Removing Paraffin-Based Wax Coatings from Old Corrugated Containers Using Supercritical Carbon Dioxide

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ABSTRACT: Supercritical carbon dioxide (SC-CO_2) extractions of paraffin-based wax coatings from saturated and curtain-coated old corrugated containers (OCC) are reported. Extractions were performed in a 500-mL reactor (300 bar, 100°C, 50 g CO_2/min and 1 h). Wax removal efficiencies of 98 and 70% for saturated and curtain-coated OCC, respectively, were obtained. Under similar conditions, extractions in the presence of water resulted in an extraction efficiency of 99% for saturated OCC. Decreasing the operating pressure to 200 bar decreased the extraction efficiency to approximately 50%. Gas chromatography (GC) of the wax coatings on OCC, before and after extraction with SC-CO_2, showed a slight shift in the molecular weight distribution of the paraffin wax (after SC-CO_2 extraction) toward higher molecular weights for both saturating wax and curtain-coating wax. There was no evidence of chemical degradation or modification of the paraffin wax coatings by SC-CO_2. The packing density, packing arrangement, and dimensions of the curtain-coated OCC in the extraction apparatus affected the extraction efficiency. Loose packing compared to tight packing, 1×1 cm squares versus 1×20 cm strips, had higher extraction efficiencies; a random packing arrangement was better than packing with the fluting material in the direction of SC-CO_2 flow. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2699–2704, 2002

Key words: recycling; fibers; renewable resources; chromatography

INTRODUCTION

Old corrugated containers (OCC) are one of the primary packaging materials currently in use today. Historically, corrugated containers have held an advantage over other forms of packaging because of their recyclability. OCC are an excellent source of strong, unbleached fibers; however, the recovery rate of OCC is currently close to a maximum level with respect to recycling technical feasibility due to the fact that wax-coated OCC is excluded from the recycle stream. Although a valuable source of fibers, wax-containing OCC will not be recycled until a technological breakthrough is developed to efficiently remove the wax.[1–3]

The majority of wax coatings typically employed in the corrugated container industry is composed of paraffin wax, which is predominantly composed of straight chain *n*-alkanes, C_{18}-C_{50} and averaging C_{20}-C_{30}. Saturating or cascading waxes are the most commonly employed waxes in the corrugated container industry. A typical recipe for saturating wax consists of 95–99% paraffin wax and 1–5% modifier, usually a polymer or synthetic wax, such as a polyethylene/maleic anhydride graft copolymer. Curtain-coating waxes, in contrast to saturating waxes, are typically

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made from a higher melting base wax and contain more modifiers.

Paraffin-based waxes are soluble in a number of organic solvents, and solvent extraction is a standard method to quantify the wax content of board. However, the use of organic solvents to remove wax on an industrial scale is both expensive and environmentally unacceptable. Wilson et al.[4] first reported the use of SC-CO_2 to remove wax. Since this time, several researchers have reported on the solubility of paraffin-based materials in both liquid and supercritical CO_2. Only a few compounds of any structure with molecular weights exceeding 500 are soluble in liquid carbon dioxide, but the solubility of high-molecular-weight alkanes (the main component of wax) dramatically increases for SC-CO_2. Bartle et al.[5] showed that higher temperatures and pressures increase the solubility of paraffinic compounds in SC-CO_2. On the basis of the work of Li and Kiran,[6] SC-CO_2 should be able to remove wax contaminants from OCC fiber without simultaneously extracting lignocellulose materials or chemically modifying the OCC fiber.

We previously reported[7] SC-CO_2 extractions of paraffin-based wax coatings from saturated and curtain-coated OCC. The operating conditions were 300 bar and 100°C with a flow rate of 3 mL/min of SC-CO_2. These preliminary laboratory-scale (3 mL) experiments quantitatively extracted paraffin-based wax coatings from both the saturated and the curtain-coated OCC. Here we report our extractions of saturated OCC by using SC-CO_2 at a 500-mL scale. The effects of water, lower pressure, sample packing, and flow rate on the extraction process are shown.

EXPERIMENTAL

Materials

Curtain-coated and saturated corrugated containers were obtained from Willamette Industries Inc. (Wilsonville, OR), as were bulk samples of curtain-coating wax and saturating wax. The bulk wax samples and wax-board containers were preconsumer products and were used as received. Cylinders of bone-dry carbon dioxide with a dip tube were obtained from National Specialty Gases and chilled to 5°C before pumping. Hexane (95% HPLC grade) was obtained from Aldrich and used as received.

A sample of wax-saturated OCC was soaked, completely submerged in water for 5 days, and subsequently extracted without drying. The weight increase was 50.2%.

Supercritical Fluid Extractions

Supercritical fluid extractions were performed with a 500-mL scale supercritical fluid extractor using pure CO_2. OCC samples were cut into strips approximately 1 cm wide and 20 cm long and placed lengthwise into the extraction vessel. Typically, the extractions were semicontinuous and were conducted for 1 h in a preheated oven set at the desired temperature. The pressure was regulated within 3 bar of the reported pressure by means of a manual, back-pressure regulator (BPR). A high-pressure, dual piston, reciprocating pump (Thar Designs, Pittsburgh, PA) was incorporated both to pressurize and to circulate the CO_2. The reactor vessel (Thar Designs) was constructed from 17-4-PH stainless steel and had an interior volume of 500 mL. The extractor vessel was located in a modified oven that served both to heat and to circulate the surrounding air bath; an auxiliary heating tape was also used to heat the vessel.

Soxhlet Extractions

Solvent extractions of OCC were performed in a Soxhlet apparatus with cellulose thimbles and with hexane as the solvent. OCC samples were cut into strips approximately 1 cm wide and approximately 10 cm long, weighed, and placed lengthwise into the thimbles. For each extraction, 400 mL hexane was used and the extractions were conducted for 24 h. After the extractions were complete, the OCC and thimbles were removed from the Soxhlet apparatus and dried in a vacuum oven at 50°C for 24 h before weighing. The solvent was analyzed by gas chromatography (GC) to determine the composition and distribution of extracted wax components. To determine the wax removal efficiency with CO_2, SC-CO_2 extracted samples were subjected to hexane extraction in a Soxhlet apparatus for 24 h.

Analysis of Wax Samples

GC analyses of wax samples were performed with a Hewlett–Packard 6890 gas chromatograph (splitless injection) with a flame ionization detector, using helium as the carrier gas. Injector and detector temperatures were 240 and 280°C, re-

Table I Results for SC—CO_2 Extractions at Various Operating Conditions and Soxhlet (Hexane) Extractions of Wax-Saturated and Curtain-Coated OCC

	Saturated OCC	Curtain-Coated OCC	Low Pressure Saturated OCC	Wet Saturated OCC
Operating conditions	300 bar, 100°C, 1 h	300 bar, 100°C, 1 h	200 bar, 100°C, 1 h	300 bar, 100°C, 1 h
Mass of OCC before SC—CO_2 (g)	85.4663	84.2430	88.7583	86.4430
Mass of OCC after soaking in water for 5 days before SC—CO_2 (g)	N/A	N/A	N/A	129.86
Mass of OCC after SC—CO_2 (g)	62.0053	76.8338	77.4628	63.8408
Mass of wax removed by SC—CO_2 (g)	22.8010	7.4092	11.2955	22.6022
Wax residue from Soxhlet extraction of SC—CO_2 extracted board (g)	0.40	1.65	13.24	0.92
% of original board weight extracted by SC—CO_2	26.5	8.8	12.7	26.1
% of original board weight extracted by Soxhlet (Hexane)	26.1	12.6	26.1	26.1

spectively. Separations were achieved on a J and W DB-5 fused silica capillary column (30 m × 0.32 mm × 0.25 μm). The oven temperature was initially set at 120°C and ramped at 10°C/min to a final temperature of 280°C. The final temperature was maintained for 45 min.

RESULTS AND DISCUSSION

Soxhlet Extractions with Hexane

It was observed that the distribution of wax (amount and uniformity) varies from board to board and on the same board. Correspondingly, variations in the determined wax content of approximately 1% are possible. To determine the extent of wax removal via SC-CO_2 extraction, duplicate samples of both curtain-coated and saturated wax board were extracted in a Soxhlet apparatus by using hexane as the solvent. The average decrease in weight for the curtain-coated samples was found to be 12.6%, whereas the average decrease in weight for the saturated samples was found to be 26.1%.

Supercritical Carbon Dioxide Extractions of Wax-Coated Corrugated Containers

We have previously demonstrated in preliminary, laboratory-scale experiments that it is possible to quantitatively remove the wax from air-dried, unpulped OCC by using SC-CO_2 extraction.[7] The initial extractions performed in the 500-mL extractor were run under similar operating conditions (i.e., 100°C and 300 bar) and OCC mass/cell volume ratio employed in the 3-mL experiments. The results of the extractions performed in the 500-mL apparatus are summarized in Table I. For the saturated OCC, the results correlate well with the 3-mL extractions. Ninety-eight percent of the initial amount of wax present was extracted via SC-CO_2. Soxhlet extractions of the SC-CO_2 extracted board (hexane, 24 h) recovered the remaining 2% (0.4 g) of residual wax.

GC traces are shown in Figure 1 for (a) saturating wax scraped directly from the saturated

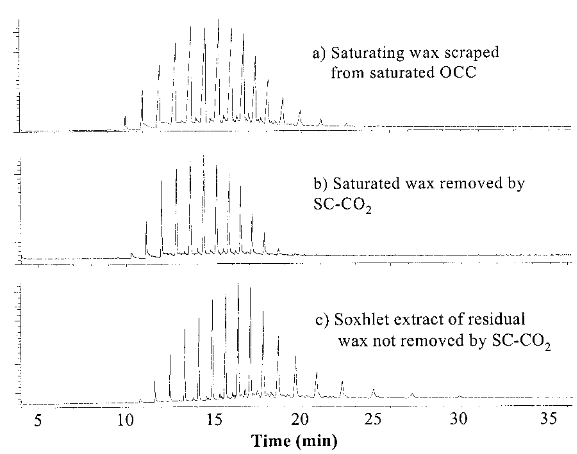

Figure 1 GC time traces of saturating wax (a) scraped from the board surface (ordinate maximum is 1,200,000 counts); (b) extracted with SC-CO_2 (ordinate maximum is 250,000 counts); and (c) Soxhlet extract of residual saturating wax not removed by SC-CO_2 (ordinate maximum is 600,000 counts).

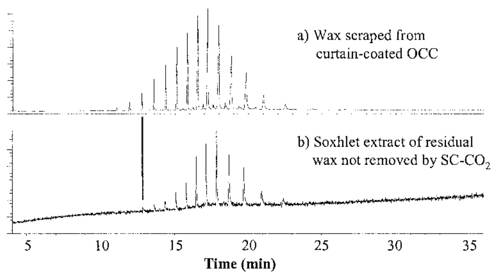

Figure 2 GC time traces showing the effect of SC-CO_2 extraction on the composition of residual curtain-coating wax. Ordinate maximum is 600,000 counts for (a) and 60,000 counts for (b).

OCC surface (before SC-CO_2), (b) saturating wax removed with SC-CO_2, and (c) the Soxhlet extracts of the previously SC-CO_2 extracted OCC. Comparison of Figure 1a and 1b shows a slight decrease in the relative abundances of the higher molecular weight components of the wax. Figure 1c shows a slight increase in the relative abundances of the higher molecular weight components of the wax. These shifts in the molecular weight distribution of the saturating wax indicate that the lower molecular weight components are more effectively removed by SC-CO_2. This higher extraction efficiency of lower molecular weight materials is consistent with the CO_2 solubility[5] and fractionation[8,9] data of paraffin wax. It is noteworthy that the molecular weight distribution of the saturating wax after SC-CO_2 extraction is very similar to that of the saturating wax scraped from the box surface. There are no additional peaks in the GC traces, indicating no chemical degradation or modification of the paraffin wax has taken place. This further suggests that the paraffin wax may be recovered in its original form to be reused.

The results obtained for the curtain-coated OCC differ remarkably from those obtained on curtain-coated OCC in the 3-mL vessel and with the wax-saturated OCC in the 500-mL vessel (Table I). For the curtain-coated OCC, extraction with SC-CO_2 in the 500-mL vessel resulted in the removal of approximately 70% (7.4 g) of wax. Interestingly, there was approximately five times more residual wax after SC-CO_2 extraction of the curtain-coated OCC than for the wax-saturated OCC. Figure 2 shows the GC traces obtained for the wax scraped directly from the curtain-coated OCC surface (before SC-CO_2) and for the Soxhlet extracts of the previously SC-CO_2-extracted OCC. Despite the higher amount of residual wax, GC analysis of the residual curtain-coated wax reveals a much lower abundance for those peaks attributed to the individual components of the paraffin wax. The observed differences in wax removal between the curtain-coated and wax-saturated OCC samples are likely due to the various polymeric modifiers incorporated into the curtain-coated wax. As with the saturating wax, there is a substantial increase in the relative abundances of the higher molecular weight components of the curtain-coating wax before and after treatment with SC-CO_2. Similar shifts were previously reported,[7] consistent with lower molecular weight species being extracted sooner than those of higher molecular weight.[9,10]

The difference in the observed results for curtain-coated and saturated waxes may be due to two major differences in the samples. First, the curtain-coating wax contains approximately 30% modifiers compared to only 1.5% modifiers for the saturated wax. Second, wax-saturated OCC contain approximately twice as much wax as do curtain-coated containers (approximately 26 and 13%, respectively), which results in a larger bulk density for the wax-saturated containers. Therefore, to have the same mass of waxed board in the 500-mL extractor, it is necessary to use approximately 40% more board area of curtain-coated OCC than wax-saturated OCC. This results in substantially tighter packing for the curtain-coated OCC, which may drastically reduce the efflux of larger wax molecules out of the interstitial fiber spaces. Additionally, excessively tight packing could result in CO_2 flow patterns that could lower the accessibility of the SC-CO_2 to the OCC surface.

Effect of Lower CO_2 Pressure on the Wax Extraction Process

The effect of lowering the pressure from 300 to 200 bar on the extraction process results in a decrease in the extraction efficiency of wax-saturated OCC by approximately 50%. At 200 bar, only 49% of the wax was removed (Table I). Figure 3 shows the GC traces for the wax removed directly from the wax-saturated OCC surface (before SC-CO_2) and the Soxhlet extracts of the previously SC-CO_2-extracted OCC. Comparison of the GC traces before and after extraction at 200 bar again shows an increase in the relative abundance of the higher molecular weight components.

The decrease in the extraction efficiency of the saturating wax is consistent with the solubility

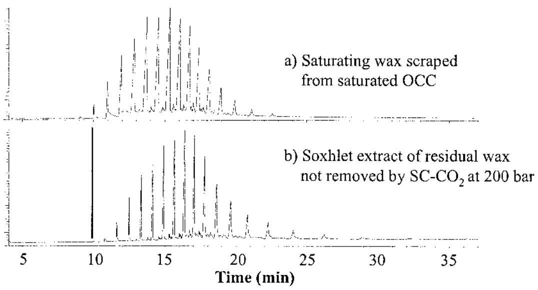

Figure 3 GC time traces showing the effect of lower pressure on the composition of residual saturating wax. Ordinate maximum is 1,200,000 counts (a) and 1600,000 counts (b).

data of octacosane (C_{28}) in SC-CO_2 at 90°C.[5] On the basis of the reduction in extraction efficiency and the octacosane solubility data, it is anticipated that extractions at 200 bar will take approximately twice as long as extractions at 300 bar.

Effect of Water on the Wax Extraction Process

The majority of wax-coated containers are used in high-moisture applications, which could, in practice, lead to substantial amounts of water entering the SC-CO_2 extractor. A sample of water-saturated wax-saturated OCC was extracted with SC-CO_2 (Table I). The extractions of the wet OCC compare well with those of the dry OCC. Soxhlet extraction (hexane, 24 h) of previously SC-CO_2-extracted wet OCC showed 1.1% (0.92 g) residual wax, indicating the presence of water does not influence the extraction efficiency.

Effect of Packing and Flow on the Wax Extraction Efficiency of Curtain-Coated OCC

It was postulated that the packing arrangement of the OCC pieces could influence the extraction efficiency. In preliminary experiments, samples were packed loosely and tightly as 1 × 20-cm strips with fluting parallel to the SC-CO_2 flow. In the case of the loosely packed strips, the loading was approximately one-half that of the tightly packed arrangement, and the SC-CO_2 flow was correspondingly reduced. The loose packing arrangement resulted in an increase in wax extraction efficiency, 81% versus 70%. A further increase in extraction efficiency to 88% was realized when the samples were cut into smaller pieces (1 × 1 cm) and loosely packed. These increases in extraction efficiency were realized even though the CO_2 flow rates were decreased (Table II). Increasing the CO_2 flow rate further increased the extraction efficiency to 92%.

It should be noted that all of the previously mentioned extractions required a 60-min preheating to raise both the oven chamber and the extraction vessel temperature to 100°C. During this heating period (especially for the curtain-coated containers), the wax melts and was observed to penetrate into the board, which can potentially affect the extraction process. It is expected that foregoing this heating process by preheating the SC-CO_2 and not the reactor vessel itself will greatly diminish the residence time of the melted wax on the board, thus lessening the diffusion of the wax into the interfiber spaces and allowing even greater extraction efficiency.

CONCLUSION

The results demonstrate that SC-CO_2 can effectively remove paraffin-based waxes from wax-coated OCC. At the conditions employed (300 bar, 100°C, ~ 50 g CO_2/min, 1 h), extraction efficiency is unaffected by extraction vessel size for wax-saturated OCC. Lowering the operating pressure from 300 to 200 bar decreases the extraction efficiency by approximately 50%. The presence of water in the OCC has no effect on the extraction efficiency. Presumably due to the presence of various modifiers,

Table II Effect of Packing and Sample Morphology on the Extraction Process

Curtain-Coated OCC	1 × 20 cm Tight Pack	1 × 20 cm Loose Pack	1 cm^2 Loose Pack	1 cm^2 Loose Pack
SC—CO_2 Flow (g SC—CO_2/g OCC)	36	28	23	67
Mass of CC-OCC before SC—CO_2 (g)	84.2430	41.9803	51.4318	45.0490
Mass of CC-OCC after SC—CO_2 (g)	76.8338	37.7727	45.7144	39.7443
Mass of wax removed by SC—CO_2 (g) (% of original wax removed)	7.4092 (70%)	4.2076 (81%)	5.7174 (88%)	5.2966 (92%)

the extraction efficiency of the wax curtain-coated OCC is reduced. OCC packing density and orientation affected the efficiency of the extraction.

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