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Towards effective recycling routes for polypropylene: Influence of a repair additive on flow characteristics and processability

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ABSTRACT

Plastic recycling is a key aspect to achieve effective polymer circularity, especially for polyolefins for which usually the mechanical recycling is considered a downcycling process. This downcycling phenomenon arises from the progressive deterioration of the polymer microstructure during reprocessing, resulting in a gradual loss of processability and properties, ultimately compromising the possibility of using recycled polyolefins for applications with high engineering requirements.

In this work, the effects of the thermomechanical degradation on the microstructure of polypropylene (PP) were assessed by subjecting the polymer to multiple extrusion cycles. The objective is investigating the evolution of the molecular weight and of the macromolecular architecture of PP typically occurring in a mechanical recycling process.

Furthermore, a commercially available additive capable of restoring the PP molecular weight was introduced, with the purpose of proposing an effective upcycling strategy for achieving recycled PP with enhanced processability. In particular, the effects of the additive were evaluated following two different strategies that simulate pre-consumer or post-consumer mechanical recycling.

The obtained results indicated that the introduction of the additive can effectively prevent the decrease of the molecular weight of reprocessed PP, also inducing some melt structuring phenomena associable with the introduction of some long chain branching and/or crosslinking. Finally, it was demonstrated that different macromolecular architectures for recycled PP can be achieved depending on the residence time during the processing in presence of the additive, opening new perspectives towards the possibility of obtaining recycled PP with modulable flow characteristics and, hence, processability.

1. Introduction

In 2022, the global plastic production increased with respect to the previous years, reaching 400.3 million tonnes (Mt), faced with a demand of 58.7 Mt in Europe [1]. Obviously, this huge amount of plastics generates as many units of wastes, which need a proper disposal in order to limit as much as possible post-consumer plastic destined for landfill [2]. According to the last available data about the plastics recycling in Europe, more than 10 Mt of postconsumer plastic wastes were sent to recycling in 2021. However only 5.5 Mt of post-consumer recycled plastics were used in new parts and products in the same year, representing about 10 % recycled content rate in plastics conversion [3]. Even though these data indicate an increasing trend compared to the previous

years, this value is still too low since the improper management of plastic wastes not only contaminates the environment but also encompasses an immense loss of economic value.

The shift toward a circular, climate-neutral economy requires investments and innovations across the entire plastics industry value chain to create novel reuse business models, boost recycled plastic production, and reduce reliance on fossil-derived oil and gas for new feedstocks [4–6]. Recent years have seen the development of new circular economy policies, driven by growing environmental awareness in society. These policies are transforming traditional approaches to designing plastic products, emphasizing durability, reusability, and high-quality recyclability [7,8]. The circular economy model advocates for the efficient use of resources and encourages the valorisation of plastics already in

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circulation through recycling strategies. However, recent market data reveal that the global plastic economy remains largely linear, with over half of the total annual plastic parts production ending up as waste with no recovery [3]. Consequently, there is an urgent need to enhance the plastic recycling rate to make the industry more sustainable and align it with circular economy principles. Furthermore, a shift towards upcycling approaches by means of closed-loop recycling processes is required in order to obtain materials derived from recycled plastic that possess at least the same quality, processability and properties of the raw materials [9].

As widely documented in the literature, plastic recycling consists of all strategies to recover materials from waste in order to reuse rather than dispose of them. This prevents the waste of potentially useful materials, reduces energy consumption and greenhouse gas emissions and limits the use of raw materials. Among the various recycling technologies, mechanical recycling stands out as the preferred option from both an energy and ecological perspective [5,8,10]. Ideally, this process allows for the complete replacement of virgin polymers with materials reclaimed from waste. Nonetheless, the degradation processes occurring during re-processing significantly impact the polymer processability and lead to a progressive deterioration of the final properties of recycled materials [11,12]. This last is also an economic disadvantage that hampers the competitiveness of recycled polymers compared to their pristine counterparts. For all the listed reasons, plastic recycling has to go towards the waste valorisation and the designing of recovered materials that have the same or even better properties with respect to the virgin ones.

Among all polymers, polyolefins, including polyethylene (PE) and polypropylene (PP), account for almost half of the plastic content of municipal solid waste [3]. Owing to their chemical-physical properties, lightness, low cost and durability over time, polyolefins are used in various industrial sectors, such as packaging, automotive, construction and electronics [12–14]. In particular, polypropylene has good chemical and heat resistance and excellent mechanical properties; for these reasons it is widely exploited in the above applications, with consequent volumes of post-consumer material to be disposed of [14].

However, it must be considered that during their useful life plastic parts undergo degrading phenomena that vary depending on the polymer and on the specific application of each product. Additionally, further degradation occurs during the reprocessing of the second raw material, affecting the molecular weight and the crystallinity degree of the polymer, as well as inducing the introduction of new functional groups and/or the modification of the chain topology [14–17]. In particular, for polypropylene the thermomechanical degradation that the polymer experiences during melt processing at high temperatures involves mainly the occurrence of chain scission reactions, which results in a decrease of the molecular weight [18]. In fact, some authors reported an increase of melt flow index (MFI) [15,16,19,20] and a progressive decrease of the PP viscosity [20–23] with increasing the number of reprocessing cycles. The observed modification of the PP microstructure causes a gradual loss of the added value of the recycled PP, which currently is only employed in applications with less-engineering requirements as compared to those of its pristine counterpart. In fact, the mechanical recycling of PP is commonly considered a downcycling (or downgrading) process. Besides, it has been demonstrated that the chemical structure of PP does not change significantly as a result of reprocessing. In this context, it has been shown through spectroscopical analyses that minimal or almost nothing appearance of signals associable with oxygen-containing functional groups coming from oxidative reactions of PP is observed [15–17,19], demonstrating that during multiple extrusion steps, the functional degradation of PP is negligible as compared to its structural degradation, strongly affecting its molecular weight.

Therefore, in order to properly valorise recycled plastics and to achieve an effective plastic circularity, improving the performances and enhancing the added value of recyclates is imperative. Several strategies for the valorisation of recycled PP have been investigated in the literature. The most used approach (also at industrial level) involves the introduction of virgin PP in blend with the recycled one, resulting in an increase of the properties and performances as compared to unmodified recycled PP [20,24]. In particular, it has been demonstrated that the mechanical performances of virgin PP can be maintained by creating a blend containing up to 70 wt.% of recycled PP [22]. Interestingly, blends of virgin/recycled PP have been also exploited for 3D printing processes, demonstrating the possibility of valorising a typical low added-value material through its use for innovative manufacturing approaches [25]. A further approach concerns the blending of the recycled PP with long-chain branched PP, inducing an enhancement of the rheological and mechanical properties as compared to the recycled PP, paving the way for the use of these materials in applications where high melt strength values are required [26]. In this context, it has been demonstrated the possible upcycling of recycled PP through blending with long-chain branched PP, leading to an increase of the melt strength but a decrease in the mechanical properties because of the presence of PE-based impurities within the post-consumer household waste [27]. The PP waste valorisation can be even carried out by means of functionalization or addition of compatibilizers or fillers [23,28,29]. Furthermore, upcycled PP with great industrial potential can be achieved by cross-linking and producing the so-called covalent adaptable networks [30]. Finally, the reactive extrusion route can be followed. In particular, enhanced mechanical properties can be achieved if contaminated recycled PP is melt-compounded with chemical species, like peroxide, that can lead to the formation of long-chain branching [31, 32]. Furthermore, PP waste has been upcycled by means of reactive extrusion obtaining long-subchain hyper-branched polypropylene starting from thermally degraded products as precursor [33]. Nevertheless, it should be highlighted that for PP there is currently no solution available to restore the molecular weight, apart from traditional cross-linking strategies (e.g. through peroxides) that, however, are not selective and do not rebuild the molecular weight through an end-to-end reattachment mechanism [34–36]. Surely, the so-called restabilization methods allow preventing chain cleavage during the reprocessing (by adding, as an example, fresh antioxidant or restabilization additives) but do not have any effects in restoring the original molecular weight, hence processability, of the virgin polymer [37].

This work aims at evaluating the thermomechanical degradation undergoes from PP during multiple reprocessing cycles and the effects of a commercially available additive (Nexamite® R201), usually employed for the enhancement of the processability and properties of recycled polyolefins. Firstly, the effect of multiple extrusions on the rheological behavior and thermal properties of PP was assessed. Then, the additive was introduced within PP following two different routes, mimicking the primary (i.e. pre-consumer) and the secondary (or post-consumer) mechanical recycling process, respectively. The additive-induced microstructural modifications of PP during the reprocessing cycles were monitored through rheological, thermal, and spectroscopic analyses. Finally, an in deep characterization of the rheological behavior and of the relaxation dynamics of the PP macromolecules with and without the additive as a function of the residence time during the processing was performed, aiming at correlating the achieved microstructural evolutions to the processability of the recycled PP.

2. Materials and methods

2.1. Materials

A homopolymer PP (Moplen HP500N supplied by Lyondellbasell) with MFR of 12 g/10 min (230 °C/2,16 kg) was used. The commercially available additive NEXAMITE® R201 (hereinafter named NEX) was provided by Nexam Chemical. The additive was introduced in PP at 5 wt.%.

2.2. Processing

The mechanical recycling of PP, with and without NEX, was simulated by subjecting the material up to 9 re-processing cycles performed using a Process 11 (Thermo Fisher Scientific) twin screw extruder (screw diameter: 11 mm; L/D: 40). The used screw profile has been already reported in our previous study [29]. The screws operated at a speed of 150 rpm (8,6 cm/s tangential speed), and a heating temperature of 190 °C was maintained across all zones. After exiting the extruder die, the material was cooled in water and pelletized. Table 1 reports the codes of the investigated materials. The samples without NEX will be distinguishable from the number of cycles reported at the end of the name (e. g. rPP n9). To investigate the effects of NEX, two strategies were followed. More specifically, the additive was introduced during the first reprocessing cycle of PP (rPP+NEX@n1), aiming at simulating the conditions that the material usually undergone during the pre-consumer or primary recycling. The sample have been named rPP+NEX@n1, where @n1 indicate the cycle in which NEX was added. Then the so-obtained material was reprocessed up to 9 times and the number of cycles will be reported at the end of the name of the sample (e.g. rPP+NEX@n1 – n9). The second strategy attempts to simulate the conditions of a post-consumer mechanical recycling process; to this aim, NEX was introduced in PP already subjected to 8 reprocessing cycles, therefore on ninth cycle (rPP+NEX@n9).

The effect of NEX on the microstructure and macromolecular architecture of PP was evaluated using a twin-screw mini-extruder (Xplore MC 15 by DSM) equipped with a recirculation channel that allows selecting the desired residence time. The processing of PP+NEX materials was carried out at 190 °C, with a screw rotation speed of 100 rpm for a residence time of 3 or 9 min. Hereinafter the specimens processed with mini-extruder will be named adding the residence time at the end of the codes: PP 3 min, PP+NEX 3 min, PP 9 min and PP+NEX 9 min.

Specimens for the rheological characterization, having a diameter of 25 mm and a thickness of 1 mm, were produced via compression moulding using a hot plate press Collin P 200T, operating at 190 °C under a pressure of 100 bar for 3 min. Thermal analyses were performed directly on the extruded materials.

2.3. Characterisation techniques

The rheological behavior of the investigated materials was assessed using a strain-controlled rheometer ARES from TA Instruments. The rheological tests were conducted under nitrogen atmosphere in parallel plate geometry (plate diameter = 25 mm). Preliminary strain sweep experiments were carried out at 190 °C and $\omega = 10$ rad/s. Subsequently, frequency sweeps measurements were carried out at 190 °C, from 10^2 to 10^{-1} rad/s, selecting a strain amplitude value within the linear viscoelastic region for each sample. Besides, the Carreau model was used to fit the experimental complex viscosity data:

$$\eta(\omega) = \eta_0 \left[1 + (\lambda\omega)^2 \right]^{\frac{n-1}{2}} \tag{1}$$

where: η_0 is the zero-shear viscosity, λ is the characteristic relaxation time and n is the power law index. Data coming from frequency sweep tests were used to calculate the weighted relaxation spectra of the materials, using the calculation procedure proposed by Honerkamp and

Weese [38].

The thermal properties were assessed through Differential Scanning Calorimetry (DSC) using a Q20 equipment by TA Instruments. The samples were subjected to double heating scan from 0 °C to 220 °C at a heating rate of 10 °C/min, in order to firstly erase the previous thermal history. The information gleaned from this assessment is the melting enthalpy (ΔH_m), which can be determined by measuring the area beneath the exothermal peak of the heat flow during the second heating. ΔH_m values are valuable indicators of the degree of crystallinity and, hence, of the molecular weight, as stated from other authors for the studies regarding the degradation of PP [39,40]. Furthermore, the melting and crystallization temperatures, as well as the crystallization enthalpy were evaluated. All DSC tests were performed in triplicate and the results averaged.

The chemical characterization of the materials was carried out by means of attenuated total reflectance infrared spectroscopy (ATR-FTIR), using Frontier spectrophotometer by Perkin Elmer (8 scans and 4 cm^{-1} resolution).

3. Results and discussion

3.1. Multiple reprocessing of pristine PP

First of all, PP was subjected to reprocessing in a twin-screw extruder up to 9 cycles to simulate the conditions that the polymer undergone during a typical mechanical recycling process. The modification of the material microstructure was monitored through rheological analyses. Fig. 1a reports the trend of the complex viscosity as a function of the frequency for the virgin sample (PP n0) and for those collected at cycle 1, 4, 6 and 9. As expected, virgin PP shows a typical Newtonian behaviour at low and intermediate frequencies, followed by a mild shear thinning at higher frequency. When increasing the number of reprocessing cycles, a progressive decrease of the complex viscosity at low frequencies can be observed. Besides, the material reprocessed for a higher number of cycles shows a progressively more pronounced Newtonian behaviour. As widely reported in the literature [20–23], both these features indicate a gradual decrease of the molecular weight of PP due to the chain-scission reactions occurring during the reprocessing. In fact, the decrease of the chain length induced by the thermomechanical degradation of PP causes a reduction of the mass average molecular weight (hence, of the complex viscosity) and, consequently, a reduction of the entanglements and intermolecular interactions. This last results in an enhancement of the macromolecular mobility, leading to a progressive more pronounced Newtonian behaviour. Furthermore, the analysis of the curves depicted in Fig. 1a highlights that the differences between the complex viscosity curves of the different samples subjected to various reprocessing cycles tend to minimize in the high frequency region, indicating a different effect on the shear thinning region. According to the literature, this behaviour can be ascribed to a progressive widening of the molecular weight distribution [20].

Fig. 1b reports the FTIR spectra collected in the range 4000–400 cm^{-1} for PP n0 and for the r-PP samples. As can be clearly noticeable, no significant variations can be observed as a function of the number of reprocessing cycles. Furthermore, the collected spectra indicate that no oxidative reactions occur during the reprocessing, as testified by the lack of peaks associated with oxygen-containing functional groups. Therefore, the obtained results suggest that during multiple extrusion steps the structural degradation of the polymer, strongly affecting its molecular weight, is significantly predominant as compared to functional degradation that can be practically neglected.

3.2. Effect of the reactive additive during multiple processing cycles

Following the first approach, the conditions of a pre-consumer or primary mechanical recycling process have been simulated by the addition of 5 wt.% NEX directly during the first processing cycle,
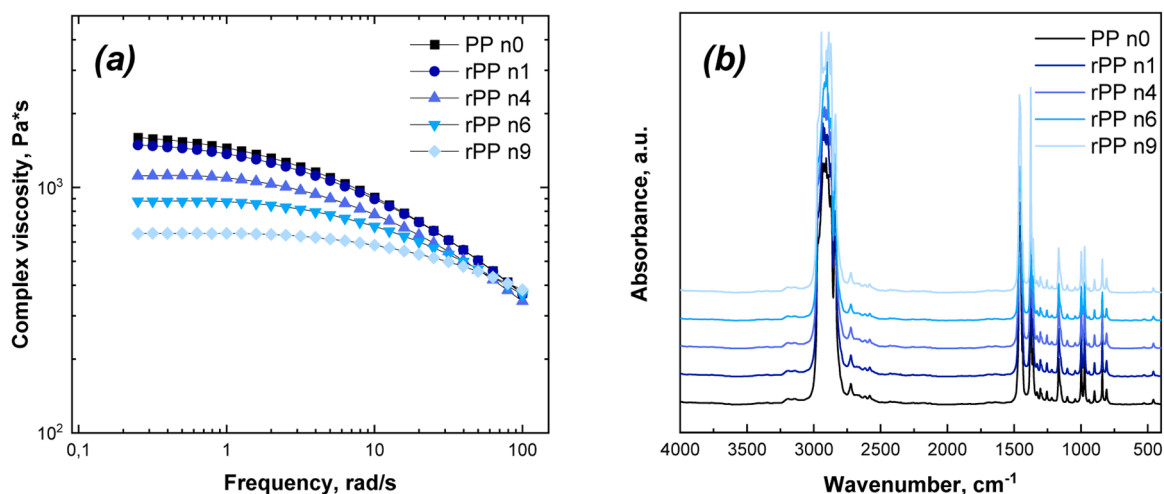
Table 1
Samples codes of virgin and reprocessed PP with and without NEX.

Number of cycles	Pristine PP	NEX@n1	NEX@n9
0	PP n0	–	–
1	rPP n1	rPP+NEX@n1 – n1	–
4	rPP n4	rPP+NEX@n1 – n4	–
6	rPP n6	rPP+NEX@n1 – n6	–
9	rPP n9	rPP+NEX@n1 – n9	rPP+NEX@n9

Fig. 1. (a) Complex viscosity curves collected at 190 °C and (b) FTIR spectra of virgin and multi-extruded rPP as a function of reprocessing cycles.

therefore on virgin PP. Then, the so-obtained material (rPP+NEX@n1) was subjected up to 9 reprocessing cycles. The complex viscosity curves of the samples containing NEX collected at cycles 1, 4, 6 and 9, reported in Fig. 2 (the complex viscosity curve of virgin PP is reported for sake of comparison), indicate a slight increase of the complex viscosity for the sample collected after the first reprocessing cycle, especially in the low frequency region. Then, a gradual decrease of the complex viscosity when increasing the number of reprocessing cycles can be observed. However, as compared to the scenario depicted in Fig. 1a, the complex viscosity is remarkably less affected by the number of reprocessing cycles, and a significant lower viscosity decreasing rate is observed. Additionally, the trend of the complex viscosity as a function of the frequency is almost unmodified as a function of the reprocessing cycles, without the amplification of the Newtonian behaviour already noticed for pristine PP. Therefore, the obtained results suggest, as also discussed for pristine PP, a progressive decrease in the molecular weight with increasing the number of reprocessing cycles because of the slight decrease in viscosity, but the introduction of NEX seems to be effective in preventing the dramatic drop of the complex viscosity, hence of the molecular weight, observed for PP reprocessed without NEX.

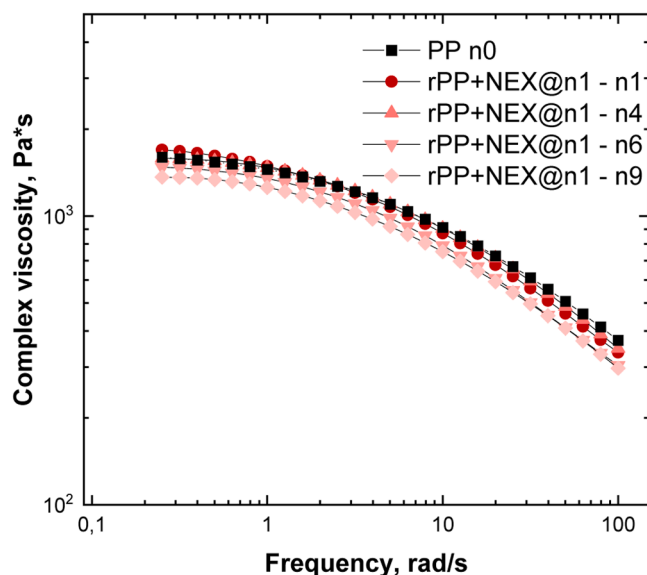According to the second proposed strategy, the conditions that

Fig. 2. Complex viscosity curves collected at 190° of rPP+NEX@n1 as a function of reprocessing cycles.

plastic parts usually experience during their secondary mechanical recycling have been simulated introducing 5 wt.% of NEX within PP already reprocessed up to eight times, therefore on ninth cycle (rPP+NEX@n9). Fig. 3a shows the trend of complex viscosity for rPP+NEX@n9 along with the curves of virgin PP (PP n0) and of pristine PP extruded 9 times (rPP n9), that are reported for completeness and clarity in the interpretation of the results. Compared to rPP reprocessed 9 times without the additive (rPP n9), the sample containing NEX exhibits higher complex viscosity values in the low frequency region. Additionally, a less pronounced Newtonian behaviour and a more prominent shear thinning at high frequency can be noticed. Besides, the trend of the complex viscosity curve tends to become very similar to that of pristine virgin PP. All these features testify that NEX is able to rebuild the molecular weight of reprocessed PP, effectively preventing the thermomechanical degradation of the polymer during the reprocessing. To further evaluate the effect of NEX also on the stability of the molecular weight of PP at high temperatures, time sweep tests have been carried out and the obtained results are depicted in Fig. 3b. For both investigated systems, a gradual decrease of the complex viscosity over time is observed. Apart from the differences in the values of complex viscosity, already observed in Fig. 3a, the introduction of NEX results in a lower rate of decrease of the viscosity as a function of the time, indicating that the beneficial effect of the additive is maintained also if the material is kept at high temperature for long times.

3.3. Additive-induced evolution of the PP macromolecular architecture

The results of the rheological characterization of the different samples subjected to multiple reprocessing cycles demonstrated that the introduction of NEX, for both exploited strategies, is beneficial in mitigating the decrease of the molecular weight of PP induced by the thermomechanical degradation experienced during the reprocessing. Aiming at quantitatively evaluating this effect, the complex viscosity data showed in Figs. 1a, 2, and 3a were fitted through the Carreau model and the values of the zero-shear viscosity η_0 (which provides useful information about the polymer molecular weight) were collected. Fig. 4 plots the values of η_0 as a function of the number of reprocessing cycles for rPP with and without the additive, following the two exploited strategies. Considering pristine PP, a sharp decrease of the η_0 can be clearly noticed, indicating a dramatic drop of the PP molecular weight passing from the virgin material to the one reprocessed 9 times. For rPP+NEX@n1, an increase of the zero-shear viscosity was observed for the material underwent 1 reprocessing cycle, suggesting the obtainment of higher molecular weight as compared to reprocessed virgin PP. With increasing the number of the reprocessing cycle, a decrease of η_0 is
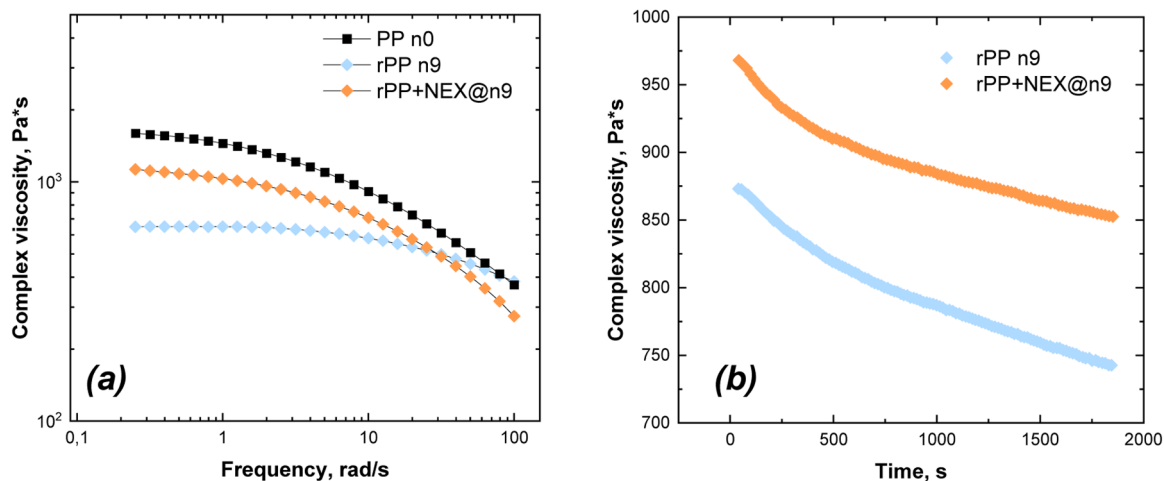
Fig. 3. Complex viscosity curves of rPP+NEX@n9 collected at 190 °C (a) as a function of frequency and (b) as a function of time.
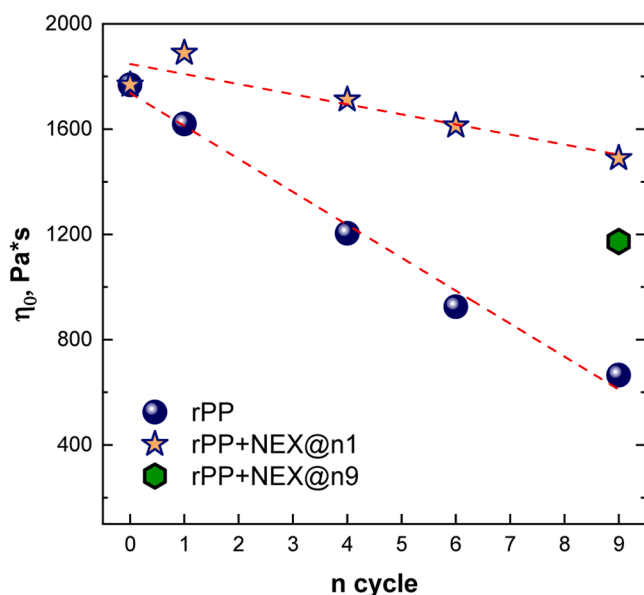

Fig. 4. Zero-shear viscosity (η_0) as a function of the number of reprocessing cycles for virgin and multi-extruded rPP, rPP+NEX@n1 and rPP+NEX@n9.

and *a* are constant values for a given polymer. For polymer macromolecules characterized by a linear topology, the Mark-Houwink equation predicts a linear relation in a η_0–M_w plot, while deviations from this linear relationship may indicate the presence of different topologies, involving branched structures [42–46]. As observable in Fig. 5, the data for reprocessed pristine PP lie on a straight line, obeying to the Mark-Houwink relation. This behaviour indicates that a progressive shortening of the PP chains occurs during the reprocessing, without any alteration of the typical linear topology of the PP macromolecules. Differently, the data for the materials containing NEX introduced at cycle n1 lie below the line for the linear samples and the deviation from the linear behaviour is progressively more pronounced for the samples subjected to increasing reprocessing cycles. More specifically, the data of the material r-PP+NEX@n1 - n1 lies on the straight line, suggesting no apparently variation of the linear structure. As PP+NEX@n1 is being reprocessed, all the data progressively tend to distance from the straight line, lying below it. This result demonstrates that NEX is able to promote some modification of the macromolecular architecture of the PP chains [47,48]. In particular, as demonstrated by Gabriel and Münsted [49], a position of η_0–M_w data beneath the linear relation indicates a branched treelike topology. Therefore, the introduction of NEX into virgin PP and

detected also for this sample. However, as already inferred from the analysis of the complex viscosity curves reported in Fig. 2, the introduction of the additive on virgin PP was beneficial in mitigating the loss of PP molecular weight. In fact, although also in this case the η_0 values show a decreasing trend as a function of the reprocessing cycle, the reduction is significantly less pronounced with respect to that of pristine PP.

As far as the rPP+NEX@n9 is concerned, also in this case a significant recover of the polymer molecular weight as compared to the pristine PP subjected to the same number of reprocessing cycles can be observed. This result confirms that the used additive is able to rebuild the structure of PP macromolecules also if it is introduced within a heavily degraded sample, hence suggesting its possible application for the recovery of the molecular weight of post-consumer recycled PP.

As widely documented in the literature [41], the polymer molecular weight can be estimated from the zero-shear viscosity through the application of the Mark-Houwink equation:

$$\eta_0 = k\, M_w^a \qquad (2)$$

where η_0 is the zero-shear viscosity, M_w is the molecular weight and K
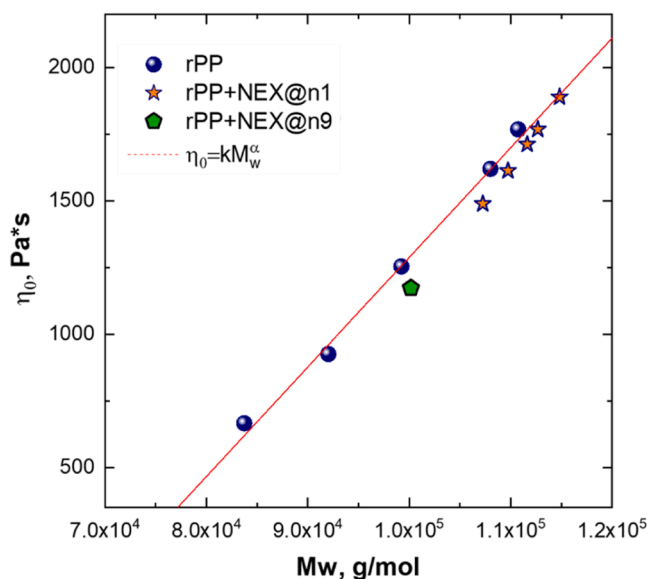

Fig. 5. Mark-Houwink plot for virgin and multi-extruded rPP, rPP+NEX@n1 and rPP+NEX@n9.

the subsequent reprocessing of the material caused not only a partial recovery of the molecular weight of the polymer, mitigating the effect of the thermomechanical degradation, but also a remarkable alteration of the macromolecular architecture through the introduction of branched structures. Interestingly, this further effect of NEX could be profitably exploited to modulate the processability of recycled PP. In fact, it is very known that the introduction of branched structures is beneficial for the processing of polymeric materials through some industrially relevant technologies in which the elongational flow is dominant (such as film blowing or melt spinning) [50,51]. Therefore, the proposed approach could allow for obtaining recycled PP endowed with a specific processability, paving the way for an effective valorisation of recyclates through a widening of their typical application field.

Finally, also the data for rPP+NEX@n9 lies below the straight line, demonstrating that even when NEX is introduced in a PP sample which has already experienced a severe degradation (i.e., typical post-consumer recycled polymers) some modification of the macromolecular architecture of PP chains occurs, involving also in this case the obtainment of branched structures.

Since the inferred alteration of the PP chains topology induced by the introduction of NEX is expected to promote some differences in the relaxation behaviour of the polymer macromolecules, the weighted relaxation spectra for the materials processed at different residence times were derived. This kind of analysis could be useful in gaining some further insights on the effect of NEX on the modification of the PP chains topology, considering the possible influence of the time interval in which the polymer and the additive are processed together.

The weighted relaxation spectra of PP with and without NEX processed for 3 or 9 min are reported in Fig. 6. When PP is processed for 3 min, a single broad peak is obtained (Fig. 6a). This last, according with the literature [52,53], can be associated with the relaxation dynamics of a single population of macromolecular chains. For the system PP+NEX processed for the same time interval, a shift of the peak towards longer relaxation times can be observed, suggesting the already inferred increase of the molecular weight of PP which causes a retarded relaxation of the polymer macromolecules.

Looking at the spectra for the materials processed for 9 min (Fig. 6b), it can be noticed that the main relaxation peak of PP (in the material without NEX) is shifted towards lower times; additionally, a secondary peak, attributable to the presence of short chains relaxing in a lower time interval, appears. In presence of NEX, the main relaxation of PP chains occurs at longer times, indicating the achievement of longer chains relaxing in a longer time interval. Besides, a distinct tail rising over the considered range is observed (Fig. 6b). This last suggests the introduction of a new dynamic specie with restricted mobility which is not able to fully relax in the tested time interval [54,48,55]. Therefore, the introduction of the additive and the processing at long residence time could promote some melt-structuring phenomena associable with the formation of treelike branched structures, as already inferred from the analysis of the Mark-Houwink plot, or also some crosslink points.

Results obtained from the analysis of the relaxation spectra thus indicate that the microstructure of PP can be profitably tuned through the introduction of NEX, depending on the residence time during the processing step, allowing for achieving different macromolecular architectures and chain topologies as a function of the processing conditions.

To further confirm the microstructural modifications occurring in PP upon the introduction of NEX, DSC analyses have been carried out. Fig. 7 shows the trend of the melting enthalpy ΔH_m as a function of the number of cycles for PP reprocessed 9 times and for the systems rPP+NEX containing the additive introduced at n1 and at n9. Furthermore, Table S1 reports the melting and crystallization temperatures, as well as the crystallization enthalpy for all the investigated materials.
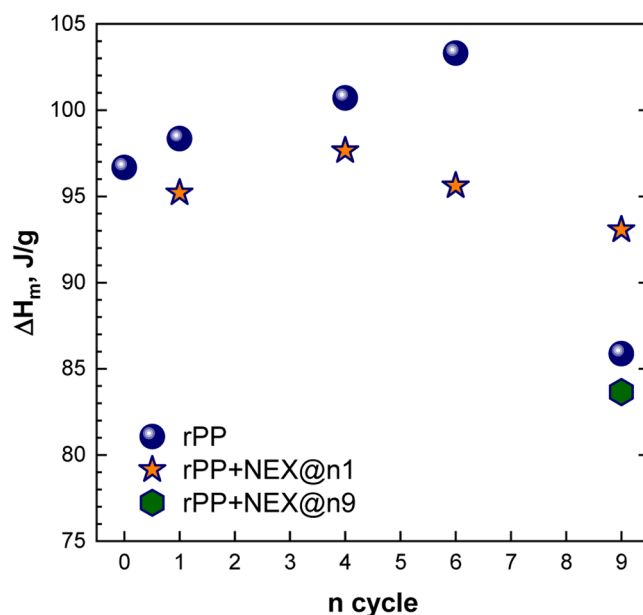

Fig. 7. Melting enthalpy values (ΔH_m) as a function of the number of cycles for virgin and multi-extruded rPP, rPP+NEX@n1 and rPP+NEX@n9.
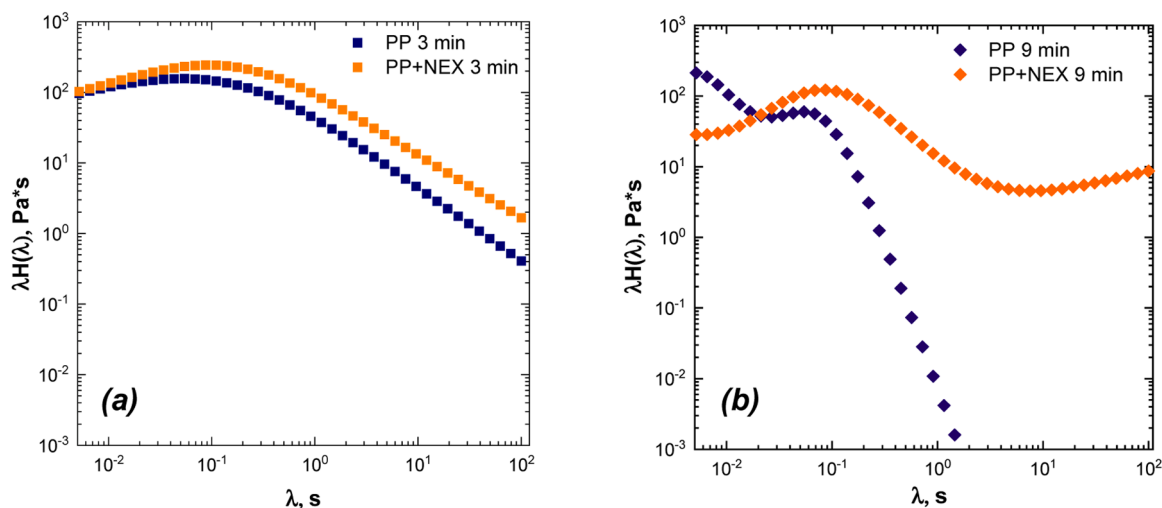

Fig. 6. Weighted relaxation spectra of PP processed for: (a) 3 min with and without NEX; (b) 9 min with and without NEX.

Considering pristine PP, when the number of reprocessing cycles increases, higher values of ΔH_m were detected until sixth cycle, then a decrease of ΔH_m can be noticed. This result can be associated with a variation of the crystallinity degree of PP with increasing the number of reprocessing cycles. In this context, other authors have already reported a similar variation of the PP crystallinity, resulting from the polymer degradation [15,16,23,39]. In particular, the increase of ΔH_m and, hence, of crystallinity can be ascribed to the occurrence of chain scission reactions, predominantly involving the amorphous portion, which causes the formation of short chains whose crystallization is enhanced as compared to primitive long macromolecular chains. On the other hand, the decrease of ΔH_m noticed at high reprocessing cycles can be explained considering that the polymer is heavily degraded at this stage; thus, the chain scission mechanism affects also the crystalline portion, with an overall decrease of the crystallinity degree of the material.

The introduction of NEX during the first reprocessing cycle results in an initial decrease of ΔH_m if compared to virgin PP. Then ΔH_m shows a slightly increase until n4 and a subsequent decrease. The lower values of ΔH_m and hence of crystallinity for rPP+NEX@n1 as compared to pristine PP can be ascribed to the already inferred increase of the molecular weight of the reprocessed PP, and also to the formation of branched structures (which are not able to crystallize) induced by the presence of NEX. For the sample rPP+NEX@n1 reprocessed 9 times, instead, the crystallinity is higher than that of pristine rPP, although the rheological characterization indicated a higher molecular weight. This result further demonstrates that the introduction of NEX is beneficial in preventing the degradation of PP during reprocessing, avoiding severe chain scission mechanisms affecting also the PP crystalline portion.

When the additive is introduced in PP already subjected to 9 reprocessing cycles (rPP+NEX@n9), ΔH_m decreases slightly with respect to rPP n9. Also in this case, the lower crystallinity of this sample as compared to reprocessed pristine PP can be attributed to the formation of branches and to the maintenance of a higher molecular weight promoted by the presence of NEX.

Besides, DSC analysis have been carried out also on the samples produced through the mini-extruder at different processing times. Table 2 reports the melting enthalpy values of virgin PP (PP n0) and of PP processed for 3 and 9 min with and without NEX.

For pristine PP, the processing for 3 min causes an increase of the enthalpy and thus crystallinity, due to the decrease of the chain length. Differently, longer processing times induce a decrease of the melting enthalpy, likely because, as already described for the samples experiencing severe thermomechanical degradation, the chain scission reactions affected also the crystalline portion. When NEX is added to PP, both for 3 and 9 min, lower melting enthalpies compared to virgin PP are obtained. The presence of the additive, in fact, can lead to an increase of the molecular weight. Moreover, comparable melting enthalpy values are obtained for either short or long residences time. This last result demonstrates that NEX is able to promote an increase of the molecular weight of PP and maintain it, without loss, even for longer processing times.

3.4. Mechanistic considerations

Considering all the obtained results about the coupled effects of the thermo-mechanical degradation experienced during multiple extrusion cycles and of the introduction of NEX on the microstructure of PP, the

following insights concerning the mechanistic of the observed behaviours emerged:

(i) the mechanical recycling of PP involves a severe thermo-mechanical degradation, which mainly involves the occurrence of chain-scission reactions causing a progressive reduction of the polymer molecular weight. This phenomenon, in turn, induces a gradual decrease of the PP complex viscosity and an amplification of its Newtonian rheological behaviour (see results reported in Fig. 1), dramatically compromising the processability of recycled PP that can not longer be processed through the same processing technology as its virgin counterpart.

(ii) The introduction of NEX in a slightly degraded PP (i.e., in a recycled pre-consumer PP) significantly alleviates the loss of the polymer molecular weight and, consequently, of its viscosity (Fig. 2). In fact, the decrease of the viscosity over the reprocessing cycles is less pronounced with respect to the pristine PP and, after 9 reprocessing cycles, the material containing NEX shows a zero-shear viscosity (Fig. 4) which could still allow processing of the recycled PP through the same processing technology of its virgin counterpart. Additionally, the additive induces some modifications of the macromolecular architecture of PP chains, promoting the introduction of branched structures (Fig. 5). Therefore, in this case, a double effect of NEX can be recognised: it is able to re-build the molecular weight of PP and, at the same time, it introduces some branches onto the backbone of the polymer. It is important to highlight that the observed NEX-induced microstructural modifications are beneficial for the future processability of recycled PP, since the achievement of a branched topology ensures the proper flow characteristics required for the processing of the polymer through technological processes in which high values of melt strength are mandatory, such as, for instance, blow molding or film blowing.

(iii) When NEX is introduced in a heavily degraded PP (i.e., in a recycled post-consumer PP) a partial recovery of the initial viscosity of the virgin polymer (see Figs. 3 and 4) is obtained. Besides, the presence of the additive helps in maintaining the viscosity of the polymer at high temperature for a longer time as compared to pristine recycled PP (Fig. 3b), exerting a sort of melt stabilization action. However, in this case, NEX seems to act as a classical chain-extender additive, able to repair the molecular weight of the PP macromolecules strongly affected by the chain scission reactions occurring during the processing, without altering the original linear topology of the polymer chains (Fig. 5). Therefore, the addition of NEX to recycled post-consumer PP allows the further utilization of the material through a processing technology requiring the same flow characteristics of the virgin polymer.

(iv) Interestingly, it has been demonstrated that the additive-induced microstructural modifications of PP can be tuned on purpose varying the processing conditions during the melt compounding. In fact, it has been shown that, depending on the residence time within the extruder, different macromolecular architectures can be obtained (Fig. 6). More specifically, while low residence times mainly cause the formation of linear chains, an increment of the processing time promotes the appearance of melt structuring phenomena, involving the introduction of branched structures and, also, some crosslink points. This last result testifies that recycled PP with adjustable processability can be easily obtained through the proper selection of the processing conditions.

4. Conclusions

In this work, the effect of a commercially available additive in rebuilding the molecular weight of a PP sample subjected to multiple reprocessing cycles was evaluated and discussed. Firstly, the

Table 2
Melting enthalpy values (ΔH_m) of virgin PP and PP processed for 3 and 9 min with and without NEX.

Sample	ΔH_m (J/g)	
PP n0	96,7	
	Pristine	*with NEX*
PP 3 min	98,1	94,3
PP 9 min	91,1	93,6

microstructural changes induced by the thermomechanical degradation that PP undergoes during a typical mechanical recycling process were evaluated through rheological and thermal analyses. The obtained results confirmed that the main mechanism of degradation of PP involves the occurrence of chain scission reactions, which result in a severe progressive decrease of the polymer molecular weight. FTIR analyses suggested that the structural degradation affecting the polymer molecular weight is predominant as compared to the functional degradation, since the oxidative degradation undergoes from PP is quite negligible. Then, the effects of the repair additive on the microstructural modifications experienced by PP during reprocessing were evaluated following two different approaches, simulating the mechanical recycling process of pre-consumer and the post-consumer polymers, respectively. A detailed rheological study allowed demonstrating that the introduction of NEX can effectively prevent the decrease of the molecular weight of PP, especially when the additive is added in a low degraded PP (i.e. in the case of pre-consumer recycling). Furthermore, it was also showed that NEX can induce some melt structuring phenomena, involving the obtainment of branched structures or crosslink points, especially if the melt processing is carried out for long residence times. Finally, the results coming from DSC analyses confirmed the inferred modification of the PP macromolecular architecture.

In all, the proposed approach demonstrated the possibility of achieving recycled PP with different macromolecular architectures and, hence, flow characteristics, endowed with tunable and adaptable processability. The obtained results can thus open new perspectives toward an effective valorisation of recycled PP through different processing technologies, allowing its employment also in applications with high-engineering requirements.

CRediT authorship contribution statement

Giulia Bernagozzi: Writing – original draft, Investigation. **Rossella Arrigo:** Writing – review & editing, Methodology, Conceptualization. **Giuseppe Ponzielli:** Writing – review & editing. **Alberto Frache:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Giulia Bernagozzi reports financial support was provided by European Union Next-GenerationEU. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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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.2024.110714.

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