

Effect of Blending β -Cyclodextrin with Poly(vinyl chloride) on the Leaching of Phthalate Ester to Hydrophilic Medium

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SYNOPSIS

β -Cyclodextrin was blended with poly(vinyl chloride) to study the influence of β -cyclodextrin on the leaching of phthalate ester from PVC. β -Cyclodextrin was found to reduce the migration of phthalate ester. The considerable effect of β -cyclodextrin on the leaching of phthalate ester was traced to the formation of an inclusion complex formation between the two components. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

β -Cyclodextrin (β CD) is well known for its ability to form inclusion complexes with a variety of components.¹⁻⁴ As a result of the complex formation, the characteristics of the included components like solubility, chemical reactivity, and spectral properties will be changed.⁵⁻⁷ This unique property of β CD has led to a wide-spread utilization of this component in pharmaceutical, food, chemical, and other industrial areas.⁸

Poly(vinyl chloride) (PVC) has been used extensively in medical applications such as tubing, storing devices for blood and related products, and IV fluids.⁹ The often-cited serious drawback of PVC is the leaching of phthalate ester plasticizer from the polymer matrix to the contacting fluids.¹⁰

Blending of β CD with PVC may be effective in curtailing the migration of phthalate ester presumably due to the complexing ability of the former. To the best of our knowledge, the effect of blending β CD with PVC with an aim to study the influence of β CD on the leaching of phthalate ester has not been reported. This note addresses our effort in this direction.

EXPERIMENTAL

Indigenously calendered PVC sheet-containing about 40% di(2-ethyl hexyl phthalate) was used for

this study. β CD (Sigma Chemicals, U.S.A.) was used after vacuum drying. All other chemicals were HPLC grade and obtained from E. Merck, India.

PVC strips and β CD were dissolved in dimethylacetamide. The concentration of β CD was 5% by weight. PVC strips without β CD was also dissolved in dimethylacetamide. Films were cast using these solutions. Vacuum-dried films having an area of 3 cm² and a thickness of 2 mm were used for the leaching studies.

A Perkin-Elmer 597 IR spectrophotometer was used for recording the infrared spectra. A Waters Associates HPLC system consisting of a Model 6000A solvent delivery pump model U6K injector and Model 486 tunable absorbance detector was used for the chromatographic analysis. A μ -Bondapak C18 column (Waters Associates) with methanol as the mobile phase was used at a flow rate of 1 mL/min for the separation and estimation. The column effluents were monitored at 254 nm and the chromatograms were obtained on an Omini scribe strip chart recorder (Houston Instruments, TX).

Estimation of Total Plasticizer Content

A known weight of PVC strips was dissolved in tetrahydrofuran. PVC resin was precipitated by adding methanol. The filtrate was concentrated and subjected to chromatographic analysis for estimating the plasticizer content.

Leaching Studies

The surface of the polymer strips with β CD and without β CD were cleaned by dipping in methanol for 30 s. These strips were then kept in 10 mL of a methanol/water mixture (3 : 1 v/v) at 30°C for 24 h, and 20 μ L of these solutions were injected onto the column. All the experiments were repeated thrice.

Preparation of DEHP- β CD Complex

β CD and DEHP were added in a 1 : 1 molar ratio to 30 mL deionized distilled water and sonicated to obtain a dispersion. The dispersion was stirred for 6 h at room temperature (30°C) and then kept overnight. The precipitate settled at the bottom was collected and vacuum-dried at 40°C. The precipitate obtained was subjected to infrared spectroscopic analysis in the form of a potassium bromide pellet.¹¹ The complex formed between β CD and DEHP (the precipitate mentioned earlier) was extracted with dichloromethane and the dichloromethane layer was subjected to spectroscopic analysis by evaporating over a sodium chloride window.

RESULTS AND DISCUSSION

Figure 1 depicts the chromatographic trace of DEHP. Under the present chromatographic conditions, DEHP has a retention time of 3 ± 0.02 min. The intensity of the peak eluted at 3 min was used for quantifying the amount of DEHP leached out.

Table I summarizes the extent of leaching of phthalate ester from PVC matrices having β CD and

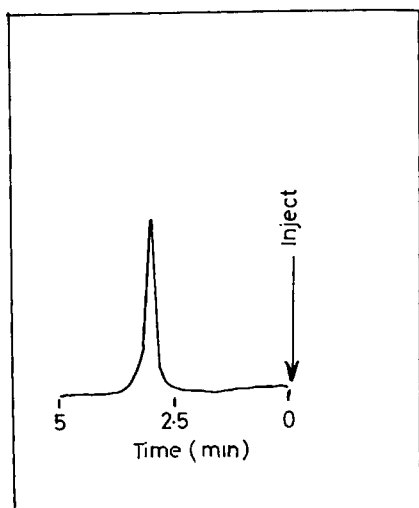


Figure 1 Chromatographic trace of DEHP.

Table I Effect of BCD on the Leaching of DEHP from PVC to Methanol : Water Mixture

| | PVC | PVC- β CD Blend |
|-----------------------------------|------------------------------------|------------------------------------|
| Weight of the polymer | 100 mg | 100 mg |
| Initial DEHP content | 34.11 mg | 33.78 mg |
| Amount of DEHP leached after 24 h | 1.84 ± 0.03 mg/cm ² | 0.87 ± 0.02 mg/cm ² |

without β CD. Though the initial DEHP content is nearly equal in both samples, the extent of DEHP leaching from the PVC- β CD blend is considerably less.

The ability of β CD to form inclusion complexes with a variety of components is well known.¹⁻⁴ The factor which is responsible for reducing the migration of DEHP in this case, we feel, could be attributed to the inherent complexing ability of β CD. It is quite reasonable to presume that DEHP molecules could form inclusion complexes with β CD already dispersed in the PVC matrix. Additionally, DEHP molecules during their migration through the PVC matrix could enter in the cavities of suitably oriented β CD molecules to form a complex.

To obtain better insight into this possibility, we studied the precipitate obtained from DEHP- β CD dispersion in water. Figure 2 illustrates the infrared spectrum of the precipitate. The spectrum clearly shows the features of both β CD and DEHP. The strong peaks centered around 3500 cm^{-1} as well as around 1100 cm^{-1} can be assigned to the —OH and —C—O—C groups of β CD. DEHP shows its presence by the strong characteristic —CO— stretching band around 1700 cm^{-1} . The characteristic doublet of the aromatic moiety centered around 1600 cm^{-1} (see Fig. 3), however, is mixed with the broad bending mode of —OH group of β CD.

It is well known that the IR spectral features of the included components, unlike UV spectra, seldom vary.¹ In that sense, the spectrum depicted in Figure 2 can be assigned to the complex formed between β CD and DEHP.

Figure 3 shows the IR spectrum of DEHP. The spectrum illustrated in Figure 4 is exactly identical to that of the DEHP spectrum shown in Figure 3. The residue obtained after the extraction was scanned from 4000 to 400 cm^{-1} . The spectrum illustrated in Figure 5 does not contain any features of DEHP, indicating the complete removal of DEHP. The spectrum shows all the features of β CD.

The gravimetric data of the complex is shown in Table II. The molecular weights of β CD and DEHP are 1135 and 390, respectively. Based on these values

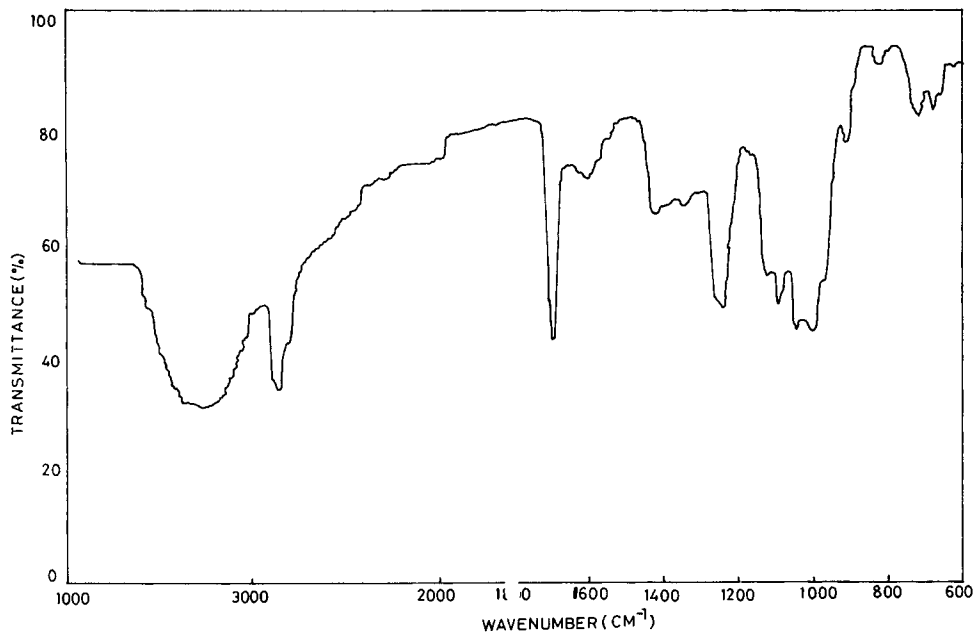


Figure 2 IR spectrum of DEHP- β CD complex.

and the weights of the complex before and after dichloromethane extraction, we arrived at the stoichiometry of the complex at 1 : 0.97 (see Table II), i.e., β CD and DEHP form a 1 : 1 inclusion complex.

The reduction of DEHP migration from PVC in the presence of β CD is quite clear in the light of the above-mentioned aspects. Some of the DEHP molecules could form complexes with β CD reducing or stopping their migration. The reduction in leaching is 44.93%, which is indeed considerable.

Table III compares some of the physicomechanical parameters of the PVC- β CD blend with PVC. The mechanical properties are decreased slightly. The presence of comparatively bulky β CD molecules could interfere with the alignment of the polymer chains during the elongation. This aspect may be responsible for the reduction of the ultimate mechanical parameters. The changes are, however, minimal, which will not affect the end-use application of PVC. Percent water absorption and specific

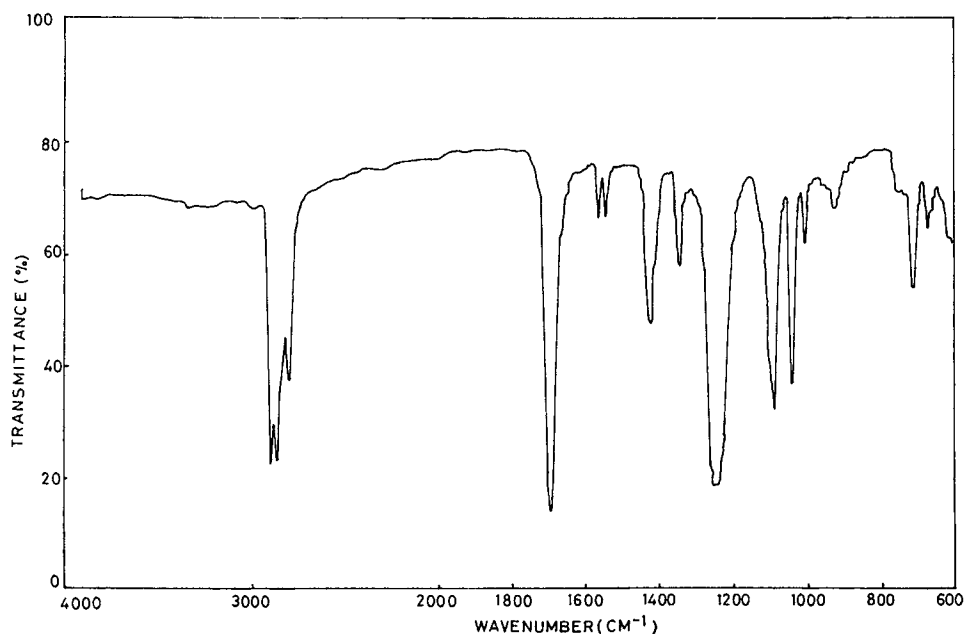


Figure 3 IR spectrum of DEHP.

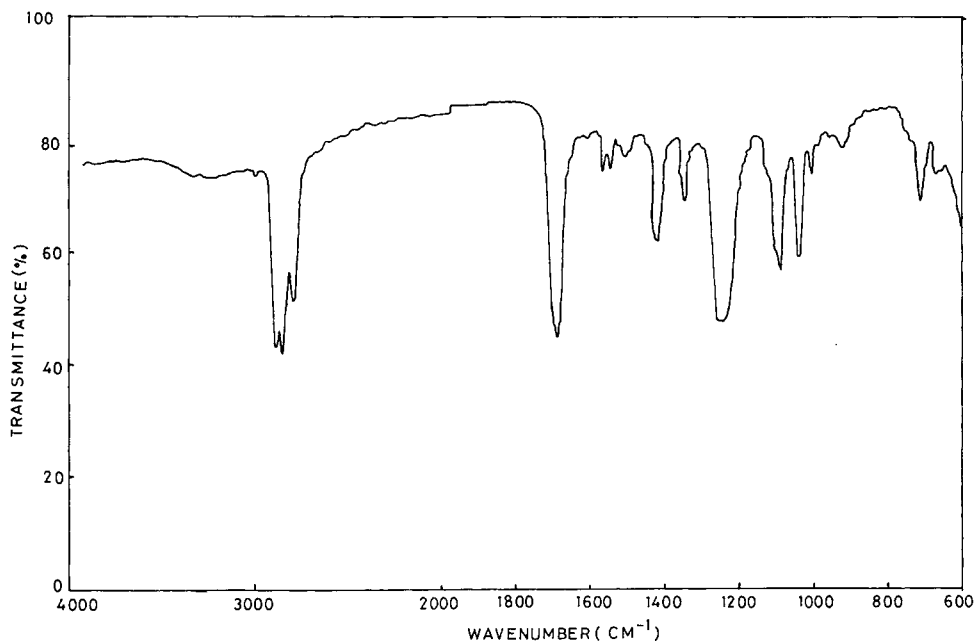


Figure 4 IR spectrum of the residue obtained after evaporating the dichloromethane extract of the β CD-DEHP complex.

gravity are slightly increased, which could be attributed to presence of β CD.

It has generally been accepted that the hydrophobic moiety of the guest molecules and the cyclodextrin cavity is a major factor governing the stability of the complex.¹² The stability of the complex is almost proportional to the hydrophobic character of the guest molecules. A complex can be dissociated using only a more hydrophobic sol-

vent. The medium used for the leaching studies is hydrophilic and the possibility of extracting the complexed DEHP is rather less. It may be relevant to point out that PVC has been widely used for storing blood, blood products, and fluids for injection. These are polar in nature and the reported method may be useful in controlling the leaching of DEHP. Our future studies will be addressed in these directions.

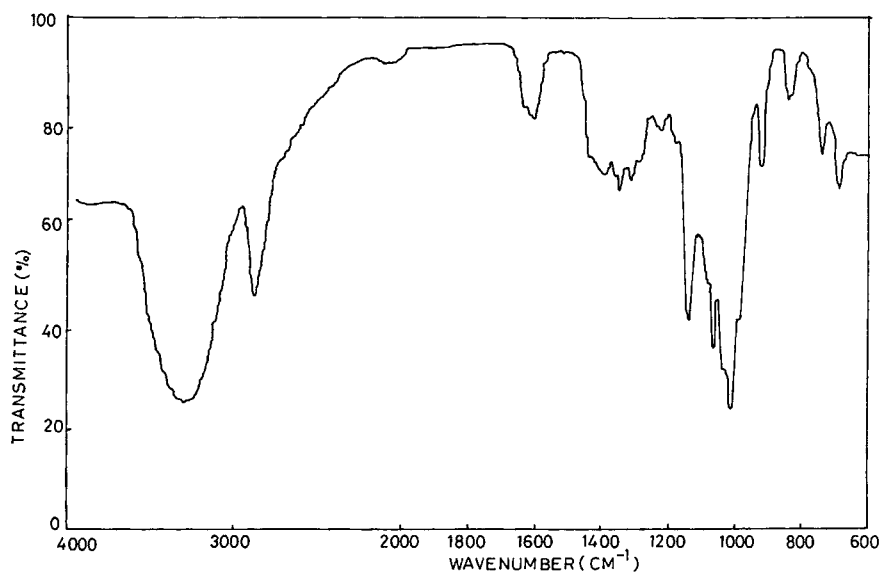


Figure 5 IR spectrum of the residue obtained after extracting β CD-DEHP complex with dichloromethane.

Table II Gravimetric Data of BCD-DEHP Complex

| Material | Weight |
|--|----------|
| BCD-DEHP complex | 20 mg |
| Amount of DEHP extracted | 4.98 mg |
| Amount of BCD left | 15.02 mg |
| Stoichiometry of the complex based on the weight | 1 : 0.97 |

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