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Effect of an Antioxidant and a Compatibilizer on the Mechanical Properties of Virgin and Thermally Aged Polypropylene Drawn Fibers

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Abstract: Polypropylene (PP), like all polymers, is susceptible to various forms of aging. Drawn fibers exhibit increased mechanical properties; however, the drawing results in non-equilibrium (decreased entropy) structures, due to the orientation of the polymer chains. Consequently, the drawn fibers are susceptible to an additional form of physical aging. In this work, the effect of common industrial additives on the mechanical strength of virgin and thermally aged PP fibers was studied. Thermogravimetry and tensile strength tests were used to characterize the drawn fibers, before and after physical thermal aging. PP drawn at 120 °C and at a drawing ratio of 7 exhibited a tensile strength of 549 MPa, while the incorporation of an antioxidant and a compatibilizer lowered the tensile strength down to 449 MPa. This reduction was related to the constraint of chain alignment due to the low molecular weight and poor dispersion of the additives. Depending on the aging temperature, shrinking occurred to different extents in pure PP fibers, accompanied by a 6–7% reduction in tensile strength. The fibers with incorporated additives exhibited higher rate and degree of shrinking. Briefly, the incorporation of such additives in drawn PP resulted in the deterioration of the fibers' mechanical tensile properties. Since such additives have an indisputable value for non-drawn samples and their usage is necessary for various reasons also in drawn samples, e.g., for their protection from chemical aging/decomposition, additives specific for drawn samples should be developed.

Keywords: isotactic polypropylene; drawing; fibers; tensile strength; aging; shrinking; additives



Citation: Tsiptsias, C.; Gkouzouma, G.; Leontiadis, K.; Tsvintzelis, I. Effect of an Antioxidant and a Compatibilizer on the Mechanical Properties of Virgin and Thermally Aged Polypropylene Drawn Fibers. *Textiles* **2022**, *2*, 499–510. <https://doi.org/10.3390/textiles2030028>

Academic Editors: Rajesh Mishra, Tao Yang and Veerakumar Arumugam

Received: 10 August 2022

Accepted: 1 September 2022

Published: 16 September 2022

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1. Introduction

Isotactic poly(propylene) (PP) is a widely produced thermoplastic used in various applications, and a large portion of its production is used in fiber-related applications. Though decades have passed since the first production of isotactic PP, the polymerization and copolymerization of propylene is still an area that attracts research interest [1]. The environmental issues related to PP (and traditional polymers, in general) disposal are well known. In this regard, the study of the aging of polymers and of the prediction of their lifetime has gained the attention of researchers [2–5]. Of course, the study of polymer aging is also important to avoid material failure in end-use applications, prior to disposal. The term aging is rather broad and is used to describe a variety of phenomena, such as physical, chemical, biological, thermal and thermo-oxidative structural changes and the deterioration of properties [6]. The term “physical” aging is used to describe reversible changes in the structure of polymers during storage, under no influence of external factors, such as mechanical stress or increased temperature, and in order to distinguish these changes from those occurring during storage that are accompanied by alterations in the chemical structure [6]. The chemical aging of polymers and of PP is well documented, e.g., thermo-oxidative aging [3,4,7,8], UV aging/photo-oxidation [9,10], aging caused by gamma-irradiation [7,8] or electron beam irradiation [11]. The effects of oxygen, temperature and aqueous media on the acceleration of PP aging have also been studied [12,13]. In

general, it has been recognized [2–4,14] that accelerated-aging experiments (e.g., at high temperatures) often fail to yield reliable predictions, and various approaches have been proposed by modelling/equations [2], studying at high exposure times (e.g., years) [3,4,8], or studying a material under real conditions [14,15]. The study of the aging of drawn PP has also been reported. Before discussing this issue, the peculiarity of drawn structures regarding aging should be highlighted.

Drawing of polymer matrices results in chain alignment/orientation in the direction of stretching and causes a significant increase of the tensile strength [16,17]. There are two main types of orientation, namely, uniaxial, characterized by a retention of the initial width, and biaxial [17]. Fibers are a typical example of materials with uniaxial orientation. Fibers, and in general drawn structures, are susceptible to both physical and chemical aging, like non-drawn structures. Increased temperature has a dual effect on polymers: it accelerates chemical aging and induces structure relaxation. Such relaxation also occurs in physical aging and is related to the enthalpy of relaxation/recovery [18]. This type of physical aging is very important for polymers like PP, for which the glass transition temperature is lower than room temperature, implying that, even at room temperature, chains in the amorphous regions have enough mobility to rearrange. Such relaxation occurs in all samples (drawn and non-drawn structures). However, in the drawn samples there is an additional contribution. This additional relaxation arises from the fact that the chain orientation induced by drawing, is related to a substantial decrease of entropy, and thus, the amorphous domains of the produced PP structure, at room temperature, are metastable (thermodynamically unstable but kinetically stable), due to the additional entropic factor related to chain alignment. This effect is well known and is used to produce thermo-shrinkable materials [19], but in all other cases the shrinkage is undesirable both for further processing and for end-use applications. The most typical way to overcome this issue is a compromise through annealing at high temperatures and controlled shrinking, e.g., of 5% [19]. Recently, the tensile properties of PP fibers, including aged fibers, have been comprehensively reviewed [5].

The physical aging of polymers, in general [6,18,20], as well as the physical aging of isotactic and syndiotactic PP [21–23] are well documented. The aging of drawn structures has also been investigated, and various studies regarding isotactic PP are available in the literature. Suggestively, it has been reported that the cold drawing of PP results in aging effects at room temperature and, more precisely, in an increase in the elastic modulus [21,24]. This effect was reported to occur in both drawn and non-drawn samples of isotactic PP [21], as well as in syndiotactic PP samples [23]. It is worth mentioning that for the (non-drawn) syndiotactic samples, though no values for stress at break were reported, it could be observed in the presented stress–strain curves that the difference in the mechanical behavior among samples subjected to different times of aging and/or annealing was intense in the elastic region, while after the yield point, such difference was smaller [23]. This effect has been related to the secondary crystallization or densification of amorphous regions [24]. Thus, besides drawing, the quenching of non-drawn samples can lead to a similar effect upon aging. In addition, the thermal expansion behavior of oriented PP was studied, and it was found that the thermal expansion coefficient in the axial direction was negative, due to the presence of internal stresses [25]. Crystallinity changes and dielectric property changes in drawn PP, induced by gamma radiation, have also been reported [8,26]. Thus, the study of aging of drawn PP concerns both physical and chemical aging. However, with few exceptions, e.g., [24], the above-mentioned entropy-driven aging, related to chain alignment, has rarely been studied. Similarly, in the development of composite PP drawn fibers, yarns, etc., this effect is rarely studied, as also observed in recent publications on PP composite fibers [27–29]). In a recent review [30] regarding the current trends and future prospects of composite PP fibers, there is no literature reference for this effect, since no adequate data could be found. No attention has been given to this effect and, especially, to its influence on the mechanical properties of fibers, most likely, because it can be tailored by controlled annealing (which is the usual industrial practice).

Recently, it was reported [27–29] that in PP composite drawn fibers various competitive effects arise, if typical industrial additives, such as antioxidants and compatibilizers, are used. For example, it was reported that PP grafted with maleic anhydride (PP-g-MA), which is used as a common compatibilizer for PP and inorganic particles, enhanced the action of a phenolic-type antioxidant [27]. The influence of such additives (antioxidant and compatibilizer) on aging, and especially on chemical aging, is also well documented for PP and PP composites (see, for example, [9,11,13]). Various types of stabilizers have also been studied, such as stabilizers of phenolic type [13], hindered amine light stabilizers [12,31], stabilizers from natural (waste) resources such as extracts from wine seeds [10] or ferulic acid-based-Bis/Trisphenols [32]. However, the effect of such additives on PP physical aging, especially, on the above-mentioned special case of physical aging, related to the decreased entropy of drawn structures, to the best of the author's knowledge, has not been reported. Such additives are typically dispersed in a PP matrix of relatively low molecular weight (to enable mixing), and this might have an influence on the properties of the drawn samples. The poor dispersion of such additives may also deteriorate the properties of drawn PP by introducing defects in the produced structure. Thus, although such additives are used for increasing the mechanical strength of composites and enhance their stability over chemical aging, they might have accountable effects on the behavior of drawn PP under physical aging. The aim of this work was to provide insights regarding the influence of the addition of typical supplements—an antioxidant and a compatibilizer—on the mechanical properties of drawn PP fibers before and after physical aging/annealing.

2. Materials and Methods

2.1. Materials and Instruments

For the experiments, isotactic PP (Ecolen HZ42Q, Hellenic Petroleum S.A., Thessaloniki, Greece) with a melting point (T_m) of 168–171 °C was used. This PP masterbatch is meant for industrial applications. The manufacturer does not provide information about the % tacticity, while in the material's Data Sheet, the melt flow index (MFI), instead of the molecular weight, is reported to be equal to 18 g/10 min (230 °C, 2.16 kg). As mentioned in the Data Sheet, the PP of this masterbatch had a very narrow molecular weight distribution. The density of the PP masterbatch was 0.9 g/cm³, while values of its modulus, tensile yield strength and % elongation at were yield equal to 1300 MPa, 33 MPa and 11%, respectively.

A masterbatch of PP grafted with maleic anhydride, PP-g-MA (Bondyram 1001, Polyram Plastic Industries LTD, Gilboa, Israel), was used as a compatibilizer, with MFI of 100 g/10 min (this MFI is the MFI of the masterbatch itself), MA content of 1% and T_m of 160 °C. A masterbatch with an antioxidant was also used (KRITILEN[®] AO PP9216, Plastika Kritis S.A., Heraklion, Greece). The antioxidant masterbatch contained 20.5 wt.% of active ingredients (a combination of phenolic and phosphite antioxidants) dispersed in the PP matrix, with MFI of 25 g/10 min (this MFI is that of the carrier polymer, not of the masterbatch itself). A four-zone twin screw extruder (Haake Rheodrive 5001) and a three-zone single-screw extruder (Noztek Xcalibur) were used. For the drawing process, a self-made apparatus was used, described in detail previously [27–29]. For the aging experiments, a simple laboratory oven was used. The Hans Schmidt & Co GmbH Universal Testing Machine ZPM equipped with a Pacific load cell model PA6110 (3 mV/V, 0.03% nonlinearity) was used for the tensile test measurements. Thermogravimetric analysis (TGA) of various samples was performed with a Shimadzu TGA-50 thermogravimetric analyzer.

2.2. Sample Preparation and Drawing

Three different filaments were produced, namely, pure PP, PP with 4 wt.% of the antioxidant masterbatch (PP-AO) and PP with 4 wt.% masterbatch of the antioxidant and 2 wt.% masterbatch of the compatibilizer (PP-AO-COMB). The non-drawn filaments, with a diameter in the range of 0.4–0.7 mm, were produced as described previously in detail [27–29]. Briefly, a first extrusion was performed in the twin-screw extruder with four heating zones operating at 190, 210, 215 and 220 °C at a motor speed of 25 rpm. The melt was cooled

in a water bath ($\sim 15^\circ\text{C}$). After pelletizing the obtained filaments, a second extrusion was performed in the single-screw extruder with three heating zones operating at 215, 225 and 210°C and at a motor speed of 20 rpm. The obtained PP filaments were drawn, as described previously [27–29], at a ratio of 7 and drawing temperatures of 100, 110, 120, 130 and 140°C . The filaments of PP-AO and PP-AO-COMB were drawn at a ratio of 7 and at a drawing temperature of 120°C . Briefly, a homemade drawing apparatus was used. A sketch of the drawing apparatus is presented in Figure 1. In this machine, the drawing ratio is tuned by varying the ratio of the diameters of two rotating drums, attached to the same axis (thus, rotating with the same speed). The diameter of the first drum was 20 mm, and that of the second drum was 140 mm, resulting in a drawing ratio of 7. The fibers before entering and after exiting the drawing oven were heated with air at 120°C in order to avoid an abrupt alteration of the samples' temperature, which could lead to undesirable internal stresses. The fiber before entering the drawing process was collected in the winder 1. After drawing, the fiber was collected in another winder (the two winders are not shown in the sketch). It is underscored that the air's temperature was 120°C , and the fiber was subjected to this air stream only for 2–3 s, thus the sample's temperature did not reach the same value.

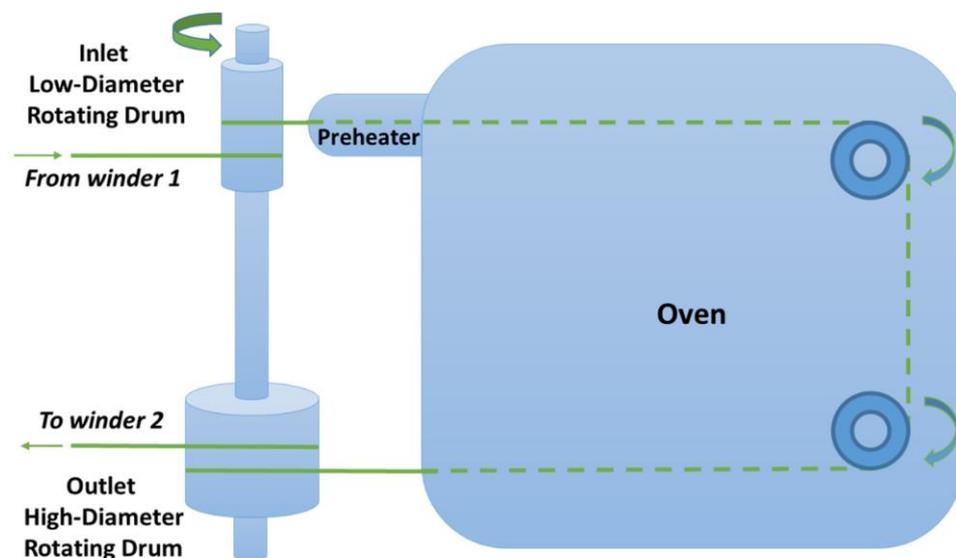


Figure 1. Sketch of the drawing apparatus. The drawing requires the rotation of two drums of different diameter at the same speed.

2.3. Aging and % Degree of Shrinking

Six pieces of PP fibers (initial length of around 35 cm), drawn at 120°C , were placed in a laboratory oven and aged for an 8 h period at two different temperatures, namely, 75 and 100°C . Six pieces of drawn fibers (initial length of around 35 cm) of PP-AO and PP-AO-COMB were aged at 100°C for 8 h. At various times, the length of the fibers was measured (by removing the fibers from the oven) with a tape measure (± 0.1 cm). Thus, the % degree of shrinking (% *S*) at time *t* was calculated by the following equation:

$$\% S(t) = \frac{\text{initial length} - \text{length at time } t}{\text{initial length}} \times 100, \quad (1)$$

The results of the % *S* are expressed as the average value \pm standard deviation from the measurements of the six different pieces for each sample.

2.4. Characterization

All the drawn virgin and aged (for 8 h) fibers were examined by a tensile strength test. At least 10 different pieces for each sample were tested at room temperature ($25 \pm 2^\circ\text{C}$). Briefly, after measuring the dimensions of a sample with a micrometer ($\pm 0.001 \mu\text{m}$), the

fiber was placed in the instrument without applying any stress (zero force). Then, the measurement was carried out with a head speed of 100 mm/min until the fracture of the sample was achieved. The reported values of elastic modulus, tensile strength (expressed as stress at break) and elongation at break are the average values \pm standard deviation of the 10 measurements.

The three masterbatches, the three non-drawn filaments and the drawn fibers (drawn at 120 °C) were examined by TGA under a nitrogen atmosphere (flow 20 mL/min) from 40 to 600 °C at a heating rate of 10 °C/min.

3. Results and Discussion

3.1. Influence of the Drawing Temperature on the Tensile Strength of Neat PP Drawn Fibers

As discussed in the Introduction, it is suspected that the low molecular weight and any poor dispersion of additives might have a negative effect on PP drawn samples. Among the most important factors that affect drawing are the drawing ratio and the drawing temperature. Thus, in order to “magnify” any possible negative effect on drawing caused by the additives, firstly, we attempted to produce PP structures with maximum possible orientation for a given drawing ratio. Consequently, since in our apparatus the maximum drawing ratio that can be accomplished in a single step is 7 (this is the common ratio in industrial practice), we examined several drawing temperatures, in order to find the most suitable one for obtaining the maximum tensile strength (corresponding to the maximum orientation). In Table 1, the elastic modulus, the tensile strength and the % elongation at break of neat PP fibers drawn at a ratio of 7 and different temperatures are presented.

Table 1. Effect of the drawing temperature on the mechanical properties of neat PP fibers drawn at a ratio of 7 (the standard deviations of at least 10 independent measurements are also reported).

Draw Temperature, °C	Elastic Modulus, MPa	Tensile Strength, MPa	% Elongation at Break
100	5741 \pm 454	513 \pm 40	41 \pm 7
110	5196 \pm 1039	503 \pm 30	29 \pm 2
120	5069 \pm 408	549 \pm 27	34 \pm 1
130	3807 \pm 895	480 \pm 80	34 \pm 2
140	2811 \pm 443	355 \pm 63	71 \pm 8

As can be seen in Table 1, the optimum drawing temperature was 120 °C. Here, it is worth mentioning that this value is highly dependent on the properties of the polymer (i.e., molecular weight, thermal history, crystallization temperature, initial crystallinity, etc.), but, due to the rather low heat transfer rate in air ovens, it is usually also dependent on the used apparatus (the nominal drawing temperature is usually not reached by the polymer matrix in industrial applications).

As mentioned above, the optimum temperature for drawing was established at 120 °C, not only because it yielded the maximum tensile strength, but also because the sample drawn at this temperature exhibited the lowest uncertainties in all three measured properties (elastic modulus, tensile strength and elongation at break). The readability of the load cell was 0.01 N, while the measured force during the tensile test was 2–3 orders of magnitude higher. Thus, the errors presented in Table 1 are much higher than the uncertainty introduced by the instrument. The main reasons for these errors are the small diameter of the fibers and the inherent heterogeneity of the fibers. Since the tensile test measurements were performed under identical conditions, it is expected that the error related to the fiber diameter would be similar in all samples. Thus, the high error in some samples regarding elastic modulus and tensile strength suggests large deviations among the 10 pieces used for the independent repetitions of the tensile test measurements and is attributed to the inhomogeneous structure and the presence of defects due to internal stresses. For example, at the higher temperatures (130 and 140 °C), these defects were most likely caused by the relaxation of the fiber after exiting the drawing oven upon cooling. Specifically, the higher drawing temperature imposed an increased cooling time to reach the room temperature, and thus, during this time period, relaxation occurred to a higher extent. For the lower

temperatures (100 and 110 °C), the increased values of the elastic modulus suggest that modules stiffening occurred, as it has been reported to occur during the aging of cold drawn PP, related either to secondary crystallization or to the densification of amorphous regions [24]. As discussed in the introduction section, this effect can be exhibited by both drawn and non-drawn samples, but from the available stress–strain curves it seems that the storage time (aging) affects mainly the elastic modulus and the yield point. This can provide an explanation, e.g., for the difference among the samples drawn at 100, 110 and 120 °C. The samples drawn at 100 and 110 °C, due to the lower temperature (cold drawing), exhibited, to a higher extent, the effect of elastic modulus stiffening, and thus, their average values were higher than those of the sample drawn at 120 °C. For the tensile strength, the difference was smaller, and there was an overlapping of the errors among these three samples. Thus, the samples with a higher elastic modulus appeared to have a lower tensile strength. This concerns the mean values, and no safe conclusion can be extracted. However, since the high standard deviations suggest a less uniform structure, and since the sample drawn at 120 °C exhibited the lowest errors in all three determined parameters, it seemed that the drawing at 120 °C resulted in a smoother structure. Consequently, for all further experiments, the temperature of drawing was kept constant and equal to 120 °C.

3.2. Influence of an Antioxidant and a Compatibilizer on the Tensile Strength of Virgin PP Drawn Fibers

In Figure 2, the TGA curves of the three masterbatches, as well as of the non-drawn filaments and the drawn fibers (drawn at 120 °C) are presented. As shown in Figure 2a, the AO masterbatch presented a rather impressive thermal stability, relatively to all samples, while the compatibilizer masterbatch was the most thermally sensitive, since it started to decompose at the lowest temperature.

As shown in Figure 2b for the non-drawn filaments, the pure PP sample appeared to be the least thermally stable sample, whereas the PP-AO sample was the most stable. Similar observations can be made for the drawn fibers, as presented in Figure 2c. In a previous work [27], it was reported that the addition of a compatibilizer enhanced the action of the AO and improved the stability of the polymer matrix over thermal oxidation during processing. Consequently, the PP-AO-COMB sample exhibited even higher thermal stability than PP-AO. In the present study, the TGA measurements were performed under nitrogen and not under air atmosphere; thus, this effect was not visible. Since in our previous works [27–29] the effects of a compatibilizer and an antioxidant were studied under oxidative (air) atmosphere, here an inert gas (nitrogen) atmosphere was chosen to study the inherent thermal stability of the used materials. In addition, the relative contents of antioxidant and compatibilizer were different in the two cases. However, it should be kept in mind that the excess of compatibilizer (which was characterized by decreased thermal stability) could indirectly contribute to the stability of the PP-AO-COMB sample by enhancing the dispersion of the antioxidant [27–29].

By comparing the PP masterbatch with the neat PP non-drawn fiber (Figure 2d), it can be observed that the non-drawn sample exhibited a slightly decreased temperature of initiation of decomposition. The difference in thermal stress between these two samples was due to two extrusions and the drawing process. From the small difference between these two samples, it can be concluded that the degradation of PP during extrusions was rather small. In addition, the non-drawn sample after 10% mass loss presented a lower mass loss rate compared to the masterbatch. Most likely, this occurred due to the presence of oxidized groups (produced during the extrusion). The drawn fibers appeared to be less thermally stable in terms of both initiation of decomposition and maximum mass loss rate temperature. Since, after two extrusions (at temperatures around 220 °C), the decomposition was rather low, the lower stability of the drawn fibers could not be attributed to the decomposition during drawing (which was carried out at a much lower temperature and for a shorter time than the extrusions). Most likely, such behavior of the drawn fibers

was influenced by their smaller diameter, which allowed for a faster heating (less thermal lag) of the sample during the TGA measurements.

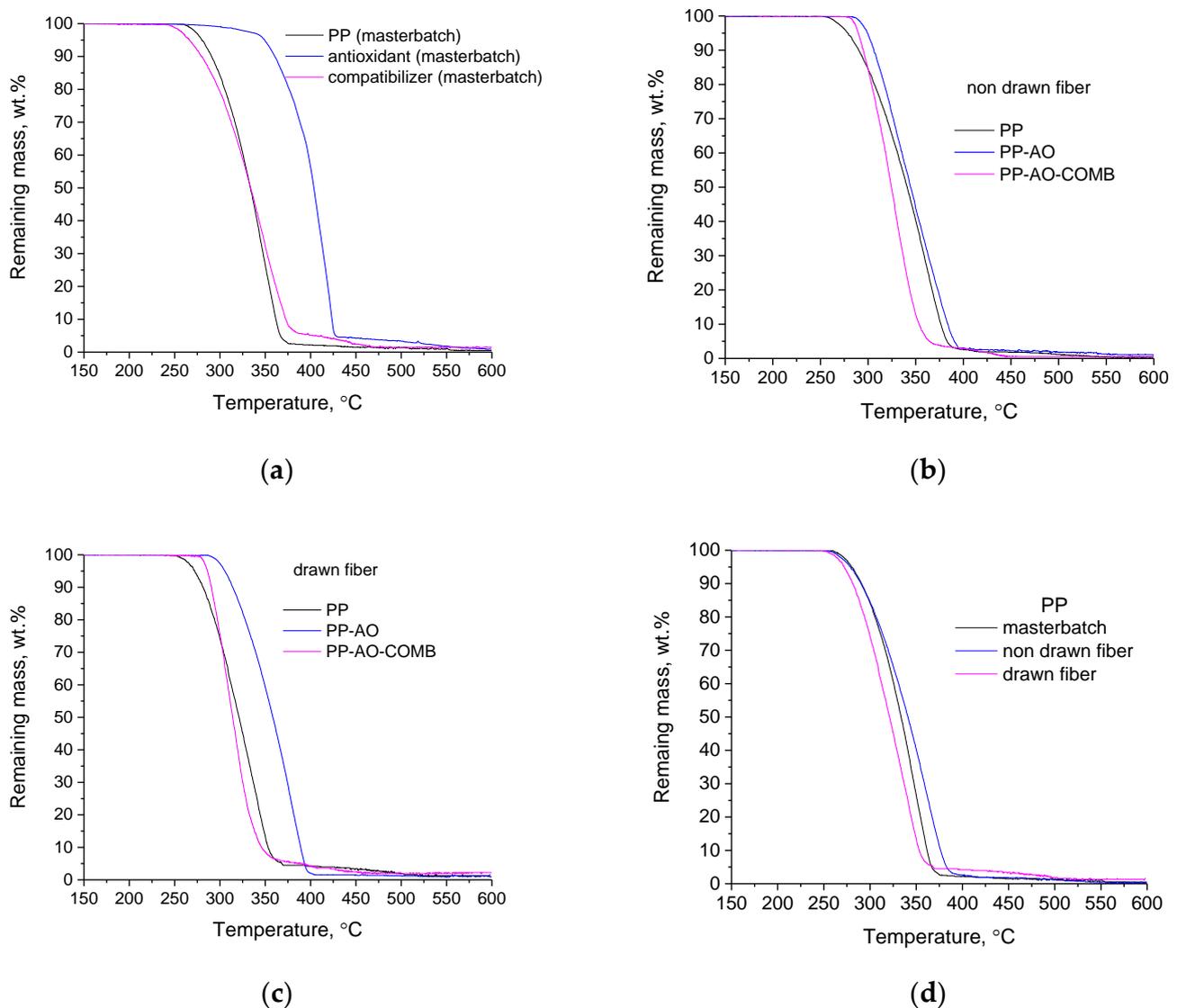


Figure 2. TGA curves of (a) masterbatches; (b) non-drawn filaments; (c) drawn fibers; (d) PP masterbatch, PP non-drawn and PP drawn fibers. Drawing was performed at 120 °C.

Regarding the mechanical properties, a different trend was observed. In Table 2, the elastic modulus, the tensile strength and the elongation at break of the drawn fibers are presented. From the results presented in Table 2, it is clear that the addition of the antioxidant masterbatch to PP countably decreased the elastic modulus and the tensile strength. The above-mentioned improvement of the properties of PP-AO caused by the addition of a compatibilizer [27], was now visible. However, although the addition of the compatibilizer induced an increase of mechanical strength, still, the pure PP sample was superior in this respect.

Table 2. Mechanical properties of virgin PP, PP-AO and PP-AO-COMB fibers drawn at 120 °C and at a drawing ratio of 7.

Sample	Elastic Modulus, MPa	Tensile Strength, MPa	% Elongation at Break
PP	5069 ± 408	549 ± 27	34 ± 1
PP-AO	4134 ± 449	448 ± 37	30 ± 1
PP-AO-COMB	4601 ± 286	487 ± 24	31 ± 1

One reason for this deterioration of the tensile strength, compared that of the neat PP, may be the lower molecular weights of the additives and the polymer used as an additive carrier (see the MFI of the additive masterbatches in Section 2.1). This interpretation is in agreement with the lower elongation of PP-AO and PP-AO-COMB compared to that of the neat PP sample. A lower molecular weight may interfere with the drawing process by two possible pathways: a) the low-molecular-weight polymer chains are overstretched, leading to deteriorated mechanical strength, b) the small chains can easily relax/shrink upon cooling and by this way they contribute to the lower values of mechanical strength. However, other explanations are possible. The molecular weight of the AO masterbatch was a bit lower than that of the neat PP, as it can be concluded from the respective MFI values mentioned in the experimental section, while the compatibilizer had a much lower molecular weight (much higher MFI). Thus, based on the above interpretation, the addition of the compatibilizer should have caused a further deterioration of the mechanical properties. The reason for observing the opposite is related to the strong intermolecular interactions that formed between the compatibilizer and the antioxidant, as recently reported [27]. These interactions lead to improved dispersion of the antioxidant in the PP matrix, and this also occurs through two possible pathways, contributing to the increase of mechanical strength, despite the lower molecular weight: (a) the better dispersion of the antioxidant results in an improved and more effective antioxidant action, and thus the thermo-oxidative decomposition during extrusions and drawing proceeds to a lower extent, (b) the better dispersion of the antioxidant results in fewer aggregates. The aggregates interfere with the chain alignment and render the drawing process less effective. This in turn leads to deteriorated mechanical properties. As a summary of this section, the addition of an antioxidant and a compatibilizer caused a countable reduction of the mechanical strength of the PP drawn fibers. This effect is not general for any polymer matrix, but specifically concerns drawn samples, since it is related to the obstruction of chain alignment through various pathways.

3.3. Influence of the Antioxidant and the Compatibilizer on the Tensile Strength of Aged PP Drawn Fibers

In Figure 3, the percentage degree of shrinking (% S), as a function of time, is presented for PP drawn fibers (at 120 °C) aged at two different temperatures (75 and 100 °C). As can be seen, the trend of the two curves is qualitatively the same at the two aging temperatures. Precisely, within 30 min of aging, shrinking proceeded rapidly and, in up to 4 h (240 min), almost reached its maximum value. Quantitatively, the shrinking at the higher temperature was higher and almost double than the one at 75 °C.

The shrinking was accompanied by the deterioration of the mechanical properties and a reduction in elastic modulus and tensile strength. In Table 3, the values of the mechanical properties of virgin and PP drawn fibers aged for 8 h, along with the reduction (%) in tensile strength, are presented. For the sample aged at a higher temperature, which exhibited a higher degree of shrinking, the % reduction in tensile strength after 8 h of aging was also higher than that of the sample aged at 75 °C. However, the % reduction can be considered low for both cases.

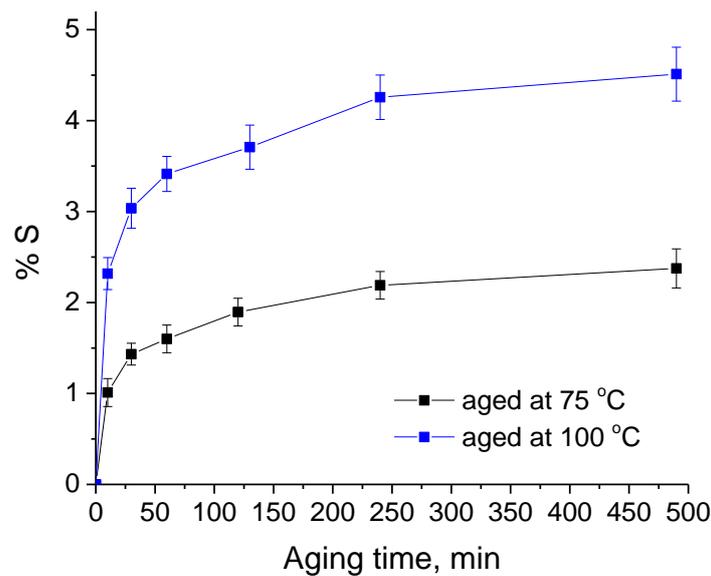


Figure 3. Degree of shrinking (% S) of PP drawn fibers (drawn at 120 °C), aged at two different temperatures, as a function of aging time.

Table 3. Mechanical properties and % reduction in tensile strength of PP fibers drawn at 120 °C before and after 8 h of aging at 75 or 100 °C.

Aging Temperature, °C	Elastic Modulus, MPa	Tensile Strength, MPa	% Elongation at Break	% Reduction of Tensile Strength
Not aged	5069 ± 408	549 ± 27	34 ± 1	-
75	4712 ± 261	516 ± 27	29 ± 1	6
100	4283 ± 419	509 ± 50	33 ± 1	7

Qualitatively, the same shrinking behavior could be observed for the PP-AO and PP-AO-COMB drawn fibers aged at 100 °C (Figure 4). However, the rate of shrinking in the first 15–30 min was quite higher, especially for PP-AO, and also, the equilibrium value was higher than the one of pure PP.

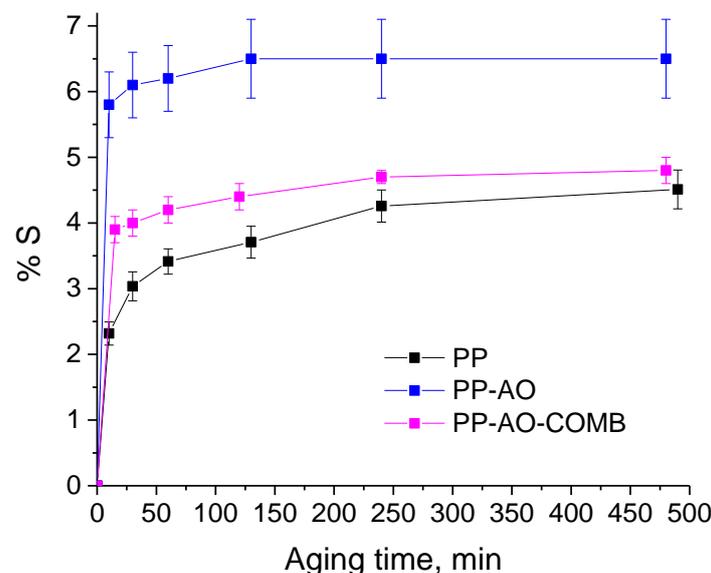


Figure 4. % Degree of shrinking (% S) of PP, PP-AO and PP-AO-COMB drawn fibers (drawn at 120 °C) aged at 100 °C, as a function of the aging time.

As shown in Table 4, the shrinking due to aging was accompanied by a reduction in elastic modulus and tensile strength for pure PP, but also for PP with additives. The % reduction in mechanical strength in the samples with the additives was of the same order of magnitude as the one for pure PP. As observed in the case of the virgin samples (see Table 2), the PP-AO appeared to be the most inferior sample.

Table 4. Mechanical properties and % reduction in the tensile strength of neat PP, PP-AO and PP-AO-COMB fibers drawn at 120 °C and aged at 100 °C for 8 h.

Sample	Elastic Modulus, MPa	Tensile Strength, MPa	% Elongation at Break	% Reduction of Tensile Strength
PP	4283 ± 419	509 ± 50	33 ± 1	7
PP-AO	3061 ± 303	414 ± 23	35 ± 1	8
PP-AO-COMB	3961 ± 377	465 ± 29	30 ± 2	5

4. Further Discussion

From the results regarding the shrinking and reduction of the tensile strength after aging, presented in the previous section, it follows that these two factors are not linearly correlated. However, some positive correlation exists, e.g., the PP-AO exhibited both the highest shrinking and the highest reduction in tensile strength.

It can also be concluded that the addition of low-molecular-weight additives in drawn PP samples had a double negative effect, i.e., not only the produced drawn fibers had reduced mechanical strength, but also the drawn fibers with additives were more sensitive to physical aging than pure PP. In the case of PP-AO, the major problem seemed to be the poor dispersion, which caused defects in the oriented structure of drawn PP. This was improved by the addition of the compatibilizer, and thus, the mechanical properties of the PP-AO-COMB sample were better compared to those of the PP-AO sample. However, the lower molecular weight of the compatibilizer interfered with the drawing process. Since this sample (PP-AO-COMB) exhibited higher shrinking than neat PP (see Figure 3) but a similar reduction in tensile strength after aging (see Table 4), it can be concluded that the of low-molecular-weight chains significantly contributed to the shrinking, but this did not result in a significant further considerable deterioration of the mechanical properties.

5. Conclusions

The incorporation of common additives such as an antioxidant and a compatibilizer in PP drawn fibers resulted in a countable decrease in elastic modulus and tensile strength. The tensile strength of pure PP was reduced from 549 MPa to 450 MPa after the incorporation of the antioxidant and the compatibilizer. Two factors may have contributed to this behavior, namely, the low molecular weight of the additives and their poor dispersion. The additives' low molecular weight, due either to overstretching or/and to increased thermal motion and subsequent easy relaxation of the small chains, can contribute to the decrease the tensile strength. The poor dispersion of AO can cause defects in the oriented structure. Thus, any positive effect, on the mechanical properties of drawn PP fibers, of the antioxidant due to the protection of PP during processing (extrusion and high-temperature drawing) was surpassed/decreased by the negative effect of its low molecular weight and poor dispersion. For similar reasons, the drawn fibers containing additives shrink faster and to a higher extent during physical aging. However, since the small chains did not contribute to a great extent to the tensile strength improvement during drawing, the reduction in tensile strength after aging was mild. In conclusion, the pure PP drawn fibers exhibited higher tensile strength than the PP-additive fibers, both prior and after physical aging. However, the used additives have an indisputable value for non-drawn samples, and their usage is necessary for various reasons, e.g., protection from chemical aging, also in drawn samples. Consequently, additives specifically designed for drawn samples should be developed.

Author Contributions: Conceptualization, C.T. and I.T.; methodology, C.T. and K.L.; software, C.T.; validation, G.G., K.L., C.T. and I.T.; formal analysis, C.T. and G.G.; investigation, G.G., K.L. and C.T.; resources, I.T.; data curation, G.G. and C.T.; writing—original draft preparation, C.T.; writing—review and editing, I.T.; visualization, G.G. and C.T.; supervision, I.T.; project administration, I.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are available upon request.

Acknowledgments: The authors would like to thank Plastika Kritis S.A. for kindly providing the antioxidant masterbatch.

Conflicts of Interest: The authors declare no conflict of interest.

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