Extraction of CdS Pigment from Waste Polyethylene

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ABSTRACT: Cadmium sulfide has often been used as a pigment in plastics such as high-density polyethylene (HDPE). Removal of CdS after the useful life of plastics is desired since it poses an environmental hazard in the waste phase of these plastics. In this study, a process is investigated to convert the insoluble CdS in the polymer matrix into $CdCl_2$ by treatment with HCl, followed by extraction of $CdCl_2$ with 1,4-butanediol (BDO). Since the diffusivity of $CdCl_2$ in HDPE is low, reducing diffusion length and enhancing interfacial area by dispersing BDO by laminar mixing of molten HDPE with BDO facilitate the extraction process. The overall mass transfer process during extraction is modeled as a combination of consecutive steps: diffusion of $CdCl_2$ through HDPE to the BDO dispersed in molten HDPE, followed by transport of the dispersed, $CdCl_2$ containing BDO to the bulk BDO phase surrounding the HDPE. This mechanism achieves reduction of $CdCl_2$ in HDPE from 1128 ppm to less than 100 ppm in 12 min. The somewhat higher melt flow index (MFI) of the HDPE after extraction (8.3 g/10 min) as compared with the MFI of the starting HDPE (6.3 g/10 min) shows some extent of degradation. However, the MFI is acceptable for HDPE recycling. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1024–1031, 2006

**Key words:** recycling; polyethylene (PE); dyes/pigments; cadmium; extraction

INTRODUCTION

Conversion of polymers into end-use-products often requires additives for improving processing characteristics and final properties. Examples of additives are antioxidants, UV-stabilizers, flame-retardants, plasticizers, nucleating, reinforcing, and coloring agents. For example, cadmium sulfide (CdS) has been widely used as a coloring agent for high-density polyethylene (HDPE) toys, as it imparts a broad range of colors (from yellow to red) in combination with other compounds. Although the heavy metal cadmium is safely trapped in the polymer matrix during its lifetime application, it can leach out from disposed material and pollute the environment.[1] For example, one conventional way of handling plastic waste is landfill,[2] but the contamination of groundwater with cadmium is then a serious risk. Another way to treat waste polymer material is incineration, but CdS gives environmental burden by dispersing through fumes and fly ashes. Thus, a preferred way of treating plastics waste is by separation of harmful additives and recycling of remaining polymer. For example, the polymer can be dissolved in a good solvent, and then filtered or extracted with another solvent to separate the additives.[3–6] However, high temperature dissolution and recovery of large quantity of potentially harmful organic solvents are high energy demanding processes. Extraction of CdS with supercritical water has been proposed,[4] but is expensive and degradation of the polymer occurs. Another proposed route is conversion of CdS with gaseous HCl into soluble $CdCl_2$ at elevated temperature.[5] Extraction of $CdCl_2$ with polar solvents such as water or glycols was also proposed, but not described. In addition, the conversion of trapped CdS with gaseous HCl at elevated temperatures demands for the use of an autoclave, which suffered, however, corrosion from the acid containing vapors. In this article, we describe the exploration of the possibility of using concentrated aquous HCl for convenient conversion for CdS in HDPE at atmospheric pressure in a glass (lined) vessel. We then present the results of a process for extraction of $CdCl_2$ from molten HDPE with 1,4-butanediol (BDO), which is not miscible with HDPE but is a good solvent for $CdCl_2$. Finally, a simple model for a description of the extraction process is presented. The model considers the extraction process to be a series combination of diffusion of $CdCl_2$ through HDPE to the BDO dispersed in molten HDPE, and transport of the BDO dispersion from HDPE melt to excess BDO.

The mechanochemical degradation of the HDPE into lower molecular weights is estimated by measuring the melt flow index (MFI).

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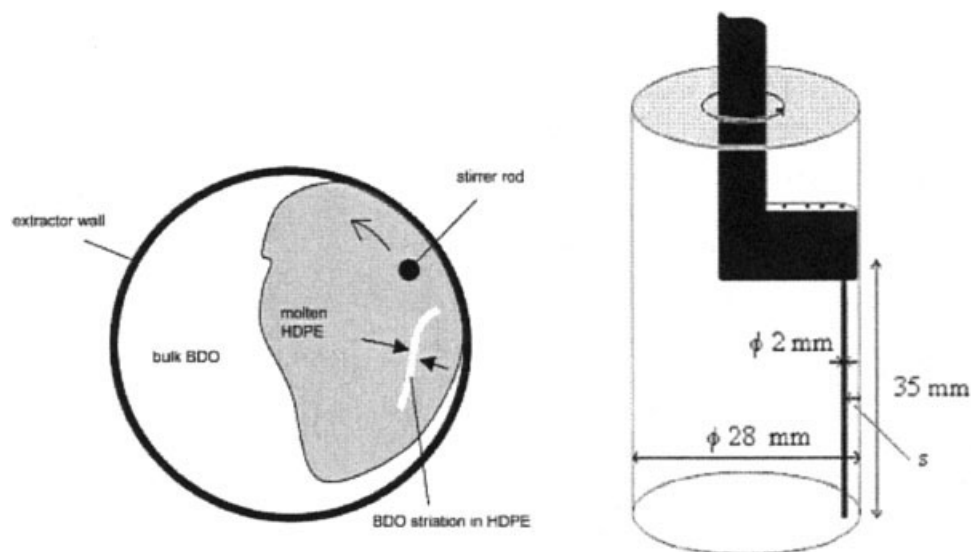
Figure 1 Schematic view of the extractor. On the left the mixing of molten HDPE (containing $CdCl_2$) with BDO in a cylindrical vessel with eccentric stirrer device (schematic overview on the right).

Theory

Chemical conversion

Jellinek and Podjaski[6] described the conversion of CdS with gaseous HCl:

$$CdS \ (s) + 2 \ HCl \ (g) \rightarrow CdCl_2 \ (s) + H_2S \ (g)$$
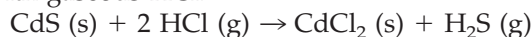
While this reaction is expected to proceed rapidly in bulk, conversion of CdS trapped in HDPE is likely to be controlled by diffusion of HCl in the HDPE matrix. At 20°C, a diffusion coefficient of gaseous HCl (D_{HCl}) in HDPE, of 8×10^{-11} m² s⁻¹ has been reported.[7] The time scale of diffusion in a spherical HDPE particle of radius r can be estimated from dimensionless time (F_o) corresponding to 99% of the HCl concentration at equilibrium.[8]

$$F_o = \frac{D \ t}{r^2} = 0.4 \qquad (1)$$

Diffusion in a polymer matrix

The diffusion coefficient of $CdCl_2$ in an HDPE matrix can be determined by examining the rate of removal of $CdCl_2$ from one surface of a HDPE plane sheet (thickness l) into surrounding solvent. For a dimensionless time, $F_o < 0.1$, i.e., the HDPE sheet can be considered semi-infinite. The extracted fraction of $CdCl_2$ can be equated as:[9]

$$\frac{M_t}{M_\infty} = 2 \sqrt{\frac{Dt}{\pi l^2}} \qquad (2)$$

where M_t is the amount of the diffusing component desorbed in time t and M_∞ is the amount of desorbed $CdCl_2$ after infinite time.

Modeling extraction of $CdCl_2$ from HDPE using BDO

We here consider a process for extraction of $CdCl_2$ from HDPE matrix into BDO. Note that BDO is immiscible with HDPE and that $CdCl_2$ is well soluble in BDO. Since diffusivities in solid polymers are low, eqs. (1) and (3) suggest that acceptable rate of transfer of $CdCl_2$ from HDPE into BDO can be achieved from small diffusion lengths in the polymer, and for large HDPE–BDO specific interfacial areas. This can possibly be achieved by making a fine dispersion of HDPE in BDO. However, enabling $CdCl_2$ diffusion out of solid HDPE within 1 h demands particle size less than 6 μm, and HDPE grinding up to this dimension would economically be hardly possible on a large scale. Alternatively, molten HDPE could be emulsified in BDO, perhaps with the aid of surfactants. However, we found that the high elasticity of HDPE melt and large viscosity difference with BDO did not allow the making of such a dispersion even with a rotor stator ultraturrax®. In the rotor stator ultraturrax, the HDPE melt tended to migrate to and remain permanently in relatively low shear regions of the system.

We therefore consider mixing of molten HDPE with BDO to disperse part of the BDO into the molten HDPE, and thus provide elongation, shear, and break up for large interfacial area for $CdCl_2$ transfer from the molten HDPE phase. This is shown schematically in Figure 1. Interfacial area generation and diffusion

have been long recognized as primary mechanisms for mixing.[10] If more BDO is used than the amount that can be dispersed (encapsulated) as droplets (or striations) in molten HDPE, an efficient macromixing of the molten HDPE (containing encapsulated BDO) with this excess BDO would result in continuous circulation of the BDO droplets into and out of the molten HDPE. So renewal of the molten HDPE interface with the encapsulated BDO will be ensured. A BDO droplet, once dispersed in the molten HDPE, will undergo striation and will spend a time (defined by a time constant τ_{mm}) within the molten HDPE, before being mixed up with the bulk BDO. Because of this exchange, the dispersed BDO and the nondispersed BDO will be in a dynamic equilibrium. Once encapsulated in the HDPE phase, the BDO striations will receive $CdCl_2$ by diffusion from the surrounding HDPE, and transport this $CdCl_2$ to the bulk BDO. So, the $CdCl_2$ mass transfer from HDPE to the bulk BDO can be considered as a series combination of two steps: the diffusion of $CdCl_2$ from the HDPE into the encapsulated BDO striations, followed by the transport of the $CdCl_2$ containing dispersed BDO phase to the bulk BDO. Both processes can be regarded as a first order process. In analogy with the two resistances in series concept,[11–13] the first order time constant of the overall $CdCl_2$ mass transfer process from the molten HDPE to the bulk BDO can be equated as:

$$\tau_{tot} = \frac{1}{k_{diff}\, a} + \tau_{mm} \qquad (3)$$

where we have neglected the contribution of transfer of $CdCl_2$ from HDPE through its direct interface with the bulk BDO. In eq. (3), $k_{diff} \times a$ stands for the volumetric mass transfer coefficient, a is the specific interfacial area between the molten HDPE and the dispersed BDO, and k_{diff} is the mass transfer coefficient, as described by penetration theory[14]:

$$k_{diff} = 2\sqrt{\frac{D}{\pi t_{exp}}} \qquad (4)$$

where D (m^2/s) is the diffusion coefficient of $CdCl_2$ in molten HDPE and t_{exp} (s) is the time of the diffusion process over which the mass transfer coefficient is evaluated. The cadmium chloride concentration profile in time is shown qualitatively in Figure 2. We take t_{exp} to be the same as τ_{mm}, the time spent by the BDO striations in the molten HDPE.

EXPERIMENTAL

Materials

HDPE (Stamylan 9089, DSM) pellets with CdS were obtained from Schoeller Wavin Systems NV, and the following characteristics were determined at TNO: M_n
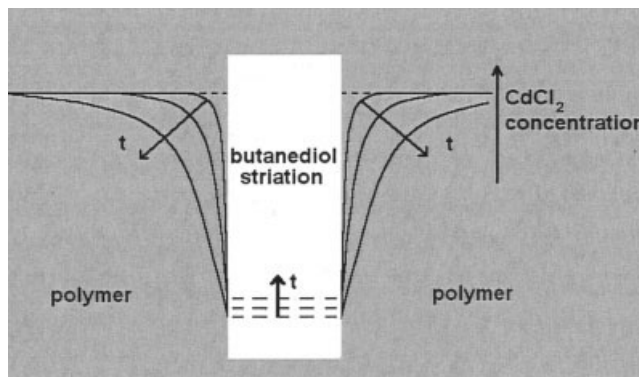
Figure 2 Qualitative view of the concentration profiles of $CdCl_2$ in a polymer sheet in contact with dispersed 1,4-butanediol at different times, t $\left(F_o = \dfrac{Dt}{l^2} < 0.1\right)$. The $CdCl_2$ profiles are shown in the polymer phase (solid line) and the BDO phase (dotted line).

= 15,000 g/mol, Cd content 1200 ppm, Zn content 260 ppm.

Hydrochloric acid (HCl, 37%), sulfuric acid (H$_2$SO$_4$, 98%), hydrogen peroxide (H$_2$O$_2$, 35%), 1,4-butanediol (BDO, HO(CH$_2$)$_4$OH, 99%), and Thymol Blue (C$_{27}$H$_{30}$O$_5$S, 95%) were obtained from Aldrich (The Netherlands). Cadmium-standard (CdCl$_2$ in H$_2$O, Titrisol) was obtained from Merck (The Netherlands). The chemicals were used as received.

Chemical conversion of CdS in polymer matrix to CdCl$_2$

HDPE pellets containing CdS were ground to a sieve size of 500 μm. The powder obtained (100 g) was introduced in a round-bottom flask (500 mL), immersed into a preheated oil-bath (53°C). Hydrochloric acid (200 mL) was added and the mixture was stirred at 250 rpm. After half an hour, the polymer was filtered off, washed with water, and dried in air.

Atomic absorption spectroscopy

Cadmium concentrations of solutions were determined by atomic absorption measurements carried out with a Schimadzu AA 6200 AAS-spectrometer. Calibration was first carried out with samples of different accurately known Cd-concentrations, obtained by dilution of the Cd standard in 0.1M HCl. Unknown samples were diluted with a 0.1M HCl solution in a volumetric flask and examined by atomic absorption spectroscopy (AAS). The results are presented in terms of cadmium concentration based on weight of the polymer.

UV-Vis spectroscopy

CdS in polymer

Polymer powder was compression molded (Collin, Presse 300G) for 1 min into 500-μm thick films at

180°C. The absorption of this film was measured with UV-Vis spectroscopy, using a Schimadzu UV-3102 PC UV-Vis-NIR scanning spectrophotometer.

Dye concentration in BDO

The concentration of Thymol blue in BDO solutions was determined measuring with UV-Vis spectrometry, using Schimadzu UV-3102 PC UV-Vis-NIR scanning spectrophotometer. For calibration, samples of known concentration of dye (Thymol Blue, maximum concentration: 2.6×10^{-5} mol/L) in BDO were prepared and their absorption was measured at 620 nm. The extinction coefficient was 3.36×10^4 L mol^{-1} cm^{-1}. The absorption of unknown samples was measured directly.

Extraction of CdCl$_2$ from HDPE

The extraction was carried out in a cylindrical vessel (i.d. = 28 mm, length = 200 mm), equipped with an inlet and an electrically driven stirrer. The stirrer was custom made to allow circular motion of a vertical bar around the vessel central axis, at an adjustable clearance from the glass wall (see Fig. 1).

It should be mentioned that using a standard stirrer, such as an anchor or helical ribbon, leads to very little dynamic contact between HDPE and BDO, because the viscous HDPE migrates to region far from the impeller zone of the extractor. The stirrer configuration applied was designed to minimize the volume of low shear zones near the extractor wall and to utilize gravity effects (large H/D) to keep the polymer for climbing, and to allow eccentric motion of the vertical stirrer bar to provide a large span even when using moderate speeds and a small stirrer surface. This system was also chosen, because it allows visible observation of the extraction process and easy sample collection.

Dried polymer powder (10 g) from the conversion experiment was introduced into the extractor immersed in a preheated oil bath (200°C). The powder was first melted. After melting, preheated BDO (30 mL, 200°C) was added. Stirring was started at the desired speed, allowing dynamic contact between the molten polymer phase and the BDO phase. Samples, with an accurately known volume between 0.5 and 1 mL, of the bulk BDO phase were withdrawn at time intervals of at least 30 s and analyzed with AAS for cadmium concentration. At the end of the experiment, the polymer phase was subjected to cadmium analysis.

Determination of cadmium in HDPE

The cadmium concentration in the polymer was determined according to the European Standard EN-1122. The polymer (0.5 g) was degraded with sulfuric acid (10 mL) and hydrogen peroxide (20 mL) under reflux until no suspended organic matter remained. The solution was analyzed on cadmium concentration with AAS.

Determination of macromixing characteristics

HDPE pellets (Stamylan 9089, 10 g) were placed in the extractor (200°C). Preheated (200°C) BDO (30 g) containing dye (Thymol Blue, 4.5 mg) was added. Mixing was carried out for 5 min at 125 rpm with a rod-wall clearance of 3 mm, allowing dynamic contact between the polymer and the dispersed BDO in the polymer phase. After the 5 min of mixing, the bulk BDO phase was poured out, allowing the polymer phase to solidify. The amount of the colored BDO dispersion in the polymer phase was determined by weighing. This solidified HDPE containing colored BDO dispersion was again introduced into a fresh extractor and melted (200°C). Fresh, preheated (200°C) BDO (60 mL) was added and stirring was started at the desired stirrer speed, allowing the dyed BDO to be transferred from the dispersed to the bulk BDO phase. Samples of the bulk BDO phase were withdrawn at desired time. These samples were analyzed for dye concentration with UV-Vis spectrometry.

Estimation of the diffusion coefficient of CdCl$_2$ in the molten polymer in contact with BDO

Dried polymer powder from the conversion experiment containing CdCl$_2$ was compression molded (Collin, Presse 300G) into films for 1 min at 180°C. A square (40×40 mm^2) sample was cut and weighed to calculate the thickness of the film. A typical thickness of the film is 1 mm. This sample was melted on an aluminum sheet and placed horizontally on a stand mounted in a preheated (200°C) conical flask. Preheated BDO (200°C) was added and stirred with a magnetic stirrer bar below the stand. BDO samples containing CdCl$_2$ were withdrawn at desired time intervals and subjected to cadmium concentration determination by AAS.

Melt flow index

MFI measurements were carried out according to the international standard ISO 1133 on a melt flow indexer equipment, Zwick 4106, with automated sampler. MFI was determined by measuring the weight of polymer samples flowing through a 2.09 mm die capillary, under an applied load of 2.16 kg at 190°C in 30 s. From this weight, the mass flow in 10 min (MFI) was calculated.

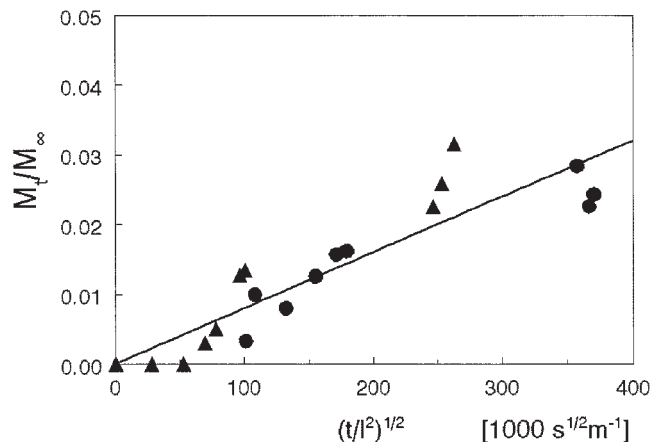## RESULTS AND DISCUSSION

Conversion of CdS in HDPE to CdCl$_2$

Conversion of CdS into CdCl$_2$ by concentrated HCl in the grinded HDPE (500 μm) (see 'Chemical Conversion' in the experimental section) at 53°C for 30 min was visually observed as a color change from bright yellow into white. This was further confirmed by examining the UV-Vis absorption of the CdS bond of HDPE films (thickness 500 μm) obtained after compression molding of the powdered HDPE before and after the conversion of CdS to CdCl$_2$, as well as of virgin HDPE, which is free of cadmium, as shown in Figure 3. For the HDPE sheet containing CdS, visible light absorption at 350–525 nm is clearly observed. According to Malik et al.,[15] this absorption corresponds to presence of CdS. Such absorption is absent for the cadmium containing HDPE sample treated with concentrated HCl, just as for the virgin HDPE sample. Thus, it supports that almost full conversion of CdS in HDPE to CdCl$_2$ was achieved with concentrated hydrochloric acid at 53°C.

Diffusion coefficient

Transport of CdCl$_2$ from the HDPE matrix to dispersed BDO occurs by diffusion of CdCl$_2$ in the HDPE. The diffusion coefficient of CdCl$_2$ in HDPE in contact with BDO is determined by monitoring its transport from a HDPE sheet (thickness l) into sur-
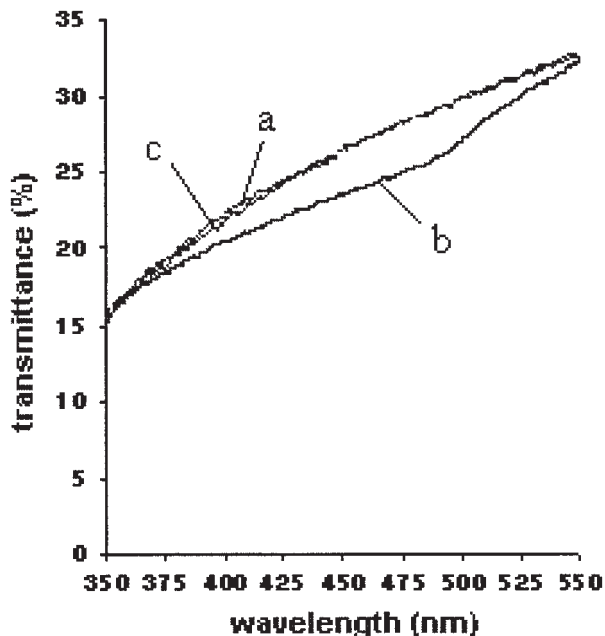
Figure 4 Progress of leaching of CdCl$_2$ from one surface of a flat HDPE sheet into BDO at 200°C. ●: sample thickness = 0.79 mm; ▲: sample thickness = 1.01 mm. Solid line is a least squares linear fit.
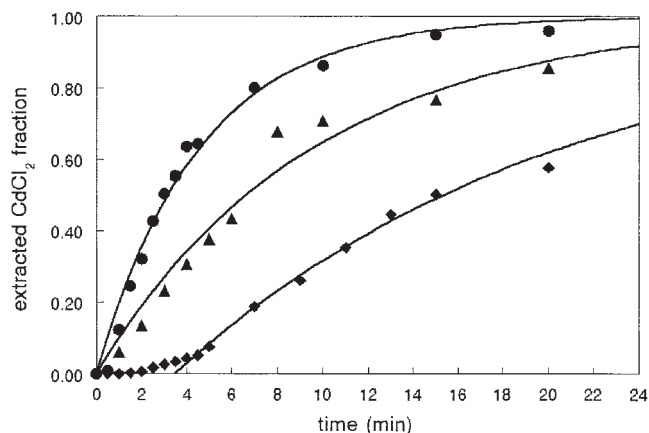
rounding BDO (see 'Estimation of Diffusion Coefficient' in the experimental section). Figure 4 shows the progress (M_t/M_∞) of CdCl$_2$ transport from the polymer sheet into BDO as a function of $\sqrt{\dfrac{t}{l^2}}$. The results in Figure 4 clearly point to a linear relationship of M_t/M_∞ with $\sqrt{\dfrac{t}{l^2}}$, so eq. (2) is applicable. Linear regression of M_t/M_∞ to eq. (2) leads to a slope, $2 \times (D/\pi)^{1/2} = 0.8 \times 10^{-7}\mathrm{s}^{1/2}\mathrm{m}^{-1}$ and a diffusion coefficient of CdCl$_2$ in HDPE of 0.7×10^{-14} m^2/s.

Extraction of CdCl$_2$

The HDPE powder containing CdCl$_2$ from the conversion experiment was molten and dynamically contacted with BDO at 200°C, using a special designed stirrer described in 'Extraction of CdCl$_2$ from HDPE' in the experimental section. The time history of the fraction (x) of CdCl$_2$ extracted from HDPE into the bulk BDO phase is shown in Figure 5 for three stirrer speeds. In the experiments collected in Figure 5, the distance between the vessel wall and the vertical bar of the stirrer was maintained at 3 mm. The solid lines are the results of fits of observed values of extracted CdCl$_2$ fraction (x) to eq. (5), in which τ_{tot} is the overall time constant for mass transfer, see eq. (3).[11]

$$x = 1 - e^{-t/\tau_{\mathrm{tot}}} \tag{5}$$

The extracted CdCl$_2$ fraction (x) for experiments at stirring speeds of 125 and 100 rpm could directly be fitted to eq. (5). The data for the experiment performed at an impeller speed of 50 rpm shows some delay at the start and allows fitting when accounting for a delay time $\tau_d = 3.5$ min as follows:
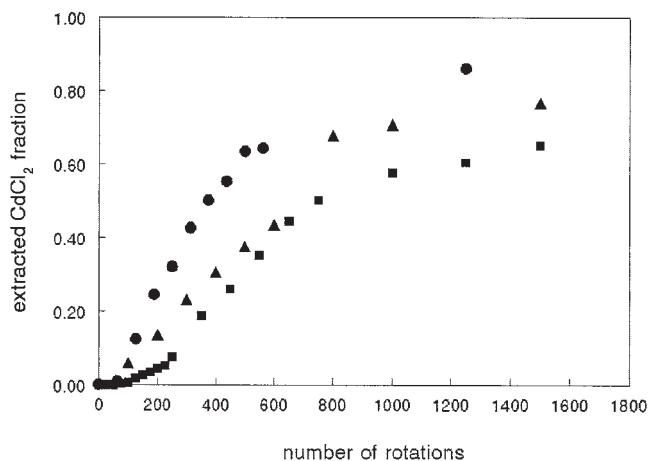

Figure 3 UV-Vis absorption of 0.5 mm thick HDPE sheets made from (a) virgin HDPE, (b) HDPE containing CdS, and (c) HDPE that originally contained CdS, after treatment with conc. HCl.

Figure 5 Progress of CdCl$_2$ extraction from HDPE matrix into bulk BDO at various stirrer speeds ●: 125 rpm; ▲: 100 rpm; ◆: 50 rpm. Solid lines are least squares fits to eq. 5 (● and▲) and 6 (◆). Clearance between stirrer rod and wall is 3 mm.

Figure 6 Progress of CdCl$_2$ extraction from HDPE matrix into bulk BDO, as a function of the number of rotations of the stirrer, at different stirring speeds. ●: 125 rpm; ▲: 100 rpm; ■: 50 rpm.

$$x = 1 - e^{(-t-\tau_d)/\tau_{tot}} \quad (6)$$

The so obtained values of the time constants of the CdCl$_2$ extraction process are collected in Table I.

We infer from Figure 5 that for the 125 rpm case, 91% of the CdCl$_2$ can be extracted in 12 min, reducing the Cd concentration in HDPE to a legally permissible value of 100 ppm. Figure 5 clearly demonstrates that higher stirrer speeds improve the performance of the extraction, as is also inferred from the decreasing value of the time constant τ_{tot}, see Table I. Investigations with higher impeller speeds than 125 rpm were hampered by this slipping of the polymer at the wall and its rotation as a lump, thus decreasing the effectiveness of the mixing process. An analogy could be found with the wall slip at higher shear stresses, a well known phenomenon in polymer melt processing.[16] The start-up delay of 3.5 min for the 50 rpm (see Fig. 5), could be due to a much lower rate of dispersing BDO into the polymer matrix. Thus, the development of a sufficient interfacial area for CdCl$_2$ transfer from

polymer matrix to dispersed BDO takes time, retarding the initial extraction rate. Following this delay, the extraction for the 50 rpm case can also be described as a first order process.

Thus, there appears to be an optimum stirrer speed for this extractor/stirrer configuration. Alternative stirrer configurations that can potentially be more efficient are kneaders and extruders, albeit with the additional operating considerations due to the low viscosity and the volatility of BDO.

It is interesting to examine if higher efficiency at higher stirring speeds can be attributed to a higher extent of shear. In Figure 6, the extracted CdCl$_2$ fraction is replotted as a function of number of stirrer rotations. Note that the number of stirrer rotations is a measure for the strain imposed on the system. A tendency of higher CdCl$_2$ fractions extracted at higher stirring speeds at the same imposed strain, even with the corresponding decrease in time available for CdCl$_2$ diffusion into striations, suggests the possible role of enhanced interfacial area of the dispersion of the BDO droplets in the polymer at higher shear rate.

TABLE I
Time Constants for Transport of CdCl$_2$ from HDPE Sheets into Bulk 1,4-Butanediol for Various Stirrer Speeds

Stirring speed (min)	τ_{tot}[a] (min)	τ_{mm}[b] (min)	$1/k_{diff} \times a$[c] (min) from eq. (4)	k_{diff}[d] (m s^{-1}) from eq. (5)	a_{cal}[e] (m2/m3) from eqs. (4) & (5)	V_{but}[f] (cm^3)
50	17.1	4.5	12.6	5.8×10^{-9}	2.2×10^5	2.01
100	9.6	2.5	7.1	7.7×10^{-9}	3.1×10^5	2.36
125	4.8	2.2	2.6	8.2×10^{-9}	7.7×10^5	2.32

[a] Total time constant (τ_{tot}) from exp. data, see Figure 5.
[b] Marcomixing time constant (τ_{tot}) from exp. data, see Figure 6.
[c] Diffusion time constant ($\tau_{diff} \times a$) from eq. (3).
[d] Mass transfer coefficient of diffusion (k_{diff}) was calculated from penetration theory, see eq. (4) with D = 0.7×10^{-14} m^2/s.
[e] a_{cal} is the calculated specific interfacial area between HDPE and 1,4-butanediol, see eqs. (4) and (5).
[f] V_{but} is the amount of incorporated 1,4-butanediol in 10 g of HDPE.
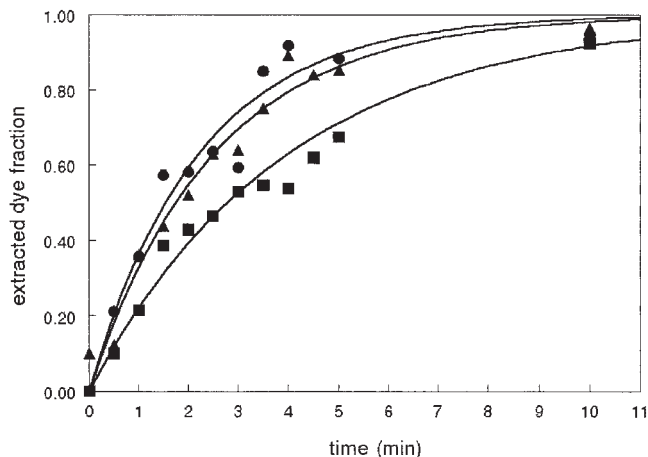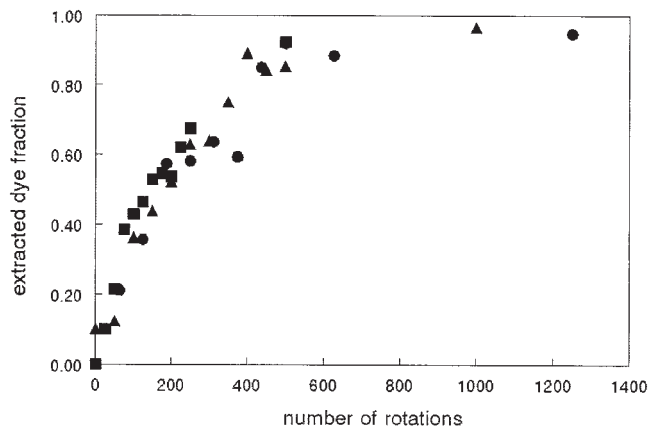
Figure 7 Progress of the transport of dyed BDO from dispersion in HDPE to bulk BDO, at various stirring speeds ●: 125 rpm; ▲: 100 rpm; ■: 50 rpm. Solid lines are fits to eq. (5), with $\tau = \tau_{mm}$. Clearance between rod and wall was 3 mm.

Macromixing characteristics

One of the steps involved in the $CdCl_2$ extraction from the HDPE matrix is macromixing, i.e., the transport of dispersed BDO from the molten HDPE to the bulk BDO. Since the mixing process is rather complex. We resorted to only a determination of a time constant τ_{mm} for the macromixing. Values of τ_{mm} for different impeller speeds are determined by dispersing dyed BDO into the HDPE matrix and then analyzing its transport to bulk BDO phase (see 'Determination of Macromixing Characteristics' in the experimental section). Figure 7 shows the progress of transport of the dyed BDO to the bulk BDO, for three different stirring speeds, while maintaining the stirring rod separation from the extractor wall at 3 mm. The results demonstrate a faster transport of the dye at higher stirring speeds. The experimental results are fitted with a first order process description, see eq. (5), with x now representing the dye extracted as a fraction of the initial amount of dye dispersed as BDO solution into HDPE. The corresponding time constants (τ_{mm}) are collected in Table I. The higher values of τ_{tot} as compared to τ_{mm} for all cases as shown in Table I indicate strong contribution of the resistance to $CdCl_2$ diffusion through the HDPE to the BDO trapped in HDPE as striations. Also, the importance of a large contact area between BDO and HDPE is clear when looking at the interfacial area (Table I), calculated from the model (eqs. (3), and (5)).

The results of the extracted dye fraction are replotted in Figure 8 as a function of the number of rotations of the stirrer, representing the extent of strain. The curves for the different stirrer speeds are not significantly different. So the results in Figure 8 indicate that the mass transfer process involving transport of the BDO encapsulations to the bulk BDO is determined by the strain imposed on the system.
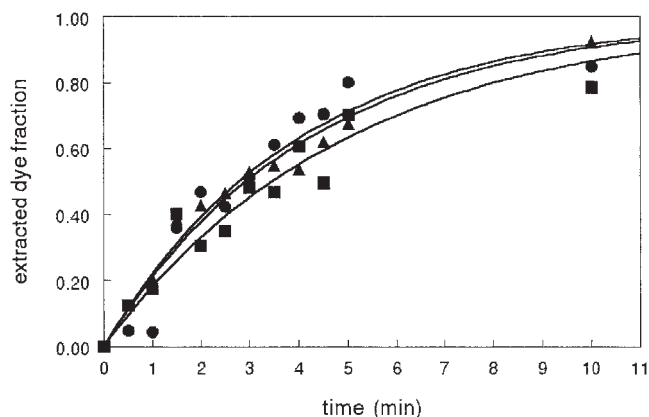

Figure 8 Progress of transport of dyed BDO from dispersion in HDPE matrix to bulk BDO, as a function of number of rotations of the stirrer, at different stirring speeds. ●: 125 rpm; ▲: 100 rpm; ■: 50 rpm.

Figure 9 shows the effect of the clearance between the stirrer rod and extractor wall, on the progress of transport of colored BDO from the polymer matrix to the bulk BDO at a stirring speed of 50 rpm. The results demonstrate that the dependence is rather small, though a slightly higher transfer rate is indicated for smaller clearances between rod and wall, corresponding to higher shear rate.

Cadmium content in HDPE following $CdCl_2$ extraction

We confirmed the extraction of $CdCl_2$ by the direct measurement of cadmium left in the polymer. This was carried out by degradation of polymer matrix with concentrated acids followed by measurement with AAS (see 'Determination of Cadmium in HDPE' in the experimental section). While the cadmium con-

Figure 9 Progress of transport of dyed BDO from polymer matrix dispersion to bulk BDO phase, for various clearances between stirrer rod and extractor wall ●: 1 mm; ▲: 3 mm; ■: 8 mm. Solid lines are least squares fits to eq. (5).

TABLE II
Cadmium Concentration and Melt Flow Index (190°C, 2.16 kg) of HDPE During the Several Process Steps for the Extraction Case of 125 rpm, Time, 30 min, and Clearance, 3 mm

	Cadmium concentration (ppm)	Melt Flow Index (g/10 min)
Before conversion	1216	6.2
After conversion	1128	6.3
After extraction	76	8.0

tent in the initial CdS-containing HDPE was found to be 1216 ppm (based on polymer matrix), the corresponding Cd concentration in the HDPE after conversion to $CdCl_2$ was found to be 1128 ppm. So extraction of up to 88 ppm Cd occurred during conversion of CdS into $CdCl_2$ with hydrochloric acid (see 'Chemical Conversion' in the experimental and results and discussion sections). When the HDPE sample was analyzed following $CdCl_2$ extraction at 125 rpm for 1 h, the corresponding Cd concentration was found as low as 76 ppm. This confirms the observations of Figure 5 that most of the $CdCl_2$ was effectively extracted by efficient mixing with BDO. Table II gives an overview of the cadmium concentration during the several process steps.

Melt flow index

Considering the possible degradation of HDPE during the HCl acid treatment and the subsequent extraction with BDO, it is interesting to evaluate the recycling potential of the HDPE after the removal of cadmium. We estimated the mechanochemical degradation into lower molecular weights by measuring the MFI (see 'Melt Flow Index' in the experimental section), which is a measure of flow rate (and hence inverse molecular weight) during a standard capillary flow under pressure flow.[2] The somewhat higher MFI (8.3 g/10 min) of the HDPE after extraction (see Table II) as compared to the starting HDPE (MFI = 6.3 g/10 min) indeed points to some degradation. However, this

MFI is acceptable for a range of possible recycling applications.

CONCLUSIONS

The insoluble pigment cadmium sulfide in HDPE matrix was easily converted into $CdCl_2$ by treatment with concentrated hydrochloric acid. Grinding the HDPE reduces the diffusion length and therefore reduces the time taken for complete conversion by the diffusion-limited reaction at 53°C to less than half an hour. Extraction of the $CdCl_2$ from the molten HDPE into BDO could be carried out by partly dispersing the two phases at 200°C. Using this procedure, more than 90% of the Cd can be removed in 12 min when working on a 0.125 L scale. The MFI of the HDPE after extraction (8.3 g/10 min) as compared to the starting HDPE (6.3 g/10 min) shows some extent of degradation. However, the MFI is acceptable for HDPE recycling.

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