

Supercritical CO₂ Extraction of Phthalate Plasticizers from PVC

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ABSTRACT: Three common phthalates, namely, dioctyl phthalate, diisodecyl phthalate, and trioctyl trimellitate, were used as plasticizers for poly(vinyl chloride) (PVC) processing, and the extraction of these plasticizers were investigated using supercritical CO₂ fluids. Factors affecting the extractions of these phthalates were focused. The molecular weight of phthalates was found to dominate the level of extraction of low temperatures, whereas the content of carbonyl groups in the phthalate was a determining factor for the level of extraction of high temperatures. Negligible extraction was observed below the critical pressure of CO₂. For 32°C, the level of the extraction is insignificant below density of ca 0.7 g/cm³, above which the level of the extraction increases roughly linearly with increasing density. For tem-

peratures above 32°C, the density of CO₂ for apparent extractions decreased with increasing temperatures. The threshold density of CO₂ for extractions was found to be independent of the amount of a given phthalate in PVC. Two extraction rates during the extraction could be determined, with a higher rate in the first hour followed by a lower rate later in the extraction for all three phthalates. The effects of the extractions of phthalates on the flexibility of PVC were also investigated as well as the effects of the extrusion conditions, which could lead to various degrees of plasticization of PVC, on the level of extractions. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 4032–4037, 2003

Key words: glass transition; poly(vinyl chloride) PVC

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most widely used polymers because of its advantageous economics of production and useful properties. PVC is extensively used as a packaging material for food items and pharmaceuticals.¹ In processing of PVC, phthalates, for example, dioctyl phthalate (DOP), diisodecyl phthalate (DIDP), and trioctyl trimellitate (TOTM), to name a few, are usually used as a plasticizer to reduce processing temperature and prevent PVC from thermal degradation.² These phthalate plasticizers may migrate over the surface of the finished PVC products and cause pollution. This pollution may prevent phthalates from using as an additive for PVC package materials for foods because of their potential toxicity to humans and the environment.³ To be safely used in the food industry as package material, it may be necessary that PVC be subjected to a removal of the phthalates before its practical application.

Supercritical fluid extraction has been reported as an efficient extraction technique for some substances.^{4–6}

Due to the carbonyl groups in the phthalates, supercritical or high-pressure CO₂ fluids may be a good solvent for the extraction of phthalates. This is based on the presence of specific interaction between the carbonyl groups of the phthalates and CO₂ according to Fourier transform infrared (FTIR) evidence.^{7–10} Eckert and coworkers¹⁰ have used the bending mode (ν_2) of CO₂ at near 660 cm⁻¹ to probe polymer–CO₂ interactions. Splitting of the ν_2 band was observed for CO₂ in polymers containing carbonyl groups acting as an electron donor and exhibiting a specific intermolecular interaction with CO₂ acting as an electron acceptor rather than as an electron donor. Johnston and coworkers¹¹ have also suggested that the interaction of CO₂ with polymers possessing acrylate groups (containing carbonyl groups) may be of a Lewis acid-base nature.

In this work, we found that supercritical CO₂ can effectively extract phthalate plasticizers from PVC. Herein, we report this environmentally friendly extraction technique. The influences of the content of carbonyl groups in the phthalate, the content of the phthalate in the PVC sample, and pressure and temperature of CO₂ on the extraction fraction per unit area of sample were systematically investigated. The influence of the extraction of the phthalates on the flexibility of PVC was investigated as well via glass transition temperature measurements.

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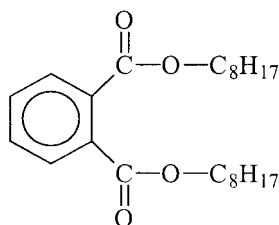
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EXPERIMENTAL

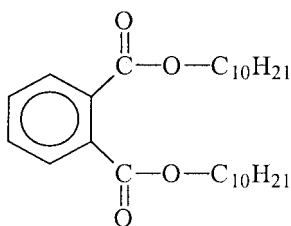
Materials

PVC, with a product number S-65 and prepared by a suspension polymerization with a degree of polymerization of about 1000, was supplied by Formosa Plastics Corporation (Taipei, Taiwan). Phthalate plasticizers including DOP, DIDP, and TOTM were supplied by Union Petrochemical Corp. (Taipei, Taiwan) and used as received. The structures of these three phthalates are shown below. Antioxidant (AO) or stabilizer is a mixture of mono-, di-, and tri-basic lead compounds, and was received from Taiwan Colors and Chemical Co. with a product number RP31M.

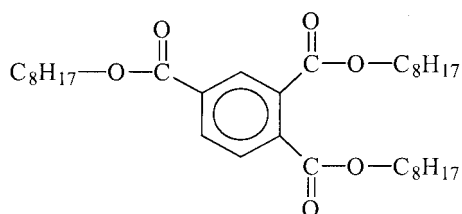
Diocetyl phthalate (DOP)



Diisodecyl phthalate (DIDP)



Triocetyl trimellitate (TOTM)



Sample preparation

The PVC plastisol (namely, the PVC/Phthalate/AO blend) was prepared by premixing 100 parts by weight of PVC, x parts by weight of phthalate, and 6.5 parts by weight of AO in a blender at 90°C for 30 min, followed by extrusion twice in a single-screw extruder (30 mm in diameter, L/D, 19, compression ratio, 3.5) at 160°C in the feeding zone, 160°C in the compression zone, and 170°C in the metering zone. After extrusions, the pelletized samples were compression molded by a hot press at 150°C for 30 s to make

coupon specimens of 1 mm in thickness, 20 mm in length, and 10 mm in width for extraction experiments.

Extraction experiments

The extraction experiments were performed in a supercritical extractor supplied by ISCO (Lincoln, NE), model SFX 2-10, which was equipped with a syringe pump, model 260D. The coupon samples were put in a 10-cm³ cell located inside the extractor pressurized by the equipped syringe-type pump. The extractor could control pressure over a range of 0–10,000 psi (680 atm) and a temperature over a range of 20–100°C. The pressurization time for reaching any preset pressure below 680 atm was 30 s. The extractor was controlled at a preset temperature prior to the pressuriza-

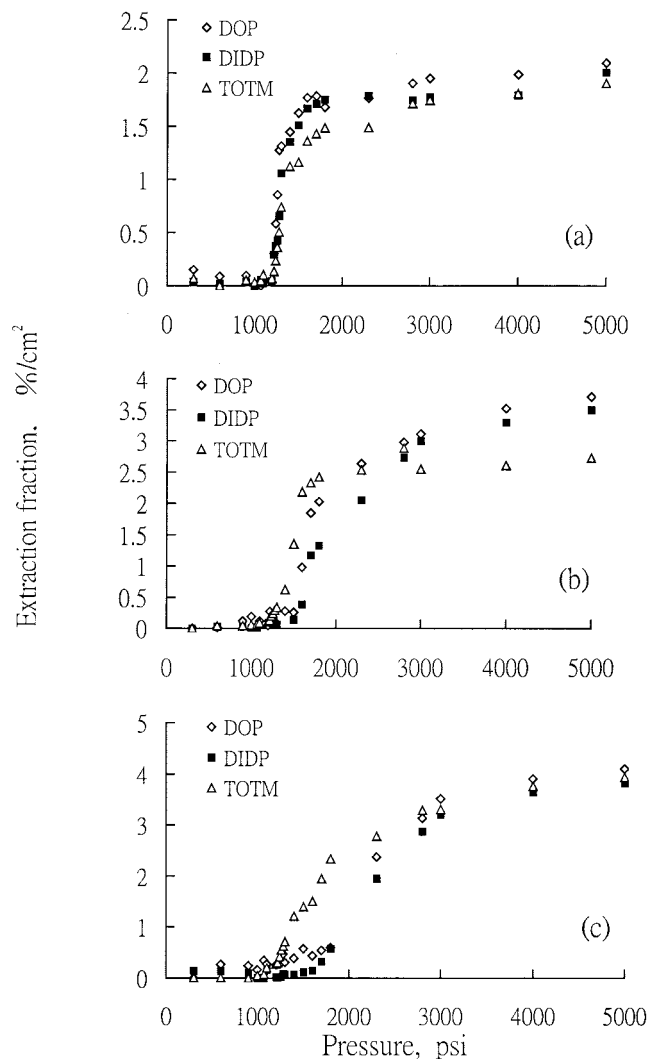


Figure 1 Extraction fraction per unit area of sample as a function of CO₂ pressure at (a) 32°C, (b) 42°C, and (c) 52°C for three PVC samples containing 30 phr of DOP, DIDP, and TOTM, respectively.

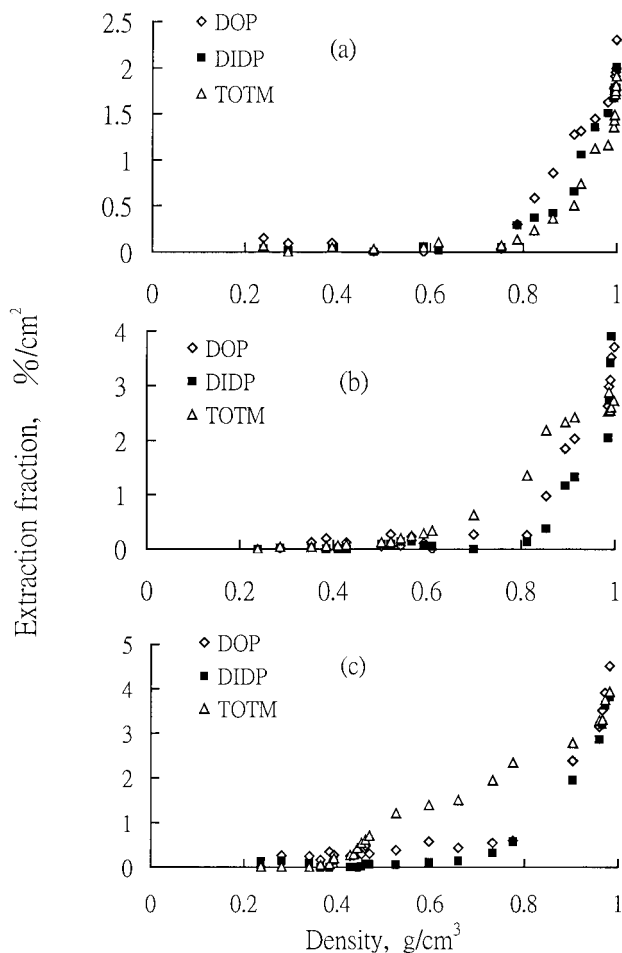


Figure 2 Extraction fraction per unit area of sample as a function of CO₂ density at (a) 32°C, (b) 42°C, and (c) 52°C for three PVC samples containing 30 phr of DOP, DIDP, and TOTM, respectively.

tion. The extraction time was 1 h (unless otherwise noted) for samples for studying the effects of CO₂ pressure and temperature, the type of plasticizers, and the content of the plasticizers on the extractions. After the extraction, the cell was depressurized and the sample was put into an 80°C oven for 30 min to evacuate all residual CO₂ in the sample. Preliminary data showed that such heating treatment could not remove the plasticizers, AO, and PVC from samples, and that CO₂ of any conditions studied could not extract AO and PVC. The extent (wt %) of the plasticizer extractions per unit area of the coupon sample was thus determined by dividing the extraction fraction as in eq. (1) by the surface area of the sample,

$$\frac{(W_0 - W_1)(100 + x + 6.5)}{W_0 x} \times 100\% \quad (1)$$

where W_0 is the sample weight before CO₂ extraction, W_1 is the sample weight after CO₂ extraction and

removal of all residual CO₂ in the sample, and x (in a unit of phr) is the amount of the plasticizer used.

DSC measurements

Glass transition temperatures of samples before and after CO₂ extractions were performed on DSC (DSC 2010, TA Instruments) at a heating rate of 10°C/min from -60 to 150°C under nitrogen.

RESULTS AND DISCUSSION

Figures 1 and 2 show extraction fractions of three phthalates per unit area of samples as a function of pressure and density, respectively, of CO₂ at three temperatures. The extraction time was 1 h. Prior to the extraction, the amounts of the three phthalates were all 30 phr, that is, 30 parts by weight per hundred parts by weight of PVC. As can be seen in Figure 1, for a given pressure at 32°C the level of extraction is in the order of DOP > DIDP > TOTM, whereas at 52°C the level of the extraction is TOTM > DOP > DIDP over a wide pressure range. This suggests that the molecular weights of phthalates may dominate the extraction process of low temperatures, whereas the content of carbonyl groups may dominate the extraction process of high temperatures. Negligible extraction is observed from Figure 1 below the critical pressure (P_c) of CO₂. From Figure 2 for 32°C, the level of the extraction is insignificant below density of ca. 0.7 g/cm³, above which the level of the extraction increases roughly linearly with increasing density. The threshold density for the extraction of a given phthalate to occur is found to decrease with increasing extraction temperature, as can be seen from Figure 2. This threshold density for a given CO₂ temperature is roughly in the order of TOTM < DOP < DIDP, an indication that the car-

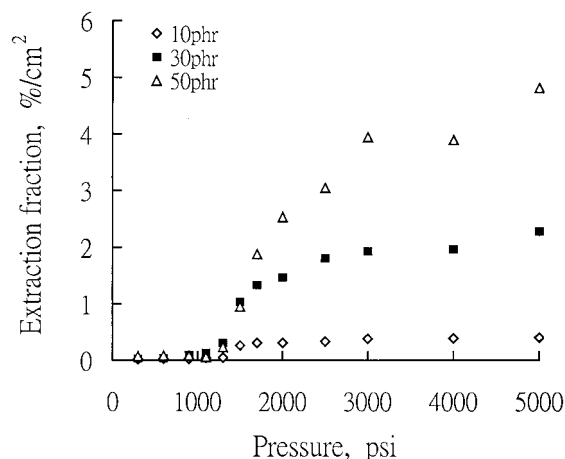


Figure 3 Extraction fraction per unit area of sample as a function of CO₂ pressure at 32°C for three PVC samples containing 10, 30, and 50 phr of DOP, respectively.

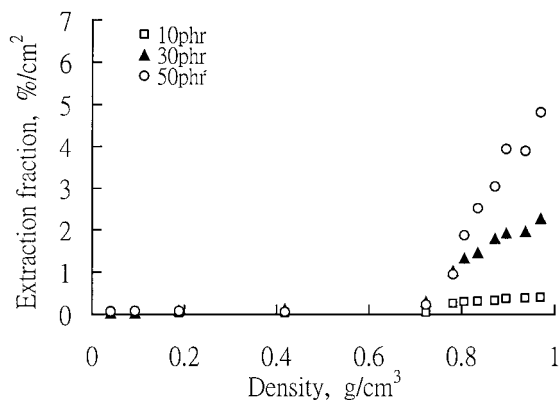


Figure 4 Extraction fraction per unit area of sample as a function of CO₂ density at 32°C for three PVC samples containing 10, 30, and 50 phr of DOP, respectively.

bonyl groups in the phthalates play an important role in the extraction process via Lewis acid-base interaction with CO₂, given that the concentration of the carbonyl group moiety in the plasticizer compound is in the order of TOTM > DOP > DIDP. A higher concentration of the carbonyl group moiety could lead to an easier extraction and thus less of a density of CO₂ is needed for the extraction to occur.

Figures 3 and 4 show extraction fractions of DOP per unit area of samples as a function of pressure and density, respectively, of CO₂ at 32°C. The extraction time was 1 h. Prior to the extraction, the amounts of DOP were 10, 30, and 50 phr. As can be seen in Figure 3, the extractions were negligible below *P_c*, whereas the extractions were apparent above *P_c*. For a given pressure above *P_c*, the higher the amount of DOP used, the higher the extraction fraction per unit area of sample. This indicates that a higher amount of DOP used could lead to the more flexible PVC that would facilitate the entering of CO₂ into the PVC sample to extract the DOP inside the sample. In addition, a higher amount of DOP inside the PVC sample could absorb more CO₂ at a given pressure to give rise to a

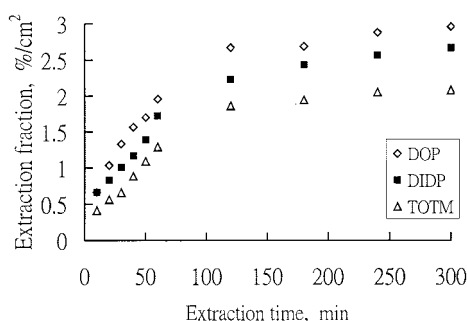


Figure 5 Extraction fraction per unit area of sample as a function of extraction time at 32°C and 3000 psi of CO₂ for three PVC samples containing DOP, DIDP, and TOTM, respectively.

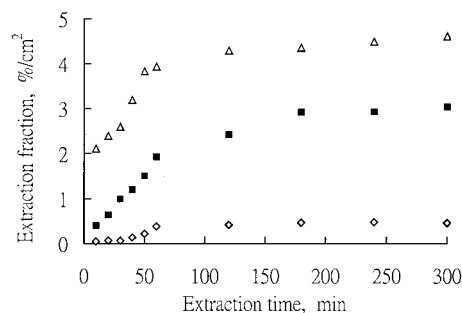


Figure 6 Extraction fraction per unit area of sample as a function of extraction time at 32°C and 3000 psi of CO₂ for three PVC samples containing 10 (◇), 30 (■), and 50 phr (△) of DOP, respectively.

higher level of extraction. In fact, in this study, the sample containing 50-phr DOP exhibited the highest level of absorption of CO₂, followed by 30-phr and by 10-phr. From Figure 4, the CO₂ with a density below 0.7 g/cm³ exhibits a negligible ability of extraction. The CO₂ with a density above 0.7 g/cm³ has extraction ability with a level depending on the amount of DOP used. The level of extraction seems to linearly increase with increasing the density of CO₂ in this high-density region. The rate of the increase of the level of the extraction as a function of the density of CO₂ increases with increasing the amount of DOP used.

Figure 5 shows extraction fractions of three phthalates per unit area of samples as a function of time at 32°C. The CO₂ pressure was 3000 psi. Prior to the extraction, the amounts of the three phthalates were all 30 phr. As can be seen in Figure 5, the extraction process includes two stages, the first hour of extraction exhibiting a higher extraction rate followed by a lower extraction rate in the later hours of extraction. These two stages correspond to two different diffusion mechanisms. For a given extraction time, the level of extraction was in the order of DOP > DIDP > TOTM. This suggests again that the molecular weight of the phthalate dominates the level of extraction at 32°C, given that a higher molecular weight of the phthalate has a lower vapor pressure or a lower diffusivity. Figure 6 shows extraction fractions of DOP per unit

TABLE I
Extraction Rates of Phthalates in PVC via Extractions by Supercritical CO₂ Fluids at 3000 psi and 32°C

PVC samples	Extraction rates, 10 ⁻² %/cm ² min	
	1st stage	2nd stage
DOP 10 phr	0.63	0.02
DOP 30 phr	2.98	0.18
DOP 50 phr	4.02	0.31
DIDP 30 phr	1.77	0.15
TOTM 30 phr	1.55	0.13

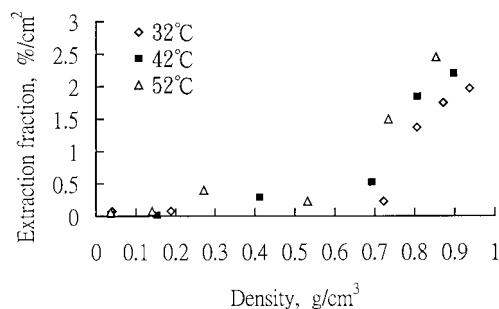


Figure 7 Extraction fraction per unit area of sample as a function of CO_2 density for PVC samples containing 30 phr of DOP after SCF CO_2 treatments at 3000 psi for 1 h at 32, 42, and 52°C.

area of samples as a function of time at 32°C. The CO_2 pressure was 3000 psi. Prior to the extraction, the amounts of DOP were 10, 30, and 50 phr. As can be seen in Figure 6, the extraction process exhibits two stages as well. For a given extraction time, the level of extraction increases with increasing DOP content in the samples. The data of each set of experiment in Figures 5 and 6 can be fairly simulated by two straight lines corresponding to the two stages of extraction. The slopes of these fitted lines can be used to account for the extraction rates, as tabulated in Table I. As can be seen in Table I for samples having 30 phr of a phthalate, the sample containing DOP exhibits the highest extraction rate, whereas the sample containing TOTM exhibits the least extraction rate. For samples containing different contents of DOP, the extraction rates of DOP increase with increasing the DOP content. The extraction rates in the initial stage of extraction are more than 10 times faster than those in the later stage of extraction.

Figure 7 shows extraction fractions of DOP per unit area of samples as a function of density of CO_2 for three temperatures. The extraction time was 1 h. Prior to the extraction, the amount of DOP in PVC was 30 phr. As can be seen in Figure 7, negligible extraction of DOP was observed below 0.7 g/cm^3 of CO_2 density. The extraction was apparent above 0.7 g/cm^3 , with the level of extraction increasing with increasing CO_2 density. The density dependence of the extraction fraction was greatest for 52°C, followed by 42 and 32°C.

Figure 8 shows T_g of PVC samples after extractions at various conditions as a function of the extraction fraction per unit area of sample. As can be seen in Figure 8, the T_g of the PVC sample after extraction increases with increasing the level of extraction. This is because the extraction of DOP from PVC reduces the flexibility of PVC and causes an increase of T_g of the sample. The T_g was significantly increased in the initial stage of extraction, below $\sim 0.15\%$ of extraction per unit area (cm^2) of sample. Above $\sim 0.15\%$ of extraction, the T_g of the sample, however, increases

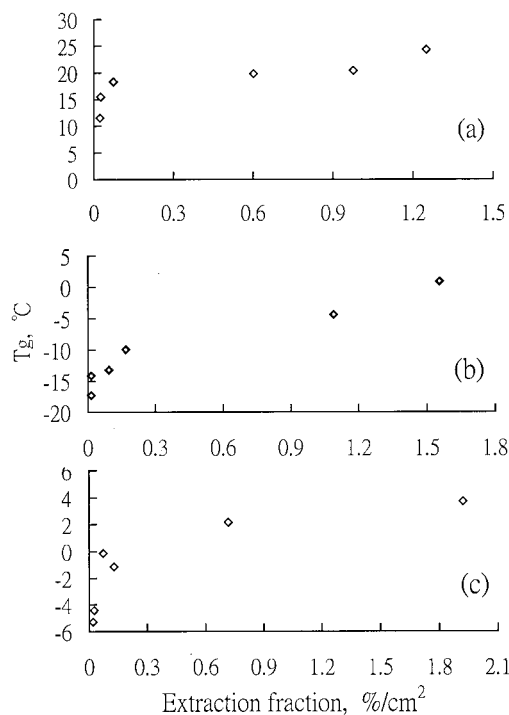


Figure 8 T_g of PVC samples as a function of extraction fraction per unit area of sample after SCF CO_2 treatments for 1 h at various pressures at (a) 32°C, (b) 42°C, and (c) 52°C.

slowly with increasing the level of extraction. This suggests that the later stage of the extraction was extracting those DOP molecules inside the bulk of the PVC sample other than the surface of the sample. Moreover, because only a small amount of sample was needed for DSC measurements and the sample for the measurements mostly came from the surface of the PVC sample other than the bulk of the sample, the observed increasing of T_g of the sample due to the extraction was thus not significant as a function of the level of extraction in the later extraction stage.

Table II demonstrates the effects of the number of extrusions on the DOP plasticization of PVC at 190°C of extrusion via T_g measurements. As can be seen in

TABLE II
Effects of the Number of Extrusions on the T_g of the Sample before and after Extraction and on the Level of Extraction

Number of extrusions	Extraction fraction, %/cm ²	T_g before	T_g after extraction, °C	T_g increases due to extraction, °C
1	13.2	24.4	27.7	3.3
2	12.9	18.4	26.6	8.2
3	11.9	14.4	23.2	8.8

The extrusion temperature was 190°C. The extractions were performed at 5000 psi, 35°C for 1 h.

TABLE III
Effects of Extrusion Temperatures on the T_g of the Sample before and after Extraction and on the Level of Extraction

Extrusion temp., °C	Extraction fraction, %/cm ²	T_g before extraction, °C	T_g after extraction, °C	T_g increases due to extraction, °C
150	11.9	26.4	35.8	9.4
170	11.2	18.4	27.9	9.5
190	9.7	14.4	23.2	8.8
210	9.7	26.4	23.5	-2.9

The number of extrusions was 3. The extractions were performed at 5000 psi, 35 °C for 1 hour.

Table II, prior to extraction of DOP, the T_g of the sample decreases with increasing number of extrusions. This indicates that the number of extrusions helps improve the plasticization of PVC and thus increases flexibility of PVC. For a given sample, the T_g of the sample is raised after SCF CO₂ treatments due to extraction of DOP. It was found that the level of extraction per unit area of the sample was the highest (13.2%) for extrusion once and the lowest (11.9%) for extrusion three times, suggesting that a better plasticization of PVC can lead to less of a level of extraction.

Table III demonstrates the effects of extrusion temperatures (150, 170, 190, and 210°C) on the DOP plasticization of PVC after extrusion three times via T_g measurements. As can be seen in Table III, prior to extraction of DOP, the T_g of the sample decreases with increasing extrusion temperatures except 210°C. This indicates that the plasticization of PVC increases with increasing extrusion temperatures except 210°C. The level of extraction per unit area of sample, however, decreases all the way with increasing extrusion temperature. This result is consistent with the change of T_g of the sample after SCF CO₂ treatments. The T_g of the sample after extrusion at 210°C shows high due to a considerable thermal decomposition, as evidenced by the brownish appearance of the sample. The thermal decomposition of PVC may cause poor plasticization,

and thus leads to a high T_g . This thermal decomposed PVC sample may be improved in plasticization via the SCF CO₂ treatments (and/or extractions), as can be seen in Table III for the 210°C extrusion where T_g after SCF CO₂ treatment (T_g 23.5°C) is lower than that before the SCF CO₂ treatment (T_g 26.4°C).

CONCLUSIONS

Three common phthalates, namely, DOP, DIDP, and TOTM, have been used as plasticizers for PVC processing, and the extraction of these plasticizers has been investigated using supercritical CO₂ fluids. Factors that can affect the extraction of these phthalates includes temperature and pressure of CO₂, the molecular weights of the phthalate, the content of carbonyl groups in the phthalate, and the extent of the plasticization of PVC. The flexibility of PVC was found to significantly reduce in the initial stage of extraction, below ~ 0.15% of extraction per unit area (cm²) of the sample. The reduced flexibility of PVC was indicated by an increased glass transition temperature of PVC from a ~ 10 to a ~ 15°C increase, depending on extraction conditions.

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