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A Method for Mitigating Degradation Effects on Polyamide Textile Yarn During Mechanical Recycling

Abstract

The phenomenon of fast fashion has resulted in high yarn consumption and growing textile waste from both manufacturing and consumers. Rising environmental awareness and evolving legislation, including landfill restrictions, have prompted the search for sustainable recycling methods to manage textile end-of-life. This study investigates the mechanical recycling of polyamide 6.6 (PA66) yarn using a chain extender (Joncryl) and antioxidant (Irganox). Thermogravimetric analysis (TGA) confirmed that thermal stability in recycled PA66 was maintained compared to the original yarn, and the presence of Joncryl further enhanced this stability. Oxidative-onset temperature (OOT), measured by differential scanning calorimetry (DSC), supported these improvements. Gas chromatography–mass spectrometry (GC/MS) identified key degradation products, which were correlated with changes in the polymer matrix. Mechanical testing showed a 31% decrease in Young's modulus after initial recycling, which was reversed with further processing. This behaviour suggests the formation of shortened semi-crystalline chains and new linkages promoted by Joncryl. Viscosity and limiting viscosity number increased by up to 50%, depending on the both additive concentrations. These findings

emphasize the critical role of additive type, concentration, and processing time in preserving material performance. Overall, Joncryl and Irganox enhanced viscosity, mechanical strength, and notably thermal stability, confirming their suitability for recyclable textile-grade PA66 yarns.

Keywords

Polyamide 66; sustainable; thermomechanical recycling; apparel; chain extender; antioxidant

1. Introduction

From a scientific perspective, there are numerous approaches to achieving a sustainable lifestyle; however, these methods are often challenging to implement them quickly and effectively under real-world, industrial conditions. Consequently, there is growing interest in reducing material use —not only in the textile industry—as it provides a straightforward and easily applicable solution. Nevertheless, recycling remains one of the key pillars of an environmentally conscious society. Recently, various factors have been compelling people to recycle everything that is produced, such as current and future projections of resource scarcity, limited landfill space, governmental policies and monetary rewards for returning items for recycling purposes. However, it is also necessary to remember about textile waste when recycling, which comprises a significant portion and often ends up in incinerators or landfills (Muthu et al., 2012). Recycling offers significant benefits for both the environment and the economy. Unfortunately, it faces many barriers, such as financial, technological, educational, legal, and infrastructural obstacles, among others, which prevent textile recycling from being a successful end-of-life option (Juanga-Labayen et al., 2022; Ponnambalam et al., 2023).

The rapidly growing textile industry, driven by fast fashion, consumes a significant amount of polymeric materials, often derived from non-renewable sources. This contributes to an increase in textile waste, polluting the environment in the process (Harmsen et al., 2021; Hirschberg and Rodrigue, 2023). Polyamide 66 (PA66), like polyamide 6, viscose, acrylic, polyester, wool, cotton, polypropylene and polyethylene's (LDPE and HDPE), belongs to the most commonly used materials from which textile fibres are produced (Harmsen et al., 2021). Approximately 70% of textile waste consists of synthetic materials, primarily polyamide and polyester. Currently, less than 1% of the materials used in clothing production are recycled into new apparels (Muthu et al., 2012).

Polyamides are widely deployed polymers for which demand is growing globally, with production projected to reach 10.4 million tons by 2027. PA66 accounts for approximately one-third of global polyamide production, while polyamide yarn represents about 7% of the polymer fibres applied worldwide (Harmsen et al., 2021; Hirschberg and Rodrigue, 2023). Tough, strong and durable, such yarn has found numerous industrial applications. Aliphatic PA66 is a type of polyamide designed for use in fibers and engineering materials. Its key properties relevant to the textile industry include high strength and durability, excellent elasticity, tear resistance, low water absorption, and resistance to rot. For example, PA66 is employed in outdoor sportswear, motorcycle apparel, ropes and parachutes (Militký et al., 2018).

PA fibers are typically processed by the melt, involving extrusion of the polymer through a spinneret at temperatures above its melting point, giving rise to the fibrous product. However, several challenges must be addressed for successful fiber production, including thermal decomposition and fiber breakage, which are common issues during the melt spinning process. Research on the re-fiberization of recycled PA materials, which are particularly prone to thermal degradation, remains very limited, with much of the existing research primarily focused on

polyester (Khan et al., 2024; Kim et al., 2024; Lindström et al., 2020; Sandin and Peters, 2018; Schmidt, 2016; Tuna and Benkreira, 2018; Xu et al., 2022).

One way of addressing degradation would be to remodel the molecular weight of the material. A more cost-effective approach, however, involves incorporation a commercially available chain-extending additive. In this process, the additive is introduced in small concentrations (~1 wt%) into recycled polymer pellets, facilitating the reconnection of cleaved polymer chains during melt extrusion (Tuna and Benkreira, 2018). Although its primary function is to enhance chain reformation and improve molecular weight, the additive is also valued for its compatibility with various polymer systems, such as polyethylene terephthalate (PET) in polyamide-based blends (Costa et al., 2022; Erdmann et al., 2023).

Another manifestation of thermal stress in PA is the oxidation of the terminal amino group, which leads to a loss of mechanical properties and causes yellowing. Stabilizers are usually added into the matrix to counteract these phenomena, for example, phenols, phosphite esters and copper salts. Irganox is one of the commercially available and commonly used antioxidants. These are primary antioxidants that act as hydrogen donors, preventing the removal of hydrogen from the polymer's core structure. Antioxidants are widely used in nearly all commercial polymers and can make up between 0.05% and 3% of their weight (Khan et al., 2024; Xu et al., 2022).

Tackling the rise in production of fast fashion and consequent textile waste certainly involves reducing consumption and raising consumer awareness of the related issues. Another approach is to increase the recycled contents of synthetic textile products, yet this often leads to a reduction in their quality (Harmsen et al., 2021). The aim of this study is to improve recycling processes in the textile and clothing industry by reprocessing the fibers while ensuring the most consistent material properties possible using currently available technologies. Furthermore, to present results on the behaviour of polyamide yarn during mechanical recycling. In this context, our

research focuses on optimizing the processing of recycled PA66 textile yarn by supplementing it with two additives known to prevent degradation mechanisms. Description is given as to how multiple recycling cycles affected samples, along with determination of the amounts of the additives required for each cycle. Material properties were evaluated by conducting mechanical, morphological and thermal tests.

2. Materials and methods

2.1. Materials

Polyamide yarn (T-582-23 PADh 66, 2 x 78 dtex f68FT full dull mat, S.C. YARNEA S.R.L.) was supplied by Sintex, a.s., Czechia. The chain extender Joncryl ADR4468 (2,3-Epoxypropyl methacrylate; BASF SE, Germany) and antioxidant Irganox 1098 (N,N′-(Hexane-1,6-diyl)bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanamide]; also BASF) were kindly provided by Pigmentum, s.r.o., Czechia. Sulphuric acid (96%) was purchased from Penta Labs (Prague, Czechia). All of the chemicals were of analytical grade and applied without further purification.

2.2. Preparation of samples

PA66 yarn, employed as a textile waste simulant, was selected as the reference material and mixed with the Joncryl and Irganox additives via a conical, counter-rotating twin-screw extruder (Thermo Scientific HAAKE MiniLab II, Karlsruhe, Germany). The temperature profile and process parameters were set to a processing temperature of 275 °C and a screw speed of 120 rpm, under a state of continuous melt discharge. The extruder chamber had a volume of 7 ml and was equipped with air cooling.

Initially, the recycling process was simulated by reprocessing the PA66 yarn, designated as cycle 1, followed by regranulation, representing the second such phase of recycling (designated as 2). Characterization was performed on the yarn (hereinafter referred to as “yarn”) as well as on the extruded samples (it means regranulates). The only exception was the tensile tests, which were conducted on monofil fibers obtained from the rheometer ((Goettfert RHEO-GRAPH 50 capillary rheometer (Göttfert Werkstoff-Prüfmaschinen GmbH, Buchen, Germany), equipped with 180° flat entrance angle die with diameter (D) of 1 mm, and a length (L) of 20mm)).

The designations of sample and additive ratios are presented in Table 1.

Table 1. Designation and formulation of the samples.

Input material*	**No. of processing cycles**	**Additive type**	**Additive dosage (%wt.)**	**Sample Designation**
Yarn	1	-	-	PA
Yarn	1	Joncryl	0.5	PA/J
Yarn	1	Joncryl + Irganox	0.5 + 0.1	PA/J/I
PA	2	-	-	2PA
PA /J	2	-	-	2PA/J
PA/J	2	Joncryl	0.5	2PA/2J
PA/J/I	2	-	-	2PA/J/I
PA/J/I	2	Joncryl + Irganox	0.5 + 0.1	2PA/2J/2I

* The initial PA66 yarn, hereinafter referred to as yarn, were subjected to two recycling cycles (1 and 2).

The effects of the additives Joncryl and Irganox (denoted as “J” and “I”, respectively), as well as their

respective concentrations during each phase of recycling, were systematically investigated. The maximum theoretical concentration of Joncryl was 1%, while that of Irganox was 0.2%.

2.3 Characterization

Changes in the chemical structures of the PA samples during the recycling treatments and the effects of the additives were determined by Fourier transform infrared spectroscopy (FTIR) on a Nicolet iS5 instrument (Thermo Fisher Scientific, Waltham, MA, USA). The spectrometer using the attenuated total reflection (ATR) technique was applied, with the diamond crystal unit set to a resolution of 2 cm^{-1} and a wavenumber range of 4000–400 cm^{-1}.

Thermogravimetric analysis (TGA) was conducted to investigate thermal decomposition on Q500 thermogravimetric analyzer (TA Instruments, Wilmington, USA), operated at a heating rate of 10°C·min^{-1} and a nitrogen flow rate of 100 ml·min^{-1}. The samples were exposed to temperatures 25–600 °C.

The thermal properties of the materials were studied by differential scanning calorimetry (DSC) using a DSC1 STARe system (Mettler Toledo, Columbus, USA). Measurements were performed at a nitrogen flow rate of 50 ml·min^{-1} at a heating/cooling rate of 10°C·min^{-1}. The following programme was followed: a heating cycle starting at 25°C and rising to 400°C, then cooling to 25°C. The melting (T_m) and crystallization temperatures (T_c) of the samples were determined from the resulting curves. The crystalline fraction was calculated via Equation (1):

$$\chi = \left(\Delta H_m / \Delta H^0 \right) \times 100 \quad (1)$$

where ΔH_m and ΔH^0 are the specific melting enthalpy of the polymer and fully crystalline PA66 (196 $J \cdot g^{-1}$) (Gültürk and Berber, 2023), respectively. It should be noted that the amounts of the chain extender and antioxidant were so low that its contribution to ΔH_m could be ignored.

Relative viscosity tests of the reference samples (the yarn and specimens without additives) and others containing the additives were performed according to ISO 307:2007 (eStudio.cz, n.d.), an Ubbelohde viscometer was employed for this purpose. According to this standard, the viscosity number was first calculated. A 250 mg of each sample dissolved in 50 ml of sulphuric acid (purity 96%) at 50°C were used. The solution was conditioned in a water bath at 25°C for 20 minutes prior to analysis. The results were expressed as the means of three measurements, including a blank. The intrinsic viscosity, and subsequently, the viscosity–average molecular weight was calculated from the relative viscosity via the equations provided below (Mao et al., 2024).

Relative viscosity: $$\eta_r = \frac{\eta}{\eta_0} \quad (2)$$

Specific viscosity: $$\eta_{sp} = \eta_r - 1 \quad (3)$$

Intrinsic viscosity: $$[\eta] = \frac{\sqrt{2(\eta_{sp} - ln\eta_r)}}{c} \quad (4)$$

Molar mass, the Mark-Houwink equation: $$[\eta] = k[M_v]^a \quad (5)$$

where k is the Mark–Houwink constant, a is the Mark–Houwink exponent related to the polymer structure, and M_v is the viscosity-average molecular weight.

Identifying target compounds in the polyamide involved measuring the molecular ions present gas chromatography on apparatus coupled to a single quadrupole mass spectrometer (GC/MS) was performed on a GCMS-QP2010 Ultra device (Shimadzu, Kyoto, Japan) equipped with a

fused silica capillary column (Rxi-5ms, 30 m × 0.25 mm × 0.25 µm, Restek, Bellefonte, PA, USA). Helium was used as the carrier gas at a flow rate of 1.10 ml·min^{-1}. The temperature of the column was held at 40°C for 2 minutes and then increased to 320°C at a rate of 20°C·min^{-1}, a temperature which was maintained for 13 minutes, respectively. The range of the scan equalled 29–600 (m/z) at a speed of 1 250, and the entire programme lasted 29 minutes in total. Peaks that appeared in the resultant TIC spectra were identified with the help of the NIST11 Spectra Library.

The oxidation stability of the samples, specifically the oxidation–onset temperature (OOT), was determined on the same DSC instrument under a state of controlled temperature in an air atmosphere.

Tensile testing was performed with adherence to ISO 527-1:2019 (“ISO 527-1,” n.d.), on an M350-5CT Testometric machine (Rochdale, UK). The samples measured for this purpose were fibers resulting from rheometric instrument. The measurement length was 50 mm in length and approximately 0.25 mm in thickness. The strain rate was set to 100 mm·min^{-1}. Mean average values were calculated from 10 independent measurements taken for each sample.

3. Results and Discussion

3.1. Structural changes

Fourier transform infrared spectroscopy (FTIR) is a technique widely deployed to detect the structural properties of samples. By applying the same baseline for all specimen graphs and the correct internal reference, it is possible to measure the integral of the band associated with an identified functional group and quantify it. This technique helps to observe how degradation occurs, as long polyamide chains are broken down into shorter oligomers with amine and

carboxylic acid end groups. Figure 1 details the FTIR spectra of the yarn and, for illustration, recycled samples after the first (a) and second (b) reprocessing cycle with selected additives. The specimen of yarn shows medium intensity bands at 3298 cm^{-1} and 2936 cm^{-1}, corresponding to N–H and C–H stretching vibrations for amino and methine groups, respectively. Distinct peaks are evident at 1534 cm^{-1} (denoting an N–H bond and C–N stretching) and 1632 cm^{-1}, linked to a C=O stretching vibration from the carbonyl group, both characteristic of amide bands (I, II). The bands at 1462 cm^{-1} and 1417 cm^{-1} assigned to $–CH_2–$ (scissor vibration) as well as at 1370 cm^{-1} corresponding to the $–CH_3$ group, were also observed. The crystalline phase of PA66 (α) is marked by a characteristic band around 934 cm^{-1}. The band located at 734 cm^{-1} is related to the presence of $–(CH_2)_n–$ chains, where $n \geq 4$. Bands at 687 cm^{-1} and 582 cm^{-1} are assigned to torsion of hydrogen bonds I and II amide mode (Farias-Aguilar et al., 2014; Fayyaz et al., 2023; Yap et al., 2024). In terms of the first recycling cycle, no significant differences between the spectra are visible, evidencing the difficulty involved in monitoring chemical changes. For the PA sample, a decrease occurs in the bands located at 3298, 1632 and 1534 cm^{-1}. These correspond to the secondary N–H, C=O stretch of amide I and II, and result from the depletion of amide groups in the amorphous phase. A reduction in the ester groups of this sample is likely, as suggested by the drop in intensity at 1740 cm^{-1} (Umarov et al., 2023).

The second recycling reprocessing procedure revealed an effect exerted on the absorbance response of samples, including the influence of additives. A decrease is seen in 2PA and 2PA/J, these being specimens absent of any additional amount of Joncryl. In contrast, the 2PA/J/I sample demonstrates the best performance, with absorbance values higher than those for the original yarn. Comparing the peak intensities, although this may not provide a definitive conclusion, it can be suggested that the 2PA/2J/2I and 2PA/2J samples exhibit similarity to the yarn sample from this analytical perspective.

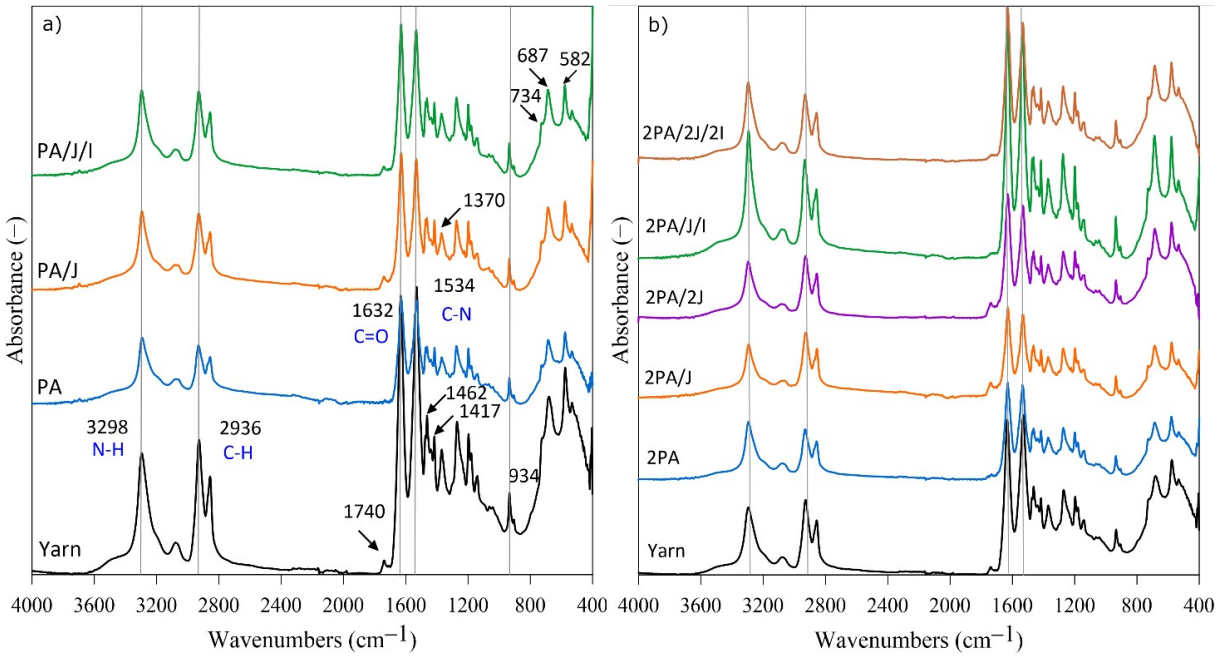

Figure 1. FTIR spectra for the original yarn sample, recycled samples with/without the additives – (a) 1st recycling cycle and (b) 2nd recycling cycle.

3.2. Thermal properties

TGA constitutes a valuable method for determining the thermal stability of polymer systems during the heating process, based on change in mass. Thermal degradation and the mechanism of decomposition, under the influence of heat, comprise crucial aspects in the optimization of process parameters.

The thermal stability of the analyzed samples was evaluated using thermogravimetric data. These data, presented in Table 2, include temperatures corresponding to initial weight loss – T_{10} (temperature for 10% weight loss), T_{50} (temperature for 50% weight loss) and T_{max} (temperature for maximum weight loss). The relative thermal stability of each sample was evaluated by comparing the decomposition temperatures at different percentage weight losses. The higher the values of T_{10}, T_{50} and T_{max}, the greater the thermal stability of the composites (Pashaei et al., 2011). The thermal properties were further complemented by additional characterization through DSC analysis, the results of which are presented in Table 3.

Thermal stability increased during the first reprocessing cycle of the yarn, potentially as a consequence of an alteration in the crystalline phase through a rise in the content of the crystalline region. This phenomenon was observed in the PA sample, which exhibited thermal degradation at 14°C (later than at T_{10}), as well as delays corresponding to 10°C and 20°C for T_{50} and T_{max}, respectively, compared to the original yarn. This effect became even more pronounced with the inclusion of additives; for example, such a delay of 22°C for PA/J for T_{10} (Salvi et al., 2025; Vasanthan and Salem, 2000).

Generally, in samples containing Joncryl, crosslinking also takes place during processing, which facilitates the reconnection of degraded chains and enhances thermal stability (Costa et al., 2022; Tuna and Benkreira, 2018). These properties were largely maintained in the second recycling phase, with the exceptions of 2PA and 2PA/J, which exhibited slight decreases in T_{max} of 3°C and 6°C, respectively. The greater content of Joncryl contributed to maintaining such thermal

properties across the two reprocessing cycles. Moreover, the Irganox additive applied in the first recycling phase supported thermal stability in the second of them. This continuation in effect eliminated the need for further supplementation of them beyond their initial incorporation.

Table 2. Values for T_{10}, T_{50} and T_{max} at 600°C for the PA66 yarn and samples following both recycling cycles, as determined from TGA curves.

Sample designation	**T_{10} (°C)**	**T_{50} (°C)**	**T_{max} (°C)**
Yarn	372	410	407
PA	386	420	426
PA/J	394	422	423
PA/J/I	390	420	423
2PA	386	418	423
2PA/J	390	418	417
2PA/2J	395	422	423
2PA/J/I	392	421	422
2PA/2J/2I	392	420	422

DSC curves from the first heating ramp, where the processing history is preserved, were chosen for the evaluation of mechanical degradation of the samples. The values in Table 3 show the changes that occurred, when thermal and mechanical stress became apparent.

In the first recycling cycle, there were no changes in the main melting peak, when the temperature was similar to that of the yarn (265°C). However, degradation could be observed in the PA sample, with the formation of a peak at ca 252°C, suggesting shorter chains had formed

during the thermal processing cycle. The Joncryl additive facilitated the binding of these shortened chains, preventing such degradation from taking place, hence the aforementioned peak was insignificant for such samples.

Sample PA/J/I experienced a drop in internal enthalpy, although it maintained the same temperatures as the original yarn, indicating a decrease and change in crystallinity (Wallner et al., 2018).

The evaluation of the cooling temperature after the first heating in the graph shows double peaks at the crystallization temperature (T_c). For all samples, the main crystallization peak (T_{c2}) was around 235°C whereas the first peak (T_{c1}) varies during cooling and arises according to the number of reprocessing cycles and the content of supplemented additives. This peak could relate to the rate and manner of crystallization of PA66 (Xu et al., 2022).

Noticeable variations exist, though. Specifically, these peaks are somewhat reduced following the first reprocessing cycle, a phenomenon clearly observed for the 2PA sample, for instance, after the second recycling phase. In specimens with the Joncryl additive, a rise in crystallinity happens that reaches a level similar to 2PA/2J, almost 50% more than that for the original yarn. The influence of thermal stress on the given material is significant, since it possesses an altered crystalline structure (e.g. in size), making it more labile. Nonetheless, the favourable properties of the first recycling phase are maintained due to the presence of the additives.

Data from the second recycling cycle was analysed to compare the samples to the original yarn. No change is noticeable in the main melting peak (T_m), which remains at ca 264°C. An interesting second peak at 252°C is evident for the PA material, differing from the yarn and other specimens, suggestive of chain disruption through the action of recycling.

Findings for the samples supplemented with just the chain extender (2PA/J and 2PA/2J) closely resembled those for the yarn. Here, the additive effectively fulfills its role by facilitating the

reconnection of shorter chains into an ordered crystalline region. As degradation progresses, long polyamide chains are cleaved into shorter oligomers with amine and carboxylic acid end groups (Brette et al., 2024).

PA66 is capable of crystallizing the triclinic α-phase and the pseudohexagonal mesophase, wherein melt quenching gives rise to α′-crystals with a non-planar hydrogen bond arrangement. The processing conducted in this study only brought about α-modifications of the crystals (Hedicke et al., 2006; Krause et al., 2019). A smaller peak appearing during recycling cycles indicates the initiation of degradation to shorter semi-crystalline chains. A decrease in crystallinity was observed for the 2PA/J/I and 2PA/2J/2I samples, the associated assumption being that both additives promoted long chain branching and physical crosslinking, thereby reducing chain regularity and hindering the crystallization of PA66 (Buccella et al., 2014).

Table *3*. DSC data on the PA yarn and PA with additives, after the first and second recycling cycles, alongside values for T_m, ΔH_m, X_m, T_c and ΔH_c gauged from the first heating ramps.

Samples designation	**T_m (°C)**	**ΔH_m (J/g)**	**T_{c1} (°C)**	**ΔH_{c1} (J/g)**	**T_{c2} (°C)**	**ΔH_{c2} (J/g)**	**χ (%)**
Yarn	264	72.0	169	6.1	235	72.5	37
PA	265	77.4	157	5.1	234	70.0	40
PA/J	265	80.3	161	5.3	235	71.3	41
PA/J/I	264	67.0	169	3.3	235	72.6	34
2PA	264	74.8	172	3.6	236	71.9	38
2PA/J	265	71.2	167	9.7	235	70.6	36
2PA/2J	264	73.4	159	7.1	235	71.6	38
2PA/J/I	264	62.0	166	10.7	235	53.1	32

2PA/2J/2I	264	65.8	163	9.1	234	68.6	34

3.3. Analysis of viscosity parameters

This characterization presents the evaluation of molecular weight-related parameters and structural characteristics of PA66 yarn that was subjected to one or two recycling cycles. The analysis focuses on relative viscosity (RV), viscosity number (VN), intrinsic viscosity (η) and viscosity-average molecular weight (M_v), in order to discern the effects of reprocessing cycles and incorporating additives on the molecular integrity and structures of samples. The results of these parameters are summarised in Table 4.

RV and VN were used to monitor changes in flow behaviour and reveal alterations in molecular architecture. Intrinsic viscosity was determined to estimate M_v and provide further insight into chain scission or possible chain extension reactions, particularly in the presence of the additives (Joncryl and Irganox).

The recycling resulted in a modest increase in the RV of the samples, by up to 15%, primarily in the presence of Joncryl. It was presumed that during processing, both the formation and reconnection of molecular chains occur, along with an increase in the crystalline phase content. No significant reduction in RV was observed for the samples containing Irganox, although a slight decrease in the crystalline phase was detected. This reduction could have contributed to the deterioration of certain properties, e.g. mechanical performance. Values for the VN went up after the second recycling cycle, suggesting that the molecular weight did not rise proportionally in line with the content of Joncryl alone. Continued processing appears to promote an increase in VN, which can be attributed to post-polycondensation reactions induced by Joncryl. Prolonged exposure to processing conditions—i.e., a combination of time and temperature—may facilitate limited chain re-linking. This outcome was anticipated and aligns with the intended objective. In

contrast, the presence of the Irganox additive suppresses this effect, and the VN values remain most similar to those of the virgin yarn, but only when a doubled dosage of the additive is applied. Furthermore, the additive demonstrates a reduction in intrinsic viscosity, which correlates with a lower viscosity-average molecular weight (M_v). This effect may be attributed to the promotion of chain branching, a phenomenon also induced by the Joncryl additive, as evidenced by the reduced crystalline phase content. One of the hypotheses is that PA66 is capable of undergoing limited crosslinking under the influence of temperature, resulting in an increase in molecular weight. The initial yarn sample may already contain a crosslinking agent, which can increase the relative viscosity during processing. To a lesser extent, this may also occur spontaneously. These structural changes subsequently influence the mechanical properties, which are discussed in the following section those of the original yarn (Okamba-Diogo et al., 2020; Schaffer et al., 2000).

Table 4. Relative viscosity (RV), viscosity number (VN), intrinsic viscosity (η), and viscosity-average molecular weight (M_v) of the PA66 yarn samples after the first and second recycling cycles.

Samples designation	**RV (–)**	**VN (ml/g)**	**[η] (dl/g)**	**M_v^* (g/mol)**
Yarn	1.76	136 ± 2	1.11	25,000
PA	1.98	137 ± 1	1.11	25,500
PA/J	1.98	134 ± 1	1.12	27,800
PA/J/I	1.95	135 ± 2	1.14	35,800
2PA	1.96	137 ± 0	1.12	27,500
2PA/J	2.01	146 ± 1	1.20	50,700

2PA/2J	2.09	149 ± 2	1.21	54,800
2PA/J/I	2.09	143 ± 1	1.15	38,100
2PA/2J/2I	2.00	139 ± 1	1.14	36,000

* $[\eta] = kM_v^a$, $k = 3.6 \times 10^{-4}$, $a = 0.85$ (Burke and Orofino, 1969)

3.4. Mass spectrometry characterisation of the PA66 pyrolysis products

This method was selected to analyse degradation products arising through the reprocessing of the textile materials, as it would facilitate qualitative identification and generate semi-quantitative data based on signal intensity, as well as potentially revealing the relative concentration of each compound investigated. Although the relative peak areas of the detected products were not determined herein, analysis focused on comparing the appearances of peaks at consistent retention times (RT), a parameter considered stable and permitting a degree of analytical confidence.

All mass spectra were evaluated manually and compared against entries in a spectral library. Correlation factors for the identified compounds were ≥80% (indicating a high specificity of the library match), and often exceeded the second-best match by more than 5%. Additionally, the results were compared with data from previously published studies addressing similar degradation phenomena (Duemichen et al., 2015; Smith et al., 2012; Wu et al., 2013).

The spectra exhibit characteristic peaks corresponding to known degradation products of PA66 generated during pyrolysis, including cyclopentanone (1), caprolactam (2) and 1,8-diazacyclotetradecane-2,7-dione (3), all primary products and their RTs are listed in Supplementary Table S1. Additionally, the samples contain appreciable quantities of compounds such as propylene, butene, 1-hexene, hexan-1-amine and octadecanal, as suggested by the relative intensities observed (Shin et al., 2011).

Reprocessing the yarn (the PA sample) led to a noticeable reduction in the concentration of the primary degradation products. Among these, cyclopentanone was identified as the principal monitored compound of PA66. It originates from the hydrolysis of hemiaminal groups, it is associated with the concomitant release of other species e.g. carbon dioxide (CO_2), ammonia (NH_3) and various aliphatic amines. Cyclopentanone (CP) acts as a key precursor for subsequent degradation reactions and is a compound considered typical for the designation PA66. It interacts with pyridine derivatives through redox and condensation reactions, potentially forming condensed cyclopentanone structures and pyridine-related compounds (Duemichen et al., 2015). It was thought that thermal reprocessing could exert a limited yet beneficial influence on the properties of polyamide materials, including a reduction in degradation products following a single reprocessing cycle (see Supplementary Figure S1). Investigation showed that the absolute intensity of cyclopentanone (CP) diminished, in conjunction with a rise in the concentrations of other compounds (e.g. octadecanal). The PA/J sample exhibited a degradation profile comparable to that of the original fibres, whereas the PA/J/I sample demonstrated elevated levels of degradation products; most notably CP, the primary degradation product, as well as a pronounced peak for caprolactam. Although the PA/J/I sample displayed a higher viscosity-average molecular weight, it also appeared to contain a greater concentration of degradation by-products. Upon further reprocessing, the intensity of CP decreased once more, with the reduction being even more evident in the sample containing Joncryl. In this case, the reprocessed PA/J/I sample exhibited CP levels comparable to those observed in the initial yarn. Nevertheless, other degradation products showed increased intensities.

Following the second reprocessing cycle of the PA sample, a theoretical decrease in the intensity of the main degradation product, CP, was observed (Supplementary Figure S2). A similar trend was noted for the 2PA/J sample, with a less pronounced one being recorded for the 2PA/2J/2I

sample. Interestingly, the intensity levels in the 2PA/2J and 2PA/J/I samples were comparable to those observed after the first recycling cycle. This is notable as these samples exhibited high relative viscosity (RV), viscosity number (VN) and viscosity-average molecular weight (M_v). One possible hypothesis is that the sample contains a sufficient number of long chains with amide groups, which were capable of forming the degradation product (Schaffer et al., 2000). Although there was an increase in degradation products in some cases, there were no significant changes in thermal stability based on the analyses mentioned above. The viscosity parameters were also not affected. Therefore, if there were significant changes, we would rather monitor changes in the mechanical behaviour of the material.

3.5. Oxidation onset temperature

This is an accelerated test that enables rapid evaluation of the performance of stabilizing additives. The oxidation-onset temperature (OOT) is measured by dynamic scanning calorimetry (DSC) under an oxygen atmosphere at a constant rate, until the exothermic peak of polymer oxidation is reached. OOT is defined as the temperature at the commencement of the exothermic oxidation peak. In this study, OOT served as a parameter for the behaviour of the polymers during the recycling cycles and the effects of the additives that mitigate degradation (Volponi, 2004).

Figure 2a illustrates that, for the yarn, the first oxidative exothermic peak with an onset occurred at 175°C, although this instance of degradation was only observed under these specific conditions of DSC. It might have happened through impregnation of the fibre, or the presence of another additive that had not been removed by washing with water, which disappeared following a recycling phase. Samples with and without additives after the first and second recycling cycles are presented in Figure 2b and 2c, respectively. The effect on the melting points for all samples

was reflected by a shift from 9°C to higher values in both reprocessing cycles. The Irganox supplemented specimen showed an exceptional shift in its OOT. This was 4°C in the first cycle, rising to 9°C in the second, but only after the amount of Irganox in the PA matrix had been doubled. Compared to the yarn, shifts in the OOT of specimens ranged from 5°C to 16°C. The effect of the phenolic antioxidant was thus confirmed, although it was necessary to either add it back into the polymer matrix in each reprocessing cycle or increase the initial dose (Xu et al., 2022). This increased thermal stability of PA66 containing Irganox in the melt state could be related to the sterically hindered phenolic groups and the high thermal stability of Irganox (Zhang et al., 2024).

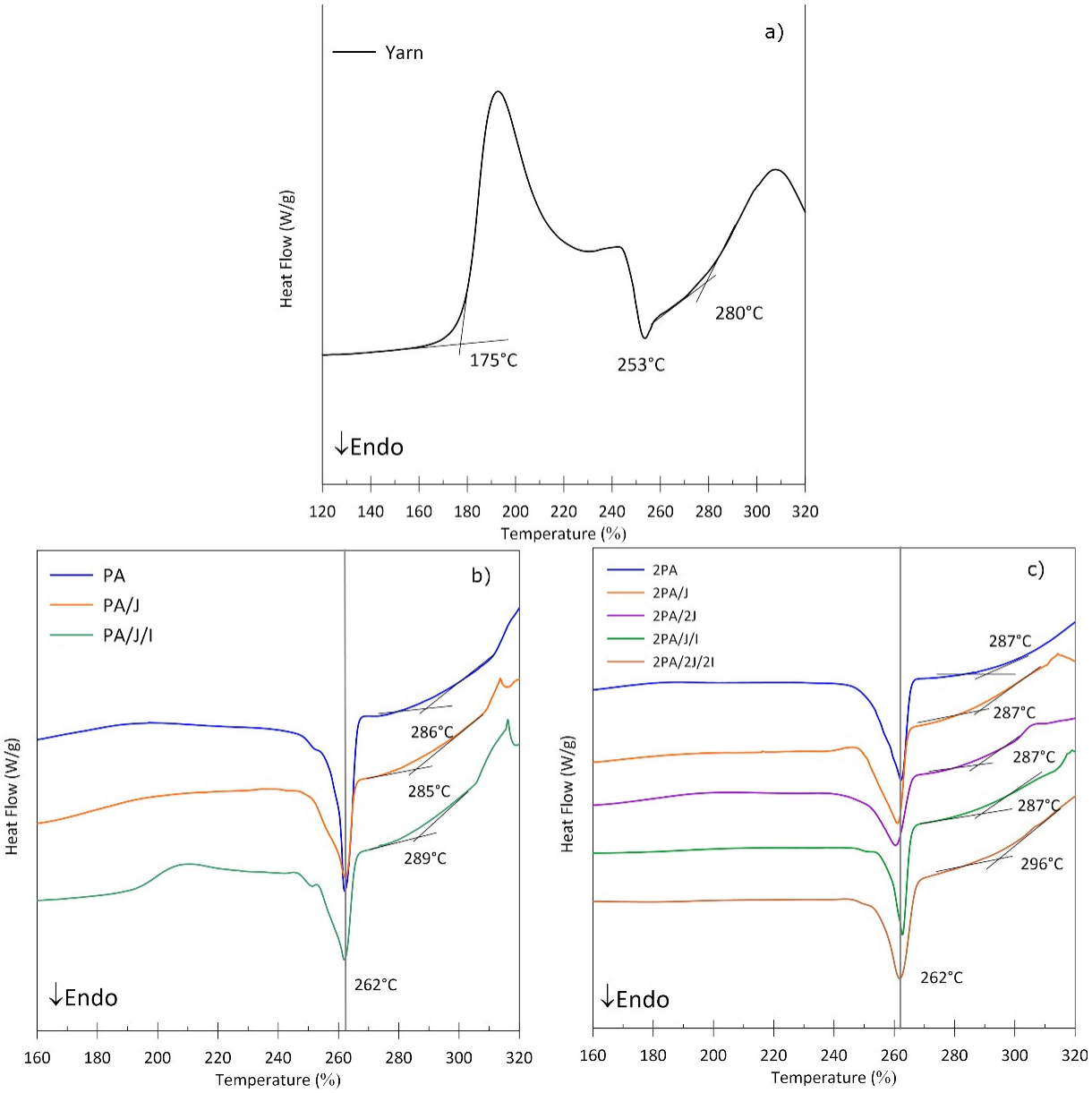

Figure 2. DSC thermograms comparing thermal transitions of (a) pristine PA yarn, recycled PA yarn and PA with additives samples after the (b) first and (c) second recycling cycle.

3.6. Mechanical properties

The mechanical behaviour of the specimens was characterized by tensile testing at a relatively low strain rate (Figure 3). Experiments were conducted tests on PA monofilament fibres and

those supplemented with additives upon completion of both recycling cycles. Assessment was made of the Young's modulus, which describes the relative stiffness of a material, and strain at break, which indicates the ability of a plastic material to resist shape changes without cracking. The initial processing of textile fibres in this case leads to an increase in Young’s modulus and a reduction in polymer elasticity, as expected. This is evident in the PA sample, where changes in the amorphous phase and enhanced crystallinity were observed, along with the rearrangement of smaller, more mobile polymer chains. In the case of the PA/J sample, this phenomenon was suppressed, with the incorporation of longer chains and crosslinking prevailing, as confirmed by the higher molecular weight and viscosity. However, this did not result in a loss of material elasticity. A different behaviour was observed for the PA/J/I sample, where a reduction in the crystalline phase may indicate the effect of the antioxidant. In this case, Young’s modulus decreased, while elongation at break increased significantly. This suggests the dominant effect of Irganox, which may increase the free volume between polymer chains (Habib et al., 2024; Sanders et al., 2022).

The second recycling cycle of the textile sample (2PA) confirms typical degradation behaviour, characterised by a decrease in Young’s modulus and an increase in elasticity, resulting from shorter chains and an increase in free volume. In samples containing only Joncryl, partial suppression of this degradation and retention of elasticity were observed.

The chain extender appears to be more effective during the second cycle, possibly due to re-incorporation or a longer processing time. Nevertheless, the samples tend to approach the properties of the original yarn. The addition of Irganox improves the tensile strength of the recycled yarn, although at the expense of elasticity, which may be undesirable in subsequent processing steps, such as fibre drawing. This behaviour is most likely caused by a dominant chain branching process.

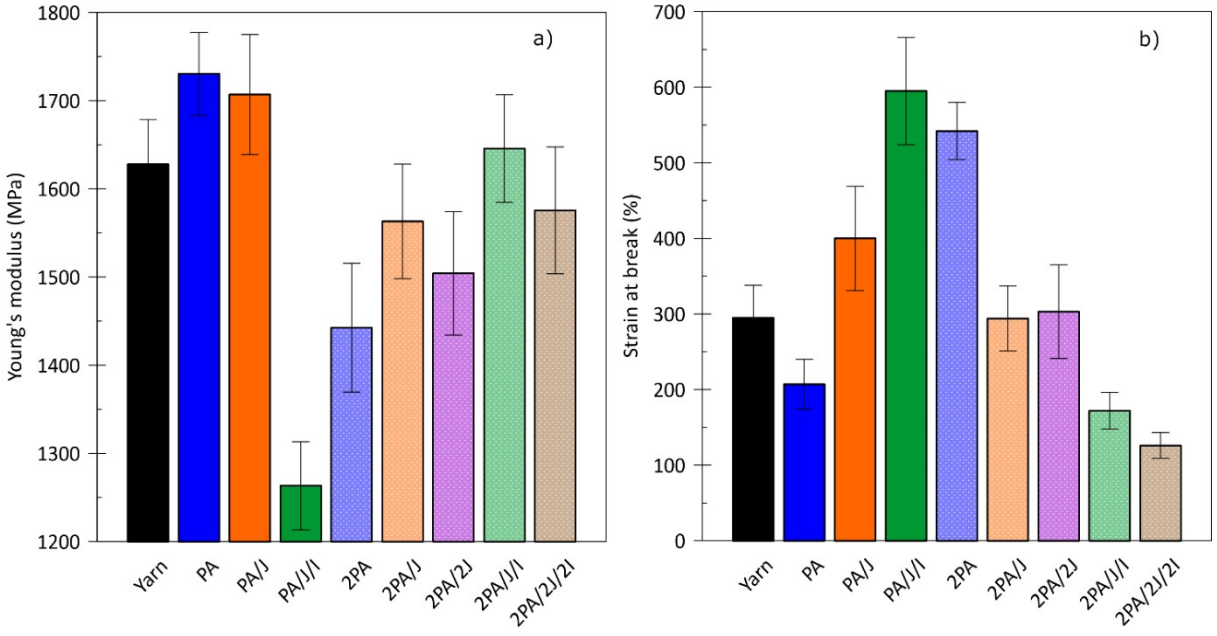

Figure 3. (a) Young's modulus and (b) strain at break for the textile yarn and samples with/without the additives as a function of the recycling cycles.

4. Conclusions

Given the growing interest in and significance of recycled materials, particularly textiles, it is imperative to develop effective strategies for reprocessing textile materials while preserving their original performance. This study aimed to mitigate degradation effects caused by the mechanical recycling of PA66 textile yarn and enable its reuse in textile applications. Commercially available additives were applied: a multifunctional chain extender (Joncryl) and a phenolic antioxidant (Irganox). The investigation focused on the influence of the recycling procedure and additive content on the PA66 matrix, with emphasis on selected thermal, chemical, and mechanical properties.

The samples generally exhibited improved thermal stability after reprocessing, suggesting partial post-polycondensation chain reactions induced by thermal and shear stress, along with changes in crystalline phase content. Minor chain crosslinking may have occurred. Joncryl significantly enhanced thermal stability, as evidenced by T_{10} increases of up to 23 °C with repeated additions during recycling. DSC revealed reduced crystallinity in Irganox-containing samples during the second cycle, while relative viscosity remained stable. This indicates structural rearrangement into branched chains, potentially limiting crystallisation.

Viscosity-related properties also increased, especially with Joncryl, which effectively enhanced the molecular weight of PA66, as confirmed by GC/MS. In samples like 2PA/2J and 2PA/J/I, significant degradation still occurred, indicating the presence of long chains that later broke down during further processing. The oxidation-onset temperature (OOT) remained stable in most cases, with PA/J/I and 2PA/2J/2I showing increases of up to 9 °C. Tensile testing revealed that mechanical properties were influenced by both additive concentration and preparation time, highlighting the importance of optimising processing conditions to maximise additive effectiveness.

Joncryl proved highly effective as an additive for recycled textile-grade PA66, particularly when supplemented in each recycling phase. Its use led to improvements in thermal stability, viscosity, and molecular weight. While combining Irganox with Joncryl provided limited additional benefits in thermal and viscosity-related properties, its presence may influence mechanical behaviour and fibre spinnability during processing.

Data Availability

The raw data required to reproduce these findings cannot be shared at this time due to ethical reasons.

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