

## Detergent impurity effect on recycled HDPE: Properties after repetitive processing

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**ABSTRACT:** High density polyethylene (rHDPE) is extruded 1 to 8 times, with and without detergent, to simulate the effects of impurities on the material and on the artificial ageing process. The mechanical properties, thermal stability, rheology, Fourier transform infrared spectroscopy (FTIR), and volatile organic compound (VOC) emissions are measured. According to the results, ageing of rHDPE increases tensile strength, reduces elongation, and enhances side chain branching of the material and thus causes rheological changes. The addition of detergent reduces changes in mechanical properties and rheological behavior but accelerates thermal degradation. VOC and FTIR measurements of the samples with detergent addition show generation of harmful 1,4-dioxane. The amount of total emission, as well as emissions of important perfumes limonene and 1R- $\alpha$ -pinene, decreases during multiple extrusion cycles. Heating of the plastics is found to be a major factor in the VOC emission reduction. Impurities have a notable effect on the artificial ageing results. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43766.

**KEYWORDS:** ageing; degradation; polyolefins; recycling

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### INTRODUCTION

The ageing of recycled plastics is commonly studied using repetitive extrusion cycles.<sup>1–5</sup> The goal is to estimate how many cycles the plastic withstands before losing its usability in a real-life situation and what are the effects on different material properties. Typically, ageing causes losses in mechanical properties, hardening of the surface layer, changes in processing behavior, and degradation in thermal properties. Artificial ageing is always a simplification of the real situation. One of the challenges in artificial ageing is to simulate the effect of different impurities present in the plastic. One likely scenario where impurities are present is recycled plastics collected from municipal waste.

High-density polyethylene (HDPE) is a commodity plastic used in many kinds of applications including packages and films. Detergent bottles are a typical application for HDPE. HDPE is a desirable plastic for recycling due to its high total annual production volume, easy processing, and many applications.<sup>6</sup> Consumer generated HDPE waste is usually collected with other packages (plastic and other materials) and separated in sorting

facilities before crushing, washing and extruding to recycled granulates. HDPE packages and bottles collected from municipal waste may contain food, chemicals or microbes. Washing of these consumer plastics in industrial-scale factories, including the first one in Finland (Ekokem, Riihimäki, 2016), is typically performed with only water and mechanical work. If the washing result is insufficient, some of these impurities, including detergents, may remain in the plastic during processing and accumulate over time. Migration of these impurities into the plastic may complicate the washing. Slow migration of these substances out of the recycled plastic during use may cause aesthetic problems to product, or in worst case, health problems to users.<sup>7,8</sup>

The goal of this work is to study the effects of detergent on the material properties as well as particle emissions, caused by the presence of the detergent in the material during processing. The study was inspired by a recycled HDPE grade that had a strong odor of limonene, a commonly used odor constituent, even though the grade was industrially washed. Therefore, this same rHDPE grade is artificially aged up to eight times, with and without added detergent, using a typical single screw extruder. These samples are then characterized with conventional material



**Figure 1.** Collected and sorted HDPE packages (A) and granulated HDPE (B). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

tests and with particle emission measurements. The effect of detergent as well as multiple ageing cycles is estimated. The secondary goal is to estimate the effects of contaminants on artificial ageing on a general level because they may cause problems yet unknown.

## EXPERIMENTAL

### Materials

rHDPE (recycled high density polyethylene) was manufactured by Ekokem Ltd. Post-consumer plastics were collected separately in Kuopio, Finland, where only hard plastic packages (high-density polyethylene, low density polyethylene, polypropylene, and polyethylene terephthalate) were allowed. A sample of 3000 kg was sorted with mobile TiTech equipment based on NIR (near infrared) technique rented from Tomra Sorting GmbH [Figure 1(a)]. The sorted rHDPE sample was washed and granulated by NGR, Next Generation Recyclingmaschinen GmbH, in Austria. The resulted rHDPE had a lilac color and strong odor of limonene [Figure 1(b)].

The detergent used was Surf Sunshine Lemons & Mandarin Flower Washing Powder by Unilever. According to the product data sheet, the product contains following substances: aqua, C11-15 parath-7, sodium dodecylbenzenesulfonate, propylene glycol, sodium laureth sulfate, TEA-hydrogenated cocoate, glycerin, parfum, sodium citrate, styrene/acrylates copolymer, sodium diethylenetriamine pentamethylene phosphonate, sodium hydroxide, sodium sulfate, DASC-4, butylphenyl methylpropional, limonene, protease, citronellol, triethanolamine, benzyl Salicylate, linalool, C12-14 sec-parath-9, boronic acid, (4-formylphenyl), sodium lauryl sulfate, hexyl cinnamal, and polyvinyl alcohol.

### Ageing

The rHDPE was aged with (rHDPE\_D) and without (rHDPE) the detergent. The procedure of one ageing cycle is presented in Table I. Drying was performed using Tamro-Apta 90-544011 laboratory oven. Extrusion was performed on Eco Ex single screw extruder produced by KFM. A standard single screw for PE extrusion with 25 L/D ratio was used. A 4 mm lace die and air cooling were used for pelletization. Both samples were aged 1, 2, 4, and 8 times. During the experiment the same screw rotational speed and temperature profiles were used, while pelletizer speed was adjusted to keep the cooling of the strings and diameter of the granules constant. It was observed that the throughput rate of rHDPE was almost twice the throughput rate of rHDPE\_D, probably because the addition of detergent made the surface of the material more slippery.

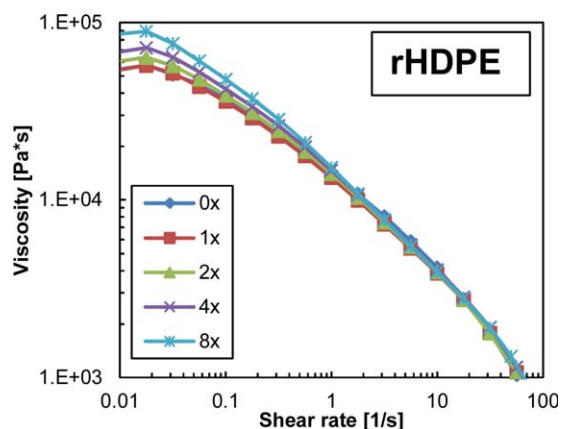
### Measurements

The rotational rheometer tests were done using Anton Paar Physica MCR 301 rheometer. All the experiments were performed at 200 °C under a nitrogen atmosphere using 25-mm plate-plate geometry. The constant shear rate was recorded with increasing frequency in the shear rate range of 0.01–100 1/s.

Samples for tensile testing were produced according to the ASTM D 638–67T standard (type I) with Engel ES 200/50HL CC90 injection molding machine. The temperature setting (hopper to die) was 220–220–220–210 °C, mold temperature 40 °C, cooling time 20 s, injection pressure 90 bar and holding pressure 72 bar. Tensile properties of the materials were tested using Testometric M 350-5CT material testing machine, according to ASTM D 638–67T standard using testing speed of 51 mm/min. Total of 15 parallel samples were tested.

**Table I.** The Procedure of One Ageing Cycle

Order	Description	rHDPE_D	rHDPE
1	Addition of the detergent	3 wt %	—
2	Drying	2 h at 80 °C, stirring every 30 min	2 h at 80 °C, stirring every 30 min
3	Extrusion	100 rpm, 180–180–190–190–200–200 °C	100 rpm, 180–180–190–190–200–200 °C
4	Pelletizing	Cutting speed 2.5–4.5 m/min	Cutting speed 2.5–4.5 m/min

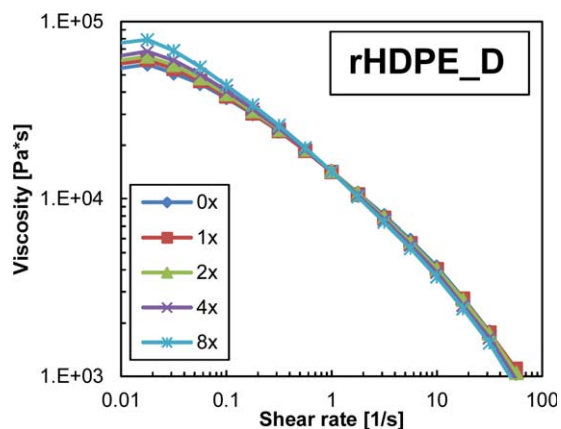


**Figure 2.** Rotational rheometer tests for HDPE measured at 200 °C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

DSC measurements were performed with Netzsch DSC 204 F1. Approximately 10 mg of sample was heated at a rate of 10 °C/min to 300 °C in an oxygen atmosphere (50 mL/min). Oxidation onset temperature was measured simultaneously. The onset point was defined as extrapolated onset from the intersection point of the baseline tangent and the tangent of the initial inflection.

For the VOC emission measurement, 100 g of granulates were stored in 250 mL glass headspace chambers for two days at room temperature ( $20 \pm 1$  °C) until the VOC concentration was stable. VOC samples, (flow rate of 140 mL/min for 30 min) were collected from the headspace chambers on commercially filled Tenax<sup>®</sup>-GR Adsorbent Resin tubes (Markes). Compounds were released from adsorbent tubes and analysed with thermodesorption-GC-MS system consisting of Thermal Desorber TD-100 (Markes), gas chromatograph 7890 A GC (Agilent Technologies), and mass spectrometer VL MSD 5975 C (Agilent Technologies).

Fourier transform infrared spectra (FTIR) of injection molded tensile testing specimens was measured with Bruker optics tensor 27 using ATR (attenuated total reflection) mode in the



**Figure 3.** Rotational rheometer tests for HDPE\_D measured at 200 °C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

wavenumber range 400–4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  and average of 32 scans.

## RESULTS AND DISCUSSION

### Rheological Properties

Rheological measurements in Figures 2 and 3 show an increase in the zero shear viscosity with increasing number of extrusion cycles. According to the literature, long chain branching is the most probable cause during the first processing cycles.<sup>1,9–11</sup> Also crosslinking has been suggested as one explanation.<sup>12,13</sup> In both cases the increase in the viscosity is caused by the growth of the molecular mass that enables more entanglements between the chains. Also the shear thinning of the material increases slightly with processing cycles; the viscosity near 100 1/s is almost independent of the number of cycles even when there is difference at the zero shear rate. This is typical for the branched polymers as the entanglements of the branched chains become more easily disentangled at higher shear rates than linear chains.<sup>14</sup> The difference between the virgin rHDPE and 8 times extruded rHDPE is relatively small and it is considered not to affect further processing.

Effect of the detergent is small but visible. Addition of detergent compensates the effects of multiple processing cycles. The detergent contains low molecular weight substances like propylene glycol and glycerin that are used as plasticizers for plastics.<sup>15</sup> The plasticizers act by spacing out the polymer chains leading to fewer entanglements between the chains and thus improve the chain mobility at low shear rates.

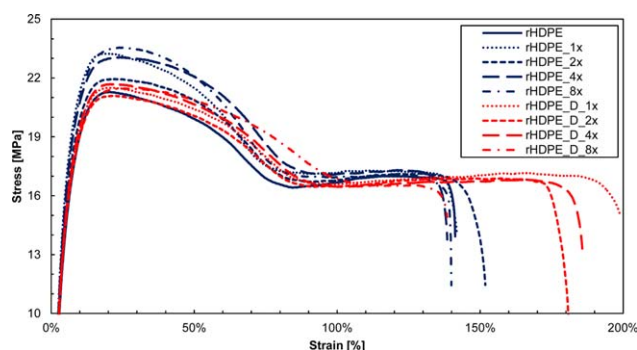
### Mechanical Properties

The results of the tensile tests are presented in Table II and typical tensile testing curves in Figure 4. The tensile strength and modulus increases and the strain at break decreases when the number of extrusion cycles increases. The increase in modulus is approximately 10–20% while the changes in other properties are smaller. The changes are likely related to the long chain branching and crosslinking of the material, discussed in the previous paragraph. Similar observations have been reported by others.<sup>16</sup>

The suggestion that the detergent is working as a plasticizer is supported by the mechanical test results as the elongation

**Table II.** Results of the Tensile Testing of Material A

Material	Tensile strength (MPa)	Strain at break (%)	Modulus (MPa)
rHDPE	22.5 ± 0.68	149 ± 31	377 ± 20
rHDPE_1x	22.7 ± 0.40	137 ± 23	450 ± 18
rHDPE_2x	22.3 ± 0.36	150 ± 21	421 ± 14
rHDPE_4x	22.9 ± 0.36	137 ± 18	429 ± 21
rHDPE_8x	23.1 ± 0.30	135 ± 23	432 ± 21
rHDPE_D_1x	21.4 ± 0.38	196 ± 15	397 ± 22
rHDPE_D_2x	21.3 ± 0.38	192 ± 23	387 ± 17
rHDPE_D_4x	21.5 ± 0.37	181 ± 20	384 ± 13
rHDPE_D_8x	21.0 ± 0.32	145 ± 23	379 ± 10



**Figure 4.** Typical tensile testing curves for rHDPE and rHDPE\_D. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

increases after the addition of the detergent. At the same time mechanical strength and modulus are slightly decreased.

### Crystallinity and Melting Point

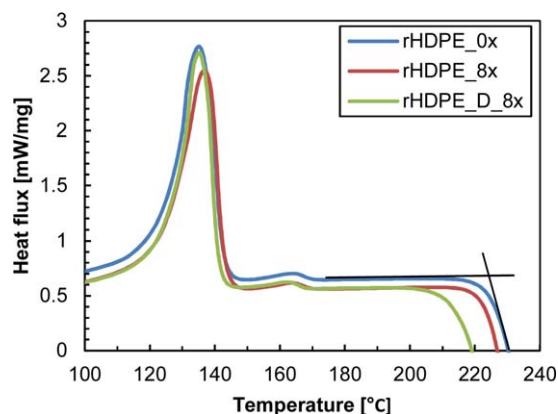
Crystallinity was calculated as the ratio of measured enthalpy of fusion and theoretical value of 293.6 J/g for 100% crystallinity.<sup>17</sup> According to the measurements the crystallinity is 66% for unaged sample. Ageing without detergent decreases this value to 62–63% and addition of detergent slightly more to 56–61%. No correlation was found between the number of ageing cycles and decrease in crystallinity but the difference was caused by material inhomogeneity and variance in measurements.

Both ageing and addition of detergent had little effect on the melting point of the material. The peak melting point for all samples was 135–138 °C.

### Oxidation Onset Temperature

Oxidation onset temperature was determined to estimate the thermal stability of the material (Figure 5). Each processing cycle changes the morphology of the material, consumes stabilizers used and typically worsens the thermal stability.<sup>2,18</sup>

The oxidation onset temperature is much lower for rHDPE\_D samples compared to rHDPE, as shown in Figure 6, indicating that the detergent accelerates the degradation during processing.



**Figure 5.** DSC curve of rHDPE\_0x, rHDPE\_8x, and rHDPE\_D\_8x, and the determination technique for oxidation onset temperature. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The onset temperature of rHDPE\_D drops steadily from 225 °C to 214 °C. The onset temperature of rHDPE is somewhat inconsistent, first rising from 225 °C to 230 °C and then returning to the original level.

### VOC Emissions

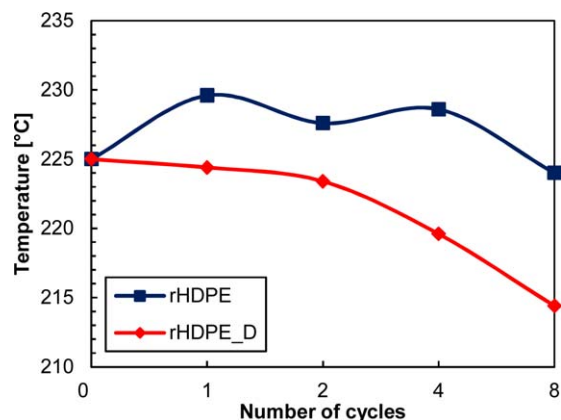
Volatile organic compounds (VOCs) were analyzed to characterize emissions of air pollutants related to ageing of recycled waste plastic (example in Figure 7). According to the results in Figure 8, rHDPE\_D releases larger amounts of TVOCs (total VOCs) than rHDPE during multiple extrusion cycles. TVOC levels of rHDPE\_D remained relatively stable as a result of detergent addition whereas the levels of rHDPE dropped steadily, most likely due to heating.

Limonene was the most abundant VOC in the measured samples. Concentration of limonene (Figure 9) and 1R- $\alpha$ -pinene (Figure 10) perfumes decreased in rHDPE and rHDPE\_D as a result of the ageing. Evidently, the effect of heating during multiple extrusion cycles was so strong that the addition of new detergent couldn't compensate the reduction in VOC amount. In real-life situations the detergent has several months' time to migrate into plastic whereas in artificial testing only a few hours which probably have some effect on the results as well.

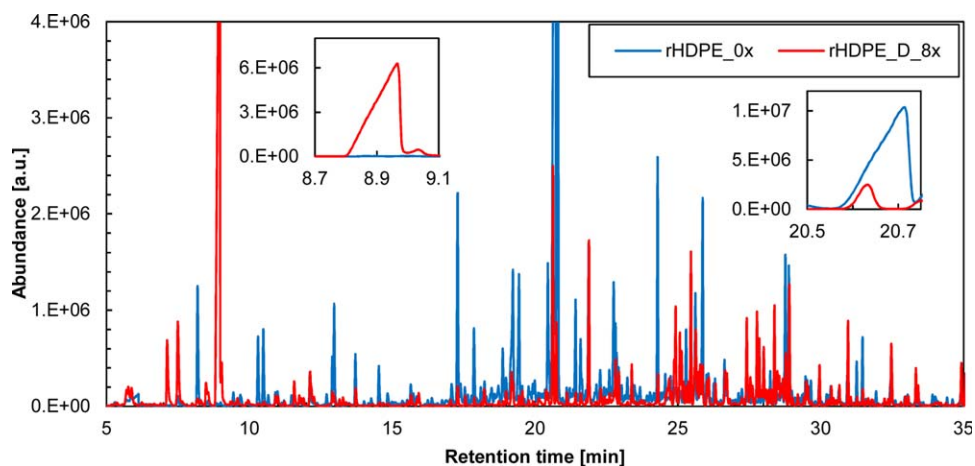
A possible human carcinogen,<sup>19,20</sup> 1,4-dioxane, accumulated into the rHDPE\_D evidently as a result of added detergent during multiple extrusion cycles (Figure 11). 1,4-dioxane is a by-product of the dimerization of ethylene oxide, which is used in the synthesis of sulphate surface active agents (e.g., sodium lauryl sulphate). This explains why 1,4-dioxane is a common contaminant in ethoxylated products such as personal care products, household detergents, and cleaners.<sup>21</sup>

### FTIR

Typically, ageing of polymers causes changes in the carbonyl group (C=O) absorption band of FTIR spectra, located in the wavenumber region 1540–1870  $\text{cm}^{-1}$ . Another typical change is the formation of a broad hydroxyl (—OH) group absorption in the 2800–3700  $\text{cm}^{-1}$  region of the spectrum. In current study, the changes in these regions are relatively small and remain hidden by the measurement noise (Figure 12). The only notable



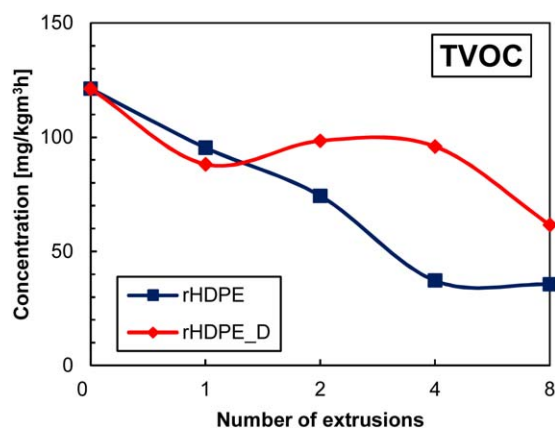
**Figure 6.** Oxidation onset temperatures for rHDPE and rHDPE\_D. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



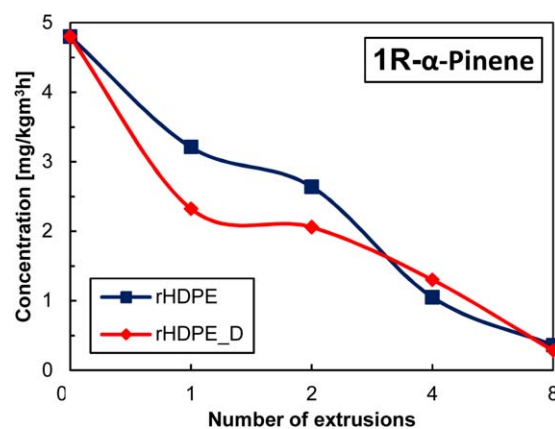
**Figure 7.** Overlaid GC-MS total ion chromatograms of rHDPE\_0x and rHDPE\_D\_8x. The retention of time of 1,4-dioxane is approximately 8.9 min and limonene 20.7 min. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

changes were found between 1050 and 1200  $\text{cm}^{-1}$  in rHDPE\_D\_4x and rHDPE\_D\_8x samples. Samples aged without detergent did not show these peaks. Typically this band corre-

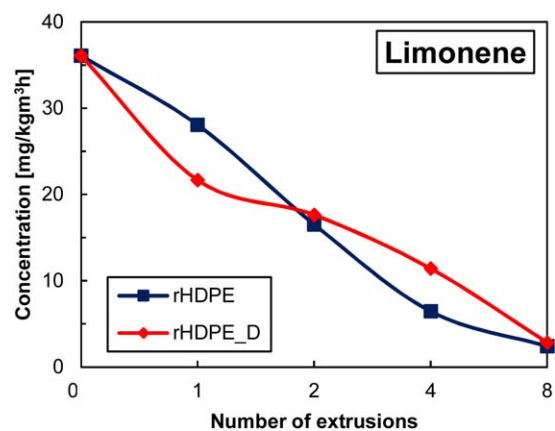
sponds to C-O stretch of alcohols, ethers, esters, and carboxylic acids. In this case the band is likely caused by 1,4-dioxane, discussed earlier in the VOC emissions paragraph. 1,4-dioxane has



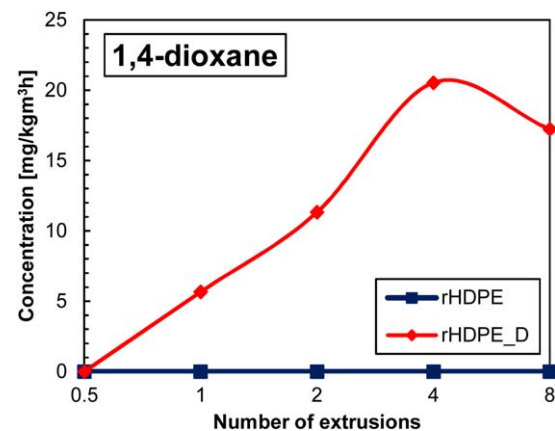
**Figure 8.** Total VOC concentration during multiple extrusion cycles. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



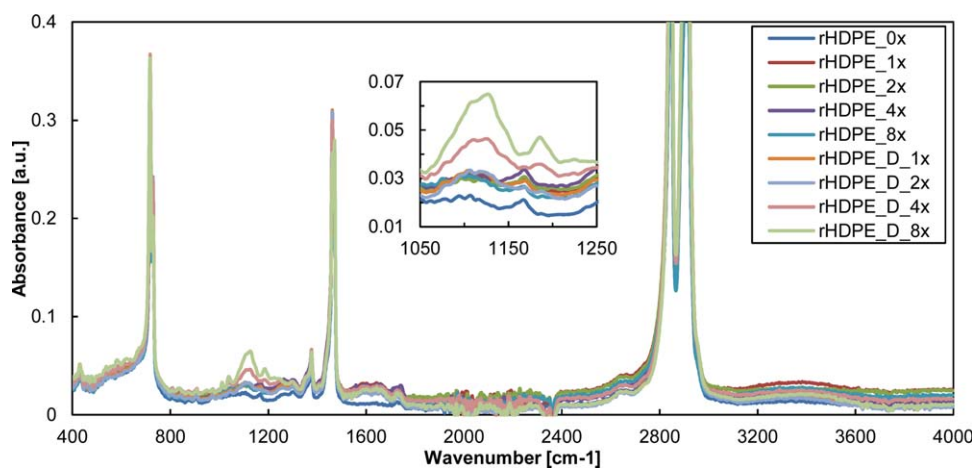
**Figure 10.** 1R- $\alpha$ -pinene concentration during multiple extrusion cycles. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 9.** Limonene concentration during multiple extrusion cycles. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 11.** 1,4-dioxane concentration during multiple extrusion cycles. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 12.** FTIR spectra of rHDPE and rHDPE\_D. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

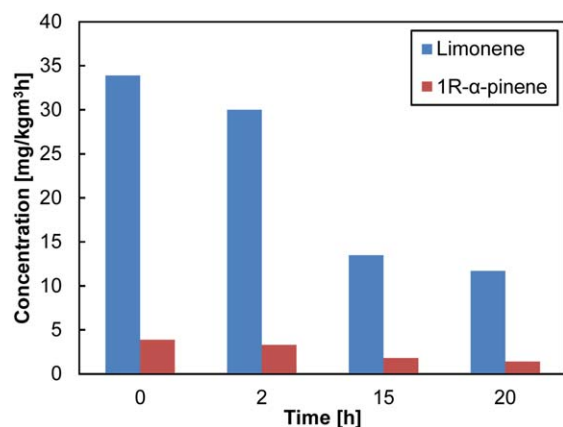
a typical wavenumber maximum between 1120 and 1220  $\text{cm}^{-1}$ .<sup>22</sup> The finding is significant because it allows following the accumulation of a toxic compound with an easy ATR-FTIR method.

#### Reduction in VOC's by Heating the Plastic

Unaged rHDPE was heated various times at 50 °C to estimate the effect of heating on the VOC emissions. According to the previous VOC measurements, the VOC amounts decrease as the number of processing cycles increases. Heating in an oven has a significant effect on the VOC emissions as well (Figure 13). Limonene concentrations reduced by 12% in 2 h, 60% in 15 h, and 65% in 20 h of heating. The change is relatively similar in the case of 1R- $\alpha$ -pinene. Even though migration may increase these concentrations afterwards, heating seems to be an easy and viable alternative to reduce the harmful VOC emissions. This technique has been taken into practice at least in the United States where heat purified plastics may pass the requirements of FDA for direct food contact use.<sup>23</sup>

#### CONCLUSIONS

Recycled HDPE was artificially aged by extruding it 1 to 8 times to study the effects of detergent impurities on the ageing of the



**Figure 13.** Reduction in limonene and 1R- $\alpha$ -pinene concentrations after heating the rHDPE various times at 50 °C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

material. The samples aged without detergent suffered from typical degradation effects of HDPE, embrittlement of the material through crosslinking, and reduction in thermal properties. Added detergent acted as a plasticizer, causing increased elongation and decreased mechanical strength. Thermal properties of rHDPE showed some inconsistencies, but still, the additional detergent clearly accelerated thermal degradation.

The study provided useful information about the impurities in recycled HDPE. In the case of detergents, FTIR could be used as an easy quality assurance tool to estimate the accumulation of harmful substances during multiple processing cycles. However, it has to be noted that other impurities may be impossible to find with non-destructive chemical inspections. FTIR confirmed the generation of toxic 1,4-dioxane compounds in the material with detergent addition. Generation and accumulation of possibly carcinogenic 1,4-dioxane is alarming and must be further studied since the recycling of dirty plastics, including HDPE bottles containing detergent, is rapidly increasing.

VOC emission measurements revealed that the amount of the total VOCs and notable perfumes such as limonene and 1R- $\alpha$ -pinene reduced even though new detergent was added between the extrusion cycles. This raises questions whether the used industrial scale washing is able to remove the contaminants on plastics, how much contaminants are migrated into plastic, and how well the test setup actually represents the real situation.

Correlation between artificial ageing and real-life is difficult and artificial ageing is often a simplification of real-life complexity. It is often justified to leave the impurities out of the artificial ageing inspection since they could break the equipment, be difficult to clean, or cause danger to the user. This study confirmed that even small amounts of impurities can change the properties of the material. Since recycled plastics often contain impurities, this fact should be taken into consideration in the reuse and life-time estimations of the material.

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