Journal of Hazardous Materials 381 (2020) 120965

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Decontamination and recycling of agrochemical plastic packaging waste

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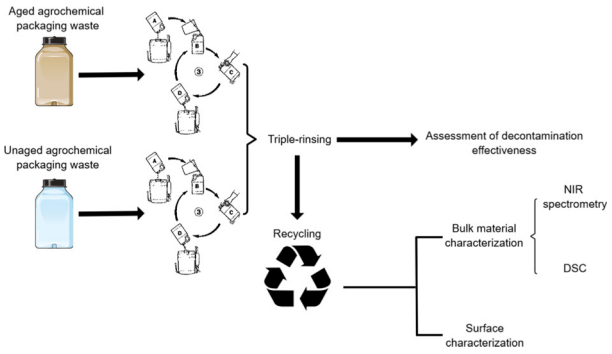
GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Deyi Hou

Keywords:
Agricultural plastic waste
Agrochemical packaging recycling
Triple-rinsing decontamination

ABSTRACT

Agrochemical containers shall undergo decontamination before being considered for recycling. This study provides an assessment on the feasibility of the triple-rinsing decontamination procedure, while evaluating the appropriateness of the material's quality for recycling. To achieve the objectives of the study, (1) the effectiveness of the decontamination procedure was investigated; (2) containers´ long storage times and changes on the polymer´s structure were assessed; and (3) the quality of the recycled material was tested. Results showed that the triple-rinsing procedure was ineffective for the container´s complete decontamination, yet a further washing step – performed during the simulation of the recycling process – allowed for an improved degree of decontamination for recycling. Photo-oxidation imposed significant changes on the chemical structure of the polymer, where the active ingredient could be detected by FTIR, even after the application of rinsing and extraction. The chemical structure of the bulk material has not changed, indicating that the pesticide mobilization was only confined to the surface. The mechanical tests showed material quality appropriateness, where tensile strength values were within the suggested ranges, providing a possibility for further utilization of this material when appropriate decontamination is applied.

1. Introduction

Agricultural plastics have been attracting greater attention in recent years due to their abundancy in all sectors of agriculture. Different forms of plastics are used in agriculture, including films, piping systems, plastic nets, fertilizer bags and agrochemical packaging

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https://doi.org/10.1016/j.jhazmat.2019.120965
Received 27 February 2019; Received in revised form 17 July 2019; Accepted 3 August 2019
Available online 08 August 2019
0304-3894/

(Briassoulis et al., 2013a), representing an easy to handle and cheaper alternative to previously used materials - e.g. glass for greenhouse covering and metal for water pipes (Picuno, 2014). In modern agriculture, agrochemicals are being extensively used. As reported by Eurostat, the total quantity of pesticides sold (expressed in active ingredient (a.i.) in 2017 for n.28 countries) was nearly 610,000 tons with Spain, France, Italy and Germany being the major consumers, consuming approximately 62% of the total of plant protection products in EU (Eurostat, 2019). From an environmental standpoint, pesticides were recently recognized amongst the main contributors, together with other persistent organic pollutants, heavy metals and radionuclides, to the world's worst pollution problems affecting the human health (Bernhardt and Gysi, 2016). Even though gaps in the current data on this issue make it difficult to provide precise predictions about the scale and trends of the problem in Europe, there is evidence that the pesticides related issues are serious and growing (Damalas and Eleftherohorinos, 2011).

In the EU, waste is declared hazardous depending on its own chemical properties or, especially applying to packaging waste, depending on the toxicity and residual concentration of hazardous chemicals contaminating the waste (European Commission, 2000). On this basis, agrochemical containers are generally declared as hazardous waste due to the presence of chemical residues after application. Nevertheless, different national legislations pursue different strategies, as long as decontamination and handling of the containers are provided. Some schemes for the management of Agrochemical Plastic Packaging Waste (APPW) have been established in a few European countries, such as in Germany (Pamira, 2017), France (Adivalor, 2018) and Spain (Sigfito, 2018). However, these schemes are incompatible with each other, and in most cases they cannot be synergistically combined with the management schemes of other agricultural plastic waste categories. This hinders the agricultural sector from achieving an optimized plastic recycling and reuse, resulting in inefficient utilization of resources, lower production efficiencies and higher associated costs. Due to the lack of education and guidance in the proper management of small quantities of agrochemical waste, hazardous chemicals are often abandoned in rural and urban areas, whereas the reuse of contaminated empty containers for domestic purposes, which has been frequently reported in many developing areas (Huici et al., 2017), is another major health risk (Damalas et al., 2008), posing technical limitations on the recycling processes as well (Briassoulis et al., 2013b).

The processes of decontamination, polymer type sorting, cleaning and reprocessing of APPW may enable a large amount of these materials to be returned to the production cycle (Briassoulis et al., 2013b). To this end, experimental investigations were performed about the possibilities of recycling post-consumer agricultural waste mechanically to produce new plastic films (Picuno et al., 2012) or rigid profiles produced by mixing plastic film with some additives, e.g., glass fibers (Dimitrijević et al., 2013). Despite of the actions promoting the transition towards sustainable farming in the EU, where sustainable waste management is considered a pivotal strategy (EUROPARC Federation, 2018), extended plastic recycling practices in the agricultural sector are still hindered by financial, management and technical aspects (Rentizelas et al., 2018). This work aims at further investigating the latter technical aspects. In this sense, the study's objectives are:

I

I assessing the effectiveness of the manual triple-rinsing decontamination procedure on aged APPW, simulating long-term storage of the pesticide containers;
II investigating the potential of agrochemical migration into the polymer´s chain or crystallization on its surface due to material aging, completing the preliminary investigations performed in Picuno et al. (Picuno et al. (2019);
III simulating a mechanical recycling process of different polymeric APPW and providing a qualitative evaluation of the recyclate performing tests.

The outcomes of this study will deliver a general assessment on the feasibility of the applied decontamination procedure, while evaluating the appropriateness of the material's quality for recycling.

2. Materials and methods

Several methods were used to provide a thorough qualitative characterization of the used materials: (a) before and after aging in contact with the pesticide, to simulate the thermo-oxidative degradation of APPW while being in contact with the product during the time they remain stored and unused for a long time, (b) after performing the decontamination procedure, to assess the effectiveness of the triple-rinsing decontamination procedure (through LC–MS/MS) as well as to investigate changes occurring on the surface (through ATR-FTIR) and in the inner structure of the polymer (by means of NIR spectrometry and DSC testing), and (c) after simulating the mechanical recycling process.

2.1. Materials

The specifications on materials used for this study, in terms of agrochemical, packaging and applied methods are summarized in Table 1. A detailed description of the aging and extraction procedures are provided in Picuno et al. (2019). The thorough description of the methods used for LC–MS/MS and for the materials surface and bulk

Table 1
Overview of the methods used on specific materials.

Sample ID*	Commercial name	Producer	Active ingredients	Packaging polymer	Applied methods
S1	Axial Pronto	Syngenta	Pinoxaden (60 g/l) Cloquintocet-mexyl (15 g/l)	PE-HD - COEX	• Aging through thermo- and photo-oxidation as in Picuno et al. (2019) • Decontamination • Extraction and • LC-MS/MS • Surface characterization (ATR-FTIR) • Bulk material characterization (FTNIR)
S2	Turboclean	Bayer Agrar	Pelargonic acid (186,7 g/l)	PE-HD - COEX	• Aging through thermo-oxidation as in Picuno et al. Picuno et al. (2019) • Decontamination • Surface characterization (ATR-FTIR) • Bulk material characterization (FTNIR and DSC)
M1a	Calypso	Bayer Agrar	Thiacloprid (480 g/l)	PE-HD	• Decontamination
M1b	Luna Experience	Bayer Agrar	Fluopyram (200 g/l) Tebuconazole (200 g/l)	PE-HD - COEX	• Extraction • Mechanical recycling
M1c	Vertimec Pro	Syngenta Agro	Abamectin (18 g/l)	PE-HD	• Surface characterization of recycled material (ATR-FTIR) • Bulk characterization of recycled material (FTNIR)

characterization is instead provided in the following sections.

*Letter S refers to samples used to test the effects of aging as well as the decontamination effectiveness. Letter M refers to samples used for simulating a mechanical recycling process.

According to the composition of the agrochemical in S1, eco-toxicity factors were taken into account. Specifically, the LC_{50} factors - defined as the concentration of a chemical in air or in water causing the death of 50% of a group of test animals (United Nations, 2017) - of Pinoxaden (LC_{50} = 10,3 mg/l on *Oncorhynchus mykiss* species) and of Cloquintocet-mexyl (LC_{50} = 76,0 mg/l on the same species) (University of Hertfordshire, 2019) were identified for further calculation of the eco-toxicity of the mixture.

2.2. APPW decontamination and extraction procedure

Manual triple-rinsing of all the containers was performed as recommended from the European Crop Protection Association (European Crop Protection Association, 2019).

Material hazardousness was firstly assessed by testing the hazardousness of the extracted solution with respect to the concentration of active ingredients after extraction. In other terms, possible migration of agrochemicals in the polymeric matrix of S1 was investigated by extracting the remaining pesticide, using a mixture of methanol and acetone (1:2 v/v). A standardized extraction procedure is not yet in place; however, there is evidence of studies performed to extract pesticides from containers of different polymeric blends (Briassoulis et al., 2014; Eras et al., 2017). For the case, the procedure suggested by Eras et al. (2017) was conducted on the APPW as described in detail in Picuno et al. (2019).

The rinsing water as well as the extraction solution for each sample were analyzed by means of Liquid Chromatography-Tandem Mass Spectrometry (LC–MS/MS), measuring the concentration of active ingredients in the water after applying triple-rinsing procedure and in the solvent mixture after the extraction step. The samples´ preparation was carried out in accordance with the QuEChERS method as in the standard DIN EN 15662 (DIN - Deutsches Institut für Normung, 2017) with alterations adapted from Muhammad et al. (2017) to better adapt the method to the investigated pesticide. After achieving a successful recovery of the spiked samples in water and solvents´ mixture (range of recovery 95% to 120%), concentration of the active ingredients of S1 were determined on two mass transitions at the LC–MS/MS.

2.3. Material´s surface characterization

2.3.1. Attenuated total reflectance - fourier transform infrared spectroscopy (ATR - FTIR)

ATR-FTIR spectrometry is a standard procedure in polymer chemistry for evaluating the polymer's quality as well as the degradation on surface (Briassoulis et al., 2012; Celina et al., 1997). Analyses were performed on S1 (aged and unaged) and S2 (aged and unaged) as well as on sample M1, resulting from the extrusion of samples M1a, M1b and M1c as further detailed in section 2.5. Spectra were acquired by means of a Bruker Vertex 70 spectrometer equipped with a platinum Attenuated Total Reflectance accessory. The measurements were performed with a scan number of 32 with a resolution of 8 cm^{-1} and at wavenumbers between 4500 cm^{-1} and 400 cm^{-1}.

2.4. Bulk material characterization

2.4.1. Near-infrared spectroscopy

Fourier Transform Near-infrared (FTNIR) Spectroscopy is a fast, non-destructive procedure relatively recently being considered for evaluating the polymer's degradation and the changes in the bulk material's chemistry (Pasquini, 2003; Alassali et al., 2018a, b). Analyses were performed by Bruker Optics FTNIR spectrometer MPA (Multi-Purpose Analyzer) on both S1 (aged and unaged) and S2 (aged and unaged) and on sample M1. The measurements were performed with a scan number of 32 with a resolution of 8 cm^{-1} and at wavenumbers range from 12500 cm^{-1} to 4000 cm^{-1}.

2.4.2. Differential scanning calorimetry (DSC)

Differential Scanning Calorimetry is used to quantitatively determine the amount of heat absorbed or evolved by a sample during a defined thermal transition, through comparing it to a reference sample Müller and Michell (2016). Heat-related properties of polymers such as the heat capacity, the temperature of glass transition, the melting temperature as well as the crystallization define unique characteristics of polymeric materials (Drzeżdżon et al., 2019). The analyses were performed on aged and unaged S2 samples using DSC1 from Mettler Toledo, cooling was done by liquid nitrogen. A heating - cooling - 2nd heating run was performed with a temperature range from −30 °C to 265 °C, applying heating and cooling rates of 10 °C/min and 20 °C/min, respectively.

Through DSC measurements the degree of crystallinity was computed applying Eq. (1) (Kong, 2002).

$$Xc(T1) = \Delta H_f(T_m) \Big/ \Delta H_f°(T_m°) \quad (1)$$

X_c: weight fraction extent of crystallinity,

$\Delta H_f(T_m)$: enthalpy of fusion measured at the melting point, Tm

$\Delta H_f°(T_m°)$: enthalpy of fusion of the totally crystalline polymer at the equilibrium melting point, Tm°.

2.5. Mechanical recycling

A lab-scale simulation of a typical mechanical recycling process (Ragaert et al., 2017) was performed on samples M1a, M1b and M1c consisting of the following steps:

1 Triple-rinsing decontamination;
2 Shredding. From this step on, samples M1a, M1b and M1c were mixed and treated as a unique sample (M1 from here on);
3 Washing and sink-float separation;
4 Extraction of agrochemical residues from the polymer matrix with acetone. For this step, the extraction procedure described in Picuno et al. (2019) was adopted;
5 Extrusion. The sample of recycled APPW was extruded in three different ratios with virgin PE-LD, to evaluate the impact of mixing the waste material with new polymers for an optimized mechanical quality of the recycled end product (i.e., ratios of APPW to virgin PE-LD: 20%:80%; 50%:50%; 80%:20% - respectively MR20; MR50 and MR80). The virgin material was provided by INEOS Olefins and Polymers Europe;
6 Injection molding to produce specimens for tensile testing. Flat dumbbell shaped samples (specimen type 1BA as defined in the DIN EN ISO 527-2 (DIN - Deutsches Institut für Normung, 2012) were prepared using *BAYBYPLAST 6/10* by the *Rambaldi Group*.
7 Analysis of tensile properties of the produced specimens in accordance to (DIN - Deutsches Institut für Normung, 2012) by means of a *zwickiLine* vertical tensile test machine by *ZwickRoell* equipped with the *videoXtens* camera.

It is worth pointing out that no information is available on whether M1a, M1b and M1c samples were decontaminated by the farmers immediately after use or stored. The material was provided by the company RIGK, responsible for managing agricultural waste in Germany.

3. Results and discussion

3.1. APPW decontamination

The triple-rinsing procedure was effective in decontaminating the

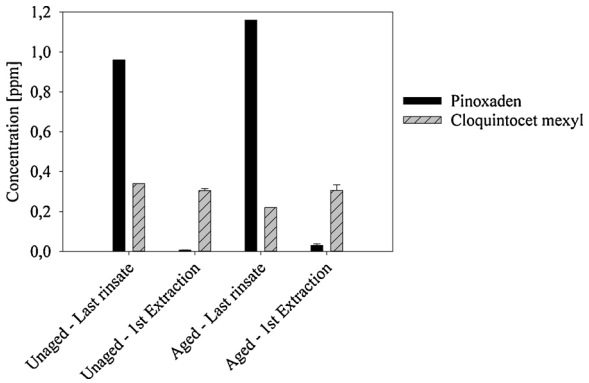

Fig. 1. concentration of the active ingredients after triple-rinsing and extraction procedures on unaged and aged APPW.

APPW from Pinoxaden, which was confirmed by the low extracted quantity of Pinoxaden, for both aged and unaged material as shown in Fig. 1. Nevertheless, Cloquintocet mexyl did not behave similarly, where the extraction procedure obtained concentrations similar to what was obtained by the last step of rinsing, indicating the existence of significant amount of Cloquintocet mexyl, even after performing the triple-rinsing. Aging the material in contact with the pesticide contributed to a less effective rinsing procedure, which could be attributed to the effect of photo- and thermo-oxidative aging on getting the chemical absorbed into the polymeric chain structure. This was observed by obtaining higher Pinoxaden concentrations in comparison to the unaged material, by both, the last washing step ("last rinsate" in Fig. 1) and the extraction procedure.

In order to evaluate the hazardousness of the obtained containers, the concentration of the extracted mixture was calculated on the basis of the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) on its last version. GHS lists the classification criteria and the hazard communication elements by type of hazard (United Nations, 2017) that is, however, not fully in line with the current European Commission regulation (European Commission, 2008). The GHS provides stricter classification ranges (e.g. the EU regulation provides one classification for short term acute aquatic hazard – Category Acute 1, whereas GHS defines three Categories with increasing thresholds). Considered the aim of this study as well as the fact that the GHS classification is the most recent one, the hazardousness assessment was performed following the latter. The GHS regulates the classification of mixtures when data are available for all components or only for some components of the mixture by applying the additivity formula for acute toxic substances based on Eq. (2) (United Nations, 2017):

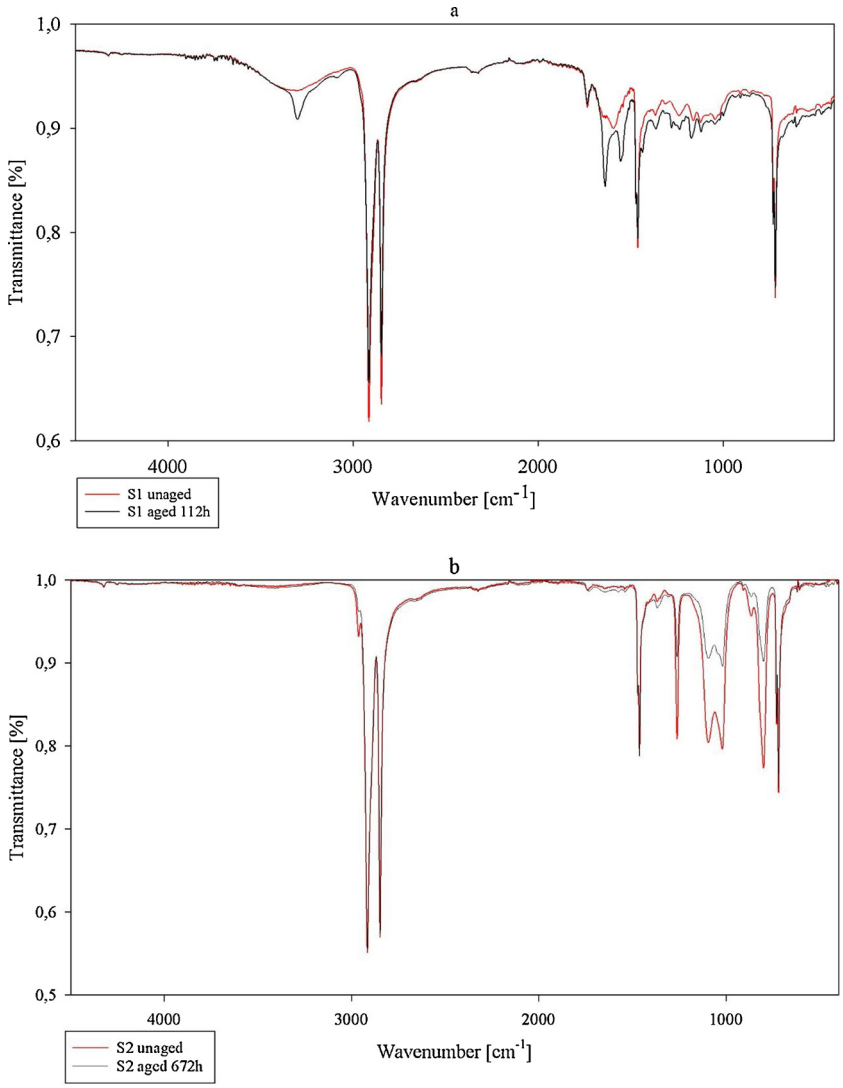

Fig. 2. ATR-FTIR spectra. a) S1 and b) S2.

$$\frac{\sum Ci}{\sum LC_{50_m}} = \sum_n \frac{Ci}{LC_{50_i}} \quad (2)$$

Ci = concentration of i component ($\%_w$)

LC_{50_i} = LC_{50} for i component (mg/l)

n = number of components

LC_{50_m} = LC_{50} of the part of the mixture with test data (mg/l)

The acute toxicity of the mixture (LC_{50m}) was calculated after the triple-rinsing procedure, in order to provide a material quality evaluation after applying the recommended treatment.

Both extraction mixtures obtained from aged and unaged APPW showed high LC_{50m} values (i.e., 10.04 mg/l and 9.83 mg/l, respectively). Applying the threshold limits defined in the GHS ($1 < LC50m \leq 10$ mg/l), both APPW fall under "Category Acute 2" limits (United Nations, 2017).

Hence, the triple-rinsing procedure was not adequate to decontaminate the APPW to be processed as non-hazardous waste. Although the investigated active ingredients do not have documented risks for health, significant consequences can be expected in the mechanical recycling phase, in which water is used for both, washing and density separation steps. As a consequence, the problem of mobilizing contaminants of emerging concern may be expected during recycling and therefore, optimized decontamination procedures are recommended.

3.2. Inner surface characterization

An increased surface roughness, in addition to pesticide crystallization on the polymeric surface due to aging was described in Picuno et al. (2019). In the following section, the effects of this degradation pattern on the surface of the polymer due to thermo-oxidative conditions are further discussed. In addition, ATR-FTIR spectra of recycled APPW are reported and discussed.

3.2.1. Thermo-oxidation effects on polymers surface

Both S1 and S2 presented spectra in correspondence with wavenumbers that are typical for PE−HD (Fig. 2): 2915 cm^{-1} (C−H stretch), 2845 cm^{-1} (C−H stretch), 1472 cm^{-1} (CH_2 bend),1462 cm^{-1} (CH_2 bend), 730 cm^{-1} (CH_2 rock), 717 cm^{-1} (CH_2 rock)) (Braun, 2013; Jung et al., 2018), (see Fig. 2). These spectra cannot be attributed to polyamides (PA) material, as for PA the transmittance response is much stronger and the spectra are much broader (Braun, 2013). However, the transmittance obtained at 1634 cm^{-1} corresponds to (C═O stretch); might be due to existence of a PA coating on the inner surface of the bottle (Jung et al., 2018). The ATR-FTIR spectra for unaged and aged S1 were identical for the wavenumbers (cm^{-1}): 2915 (C−H stretch), 2848 (C−H stretch), 1634 (C═O stretch), 1472 (CH_2 bend), 1462 (CH_2 bend), 1367 (C−H rock), 1234 (C−H wag, in alkyl halides; Cloquintocet mexyl), 730 (CH_2 rock) and 717 (CH_2 rock). When the material was aged, new spectra were formed at the following wavenumbers, indicating the formation of new chemical groups: 3300 (N−H, secondary amine), 1637 and 1556 (C═C stretch), 1437 (C−C stretch in ring), 1279 (C−N stretch), 997 (N−H wag, secondary amines). Furthermore, a transmittance peak at 1580 cm^{-1} was eliminated after aging the material, which is explained by the degradation of the coating PA layer, which, in this context, represents an N−H bend in the PA chain. There was, as well, a spectral shift from 1148 cm^{-1} to 1173 cm^{-1}, indicating the formation of alcohol groups on the cost of existing ethers, which are probably represented by the contaminating ingredient, Cloquintocet mexyl. ATR-FTIR analysis of aged and unaged S2 showed a variation in the transmittance intensity between wavenumbers 1461 cm^{-1} and 730 cm^{-1}, showing a lower transmittance value at the same wavenumbers after thermal oxidation. This response occurred most likely due to the degradation of the COEX: 1261, 1093 and 1020 cm^{-1} represent (═C−O−C, symmetric and asymmetric stretch) and 866 and 800 cm^{-1} represent (C−R stretch). Moreover, the transmittance peak representing C−H stretch group (at wavenumber 2941 cm^{-1}) was dissipated after aging, indicating either a change in the chemical structure of the polymer by having less CH_3 endings, or by the loss of plasticizer additives in the packaging material due to aging.

All in all, from the given results for both S1 and S2, it seems that the aging duration did not accelerate the processes of surface degradation and consequently of pesticide absorption on the surface. Although S2 was aged for 672 h in comparison to 112 h for S1, S1 showed more significant alterations in the material's chemical structure. Hence, the photo-oxidative aging was the limiting factor in absorbing the pesticide's components into the polymer´s chain. The role of radiation during the photo-degradation is one of the most important in abiotic degradation of polymers, leading to photolysis and initiation of photo-oxidation (Arnaud et al., 1994). Molecules in material become unstable due to absorption of photon energy (Lucas et al., 2008). Absorption of UV activates the electrons of polymer to higher reactivity; thus, bond dissociation (C−C or C−H) occurs. It produces the radical as initiation, further leading to oxidation, cleavage and other reactions (Singh and Sharma, 2008). As a result of termination, products are formed with cross linked, branched or disproportionation, dialkyl peroxydes, carbonyl species or alcohols. In this research, this was clearly provided by the ATR-FTIR analysis of the material.

3.2.2. Mechanically recycled APPW

ATR-FTIR tests performed on recycled APPW showed a spectral response (Fig. 3) typical for the PE−HD. The spectra showed no explicit signs of contamination on the surface of MR20 and MR80, indicating that the washing step in the simulated mechanical recycling process was essential for APPW decontamination. A slightly different response was obtained by the spectra of MR50, where the transmittance peaks represented higher transmittance intensities at wavenumbers: 1290, 1090 and 1044 cm^{-1} (═C−O−C, symmetric and asymmetric stretch) and ˜802 cm^{-1} (C−R stretch). This could be attributed to the existence of COEX fractions in M1b (see Table 3) and a consequent low mixing during the extrusion step.

3.3. Bulk material

3.3.1. Thermo-oxidative effects on bulk polymer

The provided NIR analysis of the full profile of the material showed no change in the bulk material after aging. For S1 (Fig. 4.a), the NIR spectra of the packaging material before and after aging were overlapping. Yet, for S2 (Fig. 4.b), although the functional groups were identically identified, the transmittance intensities slightly fluctuated. Aging provided lower transmittance intensity at: 9585 cm^{-1} (N−H stretch), which possibly happened due to the degradation of the coating material, which was also confirmed by the decrease of peak intensity at 6476 cm^{-1} (N−H stretch). Also a slight transmittance intensity decrease was observed at 7178 (i.e., C−H, methylene), indicating a possible scissoring in the chain structure of the polymer.

The NIR spectra of S1 material showed a slight shift when compared to the spectra of S2 material, which could be attributed to the difference in material's color (white for S1 and green for S2). Moreover, the NIR spectra of S2 showed a much weaker peak at 9585 cm^{-1} (N−H stretch), which almost diminished in S2 aged sample. The same trend was observed for transmittance peak at 6476 cm^{-1}. This difference could indicate that the coating layer is lower in thickness in S2 compared to that for S1. The NIR spectra did not detect material contamination with the pesticide's active ingredient.

The degree of crystallinity is a significant characteristic of a polymer in the way that it can define its mechanical properties, such as yield stress, elastic modulus and impact resistance (Kong, 2002). Results of the second heating showed a decrease in the average value of the crystal content of aged samples in comparison to unaged ones, as shown in Table 2. However, considering the larger standard deviation (± 192), crystallinity values of the material still fall within the provided reference limits (60,0%–80,0% Ehrenstein (2001). The standard

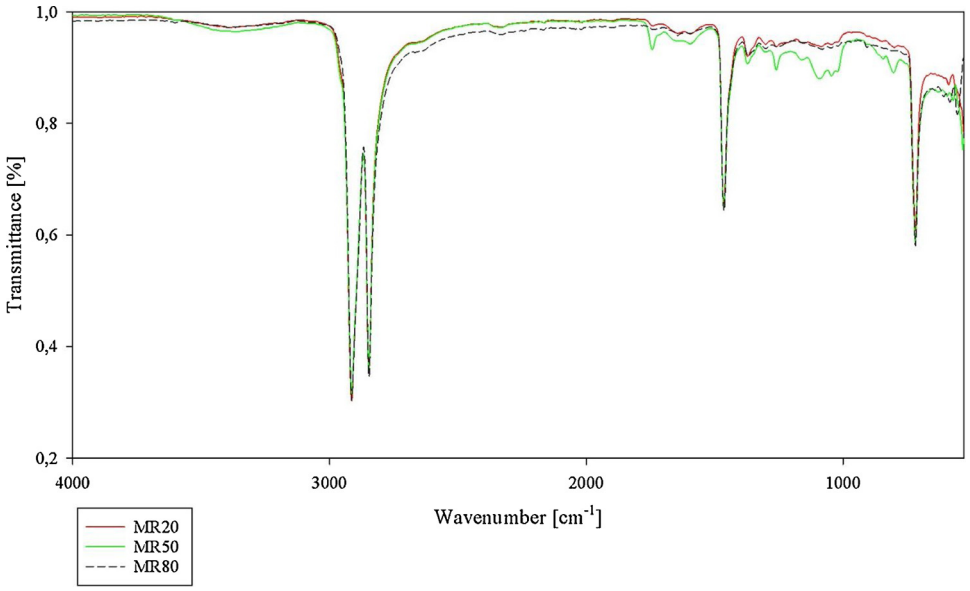

Fig. 3. ATR-FTIR spectra of mechanically recycled APPW differently diluted with virgin PE.

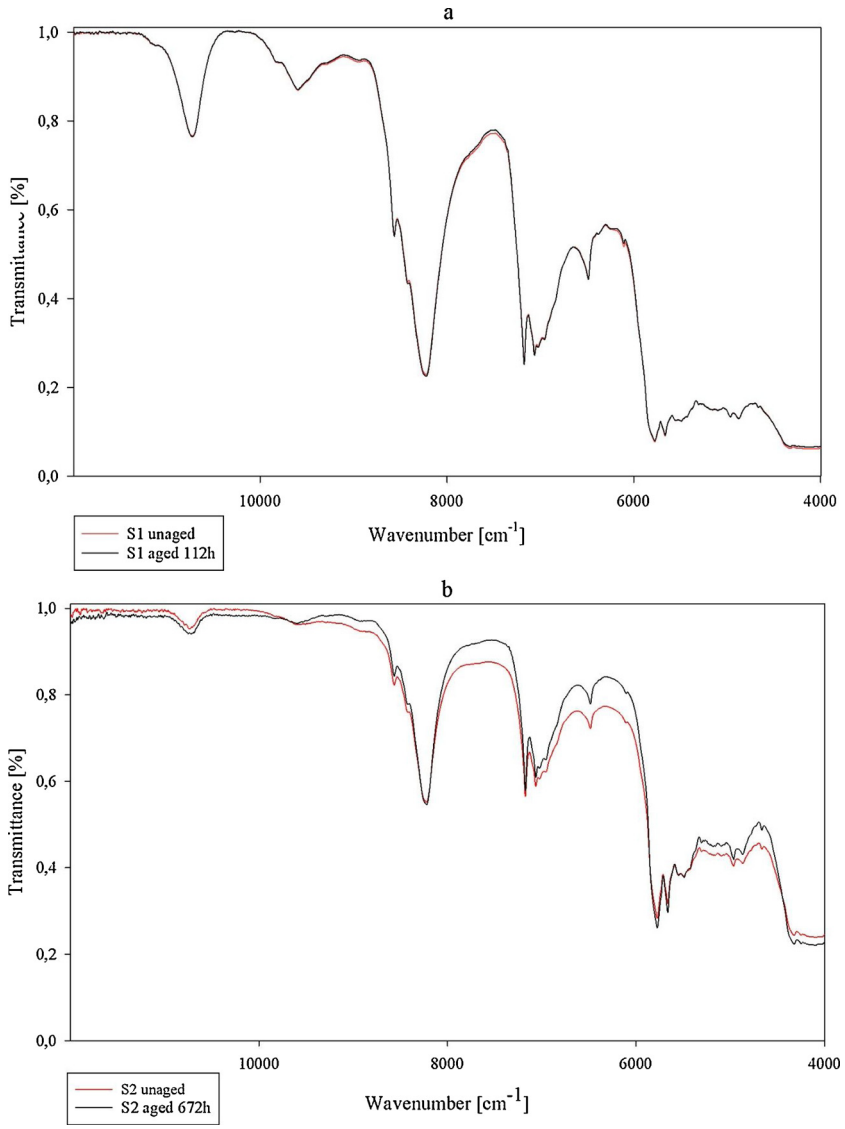

Fig. 4. FTNIR spectra. a) S1 and b) S2.

Table 2
Crystallinity changes with accelerated aging.

Typical crystallinity value for PE-HD	60 % - 80 %
Unaged	58,73 % ± 6,78 %
Aged	43,97 % ± 19,25 %

Table 3
Ratios of tensile stress over stress at break.

Proportion of recycled APPW [%]	Tensile strength σ_m [MPa]	Stress at break σ_b [MPa]	σ_m/σ_b
20	17.54 ± 0.69	14.66 ± 1.26	1.20
50	22.93 ± 0.95	18.79 ± 1.26	1.22
80	24.88 ± 0.49	14.15 ± 1.27	1.76

deviation values increased from 6,8% for the unaged material to 19,3% for aged material, indicating higher material quality variation.

3.3.2. Bulk material of mechanically recycled APPW

An assessment of the bulk material of recycled APPW through NIR spectroscopy led to the conclusion that there was no detectable contaminant in the polymeric matrix of the sample MR (refer to Fig. 5). Identical identification of the functional groups, although with slight differences in the transmittance level of differently diluted APPW with virgin PE, clearly suggested that the bulk material was pure PE−HD COEX polymer. A further confirmation of this arose from the comparison of the latter spectra with the spectral response of S1: albeit containing different active ingredients and being subjected to two utterly different processes (mechanical recycling for M1 sample and aging for S1), the spectral response was almost identical. Therefore, it is possible to conclude, with fair confidence, that the mechanically recycled material did not show contamination.

4. Tensile tests on recycled APPW

Tensile testing was performed on samples MR20, MR50, and MR80 in order to characterize the material from a mechanical perspective.

The shape of the stress-strain curve obtained for the samples containing recycled APPW was strongly affected by the concentration of APPW in the sample (refer to Fig. 6). For a ratio of 20% recycled APPW, a shorter plastic deformation before break was recorded and, for a rising amount of recycled APPW, the curve proved the material to be

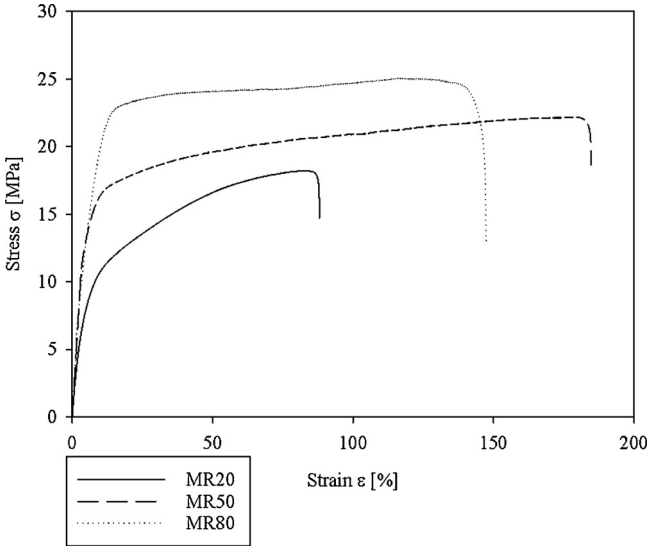

Fig. 6. Stress-strain curves of recycled APPW with different dilution ratios.

able to sustain higher stresses. This behavior can probably be traced back to the additives (from the category of plasticizers) in the PE-HD, used in agrochemical containers to improve the properties of the material with regards to the specific requirements for its application. Plasticizers provide a greater ductility, resulting in better mechanical resilience of the material and protecting the containers from brittle fractures in case of large mechanical stress (Kutz, 2011), e.g., falling down during handling or being stacked on top of each other.

However, plasticizers additionally contribute to reducing the modulus of elasticity (Houssier et al., 2017) and this tendency could be observed in the resulting mechanical parameters as in Fig. 7. In this specific case, the increase in Young´s modulus could be justified by the use of functional fillers in the production phase of packaging (Xanthos, 2005). Similarly, the tensile strength increased with an increase in amount of recycled APPW. This behavior is similar to the one observed by Shebani et al. (2018), according to whom an increase in tensile strength was attributable to an increase of crystallinity due to increasing presence of PE-HD (Shebani et al., 2018).

For the stress at break, the behavior could be explained by the influence of plasticizers as well. Higher ductility and, therefore, higher capability for plastic deformation before break, is represented in the

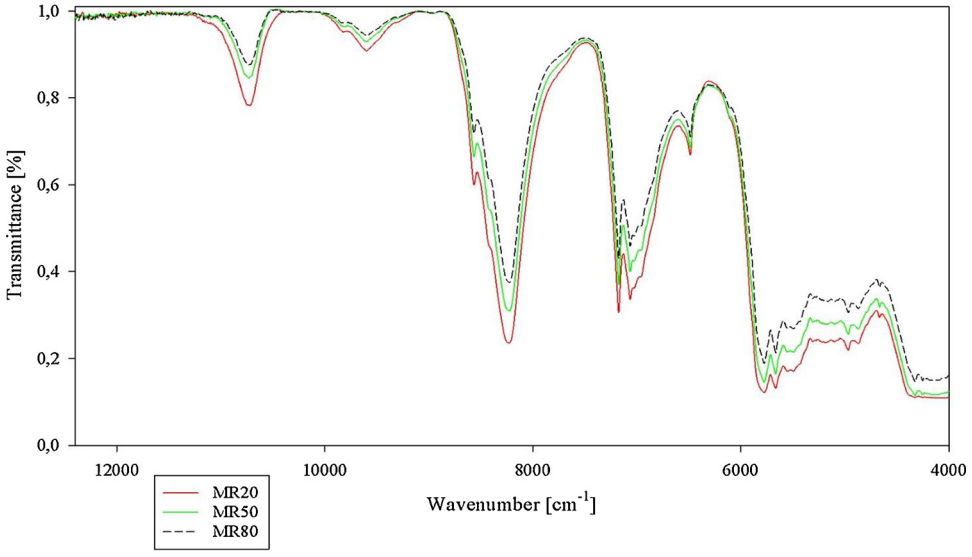

Fig. 5. FTNIR spectra of recycled APPW.

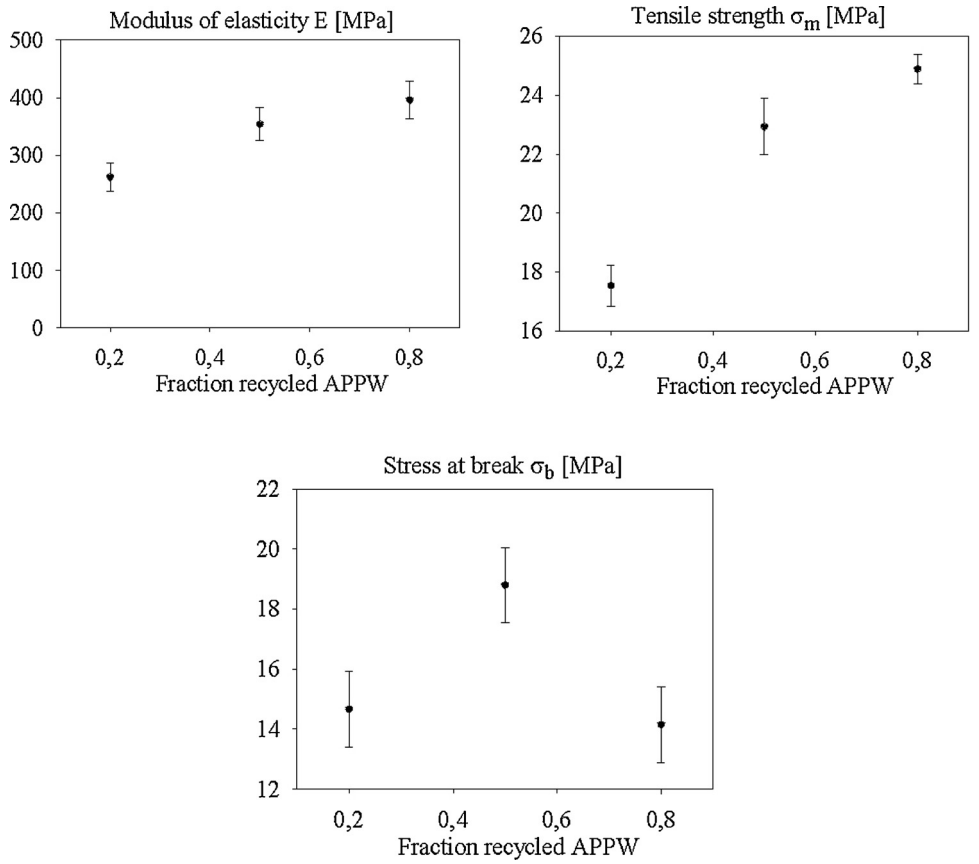

Fig. 7. Stress-strain curves derived mechanical parameters.

stress-strain curves, firstly, by the long and flat section of the stress-strain and, secondly, by a long section of strongly decreasing stress before break. Although a direct comparison of the absolute values of stress at break does not clearly indicate influence of plasticizers in the mechanical properties, a comparison of the ratios of maximum stress over stress at break does. The mean values and the standard deviation for these values listed in Table 3 prove that, as the influence of the plasticizers becomes stronger with a rising concentration of APPW, the ratio of tensile strength over stress at break increases steadily. This leads to the conclusion that the tensile strength increases at a higher rate than the stress at break, supporting the statement of the influence of plasticizers in the material increasing ductility.

As a consequence of the mechanical evaluation of the material, it can be concluded that the material could be recycled into new products for agriculture, with fairly acceptable mechanical properties for greenhouse or low-tunnel films applications, as a comparison of the mechanical parameters in Table 4 shows, or rather for simpler and low-strength applications, e.g. soil mulching (Briassoulis et al., 2013a).

5. Conclusion

The triple-rinsing procedure conducted in this research could de-contaminate the containers from the chemical Pinoxaden, yet, lower decontamination effectiveness to the chemical Cloquintocet mexyl was observed, especially when material was aged in contact with the pesticide. Generally, material contamination by Cloquintocet mexyl was only observed on the surface, suggesting mobilization and absorption of the active ingredient limited to the surface; whereas the NIR spectra showed a clean bulk material. The calculated LC_{50} value of the extracted mixture of aged and unaged agrochemical containers allowed for the classification as acute toxic within "Category Acute 2". Therefore, the APPW needs to be treated as hazardous material, even after the triple-rinsing contamination procedure. The washing step on shredded APPW, which was performed during mechanical recycling, was proved feasible as an additional decontamination procedure. This was confirmed after testing the mechanically recycled samples, where material contamination could not be detected, indicating that the washing and sink-floating step applied before extrusion could lower, if not eliminate, the material hazardousness. In addition, tensile tests proved that the recycled material is suitable for reutilization in typical agricultural practices, such as low-tunnel and greenhouse covers.

Aknowlegments

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors. The authors declare no conflict of interest. The authors gratefully acknowledge the Central Laboratory of the TUHH for the support in the analytical

Table 4
Mechanical properties of films used for agricultural applications.

	Modulus of elasticity E [MPa]	Tensile strength σ_m [MPa]
Recycled APPW	262–396	17.5–24.9
PE-LD films for greenhouse covering Briassoulis et al. (1997)	113–230	13.8–25
Blending of recycled greenhouse and low-tunnel films Picuno, 2014; Picuno et al. (2012)	110–160	12.5–35.7

procedures, the Institute of Technical and Macromolecular Chemistry of the University of Hamburg for permitting to achieve the experimental activities of this research as well as the anonymous reviewers for their constructive suggestions on a previous version of this paper.`

Declaration of Competing Interest

The authors declare no conflict of interest

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