재자원화기술

보 문

Removal of Volatile Oganic Compounds from Spent Polypropylene by High-temperature Supercritical Carbon Dioxide Extraction

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Abstract

The removal of volatile organic compounds (VOCs) from spent polypropylene (PP) sourced from the bumpers and interiors of used cars was carried out by using high-temperature supercritical carbon dioxide (scCO$_2$) extraction. The recycled polymers from the bumpers and interiors contained other additives beside PP such as polyethylene (PE), talc, and carbon black, which modified the properties of PP. The crystallinity of the recycled bumper and interior PP was significantly lower than that of the virgin PP pellet. The decomposition temperatures of the recycled bumper and interior PP was slightly higher than that of the virgin PP pellet, while the melting and crystallization points were slightly lower. The effect of process conditions on VOC removal was studied by varying the time (2 ~ 720 min), pressure (6.4 ~ 14 MPa), and temperature (298 ~ 473 K). Since VOC removal at 2 min produced satisfying results, times below 2 min (10 ~ 120 s) were also studied. The main goal of scCO$_2$ extraction was to reduce the xylene content, as the xylene content of the recycled bumpers was higher than the allowable limit. A temperature above 373 K was needed to remove the xylene from the waste PP samples. The optimum condition for VOC removal from bumper waste was determined to be 433 K, 8 MPa, and 60 s. The car interior waste had VOC content within the allowable limit, so no further treatment was needed.

Keywords : Polypropylene, Supercritical carbon dioxide, Extraction, Volatile organic compounds

1. Introduction

Polypropylene (PP) is one of the most commonly used plastics in the world[1]. Plastic waste is one of the greatest concerns in the world since it will not degrade in a long time, so it needs to be recycled for further use[2]. In using, handling, and recycling of the plastic, some of the chemicals could be transferred and attached, leading to build up of harmful substances, which are called volatile organic compounds (VOCs)[3]. VOCs have toxicity and might be harmful to humans, including carcinogenicity[4,5]. Polymer containing high VOC content cannot be reused, and thus further processing is needed to remove the VOC content under the allowable limit.

Recycled polymer sourced from bumper (PP-BP) and interior waste (PP-IN) of the end-of-life vehicle were used as raw material

in this study. There have been several studies on removal of VOCs such as devolatilization, reactive comonomer, and postpolymerization [6]. Some of the methods involved the use of solvents which need to be removed by employing additional separation process. Other studies including steam stripping, air stripping, and extraction with polyethylene glycol to remove VOC content of high-density polyethylene (HDPE) pellets[2]. These methods used a high temperature of 373 K for 2 h, which is not preferred because of the relatively long period of time and high energy consumption. Supercritical carbon dioxide (scCO$_2$) can be a good alternative solvent in extracting VOC content from polymer, since it is nontoxic, nonflammable, and environmental-friendly, and can be easily removed after the process[7,8].

Herein, we demonstrated that VOCs in the waste PP can be removed by the scCO$_2$ extraction in a short time. Xylene content

of PP-BP was higher than the allowable limit, thus the main goal is to reduce xylene content below the allowable limit. The changes in chemical and thermal characteristics of each type of waste PP prior to and after the scCO$_2$ extraction were investigated. The effect of process conditions such as time, pressure, and temperature on the VOC removal of PP-BP and PP-IN was studied. After the scCO$_2$ extraction, PP with VOC content below the allowable amount was obtained.

2. Material and methods

2.1 Chemicals

Virgin PP pellets, recycled PP pellets sourced from bumper and interior of end-of-life vehicle were provided by the Hyundai Motor Company (Republic of Korea). Liquid CO$_2$ (purity of 99.5%) was provided by Hanil Gas Company (Republic of Korea).

2.2 View cell apparatus

A representative schematic diagram of the view cell apparatus is presented in Figure 1. Before setting the temperature in the range of 298 ~ 473 K, perforated aluminum container was filled with the PP pellets and inserted into the view cell. A 260D (Teledyne ISCO, USA) syringe pump was used to flow 30 mL min^{-1} of CO$_2$ into the view cell. An ER3000SI-1 (Tescom, USA) electronic back pressure regulator was used to control the pressure in the range of 6.4 ~ 14 MPa during the extraction. After the extraction was completed, the pump was stopped, and the system was depressurized.

2.3 Determination of VOC content and odor

Analysis of VOC content and odor of virgin PP, PP-BP, PP-IN

and scCO$_2$-treated PP samples was carried out by SGS Korea Co., Ltd. (Republic of Korea) according to the MS 300-55 standard (Hyundai-Kia motors Engineering Standard/VOC test standard method). The VOCs analyzed in this study were benzene, toluene, ethyl benzene, xylene, styrene, formaldehyde, acetaldehyde, and acrolein.

2.4 Characterization of PP pellets

The chemical functionalities of the PP pellets, recycled PP bumper, and recycled PP interior were analyzed by attenuated total reflectance mode (ATR-FTIR) of IRTracer-100 (Shimadzu, Japan) Fourier-transform infrared spectrometer in the range of 4,000 to 650 cm^{-1}. Thermal properties of the samples were investigated using Q50 (TA Instruments, USA) thermogravimetric analyzer (TGA). The TGA chamber temperature was equilibrated at 35 °C, then increased to 800 °C with a ramping rate of 5 °C min^{-1} and N$_2$ flow of 60 mL min^{-1}. Nexta DSC600 (Hitachi, Japan) differential scanning calorimeter (DSC) was used to analyze the thermal transitions of the samples by heating from 20 °C to 250 °C, and then cooled to 20 °C and reheated again to 250 °C with ramping rate of 10 °C min^{-1} and under N$_2$ flow of 30 mL min^{-1}. Crystallinity of the polypropylene of the samples was calculated by using Equation (1)[9].

$$X_c = \frac{\dfrac{\Delta H}{\Delta H_0} \times 100\%}{(1 - W_{res})} \tag{1}$$

where ΔH is the value of melting enthalpy obtained in the second heating and ΔH_0 is the enthalpy of 100% crystalline PP which amounts to 207 J g^{-1}[10], and W_{res} is the percentage of the polymer's residual weight, determined using TGA.
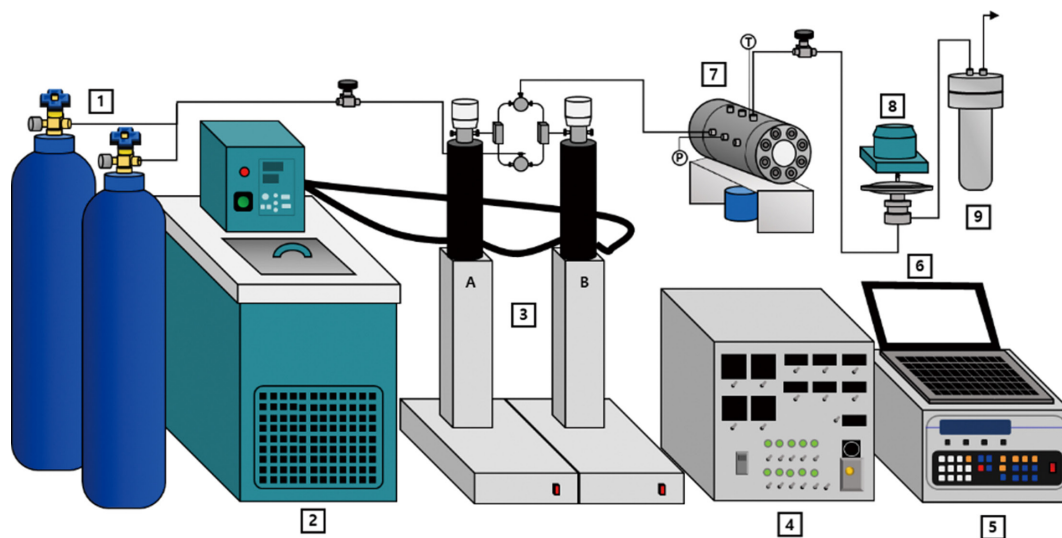

Figure 1. Figure of view cell apparatus: (1) CO$_2$ cylinder; (2) chiller; (3) ISCO pump; (4) control box; (5) ISCO pump controller; (6) laptop; (7) view cell; (8) back pressure regulator; (9) separator.
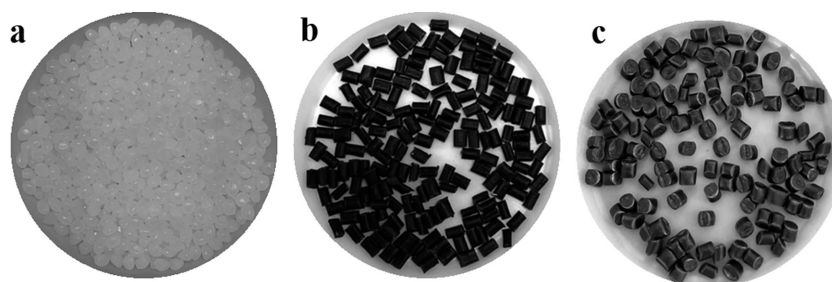
Figure 2. Picture of (a) virgin PP, (b) PP-BP, and (c) PP-IN.

3. Results and discussion

3.1 Chemical and thermal characterization of PP

Pictures of virgin PP, PP-BP, and PP-IN pellets are presented in Figure 2. The virgin PP has white color, while PP-BP and PP-IN exhibited black color because of the presence of carbon black filler. The ATR-FTIR profiles of virgin PP, PP-IN and PP-BP are shown in Figure 3. The chemical functional groups of PP-BP and PP-IN were identified and compared with those of virgin PP. the virgin PP exhibited IR bands at 809, 841, 897, 973, 997, 1,163, 1,256, 1,296, 1,377, 1,456, 2,838, 2,869, 2,919, and 2,950 cm^{-1}, which are associated with the stretching and bending vibrations of CH_2 and CH groups[11]. PP-BP and PP-IN showed additional bands by the presence of polyethylene (PE) and talc. The peaks associated with PE at 719, 1,377, 2,850, and 2,919 cm^{-1}, which correspond to CH_2 rocking deformation, symmetric CH_3 bending, symmetric CH_2 stretching and asymmetric CH_2 stretching[12]. The bands at 670 and 1,015 cm^{-1} in the waste PP samples corresponded to -OH liberation and Si-O-Si stretching vibration of talc ($Mg_3(OH)_2$ Si_4O_{10})[13]. In the waste PP samples, the intensity of the bands associated with PP were lowered than those of the virgin PP due to the presence of carbon black which has absorbing nature[14]. Some of PE peaks overlapped with PP peaks and strengthened peaks at 1,377 and 2,919 cm^{-1}.
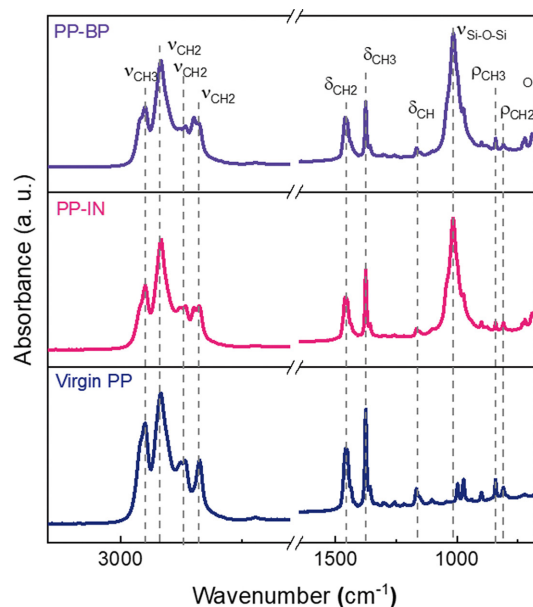
Figure 3. FTIR spectra of virgin PP, PP-BP, and PP-IN.

The TGA profiles of virgin PP, PP-IN and PP-BP are shown in Figure 4. PP-BP and PP-IN exhibited similar decomposition temperatures at 431 and 430 $^{\circ}$C, respectively, while the virgin PP exhibited lower decomposition temperature at 427 $^{\circ}$C. Residual weight of virgin PP, PP-IN and PP-BP were determined to be 0.5%, 14.4%, and 17.8%, respectively. The DSC profiles are presented

Figure 4. TGA graph of virgin PP, PP-IN and PP-BP.

Figure 5, and melting temperatures and crystallinity of the polymer are listed in Table 1. Crystallinities of virgin PP, PP-BP, and PP-IN were 50.4%, 35.9%, and 45.3%, respectively. The crystallinities of PP-BP and PP-IN were lower than that of virgin PP due to the addition of PE[15]. Melting peaks of PP and PE were observed in the DSC profiles of PP-BP and PP-IN, while the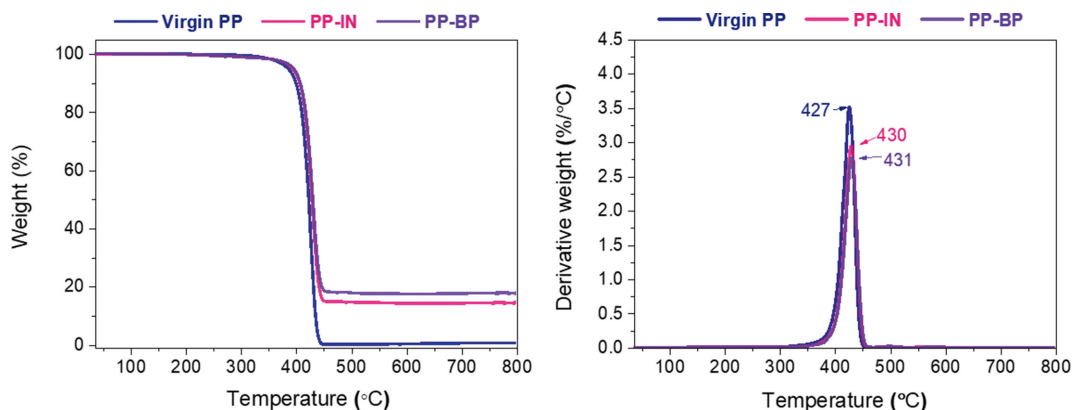 virgin PP only showed the PP melting peak. Melting peaks of PP for virgin PP, PP-BP, and PP-IN were 167.4, 165.0, 164.7 °C, respectively, while melting peaks of PE for PP-BP and PP-IN were 125.7 and 126.6 °C, respectively.
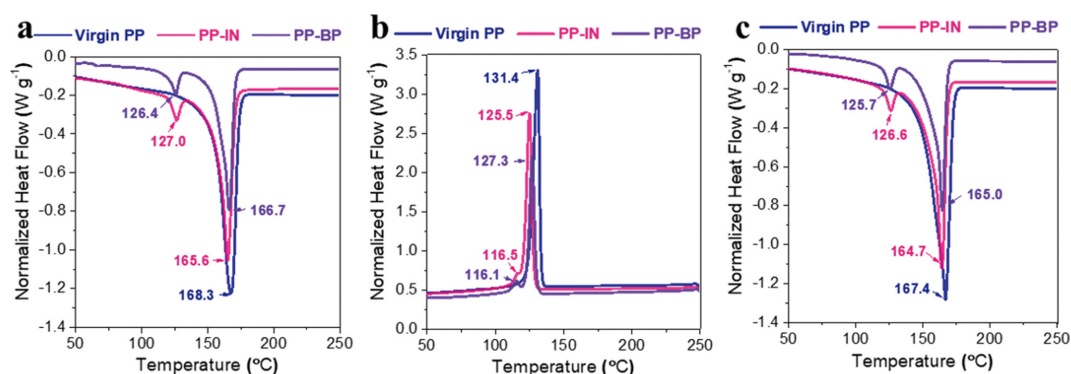
3.2 The effect of process parameters on VOC removal of PP-BP

3.2.1 The effect of time

ScCO$_2$ extraction at a high temperature of 453 K, which is above the melting temperature of PP (441 K), was chosen to extract VOCs from the melted PP samples at 14 MPa. The effect of time between 2 ~ 720 min on VOC removal is listed in Table 2. After 2 min extraction, all the VOC content in the PP-BP effectively reduced under the MS300-55 standard. In particular, the xylene content of PP-BP was higher than the allowed amount,

Figure 5. DSC graph of virgin PP, PP-IN, and PP-BP for (a) first heating; (b) cooling; (c) second heating.

Table 1. DSC data and crystallinity of new PP, PP-BP, and PP-IN

Sample name	First heating			Cooling			Second heating			Crystallinity (%)
	$T_{m,PE}$ [a] (°C)	$T_{m,PP}$ [b] (°C)	$\Delta H_{m,PP}$ [c] (J g^{-1})	$T_{c,PE}$ [d] (°C)	$T_{c,PP}$ [e] (°C)	$\Delta H_{c,PP}$ [f] (J g^{-1})	$T_{m,PE}$ (°C)	$T_{m,PP}$ (°C)	$H_{m,PP}$ (J g^{-1})	
Virgin PP	-	168.3	93.1	-	131.4	102.7	-	167.4	103.8	50.4
PP-BP	126.4	166.7	56.9	116.1	127.3	59.3	125.7	165.0	61.2	35.9
PP-IN	127.0	165.6	77.2	116.5	125.5	77.5	126.6	164.7	80.3	45.3

$T_{m,PE}$ [a], melting temperature of PE; $T_{m,PP}$ [b], melting temperature of PP; $\Delta H_{m,PP}$ [c], heat of melting of PP; $T_{c,PE}$ [d], crystallization temperature of PE, $T_{c,PP}$ [e], crystallization temperature of PP; $\Delta H_{c,PP}$ [f], heat of cooling of PP

Table 2. The effect of time on VOC removal of PP-BP at 453 K and 14 MPa

	Benzene (μg m^{-3})	Toluene (μg m^{-3})	Ethylbenzene (μg m^{-3})	Xylene (μg m^{-3})	Styrene (μg m^{-3})	Formaldehyde (μg m^{-3})	Acetaldehyde (μg m^{-3})	Acrolein (μg m^{-3})	TVOC[f] (μg m^{-3})
MDL[a]	10	10	10	20	10	20	20	20	100
Limit[b]	30	1,000	1,000	870	220	210	300	50	-
Virgin PP[c]	n.d.[e]	12	n.d.	n.d.	n.d.	n.d	n.d.	n.d.	7,100
PP-BP[d]	n.d.	193	362	2,990	174	27.7	n.d.	n.d.	33,700
2 min	n.d.	13.9	20.2	68.9	n.d.	30.7	n.d.	n.d.	3,180
10 min	n.d.	14.8	18.9	80	n.d.	26	26	n.d.	2,570
30 min	n.d.	12.6	14.6	48.2	n.d.	n.d.	n.d.	n.d.	1,320
60 min	n.d.	14.1	14.6	44.9	n.d.	n.d.	n.d.	n.d.	1,060
120 min	n.d.	n.d.	n.d.	36.7	n.d.	n.d.	n.d.	n.d.	1,810
720 min	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-

[a]MDL, Method detection limit; [b]Limit, refer to MS300-55 Table 1 Korea; [c]Virgin PP, virgin polypropylene; [d]PP-BP, recycled polypropylene from bumper; [e]n.d., not detected below MDL; [f]TVOC, total volatile organic compound

which is why xylene removal was one of the key factors in optimization of VOC removal process condition. The lowest VOC and xylene content was achieved at the longest time of 720 min, but 2 min was enough to achieve below the required VOC content.

3.2.2 The effect of pressure

Based on the above-mentioned time studies, as 2 min extraction was enough to remove the VOC content from PP-BP. Thus, 453 K and 2 min were chosen to investigate the effect of pressure on the VOC removal. Pictures of treated PP-BP in different pressure are shown in Figure 6. Above the melting point of PP, the pellets were agglomerated. The effect of pressure between 6.4 ~ 12 MPa on VOC removal is presented in Table 3. In the pressure ranges that examined in this study, there is no significant changes in the VOC removal observed. Typically, as pressure increases, the diffusion CO_2 molecules into the polymer matrix can be facilitated, which could enhance the VOC transport from the polymer matrix to the fluid phase[16]. At the high pressure, however, the increase in fluid density could decrease the diffusion of VOC molecules[16]. Because of this trade-off relationship, VOC removal may not be strongly dependent on the pressure. All of the experiments resulted in low VOC content below the requirements, but the lowest xylene content was produced at 8 MPa.
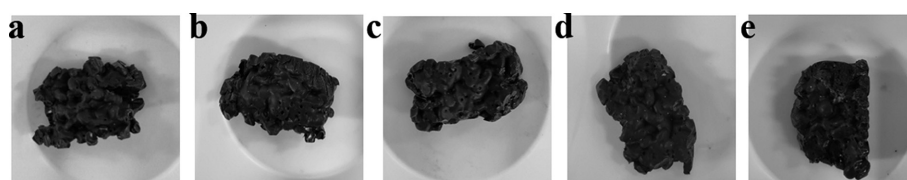

Figure 6. Picture of PP-BP after VOC removal at pressures of (a) 6.4 MPa, (b) 7.4 MPa, (c) 8.0 MPa, (d) 10 MPa, and (e) 12 MPa at a fixed temperature of 453 K and time of 2 min.

Table 3. The effect of pressure on VOC removal of PP-BP at 453 K and 2 min

	Benzene (μg m^{-3})	Toluene (μg m^{-3})	Ethylbenzene (μg m^{-3})	Xylene (μg m^{-3})	Styrene (μg m^{-3})	Formaldehyde (μg m^{-3})	Acetaldehyde (μg m^{-3})	Acrolein (μg m^{-3})	TVOC[f] (μg m^{-3})
MDL[a]	10	10	10	20	10	20	20	20	100
Limit[b]	30	1,000	1,000	870	220	210	300	50	-
Virgin PP[c]	n.d.	12	n.d.	n.d.	n.d.	n.d	n.d.	n.d.	7,100
PP-BP[d]	n.d.	193	362	2,990	174	27.7	n.d.	n.d.	33,700
6.4 MPa	15.7	42.4	66.5	483	35.6	n.d.	n.d.	n.d.	12,200
7.4 MPa	16.7	44.1	80.3	601	43.4	23.2	n.d.	n.d.	14,100
8.0 MPa	15.8	33	58.7	423	32.4	29.3	n.d.	n.d.	12,100
10.0 MPa	15.4	32.7	59.3	425	32.9	28.1	n.d.	n.d.	11,500
12.0 MPa	15.5	38.6	74.2	556	38.6	34.1	n.d.	n.d.	14,800

[a]MDL, Method detection limit; [b]Limit, refer to MS300-55 Table 1 Korea; [c]Virgin PP, virgin polypropylene; [d]PP-BP, recycled polypropylene from bumper; [e]n.d., not detected below MDL; [f]TVOC, total volatile organic compound
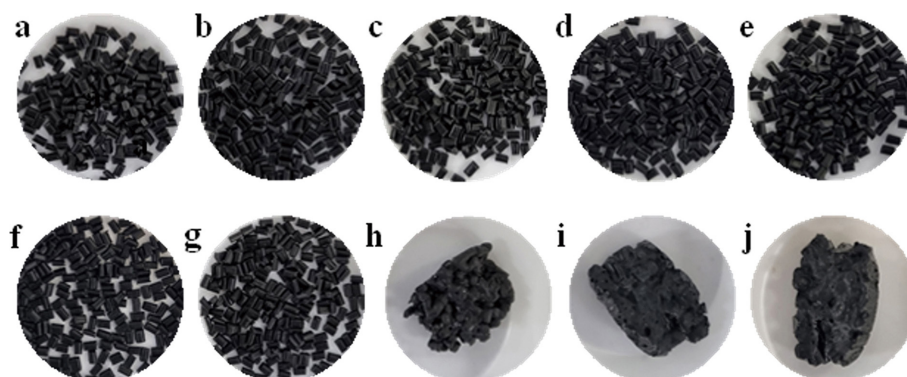

Figure 7. Picture of PP-BP after VOC removal at pressure of 12 MPa, time of 2 min, and temperature of (a) 298 K, (b) 313 K, (c) 333 K, (d) 353 K, (e) 373 K, (f) 393 K, (g) 413 K, (h) 433 K, (i) 453 K, and (j) 473 K.

3.2.3 The effect of temperature

The effect of temperature was studied at a fixed pressure of 12 MPa and time of 2 min. The pictures of treated PP-BP in different temperatures are shown in Figure 7. At the temperature above 433 K, the pellets were agglomerated. The effect of temperature from 298 ~ 473 K on VOC removal of PP-BP is presented in Table 4. As the temperature was increased from 298 to 433 K, xylene and TVOC removal value were increased, but at higher temperatures of 433 ~ 473 K, the removal of xylene and TVOC slightly decreased. The increase in temperature may contribute to facilitate the diffusion of VOC molecules into the fluid phase[16], but a further increase in temperature induce the polymer

melting and the agglomeration between neighboring particles could makes it difficult to the transport of VOC molecules from the polymer matrix to the fluid phase. To achieve xylene value below the requirement, the temperature needs to be at least 373 K. Lowest xylene and TVOC content was produced at 433 K.

3.2.4 The effect of time below 2 min

To investigate the possibility of extremely short time VOC removal, the effect of time below 2 min on VOC removal at 453 K and 12 MPa was investigated. Even under the extremely short time extraction condition, the scCO$_2$-treated PP-BP in were agglomerated (Figure 8), which could occur during the temperature

Table 4. The effect of temperature on VOC removal of PP-BP at 12 MPa and 2 min

	Benzene (µg m^{-3})	Toluene (µg m^{-3})	Ethylbenzene (µg m^{-3})	Xylene (µg m^{-3})	Styrene (µg m^{-3})	Formaldehyde (µg m^{-3})	Acetaldehyde (µg m^{-3})	Acrolein (µg m^{-3})	TVOC[f] (µg m^{-3})
MDL[a]	10	10	10	20	10	20	20	20	100
Limit[b]	30	1,000	1,000	870	220	210	300	50	-
Virgin PP[c]	n.d.	12	n.d.	n.d.	n.d.	n.d	n.d.	n.d.	7,100
PP-BP[d]	n.d.	193	362	2,990	174	27.7	n.d.	n.d.	33,700
298 K	n.d.	149	286	2,440	141	28.2	n.d.	n.d.	27,300
313 K	n.d.	159	287	2,390	140	23	n.d.	n.d.	27,500
333 K	n.d.	124	227	1,960	120	27.5	n.d.	n.d.	23,700
353 K	n.d.	61	124	1,180	64.5	27.7	n.d.	n.d.	16,900
373 K	n.d.	50.9	97	829	47.5	25.2	n.d.	n.d.	12,000
393 K	n.d.	36.2	68.6	597	36.3	26.6	n.d.	n.d.	11,300
413 K	n.d.	24.5	41.1	359	21.4	n.d.	n.d.	n.d.	8,250
433 K	n.d.	17	21.4	178	n.d.	n.d.	n.d.	n.d.	5,180
453 K	n.d.	23.9	38.2	344	17.4	24.1	n.d.	n.d.	9,230
473 K	n.d.	25.8	42.1	369	26	n.d.	n.d.	n.d.	8,890

[a]MDL, Method detection limit; [b]Limit, refer to MS300-55 Table 1 Korea; [c]Virgin PP, virgin polypropylene; [d]PP-BP, recycled polypropylene from bumper; [e]n.d., not detected below MDL; [f]TVOC, total volatile organic compound

Table 5. The effect of time below 2 min on VOC removal of PP-BP at 453 K and 12 MPa

	Benzene (µg m^{-3})	Toluene (µg m^{-3})	Ethylbenzene (µg m^{-3})	Xylene (µg m^{-3})	Styrene (µg m^{-3})	Formaldehyde (µg m^{-3})	Acetaldehyde (µg m^{-3})	Acrolein (µg m^{-3})	TVOC[f] (µg m^{-3})
MDL[a]	10	10	10	20	10	20	20	20	100
Limit[b]	30	1,000	1,000	870	220	210	300	50	-
Virgin PP[c]	n.d.	12	n.d.	n.d.	n.d.	n.d	n.d.	n.d.	7,100
PP-BP[d]	n.d.	193	362	2,990	174	27.7	n.d.	n.d.	33,700
10 s	15.6	43.2	75.9	578	42.9	29.6	n.d.	n.d.	13,900
30 s	n.d.	49.1	80.1	354	21	26.4	n.d.	n.d.	10,600
60 s	n.d.	64.7	65	269	13.2	33.7	n.d.	n.d.	9,780
90 s	n.d.	69.8	70.9	284	19.4	34	n.d.	n.d.	11,700
120 s	15.5	38.6	74.2	556	38.6	34.1	n.d.	n.d.	14,800

[a]MDL, Method detection limit; [b]Limit, refer to MS300-55 Table 1 Korea; [c]Virgin PP, virgin polypropylene; [d]PP-BP, recycled polypropylene from bumper; [e]n.d., not detected below MDL; [f]TVOC, total volatile organic compound
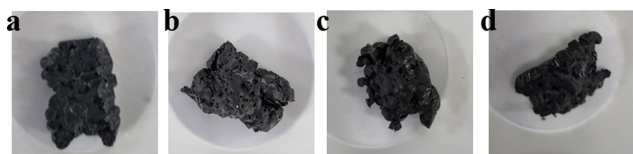
Figure 8. Picture of PP-BP after VOC removal at temperature of 453 K, pressure of 12 MPa, and time of (a) 10 s, (b) 30 s, (c) 60 s, and (d) 90 s.

ramping. The effect of time between 10 ~ 120 s is presented in Table 5. The lowest value of xylene and TVOC was achieved at time of 60 s. This result implies that in scCO$_2$ environment, VOC molecules rapidly diffuse from the bulk polymer, which is why

only a short time is enough for the VOC removal.

3.3 The effect of process parameters on VOC removal of PP-IN

The effect of time on VOC removal of PP-IN was investigated at 453 K and 14 MPa. The effect of time between 2 ~ 720 min on VOC removal of PP-IN is presented in Table 6. Prior the scCO$_2$ extraction, the VOC content of PP-IN was already lower than the allowed amount, but the lowest xylene content was achieved at 720 min.

At a pressure of 12 MPa and time of 2 min, the effect of temperature between 298 ~ 473 K on VOC removal of PP-IN

Table 6. The effect of time on VOC removal of PP-IN at 453 K and 14 MPa

	Benzene (µg m^{-3})	Toluene (µg m^{-3})	Ethylbenzene (µg m^{-3})	Xylene (µg m^{-3})	Styrene (µg m^{-3})	Formaldehyde (µg m^{-3})	Acetaldehyde (µg m^{-3})	Acrolein (µg m^{-3})	TVOC[f] (µg m^{-3})
MDL[a]	10	10	10	20	10	20	20	20	100
Limit[b]	30	1,000	1,000	870	220	210	300	50	-
Virgin PP[c]	n.d.	12	n.d.	n.d.	n.d.	n.d	n.d.	n.d.	7,100
PP-IN[d]	15.7	35.8	25.3	99	20.4	n.d	n.d.	n.d.	4,400
2 min	n.d.	18.7	21.2	97.1	n.d.	n.d.	n.d.	n.d.	3,020
10 min	n.d.	15	17.1	69.7	n.d.	n.d.	n.d.	n.d.	2,050
30 min	n.d.	16.5	15.7	49.8	n.d.	n.d.	n.d.	n.d.	1,560
60 min	n.d.	13.5	15	38	n.d.	n.d.	n.d.	n.d.	622
120 min	n.d.	12.8	15	37.8	n.d.	n.d.	n.d.	n.d.	1,090
720 min	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

[a]MDL, Method detection limit; [b]Limit, refer to MS300-55 Table 1 Korea; [c]Virgin PP, virgin polypropylene; [d]PP-BP, recycled polypropylene from bumper; [e]n.d., not detected below MDL; [f]TVOC, total volatile organic compound

Table 7. The effect of temperature on VOC removal of PP-IN at 12 MPa and 2 min

	Benzene (µg m^{-3})	Toluene (µg m^{-3})	Ethylbenzene (µg m^{-3})	Xylene (µg m^{-3})	Styrene (µg m^{-3})	Formaldehyde (µg m^{-3})	Acetaldehyde (µg m^{-3})	Acrolein (µg m^{-3})	TVOC[f] (µg m^{-3})
MDL[a]	10	10	10	20	10	20	20	20	100
Limit[b]	30	1,000	1,000	870	220	210	300	50	-
Virgin PP[c]	n.d.	12	n.d.	n.d.	n.d.	n.d	n.d.	n.d.	7,100
PP-BP[d]	15.7	35.8	25.3	99	20.4	n.d	n.d.	n.d.	4,400
298 K	n.d.	17.6	n.d.	63	n.d.	n.d.	n.d.	n.d.	2,860
313 K	n.d.	19.3	n.d.	61	n.d.	n.d.	n.d.	n.d.	2,310
333 K	n.d.	17.2	18.3	147	11.5	n.d.	n.d.	n.d.	3,730
353 K	n.d.	20.8	23.2	184	12.8	n.d.	n.d.	n.d.	3,910
373 K	n.d.	22.5	24.7	201	14	n.d.	n.d.	n.d.	4,440
393 K	n.d.	17.7	23.9	199	13.1	n.d.	n.d.	n.d.	4,570
413 K	n.d.	15.4	20	172	11	n.d.	n.d.	n.d.	4,290
433 K	n.d.	21.7	14.2	106	n.d.	n.d.	n.d.	n.d.	2,890
453 K	n.d.	25.5	23.6	165	n.d.	n.d.	n.d.	n.d.	4,680
473 K	n.d.	19.2	22.9	164	12.3	n.d.	n.d.	n.d.	4,840

[a]MDL, Method detection limit; [b]Limit, refer to MS300-55 Table 1 Korea; [c]Virgin PP, virgin polypropylene; [d]PP-BP, recycled polypropylene from bumper; [e]n.d., not detected below MDL; [f]TVOC, total volatile organic compound

Table 8. The effect of time below 2 min on VOC removal of PP-IN at 453 K and 12 MPa

	Benzene ($\mu g\,m^{-3}$)	Toluene ($\mu g\,m^{-3}$)	Ethylbenzene ($\mu g\,m^{-3}$)	Xylene ($\mu g\,m^{-3}$)	Styrene ($\mu g\,m^{-3}$)	Formaldehyde ($\mu g\,m^{-3}$)	Acetaldehyde ($\mu g\,m^{-3}$)	Acrolein ($\mu g\,m^{-3}$)	TVOC[f] ($\mu g\,m^{-3}$)
MDL[a]	10	10	10	20	10	20	20	20	100
Limit[b]	30	1,000	1,000	870	220	210	300	50	-
Virgin PP[c]	n.d.	12	n.d.	n.d.	n.d.	n.d	n.d.	n.d.	7,100
PP-IN[d]	15.7	35.8	25.3	99	20.4	n.d	n.d.	n.d.	4,400
10 s	n.d.	52.2	30	155	12.5	n.d.	n.d.	n.d.	7,120
30 s	n.d.	30.1	30.6	167	13.2	n.d.	n.d.	n.d.	8,040
60 s	n.d.	26.7	30.1	168	13.2	n.d.	n.d.	n.d.	7,170
90 s	n.d.	16.6	26.4	135	10.4	n.d.	n.d.	n.d.	6,910
120 s	16.5	45.9	46.3	254	26.6	n.d.	n.d.	n.d.	8,880

[a]MDL, Method detection limit; [b]Limit, refer to MS300-55 Table 1 Korea; [c]Virgin PP, virgin polypropylene; [d]PP-BP, recycled polypropylene from bumper; [e]n.d., not detected below MDL; [f]TVOC, total volatile organic compound

was investigated, and the results are presented in Table 7. Lower temperatures were preferred in resulting lower xylene and TVOC content, in which temperature of 313 K gave the best result.

At a temperature of 453 K and a pressure of 12 MPa, the effect of time below 2 min on VOC removal of PP-IN was analyzed and presented in Table 8. A slight increase of TVOC and xylene was observed after the treatment using $scCO_2$, but the value is still under the allowable amount.

4. Conclusions

Recycled car bumper and interior waste consisted primarily of PP, with addition of PE, talc and carbon black, which modified the chemical and thermal properties of the recycled polymer. VOC removal from PP-BP was successfully done using CO_2, while PP-IN has VOC content below the allowed amount and can be used as it is for further processing. The optimized condition to remove VOC content from PP-BP was determined to be temperature of 433 K, pressure of 8 MPa, and time of 60 s.

Acknowledgement

Nomenclature

ΔH: melting enthalpy, $J\,g^{-1}$

ΔH_0: enthalpy of 100% crystalline PP, $J\,g^{-1}$

CO_2: carbon dioxide

PE: polyethylene

PP: polypropylene

$scCO_2$: supercritical carbon dioxide

TVOC: total volatile organic compounds

VOC: volatile organic compounds

X_c: crystallinity, %

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