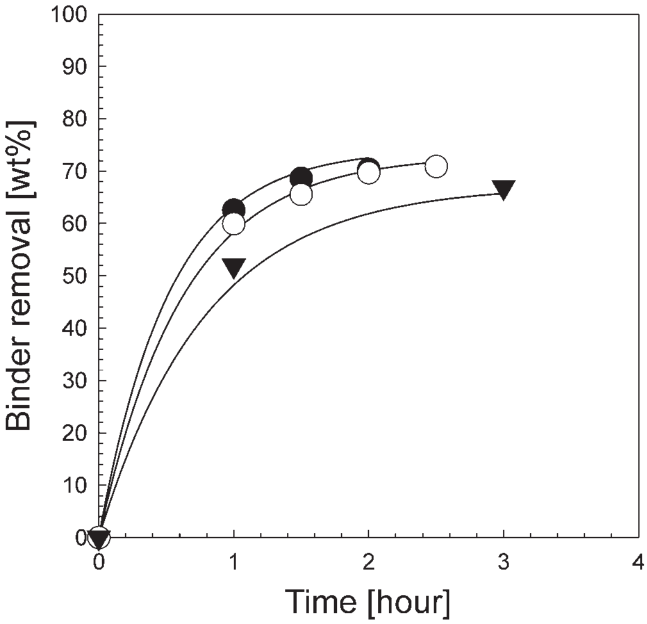

Figure 5. Effect of the pressure on binder removal rate at constant temperature at 348.15 K. *Key:* ●, 28 MPa, ○, 25 MPa; and ▼, 20 MPa; ——, calculated by Eq. (4).

reason, to enhance the extraction efficiency in the supercritical extraction process, the method of adding cosolvent is widely used. Figure 7 displays the effect of different cosolvents, which are used for the enhancement of debinding efficiencies, on supercritical CO_2. For 1 hr debinding at 348.15 K, 25 MPa, the binder removal rates were 69.8% (*n*-hexane), 63.1% (dichloromethane), 36.4% (1-butanol), and 51.2% (methanol), respectively. As can be seen in Fig. 7, the addition of cosolvent such as *n*-hexane and dichloromethane, which behave primarily through dispersion force, achieved enhancement of binder removal rate when compared to pure supercritical CO_2. However, methanol and 1-butanol, as polar cosolvent, did not achieve enhancement of binder removal rate compared to pure supercritical CO_2. Solubilities of nonpolar solute, paraffin waxes, in supercritical CO_2 can be greatly weakened by decreasing their solvating power via addition of various polar cosolvents. Therefore, *n*-hexane is shown to be a much stronger cosolvent for debinding removed paraffin waxes from an injection molded part than dichloromethane, methanol, and 1-butanol. For example, in case of addition of 5 wt% *n*-hexane in the supercritical CO_2, the debinding rate was enhanced more than two times comparing to using only pure supercritical CO_2 under 348.13 K, 25 MPa. We can explain this reason from the characteristic

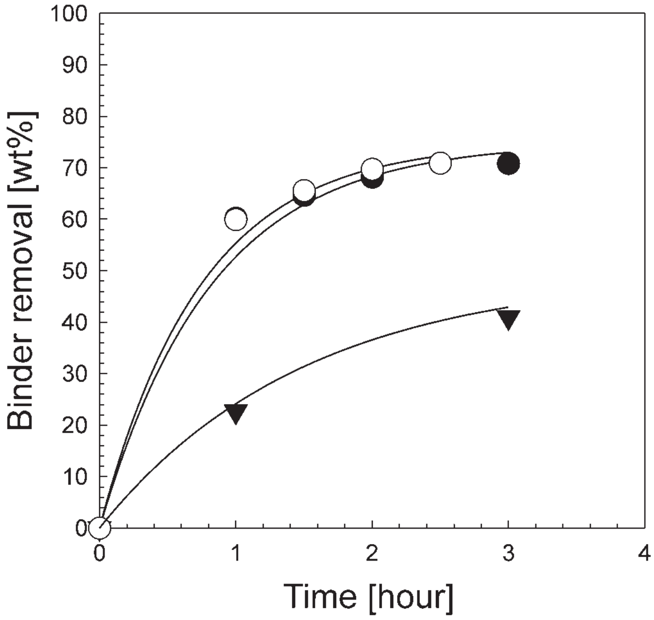

Figure 6. Effect of the temperature on binder removal rate at 25 MPa. *Key:* ●, 358.15 K, ○, 348.15 K; and ▼, 333.15 K; ——, calculated by Eq. (4).

molecular structure of a paraffin wax. The paraffin wax consists predominantly of the mixture of straight-chain alkanes. The solubility behavior of a paraffin wax in terms of molecular interactions will be dominated by its large hydrocarbon structure (i.e., dispersion interaction). The fact that the solubility of a paraffin wax is higher in a nonpolar cosolvent than a polar cosolvent indicates that the solubility of a paraffin wax is affected by the dispersion interactions.[20,21]

Effect Variation of Cosolvent Concentrations and Pressure in Supercritical CO_2 Debinding with Cosolvent

Figure 8 shows the effect of concentrations of dichloromethane, which behaves as a primarily dispersion force, in supercritical CO_2 debinding. According to Fig. 8, it was found that the debinding time could be further reduced with increasing concentration of dichloromethane, in other words, debinding time can be reduced 50% by increasing from 5 to 10 wt% concentration of dichloromethane at 348.15 K, 25 MPa. Table 3 presents values of diffusivities in each case of variation concentrations under 348.15 K, 25 MPa. Figure 9 shows the effect of pressure in supercritical CO_2 debinding

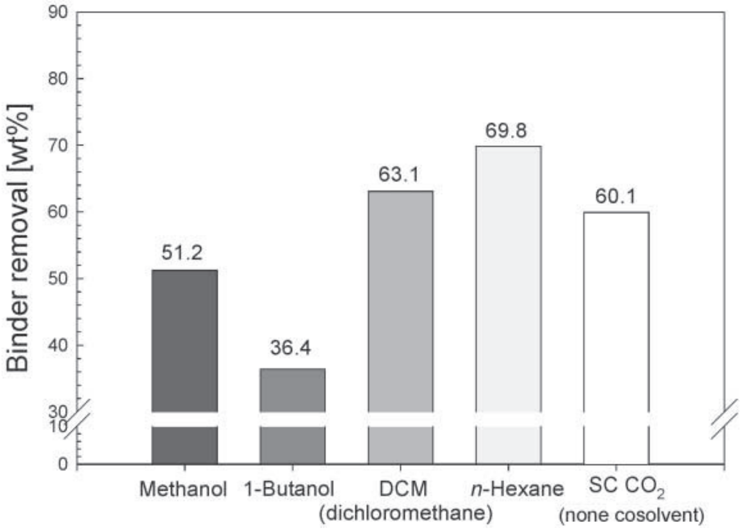

Figure 7. Effect of cosolvent on binder removal rate in supercritical CO_2 debinding for 1 hr at 348.15 K, 25 MPa; the concentration of each cosolvent is 5 wt%.

with the constant concentration of a cosolvent. In general, the solvent power (i.e., solubility of paraffin wax) increases with increasing pressure at constant temperature, therefore almost all paraffin waxes (71 wt% of binder mixture) were removed in 1 hr at 348.15 K, 28 MPa, with 10 wt% dichloromethane. Diffusivities in each case of increasing pressure are displayed in Table 4. This shows that diffusivity will increase with increasing pressure at constant temperature. This might be explained because higher pressure (density) enhances the solubility of paraffin wax in the supercritical CO_2 and that is affected by increase solute mass transfer and diffusivity.[22] In Figs. 8 and 9, solid lines were evaluated by Eq. (4), the experimental results were compared with theoretical predictions based on the Fick's diffusion model and the kinetic of debinding calculated by Fick's model showed good agreement with experimental data.

Use of a Binary Supercritical Fluid Mixture

Effect of a Binary Mixture of Propane and CO_2, as Supercritical Solvent

Supercritical propane as solvent is more effective than supercritical CO_2; however, it is relatively expensive and flammable. On the other hand,

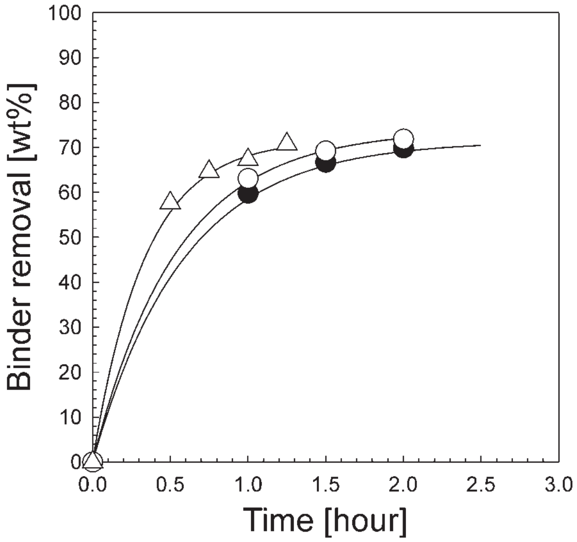

Figure 8. Effect of the concentration of dichloromethane on binder removal rate in supercritical CO_2 debinding at 348.15 K, 25 MPa; *Key:* △, 10 wt%, ○, 5 wt%; ● using the pure SC CO_2; ——, calculated by Eq. (4).

supercritical CO_2 has lower solvent power than supercritical propane, however, it is nonflammable and very cheap. Therefore, binary mixtures of the two compounds may have good potential as an alternative supercritical solvent. The effects of a binary mixture propane + CO_2 as solvent, which remove paraffin waxes in metal injection molded part, are depicted in Fig. 10. In this work, we experimented on various concentration of propane from 10 to 50 wt%. As presented in "Use of supercritical CO_2 in debinding process," binder removal rate was not enhanced above 348.15 K, so temperature was maintained at 348.15 K in this work. Figure 4 shows the effect of pro-

Table 3. Comparison of diffusivities calculated by the Fick's law with concentration of cosolvent.

Temperature (K)	Pressure (MPa)	Concentration (wt%)	Diffusivity (m^2/sec)
348.15	25	10	5.015×10^{-10}
348.15	25	5	3.492×10^{-10}
348.15	25	0	2.735×10^{-10}

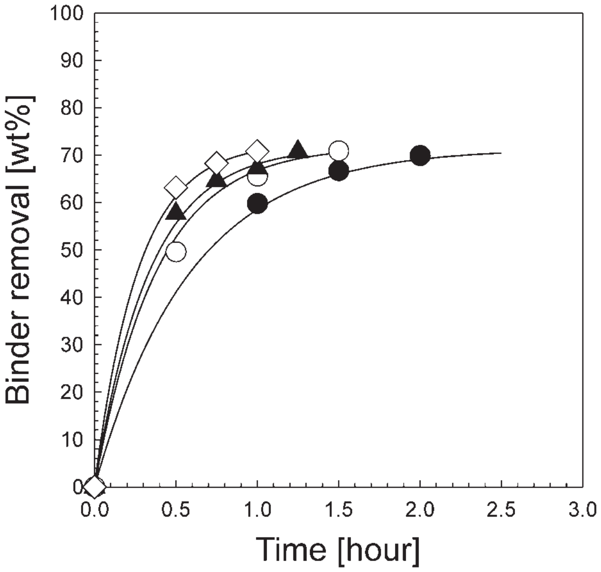

Figure 9. Effect of pressure on binder removal rate in supercritical CO_2 debinding with 10 wt% dichloromethane at 348.15 K. *Key:* ◇, 28 MPa, ▲, 25 MPa, ○, 20 MPa; ● using the pure SC CO_2 at 25 MPa; —, calculated by Eq. (4).

pane weight ratio on the binder removal rate at the experimental condition of 348.15 K and 15 MPa. As can bee seen in this figure, except for 10 wt% propane mixture, binder removal rate in case of others enhanced remarkably. To put it more concretely, all paraffin waxes (71 wt% of total binder mixture contained in injection molded part) were removed in 60, 45, 30, and 15 min when the ratio of propane was 20, 30, 40, and 50 wt%, respectively. In case of increasing pressure up to 20 MPa at 348.15 K, the supercritical CO_2 debinding mixed with only 10 wt% propane showed a good efficiency, that

Table 4. Comparison of diffusivities calculated by the Fick's law with pressure at constant concentration of cosolvent.

Temperature (K)	Cosolvent	Pressure (MPa)	Diffusivity (m^2/sec)
348.15	10 wt% Dichloromethane	28	6.492×10^{-10}
348.15	10 wt% Dichloromethane	25	5.015×10^{-10}
348.15	10 wt% Dichloromethane	20	4.394×10^{-10}
348.15	None	25	2.735×10^{-10}

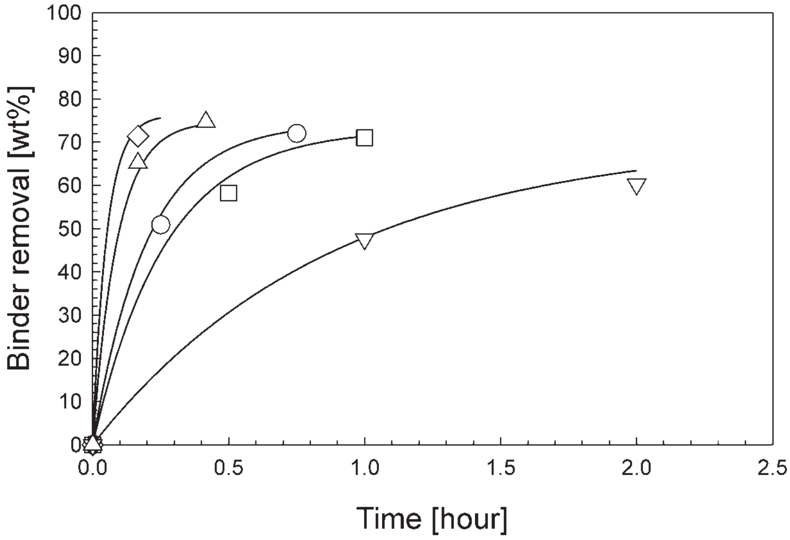

Figure 10. Comparison of binder removal rate with various concentration of propane at 348.15 K, 15 MPa. *Key:* ▽, 10 wt%, □, 20 wt%, ○, 30 wt%, △, 40 wt%, ◇, 50 wt%; ——, calculated by Eq. (4).

is, most paraffin waxes were removed in 90 min. This result appears in Fig. 11. As can be seen in this figure, in each case of the propane weight ratio 20, 30, 40, and 50 wt%, all paraffin waxes (71 wt% of total binder mixture contained in injection molded part) were removed in 40, 30, 15, and 5 min, respectively. The last points of the each data mean the time in which debinding was done. Moreover, we can predict the kinetics of debinding using the diffusion equation. Figure 12 shows binder removal rate at 348.15 K, 25 MPa. As depicted in this figure, most paraffin waxes were removed in 5 min at a mixture of 40% propane–60% CO_2. Furthermore, in case of 50% to 50% mixture, debinding was completed after the lapse of 4 min. The results obtained in this study demonstrated that using binary mixture propane + CO_2, as supercritical solvent, is a very effective method, in comparison with using pure supercritical CO_2. In addition, we calculated diffusivities of paraffin wax by Fick's law using Eq. (5) and compared them with experimental data. All the theoretical curves calculated with Eq. (4) are also shown in Figs. 10–12. As can be seen in these figures, the calculated values represent relatively good agreement with the experimental data. Diffusivities calculated by Fick's model in temperature, pressure, and concentration of propane are each summarized in Table 5. It was believed to us that the method suggested in this

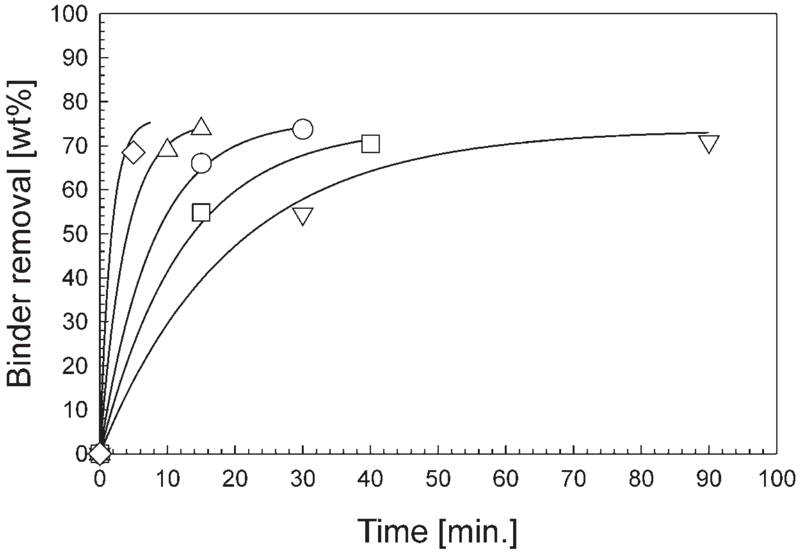

Figure 11. Comparison of binder removal rate with various concentration of propane at 348.15 K, 20 MPa. *Key:* ▽, 10 wt%, □, 20 wt%, ○, 30 wt%, △, 40 wt%, ◇, 50 wt%; —, calculated by Eq. (4).

work, that is, using a binary supercritical fluid mixture of CO_2 + propane for debinding in the MIM process is a unique and outstanding method for use as an alternative to conventional debinding. The experimental results that were obtained at 348.15 K among previous mentioned results described above are shown in Fig. 13. We could know through this figure not only the method to add cosolvent but the method to mix propane and CO_2 that could further decrease debinding time as well as lower operating conditions than those of pure supercritical CO_2 debinding.

CONCLUSIONS

The objective of this study was to suggest a supercritical CO_2 debinding and an improved method to supercritical CO_2 debinding. In addition, the critical point of a binary mixture propane + CO_2 was calculated by the equation-of-state method, as stated at the theory in the introduction and the diffusivities were calculated by the Fick's diffusion model. Good agreement was obtained between the experimental and the calculated data. It was found from supercritical CO_2 debinding that when the supercritical CO_2 debinding was carried

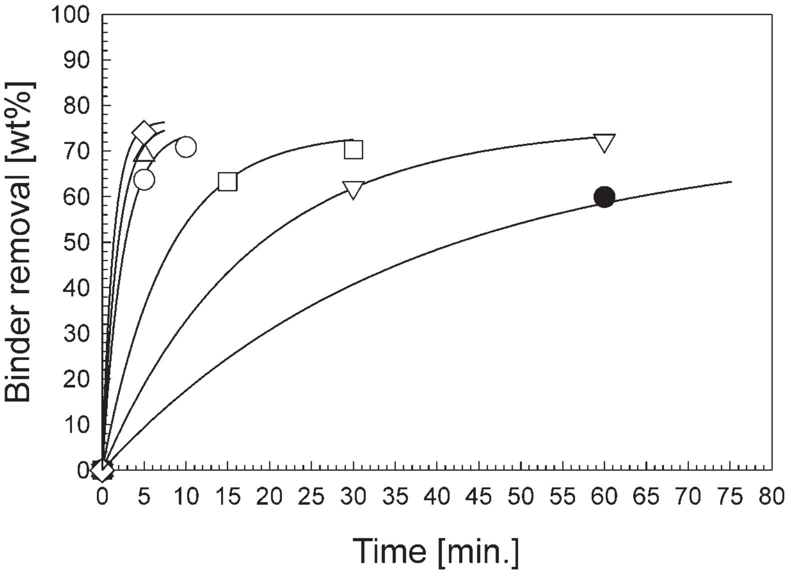

Figure 12. Comparison of binder removal rate with various concentration of propane at 348.15 K, 25 MPa. ▽, 10 wt%, □, 20 wt%, ○, 30 wt%, △, 40 wt%, ◇, 50 wt%, ● using the pure SC CO_2; —, calculated by Eq. (4).

out at 348.15 K, almost all paraffin waxes (71 wt% of binder mixture) were removed in 2 hr under 28 MPa, and in 2.5 hr under 25 MPa, respectively. As can be seen in results obtained from using an experimental cosolvent, the supercritical CO_2 debinding with *n*-hexane seems to show the best result among our results presented in this paper. In this case, almost all waxes (71 wt% of binder mixture) were removed in 1 hr at 348.15 K, 25 MPa. First

Table 5. Diffusivities of paraffin wax versus weight ratio of propane at various pressures.

Weight ratio of propane (wt%)	Diffusivity (m^2/sec)		
	15 MPa	20 MPa	25 MPa
10	1.949×10^{-10}	5.450×10^{-10}	7.265×10^{-10}
20	6.656×10^{-10}	9.538×10^{-10}	1.469×10^{-9}
30	9.119×10^{-10}	1.633×10^{-9}	3.918×10^{-9}
40	2.166×10^{-9}	3.287×10^{-9}	6.996×10^{-9}
50	4.208×10^{-9}	6.744×10^{-9}	1.042×10^{-8}

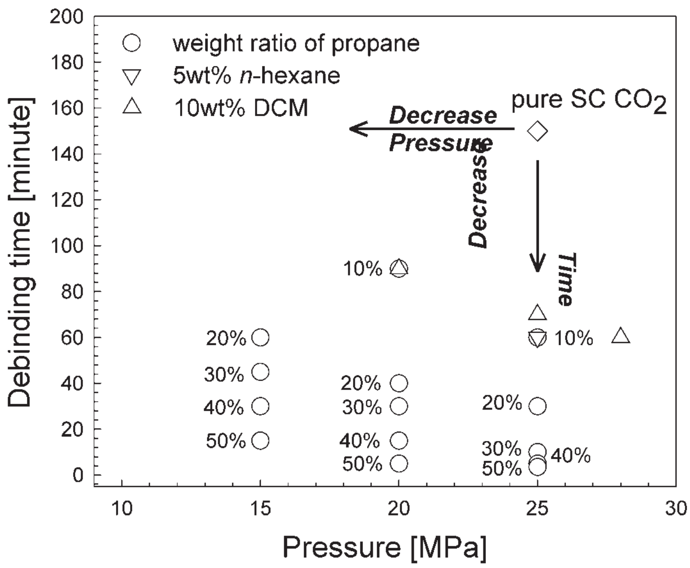

Figure 13. Comparison of an improved SC CO_2 debinding with pure SC CO_2 debinding when completed debinding at 348.15 K.

of all, what is important in this study is to use a binary mixture propane + CO_2 for supercritical solvent. Under 25 MPa, 348.15 K, when the mixture of supercritical propane + CO_2 is a one to one ratio, dewaxing could be completed in 4 min. It was found from this result that binder removal rate was enhanced more than 30 times in comparison with pure supercritical CO_2 debinding at same condition.

These results lead us to the conclusion that supercritical CO_2 debinding might offer a short debinding time and safety working environment alternative to the current conventional debinding methods, such as the solvent extraction or thermal debinding. Also, effective debinding methods of reducing debinding time as well as lowering operation condition would be to add cosolvents (*n*-hexane and dichloromethane) to supercritical CO_2 and to use the mixture of propane and CO_2, as supercritical solvent, in comparison with using pure supercritical CO_2.

NOMENCLATURE

a energy parameter in Redlich–Kwong EOS ($K^{1/2}$ bar cm^6/g mol^2)

b	size parameter in Redlich–Kwong EOS (cm^3 gmol)
c, c_0	concentration of solute, initial concentration of solute, respectively (g)
$\bar{c}$	average concentration of remaining solute (g)
D	diffusivity of solute (m^2/sec)
l	thickness of injection molded part (m)
P	pressure (MPa)
P_{ci}, P_{cT}	critical pressure of component i, critical pressure of a mixture, respectively (MPa)
θ	surface fraction
R	ideal gas constant (J/mol K)
T	temperature (K)
T_{ci}, T_{cij}, T_{cT}	critical temperature of component i, characteristic temperature of i–j interaction, critical temperature of a mixture, respectively (K)
t	time (sec)
τ_{ij}	correlating parameter for critical temperature (K)
v	molar volume (cm^3/mol)
v_{ci}, v_{cT}, v_{ij}	critical volume of component i, critical volume of a mixture, correlating parameter for critical volume, respectively (cm^3/mol)
ω	acentric factor
Ω_a, Ω_b	dimensionless constants in Redlich–Kwong equation
x	mole fraction

ACKNOWLEDGMENT

This work was supported by Ministry of Science and Technology of Korea, and the National Research Laboratory Program for Supercritical Fluid. The financial contribution is greatly appreciated.

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Received July 2003
Accepted January 2004

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