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Mechanical recycling of HDPE-based packaging: Interplay between cross contamination, aging and reprocessing

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ABSTRACT

Achieving effective mechanical recycling strategies for polyolefins remains a major challenge for several reasons. Firstly, the thermo-mechanical degradation underwent during reprocessing, as well as the different degradation forms experienced during the service life, cause a severe modification of polyolefin microstructure, ultimately leading to a progressive deterioration of their performance. On the other hand, due to non-fully accurate sorting technologies, low levels of cross-contamination are commonly encountered in recycled polyolefins. All these features result in the obtainment recyclates with a heterogeneous and complex morphology, which significantly affects their final properties, often limiting their possible future applications. This work aims at addressing these issues, evaluating the combined effect of cross-contamination and of the degradation undergone by the polymers during service life and reprocessing for high-density polyethylene (HDPE) containing low amounts of polypropylene (PP) and polyethylene terephthalate (PET) as contaminants. In particular, pristine and cross-contaminated HDPE were subjected to photo-oxidative or thermo-oxidative treatments and the aged materials were reprocessed, aiming at simulating the real conditions of a typical mechanical recycling process. The obtained results demonstrated that cross-contamination minimises the functional degradation of HDPE, especially under photo-oxidative conditions. Conversely, the microstructural characterization pointed out that different microstructures can be achieved depending on the level of cross-contamination and on the aging treatment. Finally, it was shown that the presence of PP and PET as contaminants has a detrimental impact on the HDPE ductility, especially under thermo-oxidative conditions, while for photo-oxidised materials exerts a marginal role.

1. Introduction

Nowadays, it is widely accepted that the transition to a circular plastics economy could significantly alleviate the environmental issues associated with plastic waste [1–2]. In fact, the complete reintroduction of end-of-life plastics into the production and consumption cycle through repair, reuse or recycling strategies, would significantly change their ultimate fate, which is currently largely landfilling (causing soil pollution, micro- and nano-plastics generation and marine litter) or incineration (leading to the release of carbon dioxide and other harmful gases, further contributing to climate change) [3].

At the same time, the accomplishments of a full plastics circularity would also have a positive impact on the industry's dependence on fossil fuel feedstocks. In fact, recent studies have reported that, even considering a moderate scenario, the circular plastics economy model may lead to a reduction in demand for hydrocarbons in petrochemical industry of 5–10 % by 2050, as compared to the business-as-usual case [4].

At present, recycled plastics are almost exclusively obtained through mechanical processes [5–6]. Despite the huge technological progress made in mechanical recycling over the last decades, there are still some shortcomings negatively affecting the achievement of a full plastic circularity. The main challenge associated with the mechanical recycling is the transformation of end-of-life plastics into materials with an added economic value [7–8]. In fact, although mechanical recycling strategies are undoubtedly potentially able to generate economic and environmental benefits, in order to achieve a circular plastics economy, it is essential to maintain the value of the material, by preserving its structural integrity [9]. Unfortunately, the various degradation forms (such as, photo-oxidation, thermo-oxidation and thermo-mechanical degradation) at which the polymeric materials are subjected during

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both their service life and re-processing severely modify their macromolecular microstructure [10–11]. In particular, all these degradative processes result in changes in the polymer molecular weight, chain architecture, processability, mechanical and functional properties, and aesthetic appealing, significantly affecting the final performance of recycled plastics, which could no longer meet the requirements for a certain application [12]. For all these reasons, recycled polymers are often used to formulate products of lower quality and value rather than for the same original application as their virgin counterparts, resulting in what is known as downcycling. In fact, according to the latest available data, only 8.5 % of new goods and products are currently made from recycled polymers, indicating a preference by manufactures for virgin over recycled polymers [13].

Another aspect to be considered in mechanical recycling is the possible contamination of the recycled polymer with inorganic (e.g., glass or metals) or organic (such as additives or food residues) materials or, even more importantly, with other polymers [14]. In particular, due to ineffectiveness of the sorting techniques exploited for the selection of polymeric materials prior to mechanical recycling, recycled materials often contain contaminants or mis-sorted polymers, whose presence can lead to a worsening of polymer properties (either during or after the reprocessing), ultimately resulting in a further reduction of the quality of recyclates [5,15–16]. Cross-contamination is particularly relevant for recycled polyolefins, such as polyethylene and polypropylene. Both polymers are extensively used for packaging applications and represent the most discarded plastics every year, constituting most of the light fraction of plastic waste stream. The very similar value of density of the two polymers makes very difficult the obtainment of an accurate sorting by float-sink separation [17]. Although there exist alternative technologies with higher separation capacity, they usually involve high costs and complex equipment that are not justified by the value of the recovered materials [15]. For this reason, recycled polyolefins typically contain an amount of other polyolefins ranging from 10 to 15 % [18]. For instance, it has been shown that commercial recycled high-density polyethylene (HDPE) collected from different European companies contains from 2 to 13 wt% of polypropylene (PP) [19].

While a few works evaluating the impact of polyolefin contamination on the final properties of recyclates are already available in the literature [15–16,20–23], the combined effect of such cross-contamination with the degradation experienced by the polymers during service life and reprocessing has not been assessed, yet. However, the interplay between aging and cross-contamination may result in complex and interrelated chemical and microstructural effects influencing each other. Firstly, it should be considered that, due to the typical immiscibility between polyolefins, cross-contamination causes the obtainment of materials with heterogeneous morphologies, which could evolve in different ways depending on the processing conditions imposed during the reprocessing. Most importantly, the material microstructure can influence the response to the aging [24]. On the other hand, the effect of the aging and the consequent degradation (i.e., photo-oxidation or thermo-oxidation or thermo-mechanical degradation) on the various polymeric phases present in contaminated recyclates can significantly differ. For instance, thermo-mechanical degradation proceeds through chain-scission reactions for PP, causing a decrease of the polymer molecular weight [7]; otherwise, HDPE apart chain scission experiences also branching and crosslinking leading to a profound modification of its macromolecular architecture [25]. Once again, all these issues result in a modification of the material morphology. Considering that the final properties of recyclates are largely dependent on their microstructure, the knowledge of the different combined effects deriving from aging and cross-contamination is thus mandatory for effectively assessing the performance (hence, the possible applications) of recycled polymers.

This work aims at evaluating the impact of cross-contamination and different form of aging (namely, photo- and thermo-oxidation) on the mechanical recycling of HDPE. More specifically, starting from the typical composition of a HDPE bottle [26], HDPE-based systems containing small amounts of PP and polyethylene terephthalate (PET) contaminations were subjected to photo- or thermo-oxidative treatments and the aged materials were reprocessed, aiming at simulating a typical mechanical recycling process. The interplay between the presence of cross-contamination, the aging treatment and the thermo-mechanical degradation underwent by the material during the reprocessing was evaluated, considering either the functional or microstructural modifications induced in HDPE by the different aspects. Finally, the tensile behaviour of all investigated systems was assessed, and the obtained results were associated to the inferred evolution of the material microstructure.

2. Materials and methods

2.1. Materials

HDPE ERACLENE ® BB82 (Melt Flow Rate (190 °C, 5 kg) = 0.15 g/10 min) supplied by Versalis, PP Moplen HP500 N (Melt Flow Rate (230 °C, 2.16 kg) =12 g/10 min) supplied by LyondellBasell and PET PPK FR (Intrinsic Viscosity=0.8 dl/g) supplied by Plastipak Italia were employed.

2.2. Processing

The three following systems have been produced:

- pristine HDPE,
- HDPE with 10 wt% PP
- HDPE with 10 wt% PP and 2 wt% PET.

Before processing, PET has been vacuum dried at 80 °C overnight.

The compounding step was carried out using a Process 11 (Thermo Fisher) twin-screw extruder. The screws rotation speed was set at 100 rpm, and the temperature profile was 230–230–230–240–240–240–250–250–250 °C from hopper to die.

Specimens for the subsequent aging treatments (thickness: 2 mm) and for rheological (thickness: 1 mm) and mechanical (thickness: 0.6 mm) characterizations were produced through a compression molding step, using a Collin P200T press at 100 bar; the temperature has been set at 230 °C for pristine matrix and 250 °C for HDPE-based systems.

2.3. Aging

Two different aging treatments were considered:

- Photoaging by subjecting the specimens to UV irradiation (irradiance = 90 W/m^2 [27–28]) in a SEPAP 12/24 (Atlas) apparatus, equipped with mercury vapor lamps releasing discrete radiation at wavelengths higher than 300 nm for subjecting polymeric materials to photo-oxidation in artificial conditions [29]. All the investigated materials were treated for 300 h at 60 °C in air;
- thermo-oxidative treatment at 80 °C in oven at RH 100 % for 300 h.

After the aging treatments (i.e. after photo- or thermo-oxidative aging) all the systems have been reprocessed through ThermoFischer Process 11 twin-screw extruder with screws speed equal to 100 rpm and a temperature profile set to 250 °C for all the heated zones and the die. Specimens for the subsequent characterizations were produced through a compression molding step using the same equipment and processing conditions described above. Table 1 reports the codes associated with all the investigated materials, containing cross-contamination and/or subjected to the aging treatment and the re-processing step.

2.4. Characterization techniques

An ARES (TA Instrument) rotational rheometer has been employed

Table 1
Investigated materials and codes.

Material	Code
HDPE	**HDPE**
HDPE+10wt%PP	**HDPE/PP**
HDPE+10wt%PP+2wt%PET	**HDPE/PP/PET**
HDPE photo-oxidised and reprocessed	**HDPE_ph**
HDPE+10wt%PP photo-oxidised and reprocessed	**HDPE/PP _ph**
HDPE+10wt%PP+2wt%PET photo-oxidised and reprocessed	**HDPE/PP/ PET_ph**
HDPE thermo-oxidised and reprocessed	**HDPE_th**
HDPE+10wt%PP thermo-oxidised and reprocessed	**HDPE/PP_th**
HDPE+10wt%PP+2wt%PET thermo-oxidised and reprocessed	**HDPE/PP/PET_th**

in order to perform rheological analyses. Frequency sweep tests were performed under nitrogen atmosphere, at 230 °C and frequency ranging from 100 to 0.1 rad/s. The strain amplitude was selected within the linear viscoelastic range of each sample, preliminary evaluated through strain sweep measurements at the same temperature.

Spectroscopic characterization was carried out through FTIR-ATR Frontier (Perkin Elmer) equipped with a diamond crystal. The spectra were acquired through 16 scans, resolution of 2 cm^{-1}, in a range of wavelength between 4000 and 400 cm^{-1}. For both non-aged and aged systems, carbonyl index (C.I.) was assessed through the following formula (Eq. (1)):

$$C.I. = \frac{A_{peak}}{A_{reference}} \quad (1)$$

where: A_{peak} is the absorbance of the carbonyl peak at 1720 cm^{-1}, and $A_{reference}$ is the absorbance of the reference peak at 1472 cm^{-1} attributed to CH_2 bending for HDPE systems [2].

DSC analyses were performed via DSC Q20 (TA Instruments). For all systems, the tests consisted of three scans: (*i*) first heating from 0 °C to 300 °C, heating rate of 10 °C/min, *(ii)* cooling from 300 °C to 0 °C, cooling rate of 10 °C/min, *(iii)* second heating from 0 to 300 °C, heating rate of 10 °C/min. The HDPE crystallinity content was estimated by using the following formula (Eq. (2)):

$$\chi_C = 100\frac{\Delta H_M}{\Delta H_{M100\%}(1-x)} \quad (2)$$

where: ΔH_M is the melting enthalpy (evaluated as the area of the melting peak recorded during the second heating scan), $\Delta H_{M100\ \%}$ is the melting enthalpy of a 100 % crystalline HDPE (290 J/g [30]), and x is the cross-contamination content. DSC analyses were performed in triplicate (uncertainty < 5 %.) and the results averaged.

Scanning electron microscopy (SEM) EVO 15 by Zeiss was employed to perform the morphological characterization. Before the SEM observations, brittle fracture surfaces were obtained by treating the samples with liquid nitrogen and the observed surfaces were gold sputtered.

Finally, mechanical tensile tests were carried out using a 5966 Instron dynamometer equipped with a 2 kN cell load and 250 N clamps. The crosshead speed was maintained at 1 mm/min up to 0.25 % of deformation, then was increased to 10 mm/min until specimen breaking. The tensile tests performed on five specimens and the results averaged.

3. Results and discussion

As briefly anticipated before, HDPE-based systems containing PP and PET cross-contaminations were subjected to photo or thermo-oxidative treatment before reprocessing in order to simulate the typical aging that polymers underwent during their service life. In the following sections, the results coming from the different characterizations will be discussed taking into consideration the combined effect of the cross-contamination, the aging treatment (photo- or thermo-oxidative) and the subsequent reprocessing step.

3.1. Functional modifications induced by aging and reprocessing

Firstly, ATR-FTIR analyses were carried out either on pristine or aged and reprocessed materials aiming at evaluating the possible impact of cross-contaminations on the typical degradation experienced by HDPE under photo- or thermo-oxidative conditions and also due to the thermomechanical degradation during processing. As anticipated in the experimental section, the collected ATR-FTIR spectra were analysed, deriving the values of the Carbonyl Index (C.I.) reported in Fig. 1.

As widely reported in the literature [31–32], the degradation of HDPE in both photo- and thermo-oxidative conditions proceeds through the formation of ketone groups, recognisable from FTIR analyses through the appearance of two absorption peaks at 1720 cm^{-1} [31] and 1410 cm^{-1} [32]. As observable from the C.I. values reported in Fig. 1, HDPE degraded faster under photo-oxidative aging conditions than thermo-oxidative aging ones at the considered time scale. As a result, higher values of C.I. are obtained for HDPE_pH than for HDPE_th.

The introduction of PP as contaminant causes the achievement of lower C.I. values as compared to pristine HDPE, either before or after the photoaging, while it has a negligible effect when the material is subjected to thermo-oxidative treatment. A very similar behavior was already observed in the literature [33]. In particular, Madi et al. [34] showed that when PP is present in recycled HDPE at small concentrations (namely, < 5wt%) the resulting material is more stable than pristine HDPE, while higher amounts of PP cause an opposite behavior. This result can be explained considering that the degradation mechanism of PP involves a faster formation of radicals as compared to HDPE, due to presence of tertiary hydrogens [35]. As a consequence, PP acts as a sort of sacrificial oxidisable phase, exerting a stabilizing effect towards the oxidation of HDPE. Upon thermo-oxidative conditions this effect is less pronounced; however, it should be considered that also the degradation of pristine (i.e., without cross-contamination) HDPE is significantly less severe with respect to photoaging, at least at the exploited time scale. Therefore, all the effects related to the presence of PP are minimized. Conversely, the contemporary introduction of PP and PET induces the achievement of higher C.I. values as compared to the pristine polymer, both under photo- and thermo-oxidative treatments, although the absorption peaks in the carbonyl range used to monitor the

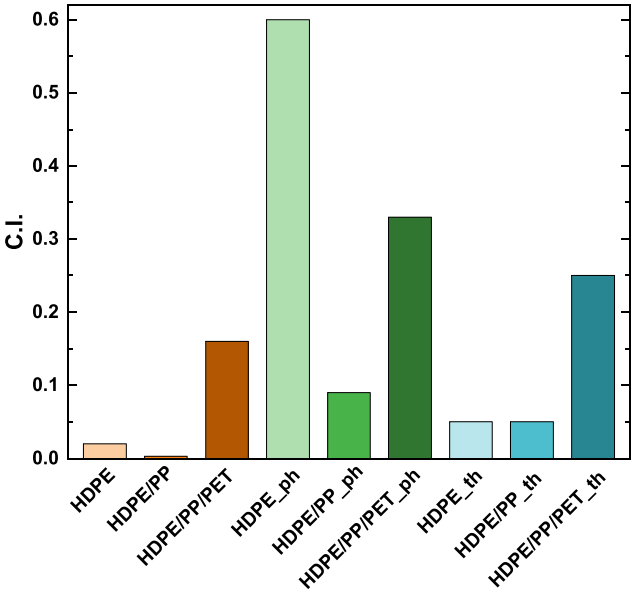


Fig. 1. Carbonyl index for HDPE and HDPE-based systems subjected to the aging treatments and reprocessing. The values for pristine samples are also reported.

degradation of HDPE are already present in the ATR-FTIR spectrum of pristine PET.

3.2. Microstructural modifications induced by aging and reprocessing

Fig. 2 reports the curves of complex viscosity as a function of frequency for the processed (Fig. 2a), photo-oxidised and reprocessed Fig. 2b) and thermo-oxidized and reprocessed (Fig. 2c) HDPE-based systems. Looking at the different behaviours obtained for the different investigated materials it is possible to infer that either the presence of contaminants or the aging and the reprocessing greatly affect the rheological response, hence the microstructure, of HDPE.

Concerning the rheological behaviour of HDPE containing cross-contamination before the aging treatments (Fig. 1a), the introduction of PP and PET leads to the achievement of higher viscosity values as compared to the pristine polymer, while maintaining almost unaffected the trend of the complex viscosity as a function of the frequency. As a matter of fact, given the typical immiscibility of the considered polymers, the cross-contaminated HDPE materials are immiscible blends whose morphology, as shown by the SEM micrograph reported in Fig. 3a, is characterized by the presence of droplets of the dispersed phases embedded in the polyethylene matrix. These inclusions are able to interfere with the relaxation dynamics of HDPE macromolecules, causing the obtainment of higher complex viscosity values [36].

Looking at the curves reported in Fig. 2b, it can be clearly noticed that the photo-oxidative treatment and the subsequent reprocessing severely affect the rheological response of pristine HDPE. In particular, HDPE_pH shows a more pronounced non-Newtonian behavior with respect to the pristine polymer, which causes the achievement of higher complex viscosity values especially in the low frequency range. As widely reported in the literature [37–39], for HDPE both photo-oxidative and thermo-mechanical degradations involve the concurrent occurrence of different phenomena, such as chains scission, long-chain branching formation and crosslinking which result in a significant modification of the macromolecular architecture of the polymer chains. Therefore, the more prominent non-Newtonian characteristics of HDPE_pH can be related to the decreased chain mobility caused by the formation of a branching structure or by the introduction of some

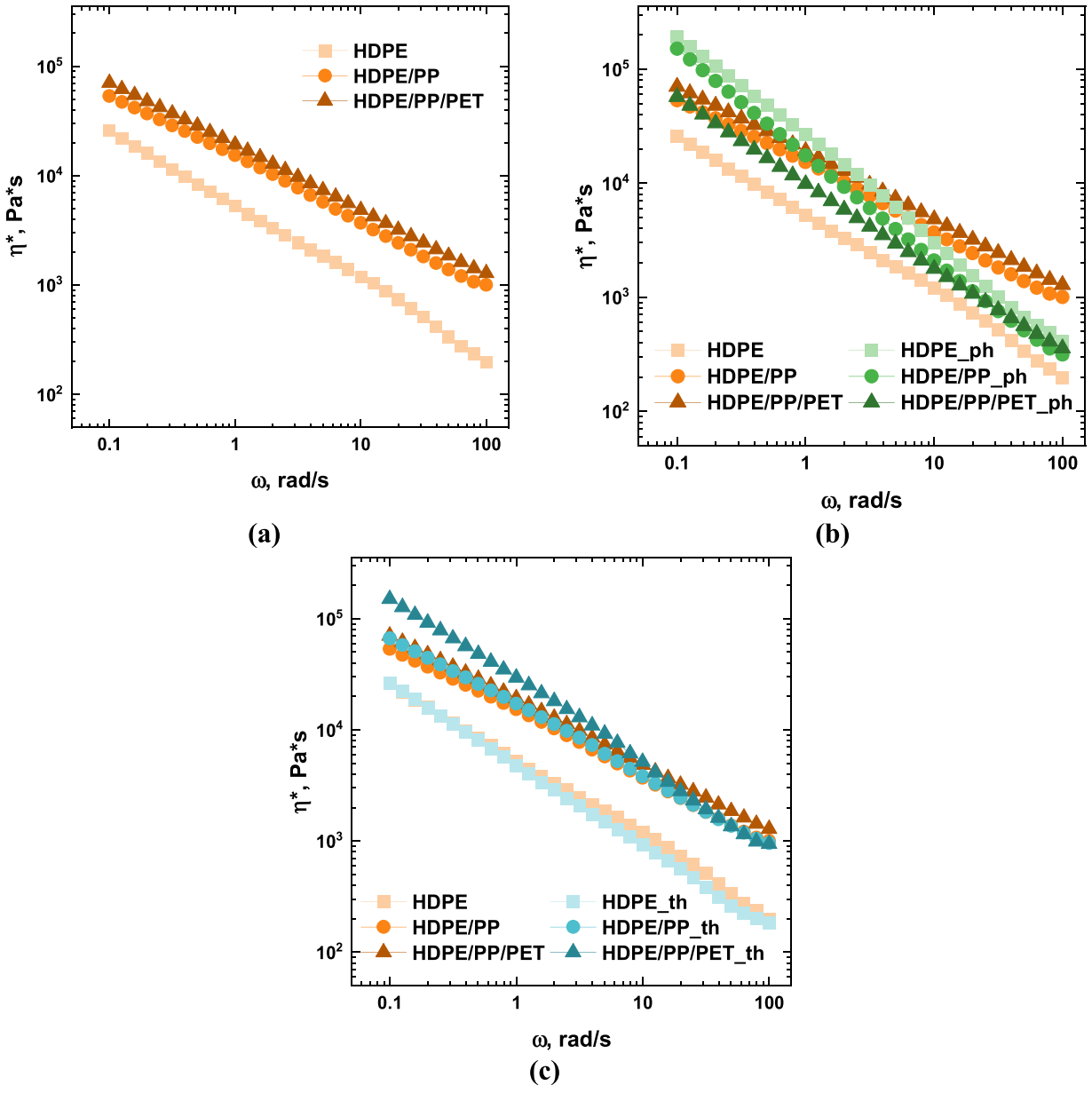


Fig. 2. Complex viscosity curves of processed (a), photo-oxidised and reprocessed (b) and thermo-oxidised and reprocessed (c) HDPE systems.

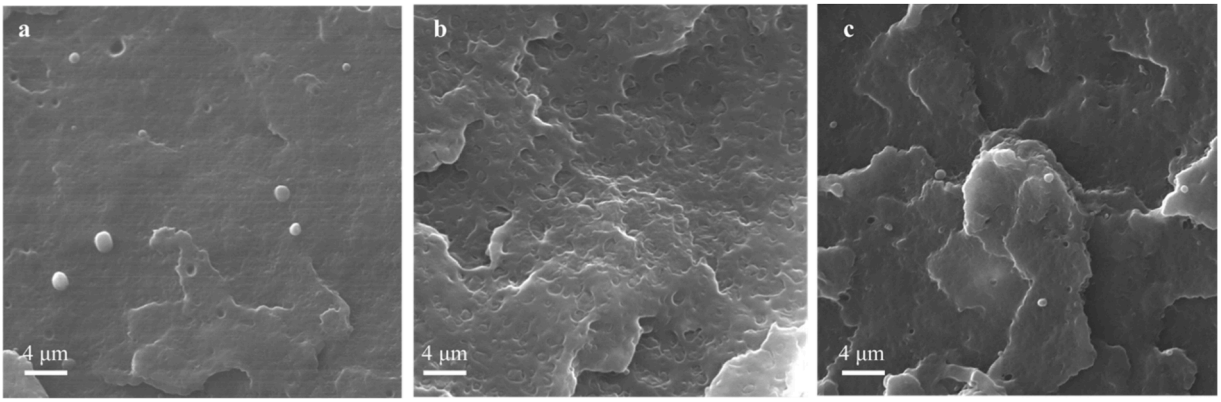


Fig. 3. SEM micrograph of HDPE/PP/PET (a), HDPE/PP/PET _pH (b) and HDPE/PP/PET_th (c).

crosslinks.

The behavior of the HDPE/PP_pH sample is quite similar to that of the non-contaminated polymer, and the complex viscosity curves of the two materials tend to superimpose in the whole investigated frequency range. At variance, the contemporary presence of PP and PET cross-contaminations results in a different rheological behavior. In fact, after the photo-oxidative treatment and the subsequent reprocessing, HDPE/PP/PET_pH exhibits less pronounced non-Newtonian behavior and lower complex viscosity values in the low-frequency region as compared to other aged systems, but also to its non-aged counterpart. These noticed modifications of the rheological response of this system can be associated to the morphological alterations induced by the aging and the reprocessing, as observable in the SEM micrograph reported in Fig. 3b. In particular, for this material a quite homogeneous morphology was obtained and, as compared to the non-aged system, the particles of the dispersed phases are barely recognisable. It is known that [40–41], in the case of immiscible polymer blends, the final morphology and the dimensions and shape of the domains of the dispersed phase depend on the occurrence of breaking and coalescence phenomena, which are in turn governed by the viscosity ratio between the dispersed phase and the matrix. In particular, in presence of high viscosity matrices coalescence phenomena are prevented, leading to the reduction of the particles main size [42]. The rheological characterization demonstrated that photo-oxidative treatment and reprocessing induced an increase of the viscosity of HDPE, which prevents coalescence phenomena between the dispersed phase inclusions during the reprocessing stage, resulting in the obtainment of a more refined and homogeneous morphology.

As far as the influence of the thermo-oxidative treatment and the reprocessing is concerned, as already highlighted for functional degradation, also the microstructural modifications of HDPE and HDPE-based systems are less severe as compared to those resulting from photo-oxidation. This last, due to the less advanced HDPE thermo-oxidative degradation phenomenon as compared to the photo-oxidative one in the time scale considered for the thermo-oxidative aging [43]. In particular, as testified by the complex viscosity curves depicted in Fig. 2c, for HDPE and HDPE/PP materials no remarkable differences are noticed, as the response of the aged samples is practically coincident to that of the corresponding non-aged materials in the whole tested frequency interval. Differently, HDPE/PP/PET_th sample shows a more pronounced non-Newtonian response as compared to its non-aged counterpart, resulting in higher viscosity values at the lowest explored frequencies. Therefore, the thermo-oxidative treatment has an opposite effect on the rheological behavior of this material as compared to photo-oxidation. Once again, it should be considered that the rheological response of such a complex system is strongly dependent on its morphology. As observable in the SEM micrograph reported in Fig. 3c, for this material a droplet-like morphology very similar to that of the non-aged sample is obtained. In this case, in fact, the viscosity of the HDPE matrix does not show significant modifications upon aging. Therefore, during the subsequent reprocessing, breaking and coalescence phenomena involving the domains of the dispersed phase occur in a very similar way as the non-aged sample, resulting in the achievement of a quite unmodified morphology. The amplification of the non-Newtonian behavior as compared to the non-aged sample could be likely attributed to some alterations of the main size and shape of the dispersed phase inclusions or of their extent of dispersion within the matrix, further disturbing the relaxation dynamics of HDPE macromolecules.

Table 2 reports the main thermal characteristics (i.e., crystallization temperature T_C, melting temperature T_M, melting enthalpy ΔH_M and crystallinity degree χ_C) evaluated from DSC thermograms collected during the cooling and the second heating scans for all investigated HDPE-based materials.

Looking at the results obtained for the samples before aging, it can be observed that neither the crystallization nor the melting temperatures of HDPE are affected by cross-contamination, which conversely has a not negligible impact on the crystallinity content when PET is present. To explain these results, it should be considered that, as also demonstrated by morphological analyses, the HDPE-based materials containing cross-contaminations are immiscible blends, for which modifications in crystallinity are typically observed due to several concurrently occurring phenomena such as fractionized crystallization and nucleating action of the interfaces [44].

Focusing on the photo-oxidised samples, it can firstly be noticed that, regardless of the presence of PP and PET contaminants, a secondary crystallization peak appears at lower temperatures as compared to the main one. As demonstrated by the rheological characterization, the typical linear architecture of the HDPE macromolecules evolves due to photo-oxidation, with the formation of branched structures and cross-linking, which can disturb the reorganisation and the chain folding during the crystallization process, thereby promoting the formation of a low content of imperfect crystallites having small dimensions [45]. Furthermore, the system containing PP and subjected to photo-oxidative

Table 2
DSC results for all investigated systems.

	T_{C1} (°C)	T_{C2} (°C)	T_M (°C)	ΔH_M (J/g)	χ_C (%)
HDPE	114.9	–	134.7	211.7	72
HDPE/PP	115.9	–	133.8	191.5	73
HDPE/PP/PET	115.8	–	133.7	203.9	79
HDPE_ph	111.7	80.1	134.5	211.3	72
HDPE/PP_ph	110.5	79.1	134.3	161.2	61
HDPE/PP/PET_ph	113.3	79.0	134.5	191.6	74
HDPE_th	115.2	–	134.1	202.9	69
HDPE/PP_th	115.5	–	134.2	186.1	71
HDPE/PP/PET_th	115.1	–	134.2	187.9	73

treatment shows decreased crystallinity degree as compared to pristine HDPE, suggesting that the presence of the droplets of the dispersed PP phase cause a delay in the HDPE crystal growth rate as already demonstrated for recycled HDPE-PP blends [34]. On the other hand, this phenomenon is minimised when PET is present as well, similarly to what noticed for non-aged systems.

The thermo-oxidative treatment, as already remarked before, has a less pronounced impact on the HDPE microstructure as compared to photoaging, at least at the exploited time scale, resulting in quite unmodified thermal properties of the aged materials as compared to the not-aged ones.

3.3. *Effect of cross-contamination, aging and reprocessing on hdpe mechanical behavior*

All the noticed chemical and microstructural alterations of HDPE when subjected to aging and reprocessing in presence of cross-contamination could likely impact its mechanical performance. To verify this feature, tensile tests were carried out on all investigated materials, and the obtained results in terms of elastic modulus (E), maximum tensile strength (σ_{MAX}) and elongation at break (ε_{MAX}) are reported in Fig. 4. From a general point of view, the presence of contaminants and the aging phenomena do not remarkably influence the HDPE elastic modulus and tensile strength, while dramatically affect its ductility. Considering the materials before the aging, the introduction of PP as contaminant has a negligible effect on the matrix tensile properties, while the contemporary presence of PP and PET causes a significant fall of the elongation at break, indicating a remarkable embrittlement effect exerted by the PET phase. According to the literature, this behavior can be ascribed to the inherent brittle characteristics of PET, as well as to the stress concentration around the dispersed phase domains, weakly interacting with the surrounding HDPE matrix [44].

As a consequence of the photo-oxidative treatment and reprocessing, HDPE-based samples exhibit a dramatic embrittlement, which is even

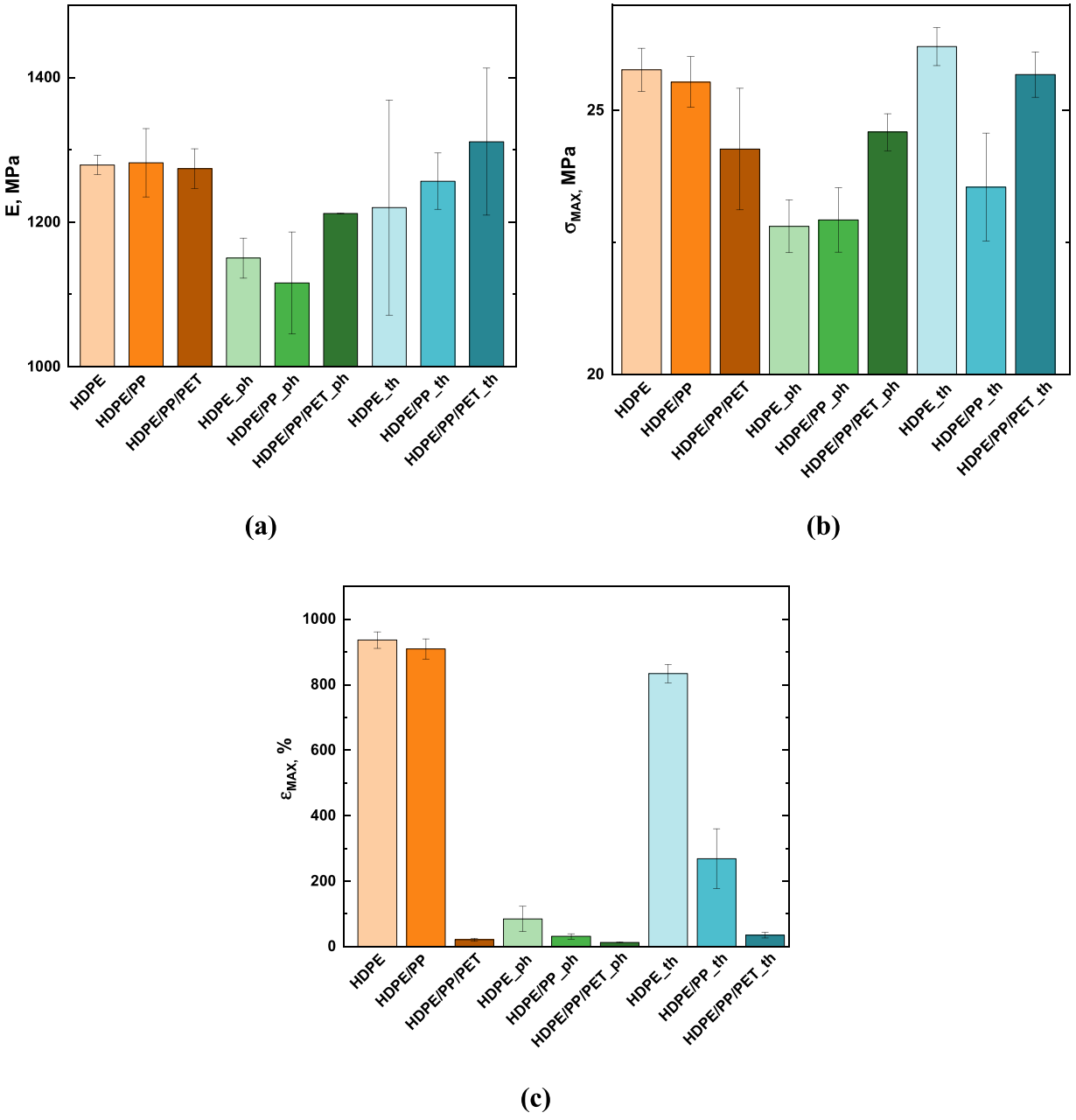


Fig. 4. Mechanical properties of HDPE systems (a: elastic modulus, b: tensile strength, c: elongation at break).

more severe for cross-contaminated materials (Fig. 4c). As already pointed out before and as widely documented in the literature, both photo-oxidative and thermo-mechanical degradation (underwent by HDPE during UV treatment and reprocessing, respectively) result in a considerable modification of the polymer macromolecular architecture, due to the concurrent mechanisms of chain-scission, branching and crosslinking. As a result, the final microstructure of the aged and reprocessed material is quite heterogeneous, and this issue severely affects its final mechanical properties and, especially, its ductility [46–47].

On the other hand, as expected considering the results of the microstructural analyses, thermo-oxidative aging does not significantly impact the tensile properties of pristine HDPE. Differently, a very different behavior is observed for the samples containing cross-contaminations. In this case, in fact, similarly to photoaged samples, the thermo-oxidative treatment and the reprocessing induced a decrease in the elongation at break as compared to HDPE without PP and PET contaminants.

To sum up, under thermo-oxidative conditions, PP and PET cross-contaminations have a detrimental role for the ductility of reprocessed HDPE, thereby potential affecting any possible reutilization of the material for the same application as its virgin counterpart. At variance, in the case of the photo-oxidative treatment the main aspect remarkably reducing the HDPE elongation at break is the severe degradation underwent by the polymer, while the presence of cross-contaminants exerts a marginal effect.

4. Conclusions

In this work, the interplay between the degradation experienced by HDPE during its service life and reprocessing and the presence of PP and PET cross-contamination was assessed, aiming at simulating the conditions underwent by the polymer during a mechanical recycling process. In particular, starting from the typical composition of a HDPE bottle, HDPE-based materials containing cross-contaminations were formulated and subjected to photo-oxidative or thermo-oxidative aging treatments. The so-obtained systems were further reprocessed and characterized, aiming at assessing the possible functional and microstructural modifications induced by the combined effects of cross-contamination and degradation, and the resulting impact on the final mechanical properties of HDPE.

Firstly, it was shown that the formation of oxygen-containing functional groups deriving from photo- and thermo-oxidative treatments is minimised when cross-contaminations are present, especially for photo-oxidised materials. Furthermore, the introduction of PP and PET resulted in the obtainment of immiscible blends, whose final microstructure strictly depends on the effect of the specific aging treatment on the viscosity of the HDPE matrix phase. In particular, the sample HDPE/PP/PET_pH showed significant morphological alterations, induced by both the aging and the reprocessing, resulting on the achievement of a more refined morphology as compared to its non-aged counterpart. Finally, the results of the tensile characterization demonstrated the prominent role of the cross-contamination presence in inducing a severe embrittlement of HDPE for thermo-oxidised materials; at variance, in the case of photo-oxidative aging, the presence of PP and PET has a negligible impact on the HDPE ductility, which is already significantly compromised due to degradation.

CRediT authorship contribution statement

Chiara Gnoffo: Writing – original draft, Formal analysis, Data curation. **Rossella Arrigo:** Writing – review & editing, Methodology, Data curation. **Alberto Frache:** Writing – review & editing, Supervision, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.polymdegradstab.2025.111290.

Data availability

Data will be made available on request.

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