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Alkaline hydrolysis of PVC-coated PET fibers for simultaneous recycling of PET and PVC

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Abstract Polyvinyl chloride (PVC)-coated poly(ethylene terephthalate) (PET) woven fibers are one of the hardest-to-recycle polymeric materials. Herein we investigate the possibility of recycling both PVC and PET through alkaline hydrolysis of PET. The coated woven fabrics were treated with NaOH, hydrolyzing the PET fibers into water-soluble sodium terephthalate, while the PVC could be removed by filtration. The PET fibers were completely hydrolyzed between 120 and 180 °C in the presence of 1 M NaOH solution, quantitatively yielding terephthalic acid. A minimum PVC dechlorination rate of 1% was simultaneously achieved at 120 °C. Furthermore, no alkaline hydrolysis of the plasticizer contained in the PVC, di(2-ethylhexyl)phthalate, was observed. Thus, the possibility of simultaneously recycling PET and PVC from PVC-coated woven fabrics was demonstrated. Kinetic analyses of PET hydrolysis and PVC dechlorination revealed that the simultaneously occurring reaction processes did not affect the progress of each other. Thus, the absence of interactions between PET, PVC, or their degradation products enables the design of a simplified recycling process without considering the interactions between the materials derived from coated woven fabrics.

Keywords Feedstock recycling · Hydrolysis · Kinetics · PET · PVC

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Introduction

Fabrics woven from poly(ethylene terephthalate) (PET) fibers and coated with a layer of polyvinyl chloride (PVC) are commonly used as ceiling materials for large dome structures or storehouses because of their high durability and low weight compared with standard building materials such as gypsum board, which can weigh forty times as much as the woven fabrics. The PET fibers provide tensile strength, dimensional stability, and flexibility [1], while the PVC imparts excellent features such as weatherability and durability. In Japan, Article 39 of the Order for the Enforcement of the Building Standards Act has required improved safety measures against ceiling collapse [2]; therefore, the demand for lightweight coated woven materials is expected to rise. Consequently, increased amounts of coated fabric waste will be generated in the future. Unfortunately, most of this will be sent to landfills or incinerated.

Waste plastics are treated by mechanical recycling, feedstock recycling, energy recovery, incineration without any recovery, and landfilling. This hierarchy is a fundamental policy for treating waste plastics. Mechanical recycling is the best way to retain the advantageous features of plastics, although it is limited to well-separated high-purity waste plastics. In the case of coated woven fabrics, the PET fibers and PVC coating are adhered together, which makes their separation by physical

crushing difficult. Furthermore, the similar densities of PET (1.380 g cm^{-3}) and PVC (1.385 g cm^{-3}) [3] preclude their effective physical separation by flotation.

Pyrolysis is one option for converting polymers into useful gases, liquids, and/or solids at high temperatures in the absence of oxygen. This process cleaves various chemical bonds in polymers and additives solely by the action of heat, which is advantageous for low-purity waste that cannot be treated by mechanical recycling. However, the pyrolysis of PVC and PET resins tends to suffer from problems such as the corrosion and clogging of the treatment facilities [4, 5], as well as the production of undesirable chlorinated organic compounds [6, 7]. Thus, the pyrolysis of these two polymers does not yield useful products. Blast furnace reduction and coke oven treatments are also categorized as feedstock recycling methods in Japan. However, since these processes limit the chlorine content in the plastics, a dechlorination pretreatment would be necessary for PVC-containing materials.

Energy recovery or incineration without any recovery also generates corrosive HCl from PVC. The formation of hazardous polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) during the incineration of PVC at lower temperatures (e.g., 300 °C) in the presence of CuO has been reported [8]. Landfilling produces no benefit for the environment. Thus, PVC-coated PET fibers can be considered one of the most difficult-to-recycle polymeric materials.

To overcome these obstacles, the separation of PET and PVC by dissolution of the PVC using organic solvents has been reported. PET is resistant to attack from most solvents, while PVC is fairly soluble in many common organic solvents. The undissolved PET fiber is recovered by filtration and the PVC is recovered by the evaporation of the solvent. The Vinyloop® process makes use of methyl ethyl ketone (MEK) as the solvent and is also suitable for the recycling of PVC-coated fabrics; in this case, it is called the Texyloop® process [9]. Grause et al. [10] reported the relationship between the solubility parameters of 30 solvents and the separation efficiency of PVC and PET, which is a helpful guide for determining a suitable solvent. These processes enable the simultaneous recovery of high-purity PVC and PET. However, since they also require large volumes of organic solvents, few recyclers are available with sufficient capacity, and the secondary problem of treating the organic solvents must be considered.

Here, we report a new approach for the recycling of both PET and PVC through the alkaline hydrolysis of PET using NaOH solution, which does not require organic solvent use. The hydrolysis of PET in the presence of NaOH produces water-soluble sodium terephthalate (Na$_2$TP), allowing the separate recovery of the PVC as a solid by filtration. The Na$_2$TP is neutralized by acid, yielding terephthalic acid

(TPA), the monomer of PET. The hydrolysis of PET is a mature reaction process that has been widely investigated under neutral [11–14], basic [15–18], and acidic [19–21] conditions. On the other hand, it may be expected that the OH$^-$ in the solution will also dechlorinate PVC by nucleophilic attack [22, 23] during PET hydrolysis. This would negatively affect the recycling efficiency of the PVC resin, although it positively impacts other feedstock recycling processes such as liquefaction, gasification, and blast furnace reduction. To the best of our knowledge, there is no report on the recovery of TPA and PVC resin from coated woven fabrics using alkaline hydrolysis. Furthermore, there is no information on the influence of PET, PVC, and their decomposition products (e.g., Cl$^-$) on the alkaline hydrolysis of PET or the dechlorination of PVC.

In this work, PVC-coated PET fibers were treated with NaOH solution between 120 and 180 °C in a batch reactor. We first evaluated the possibility of the simultaneous recovery of TPA and PVC on the basis of the TPA yield, PVC dechlorination rate, and plasticizer leaching rate from PVC. Next, kinetic analyses of PET hydrolysis and PVC dechlorination were performed using the master curve and model-fitting methods to investigate any interactions between PET and PVC. For comparison, a mixture of PET flakes and PVC powder, as well as pure PET flakes, were tested under the same conditions as the coated woven fabrics.
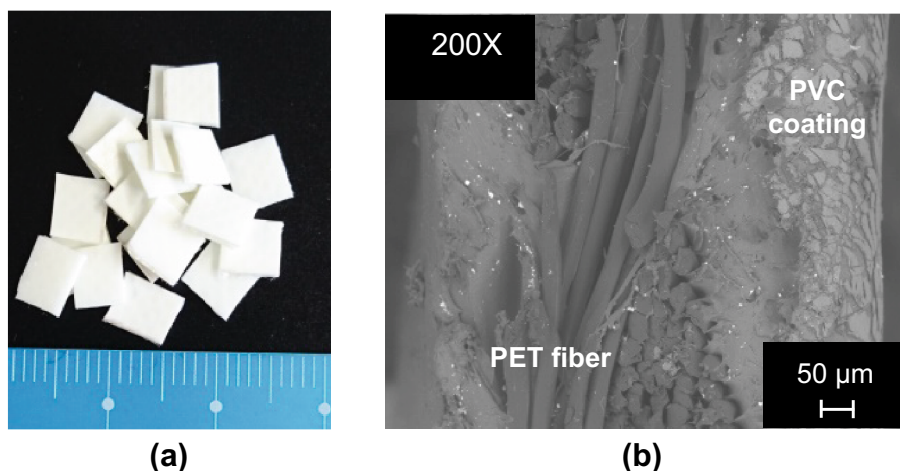
Experimental

Materials

Coated woven fabrics provided by the Taiyo Kogyo Corporation (Osaka) were cut into 5.0 mm × 5.0 mm pieces (Fig. 1a). The thickness of the sample was 0.5 mm. They consisted of PET woven fibers covered with a layer of PVC, and therefore, the PET fibers were only exposed at the cut surface (Fig. 1b). The thickness of the sheets was about 0.5 mm. The PVC coating included di(2-ethyl-hexyl)phthalate (DEHP) as a plasticizer and other additives such as TiO$_2$ pigment. The sample consisted of 40.5 ± 0.7 wt% PVC, 30.0 ± 1.2 wt% PET, 20.5 ± 0.6 wt% DEHP, and 9.0 ± 0.2 wt% other additives [10].

A mixture of bottle PET (5 mm × 5 mm pieces) and PVC powder (PET/PVC), and bottle PET alone (5 mm × 5 mm pieces) were used for comparison with the coated woven fabrics. The PVC powder and other chemicals were purchased from Kanto Chemical Co., Inc. (Tokyo).

Alkaline hydrolysis tests

Alkaline hydrolysis was carried out in a 5 mL stainless steel batch reactor. The inner reactor wall was deactivated

Fig. 1 a PVC-coated PET fibers (5.0 mm × 5.0 mm pieces). **b** SEM image of the cut surface of the PVC-coated PET fibers

by pretreatment with H_2O_2 before the experiments. Then, the coated woven fabrics (0.4 g), PET/PVC [0.28 g, (0.12 g PET + 0.16 g PVC)], or PET (0.12 g) and 1 M NaOH solution (2.5 mL, PET:NaOH molar ratio = 1:4) were placed into the reactor. The weights of PET and PVC used comparatively were equivalent to the respective amounts in the coated woven fabrics sample. Then, the air inside the reactor was replaced with argon. The reactor was heated to 120, 150, or 180 °C by immersion into a silicone oil bath, and held for the desired reaction time. The reaction time did not include the period required for the vessel to come to the desired temperature. After terminating the experiments, the reactor was quenched by immersion in a water bath. The inside of the reactor was washed with deionized water, and the unreacted solid was filtered and washed with deionized water. The filtrate, containing Na_2TP, was neutralized with 1 M H_2SO_4 solution to precipitate TPA. The precipitated TPA was filtered, washed with deionized water, and dried overnight at 40 °C in a vacuum dryer.

The recovered TPA was analyzed by elemental analysis, proton nuclear magnetic resonance spectroscopy (^{1}H-NMR), Fourier-transform infrared spectroscopy (FT-IR), and thermogravimetric analysis (TG). The detailed analytical conditions are summarized in the Supporting Information. The unreacted coated woven fabrics were weighed and examined by scanning electron microscopy (SEM). The DEHP remaining in the unreacted coated woven fabrics was quantified via Soxhlet extraction following our previous report [24]. The Cl^- content in the solution due to dechlorination was quantified by ion chromatography (DX-120, DIONEX, column: AS-12A, suppressor: ASRS-ULTRA II 4 mm, eluent: 3.5 mM Na_2CO_3/0.3 mM $NaHCO_3$).

Definitions

The TPA yield, dechlorination rate, and DEHP leaching rate are defined as follows:

$$TPA\ yield\ [\%] = \frac{Weight\ of\ product\ TPA\ [g]}{Weight\ of\ theoretical\ TPA\ in\ the\ sample\ [g]} \times 100\%$$

$$(1)$$

$$Dechlorination\ rate\ [\%] = \frac{Weight\ of\ dechlorinated\ Cl\ [g]}{Weight\ of\ theoretical\ Cl\ in\ the\ sample\ [g]} \times 100\%$$

$$(2)$$

$$DEHP\ leaching\ rate\ [\%] = \frac{Weight\ of\ leached\ DEHP\ [g]}{Weight\ of\ theoretical\ DEHP\ in\ the\ sample\ [g]} \times 100\%$$

$$(3)$$

Kinetic analysis

Determination of possible kinetic reaction models by master curve method

The PET decomposition rates and PVC dechlorination rates obtained for the coated woven fabrics, PET/PVC, and PET flakes under each set of conditions were fitted to the 15 kinetic models summarized in Table S1 [25, 26]. The models are based on common solid-state reaction models. The master curve method was carried out for each set of conditions to determine the possible reaction models. The integral form of the master curve plot can be expressed as follows:

$$\frac{g(\alpha)}{g(0.5)} = \frac{t}{t_{\alpha=0.5}} \qquad (4)$$

where α is the conversion expressed by $\alpha = x/x_{\mathrm{f}}$, where x and x_{f} are the actual and final TPA yields or dechlorination rates; t is the actual time; $t_{\alpha=0.5}$ is the time corresponding to $\alpha = 0.5$; and $g(\alpha)$ is the integrated form of the kinetic reaction model. The master plot for each reaction model (left side of Eq. 4) was compared with the experimentally determined reduced-time master plot (right side of Eq. 4). This yielded several possible models.

Determination of the three best-fitting models by the model-fitting method

The possible models selected by the master curve method were evaluated further on the basis of the linearity, r_{Model}, and the intercept (error from the origin), $r_{\mathrm{Intercept}}$, of the t versus $g(x)$ plot based on the integrated form of Eq. (5). The model fitting was carried out for the same degradation ranges as those used in the case of the master curve method. The evaluation factors, R_{Model} and $R_{\mathrm{Intercept}}$, were respectively calculated using Eqs. (6) and (7) to improve visualization, where higher values indicate a better fit. Then, the three best-fitting models were selected. The apparent reaction rate constant, k_{app}, was determined from the slope of the t versus $g(x)$ plot, and the apparent activation energy, E_{app}, and pre-exponential factor, k_0, were determined from the Arrhenius plot.

$$g(x) = k_{\mathrm{app}} t \qquad (5)$$

$$R_{\mathrm{Model}} = -\log(1 - r_{\mathrm{Model}}^2) \qquad (6)$$

$$R_{\mathrm{Intercept}} = -\log(r_{\mathrm{Intercept}}^2) \qquad (7)$$

Results and discussion

TPA recovery through alkaline hydrolysis of PVC-coated PET fibers

The alkaline hydrolysis of 5.0 mm × 5.0 mm pieces of coated woven fabrics was performed at different temperatures, as summarized in Fig. 2a. The analytical results and characterization details for the recovered TPA, summarized in Figure S1 in the Supporting Information, verify the recovery of TPA and the absence of phthalic acid which could have been derived from the hydrolysis of DEHP. TPA was recovered from coated woven fabrics in >97% yield at all temperatures, and the decomposition rate was significantly influenced by temperature.

To inspect the morphological changes in the fibers during the course of the hydrolysis reaction, the PVC coating was manually scraped away from one side of the woven fibers and the exposed PET fibers were analyzed by SEM (Fig. 3). After 3 h at 120 °C, woven PET fibers can still be clearly observed (Fig. 3a), but these decreased and grew thinner as PET hydrolysis progressed (Fig. 3b). After 48 h, the fibers had completely decomposed and only the other side of the PVC covering remained (Fig. 3c). Similarly, the PET fibers progressively hydrolyzed and grew thinner at 150 °C (Fig. 3d–f), with PET hydrolysis nearing completion within 24 h. The PET fibers observed after 0.5 h at 180 °C (Fig. 3g) showed many cracks in the fiber surfaces, which were not observed at 120 or 150 °C. Under these conditions, the hydrolysis of the PET fibers was nearly complete after 2 h (Fig. 3h, i).

For comparison, the PET/PVC and PET flakes were hydrolyzed under the same conditions (Fig. 2b, c). The hydrolysis rates of PET/PVC at 120 and 150 °C were
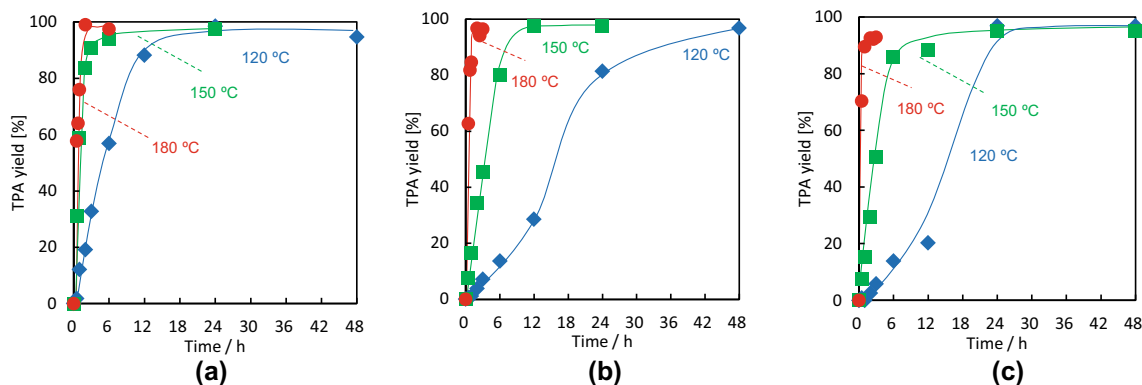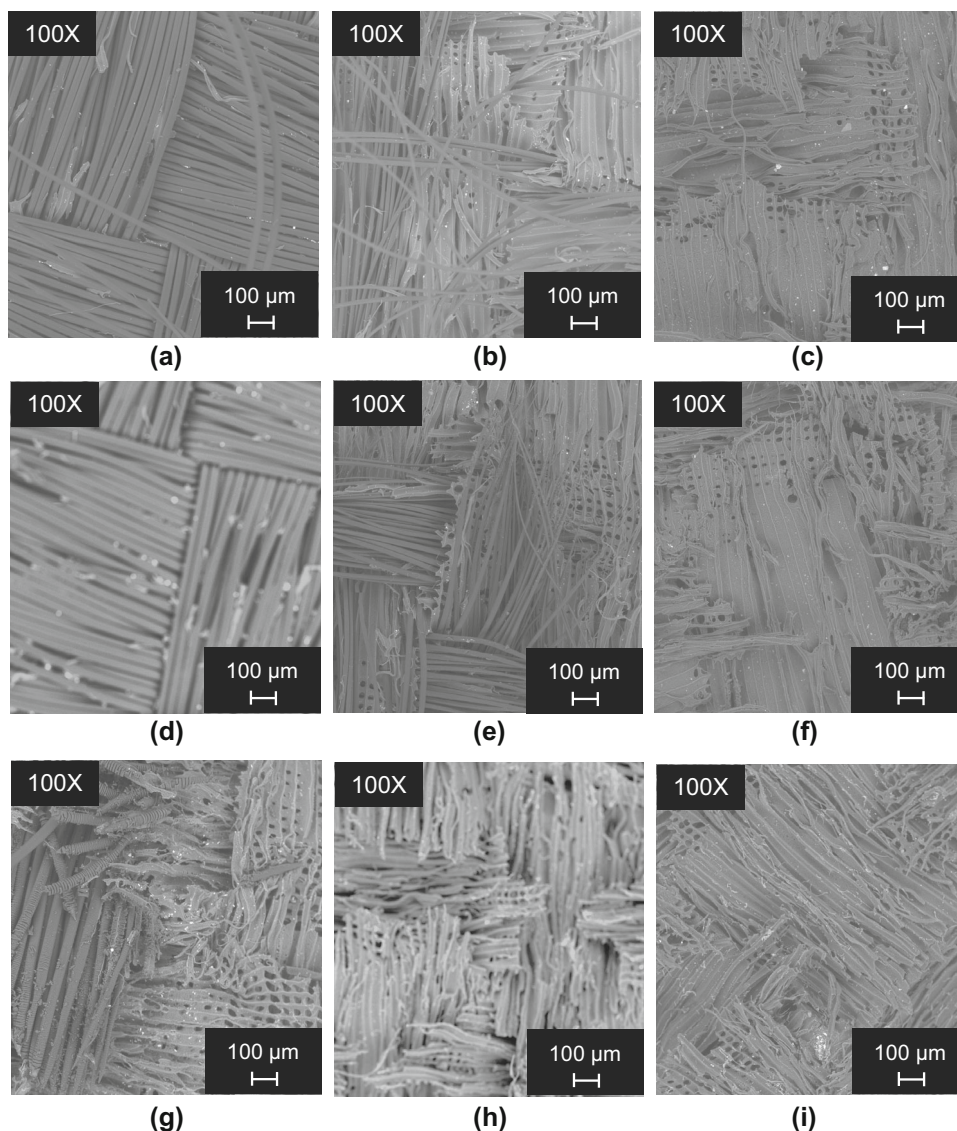

Fig. 2 TPA yields from **a** coated woven fibers, **b** PET/PVC mixture, and **c** PET flakes

Fig. 3 SEM images of recovered woven PET fibers with the PVC coating removed from one side. **a** 120 °C, 3 h, **b** 120 °C, 12 h, **c** 120 °C, 48 h; **d** 150 °C, 0.5 h, **e** 150 °C, 3 h, **f** 150 °C, 6 h; and **g** 180 °C, 0.5 h, **h** 180 °C, 2 h, and **i** 180 °C, 6 h

apparently slower than those observed for the coated woven fabrics, whereas that of the PET/PVC mixture at 180 °C was comparable. This might be due to the different accessibilities of OH⁻ and water to the PET in coated woven fabrics and the PET flakes. We expected that the PET in the coated woven fabrics would initially be more difficult to hydrolyze than in the PET flakes because the PET fibers were covered by PVC. However, the results indicate that OH⁻ and water could effectively penetrate the woven PET fibers, perhaps by filling the fiber interstices. In contrast, no difference was observed between the coated woven fabrics and the PET/PVC mixtures at 180 °C, which may be due to the formation of cracks on the surface of the PET flakes, similar to those observed on the PET fibers (Fig. 3g). Therefore, the hydrolytic advantage of the woven PET in the coated woven fabrics might be equalized by the significant increase in the surface area of the PET flakes

due to crack formation. There was no difference between the PET/PVC and PET flakes, suggesting that alkaline hydrolysis was not influenced by either the PVC or generated Cl⁻. To confirm the lack of influence of Cl⁻ on PET hydrolysis, PET hydrolyses were carried out in 1 M NaOH at 180 °C in the presence and absence of 0.5 M NaCl (Figure S2); no differences were observed.

Dechlorination of PVC

The dechlorination of PVC can occur in the presence of OH⁻ through two known pathways, E2 elimination and S_N2 substitution. The influence of temperature on the dechlorination rate during the alkaline hydrolysis of coated woven fabrics is presented in Fig. 4a. The dechlorination rate significantly increased from 1% when hydrolysis was performed at 120 °C for 48 h to 22% when performed at 180 °C for 2 h. For

Fig. 4 Dechlorination behavior obtained from the hydrolysis of **a** coated woven fabrics and **b** PET/PVC at different temperatures

(a)

(b)
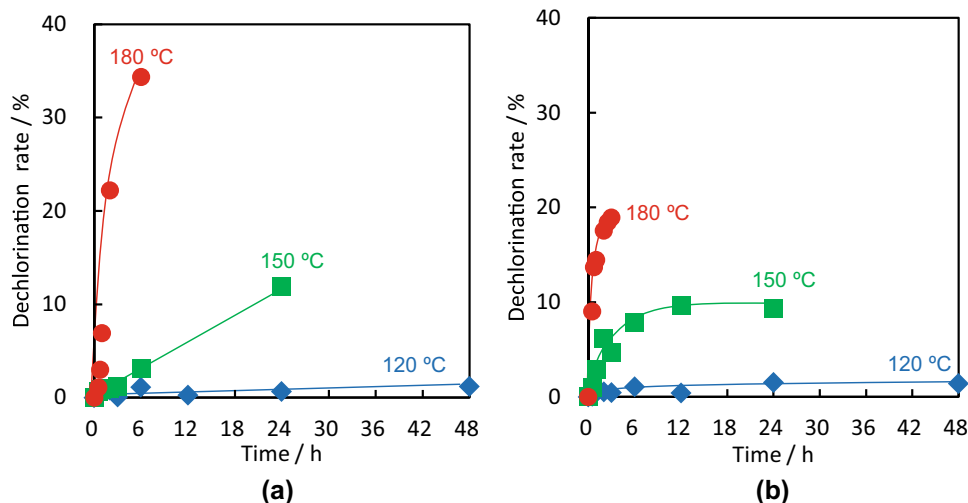
comparison, the dechlorination behavior of PET/PVC was also investigated under the same conditions, which are shown in Fig. 4b. The final dechlorination rates obtained for PET/PVC at each temperature (120, 150, and 180 °C) were comparable with those obtained from coated woven fabrics, i.e., 1% at 48 h, 9% at 24 h, and 18% at 2 h. The initial increases in the dechlorination rates obtained from the coated woven fabrics at 120 and 150 °C were slightly slower than those of PET/PVC, which was due to the film shape of the PVC coating. Therefore, time was required for OH^- to penetrate the bulk PVC and for the diffusion of Cl^- from the bulk PVC. In contrast, the similarity of the final dechlorination rates of the coated woven fabrics and the PET/PVC suggests that OH^- penetrated the coated woven fabrics well over the investigated reaction period.

DEHP leaching from PVC

The DEHP leaching rate obtained during the coated woven fabric hydrolysis is shown in Fig. 5. No leaching was
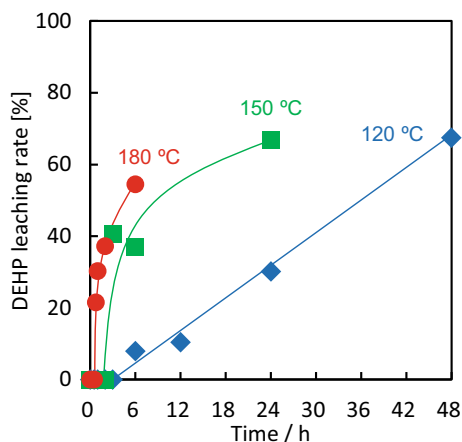

Fig. 5 DEHP leaching rates obtained from the hydrolysis of coated woven fabrics at different temperatures

observed until 3, 2, and 0.5 h had elapsed at 120, 150, and 180 °C, respectively, which was the time required for water penetration into the PVC, PVC swelling, and diffusion of DEHP from the PVC bulk into solution. The leaching rate accelerated as temperature increased because water penetration and DEHP diffusion were enhanced at higher temperature. It has also been reported that the PVC swelling rate increases with increasing temperature [27]. When PET hydrolysis was nearly complete, 67, 67, and 54% of the DEHP had leached from the PVC coating at 120, 150, and 180 °C, respectively. We also confirmed that DEHP was not hydrolyzed under the present conditions (Supporting Information).

Kinetic analysis of PET hydrolysis

A kinetic analysis based on the results shown in Fig. 2a was performed. The experimental and master curve plots for each reaction model under each condition are shown in Fig. 6. Similar plots constructed for the PET/PVC and PET flakes are presented in Figure S3. For the cases in which there was a significant difference between the experimental plot and the master plot for any model, the model was excluded. As can be seen from the figures, all the diffusion models as well as all the nucleation models were apparently inadequate. In addition, models F_2, and F_3 were unsuitable. Thus, the possible models were narrowed to chemical reaction models $F_{1/3}$, $F_{3/4}$, and F_1, and contraction models R_2 and R_3.

The three best-fitting of the selected possible models were determined by a linear-fitting method (Table 1). An adequate model showed higher values of R_{Model} (close to linearity) and $R_{Intercept}$ (intercept close to zero). The phase-boundary-controlled reaction models R_2 ($F_{1/2}$) and R_3 ($F_{2/3}$) were selected as the common models for all sets of conditions, representing the contracting cylinder and sphere
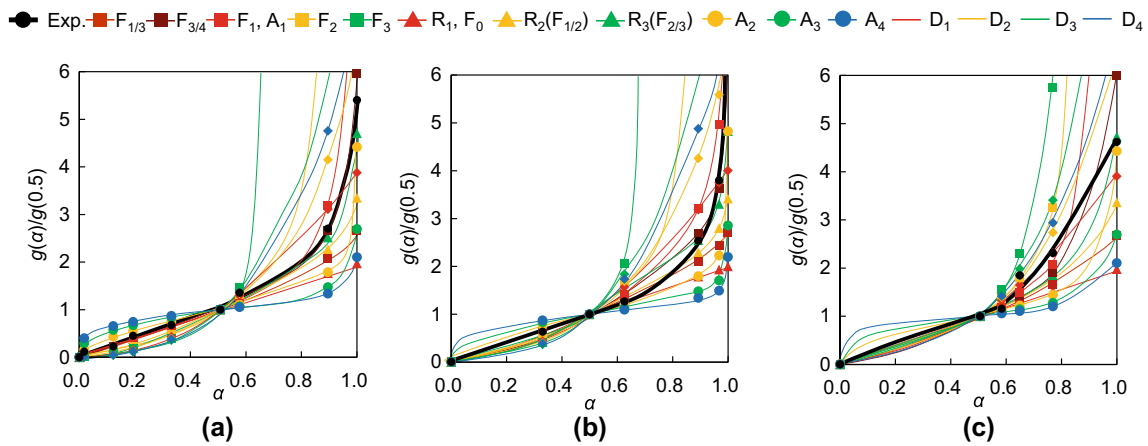
Legend: Exp. — $F_{1/3}$ — $F_{3/4}$ — F_1, A_1 — F_2 — F_3 — R_1, F_0 — $R_2(F_{1/2})$ — $R_3(F_{2/3})$ — A_2 — A_3 — A_4 — D_1 — D_2 — D_3 — D_4

Fig. 6 Experimental and master plots for PET decomposition in PVC-coated woven fabrics at **a** 120, **b** 150, and **c** 180 °C. R_n Phase-boundary-controlled reaction models ($n = 1, 2, 3$), F_n Chemical reaction models ($n = 0, 1/3, 1/2, 2/3, 3/4, 1, 2, 3$), A_n Avrami–Eroféev models ($n = 1, 2, 3, 4$), and D_n Diffusion models ($n = 1, 2, 3, 4$)

Table 1 Three best-fitting models and values of R_{Model}, $R_{Intercept}$, and k_{app} obtained from PVC-coated PET fibers, PET/PVC, and PET for PET hydrolysis

Sample	Temperature/°C	Three best-fitting models	R_{Model}	$R_{Intercept}$	k_{app}/h^{-1}
PVC-coated PET fibers	120	$F_{3/4}$	1.7	3.6	2.8×10^{-2}
		$R_3 (F_{2/3})$	1.5	3.0	3.2×10^{-2}
		$R_2 (F_{1/2})$	1.2	2.3	3.7×10^{-2}
	150	$F_{3/4}$	0.7	1.8	1.3×10^{-1}
		$R_3 (F_{2/3})$	0.7	1.5	1.8×10^{-1}
		$R_2 (F_{1/2})$	0.6	1.2	2.6×10^{-1}
	180	$R_2 (F_{1/2})$	2.1	1.6	3.4×10^{-1}
		$R_3 (F_{2/3})$	2.0	2.3	3.2×10^{-1}
		$F_{3/4}$	1.9	3.0	2.8×10^{-1}
PET/PVC	120	$R_3 (F_{2/3})$	1.5	3.0	1.5×10^{-2}
		$R_2 (F_{1/2})$	1.4	3.3	1.8×10^{-2}
		$F_{1/3}$	1.3	3.7	2.0×10^{-2}
	150	$F_{3/4}$	2.3	6.2	5.2×10^{-2}
		$R_3 (F_{2/3})$	2.1	4.3	6.0×10^{-2}
		$R_2 (F_{1/2})$	1.6	4.5	7.1×10^{-2}
	180	$F_{3/4}$	1.2	1.9	2.4×10^{-1}
		$R_3 (F_{2/3})$	1.1	1.6	2.8×10^{-1}
		$R_2 (F_{1/2})$	0.9	1.2	3.0×10^{-1}
PET	120	$R_2 (F_{1/2})$	1.6	3.4	1.8×10^{-2}
		$R_3 (F_{2/3})$	1.6	3.2	1.5×10^{-2}
		$F_{1/3}$	1.4	4.1	1.9×10^{-2}
	150	$F_{3/4}$	0.7	2.1	2.2×10^{-2}
		$R_3 (F_{2/3})$	0.7	1.9	2.6×10^{-2}
		$R_2 (F_{1/2})$	0.6	1.5	3.1×10^{-2}
	180	$F_{3/4}$	0.7	1.6	1.8×10^{-1}
		$R_3 (F_{2/3})$	0.7	1.3	2.1×10^{-1}
		$R_2 (F_{1/2})$	0.6	1.0	2.4×10^{-1}

shapes, respectively. Therefore, the rate-determining step in the hydrolysis of all the PET samples used in the present work is the contraction of the phase boundary. The fitted models are reasonable because it is known that PET hydrolysis is well expressed by the modified shrinking core model [18–20, 28]. Notably, kinetic analysis using the modified shrinking core model is inadequate in the present work because that model requires the surface area as a

Table 2 Apparent activation energy, E_{app}, and pre-exponential factor, k_0, calculated for PET hydrolysis of PVC-coated PET fibers, PET/PVC, and PET using R_2 ($F_{1/2}$) and R_3 ($F_{2/3}$) models

Sample	Models	E_{app}/kJ mol^{-1}	log k_0
PVC-coated PET fibers	R_3 ($F_{2/3}$)	57	6.1
	R_2 ($F_{1/2}$)	56	6.1
PET/PVC	R_3 ($F_{2/3}$)	72	7.7
	R_2 ($F_{1/2}$)	69	7.4
PET	R_3 ($F_{2/3}$)	65	6.6
	R_2 ($F_{1/2}$)	63	6.6

Table 4 Apparent activation energy, E_{app}, and pre-exponential factor, k_0, calculated for PVC dechlorination of PVC-coated PET fibers and PET/PVC using D_4 and D_2 models

Sample	Models	E_{app}/kJ mol^{-1}	log k_0
Tarpaulin	D_4	185	18.8
	D_2	184	19.3
PET/PVC	D_4	175	17.4
	D_2	174	18.0

parameter during the hydrolysis reaction, which would be difficult to determine for the sample consisting of woven PET covered by PVC. The apparent activation energy, E_{app}, and pre-exponential factor, k_0, were calculated using the common R_2 ($F_{1/2}$) and R_3 ($F_{2/3}$) models; the obtained values are listed in Table 2. The values of E_{app} and log k_0 determined using R_3 ($F_{2/3}$) were 56.9 kJ mol^{-1} and 6.1, respectively, which were comparable to the values determined using R_2 ($F_{1/2}$), 55.6 kJ mol^{-1} and 6.1, respectively. On the other hand, the E_{app} and log k_0 kinetic parameters obtained from PET/PVC were 71.5 kJ mol^{-1} and 7.7 using R_3 ($F_{2/3}$) and 68.7 kJ mol^{-1} and 7.4 using R_2 ($F_{1/2}$), respectively. The PET flakes afford kinetic parameters comparable with those of PET/PVC. The activation energies for PET hydrolysis in the presence of NaOH or KOH reported in several works [15, 16, 29] fall in the range of 60–70 kJ mol^{-1}, in accord with the E_{app} values for PET/PVC and PET obtained in the present work. The lack of any significantly different kinetic parameters between the

PET/PVC and PET experiments suggest that PVC and/or the liberated Cl$^-$ have no influence on PET hydrolysis. We also confirmed that the TiO$_2$ pigment included in the coated woven fabrics has no catalytic effects on the alkaline hydrolysis under the present conditions by another test (Figure S4), although anatase TiO$_2$ reportedly catalyzes the alkaline glycolysis of PET [30]. Thus, the slightly lower E_{app} obtained for coated woven fabrics than that obtained for the PET flakes might be due to the better diffusion of OH$^-$ and water into the woven PET fibers.

Kinetic analysis of PVC dechlorination

Based on the results shown in Fig. 4, a kinetic analysis of the dechlorination was performed using the master curve and model-fitting methods, analogously to the PET hydrolysis analysis. The experimental and master plots for coated woven fabrics and the PET/PVC mixture are presented in Figure S5. The three best-fitting models are summarized in Table 3. The model-fitting results indicate

Table 3 Three best-fitting models and values of R_{Model}, $R_{Intercept}$, and k_{app} obtained from PVC-coated PET fibers and PET/PVC for PVC dechlorination

Sample	Temperature/°C	Three best-fitting models	R_{Model}	$R_{Intercept}$	k_{app}/h^{-1}
PVC-coated PET fibers	120	$F_{3/4}$	2.5	5.6	1.9×10^{-4}
		R_3 ($F_{2/3}$)	2.5	5.3	2.5×10^{-4}
		D_4	2.2	10.7	1.6×10^{-6}
	150	$F_{3/4}$	2.4	7.4	1.3×10^{-3}
		R_3 ($F_{2/3}$)	2.4	7.1	1.7×10^{-3}
		D_4	1.6	7.7	7.3×10^{-5}
	180	D_4	1.6	5.6	2.9×10^{-3}
		D_2	1.6	4.4	1.3×10^{-2}
		D_1	1.0	5.2	1.7×10^{-2}
PET/PVC	120	D_4	1.1	11.4	1.0×10^{-6}
		D_2	1.1	10.1	4.7×10^{-6}
		$F_{3/4}$	0.7	6.0	1.3×10^{-4}
	150	D_4	1.1	8.1	8.7×10^{-5}
		D_2	1.1	6.8	3.9×10^{-4}
		$F_{3/4}$	0.7	4.3	1.7×10^{-3}
	180	D_4	1.1	6.0	1.2×10^{-3}
		D_2	1.0	4.7	5.4×10^{-3}
		$F_{3/4}$	0.8	3.2	9.5×10^{-3}

that the diffusion-controlled models are the common predominant models for the dechlorination of PVC in the coated woven fabrics and PET/PVC. In particular, the three-dimensional D_4 and the two-dimensional models are well fitted for all sets of conditions. The sequence of the dechlorination process can be assumed as follows. First, OH^- penetrates the PVC by diffusion and swelling; next,

the PVC is dechlorinated by the attack of OH^-. Finally, Cl^- is eluted from the PVC into the water by diffusion. The fitting results indicate that the dechlorination step is fast, so that the three- or two-dimensional diffusion is the rate-determining step. Each coated woven fabrics piece is initially 5 mm × 5 mm × 0.5 mm, but becomes slightly swollen during alkaline hydrolysis; therefore, both two-
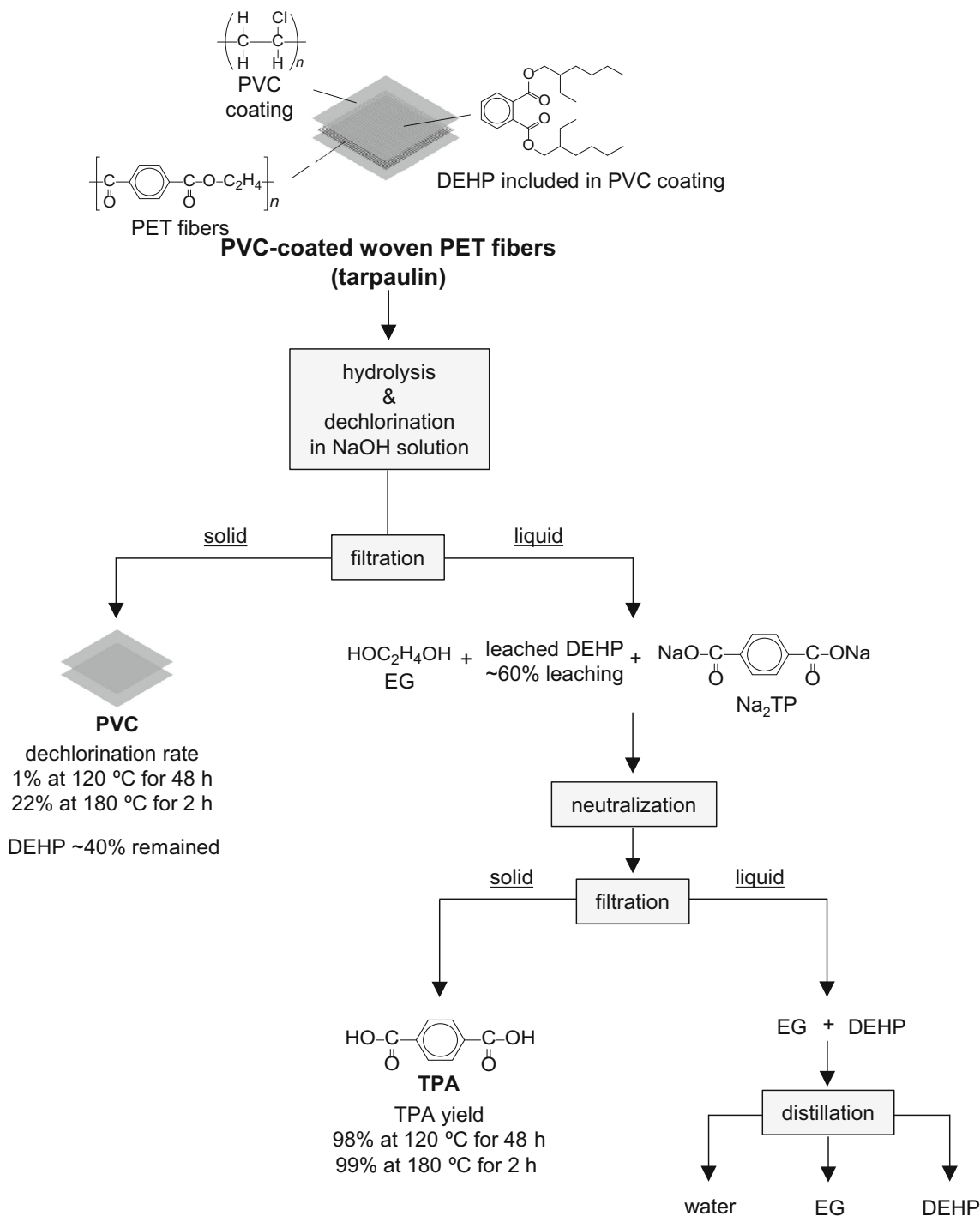

Fig. 7 Suggested recycling scheme for PVC-coated woven PET fibers using alkaline hydrolysis

and three-dimensional diffusion are reasonable. The kinetic parameters for PVC dechlorination were determined using the D_4 and D_2 models (Table 4). E_{app} and log k_0 for coated woven fabrics using the D_4 model were 185.3 kJ mol^{-1} and 18.8, respectively. Comparable values of 184.2 kJ mol^{-1} and 19.3 were obtained using the D_2 model, respectively. By the same analysis, E_{app} and log k_0 values of 175 kJ mol^{-1} and 17.4 (D_4 model) and 174 kJ mol^{-1} and 18.0 (D_2 model) were obtained from PET/PVC, respectively. These results are consistent with a previous work that reported an activation energy of 179 kJ mol^{-1} for the dechlorination of a flexible PVC film in 1 M NaOH solution [27]. Thus, the present work indicates that neither PET nor its hydrolysis products influence PVC dechlorination.

Conclusion

The alkaline hydrolysis of PVC-coated PET fibers was performed to investigate the possibility of simultaneously recycling PET and PVC. A suggested PVC-coated PET fibers recycling scheme based on our results is presented in Fig. 7. Hydrolysis of the coated woven fibers in the presence of NaOH yields water-soluble Na$_2$TP after filtration of the PVC. The recovered PVC was dechlorinated by only 1% at 120 °C, and 48 h was required for complete PET hydrolysis. The leaching of DEHP (54–67%) might be unavoidable under the present conditions. However, the amount of plasticizer needed in the PVC depends on the desired reuse; should the recovered PVC be directly available for another product, the shortage of plasticizer can be corrected. The Na$_2$TP is precipitated by neutralization with acid, and simple filtration results in a maximum 98% yield of TPA after treatment at 120 °C. The filtrate, containing ethylene glycol (EG) and the partially leached DEHP, can be separated into water, EG, and the plasticizer by distillation [31, 32]. A maximum TPA recovery of 99% was achieved at 180 °C within 2 h, with a dechlorination rate for the recovered PVC of 22%. These results imply that the higher temperature is suitable for TPA recovery with a high degree of PVC dechlorination, which would be useful for feedstock recycling as a low-chlorine-content carbon resource.

The kinetic analyses of PET hydrolysis and PVC dechlorination revealed that both processes progressed simultaneously and independently. Thus, there is no interaction between the PET, PVC, and their degradation products, which simplifies the recycling process design as interactions between the materials derived from PVC-coated PET fibers need not be considered.

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