Chain Extension Behavior and Thermo-Mechanical Properties of Polyamide 6 Chemically Modified With 1,1′-Carbonyl-Bis-Caprolactam

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A chain-extender based on 1,1′-Carbonyl-Bis-Caprolactam (CBC) was melt compounded with a commercial Polyamide 6 (PA6) by using a twin screw extruder. Rheological, thermal, and mechanical tests were performed on the resulting materials to evaluate the chain extension capability of CBC. Rheological tests on the compounded pellets and relative viscosity measurements on solubilized samples evidenced an increase of the viscosity values with the chain-extender amount, while the opposite trend was determined increasing the high temperature residence time. Terminal group analysis confirmed the increase of the molecular weight with the CBC content and highlighted a preferential reactivity of the chain-extender with aminic end groups. Differential scanning calorimetry (DSC) tests showed how both melting and relative crystallinity of the up-graded samples decreased with the CBC amount. Elastic and yield properties of chain-extended PA6 were similar to those of neat PA6 grades at different molecular weight, while crystallinity drop due to chain extension was responsible of an increase of the strain at break values. POLYM. ENG. SCI., 54:158–165, 2014.

INTRODUCTION

In the last years, the attention of the scientific community toward the environmental pollution and the consumption of fossil resources considerably increased. Therefore, the problem of plastics recycling has gained an increasing importance in many areas of the human activities [1]. It was also widely recognized that collection and recycling of plastic wastes is the only feasible way to limit environmental pollution [2, 3]. Basically, four different treatments can be applied to manage plastic wastes: energy recovery (incineration), landfilling, chemical processing (de-polymerization), and material recycling [4].

It was demonstrated that landfilling is in many cases environmentally and economically unacceptable, while incineration is unsafe and not environmentally viable [5]. Material recycling is often the easiest option to operate the disposal of plastic wastes in a convenient way [6]. Reprocessing plastic wastes into a new polymer is a suitable solution for material recycling only if a single-sort industrial plastic waste is treated. In fact, recycling polymers coming from different sources can be very complex, and the resulting materials possess mediocre mechanical performances, because of the relative incompatibility of most polymer pairs [7]. In many cases, the addition of a compatibilizing agent makes the process too complicated and expensive [8].

Polyamides (PAs), also known as Nylon, are one of the most important commercial engineering plastics [9]. From a chemical point of view, Polyamide 6 (PA6) is a linear polymer constituted by amide (—CONH—) repeating units, polymerized by the ring opening polymerization (ROP) of caprolactam (CPL). Every year, about 4.3 million tons of CPL are produced worldwide to synthesize Nylon 6. Because of their good drawability and their similarity with silk fibers, PAs were initially used in the production of socks, carpets, rugs. Only subsequently their excellent mechanical and chemical properties were applied for engineering purposes, and nowadays PAs are widely used in fiber, film, packaging, and molding applications [10]. In Europe, about 1.3 million tons of PA is utilized for textile yarns, industrial yarns, and flooring [11]. PA fibers dominate the scenario of recycled carpet materials, and it is therefore evident the strategic interest in PA carpet recycling. According to the last CARE Report, in 2011 only the 7 wt % of post-consumer US carpet discards has been recycled [11].

Generally speaking, plastic recycling can be performed by using two different technologies: down-grading and

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up-grading processes. Down-grading plastic recycling technology was widely adopted in the last decades, but the material recovered after use can be only utilized for less noble application due to the progressive loss of the material properties, up to the final disposal by landfill or incineration. On the contrary, in the up-grading process plastic wastes are recovered to their original inherent quality [12]. Therefore, plastics recycling through up-grading has no limit and can be repeated several times, at least from a theoretical point of view. During their service life, the degradative action of the UV radiation and of the thermal and mechanical stresses tends to lower the molecular weight and mechanical performances of the engineering plastics. In the up-grading recycling process, different types of additives (i.e., chain-extenders) can be added during the compounding process to restore the original properties of the degraded polymers. Chain-extenders are low molecular weight compounds that can be added either during polymerization or during reactive extrusion processes. The optimal choice of the additive is a very complex issue that depends from the processing technology. For instance, the use of a chain-extender, having two or more functionalities on injection molded products may lead to their partial curing, increasing thus the stiffness of the resulting materials. On the other hand, chain-extenders for spinned polymers must be as linear as possible, to promote chain alignment and crystallization of drawn fibers. The key parameters for the reactive extrusion process are the concentration of chain-extender, the residence time of the polymer in the extruder and the temperature profile [13].

During the up-grading recycling of PAs, chain-extender functionalities react with amino and carboxylic end groups of PA macromolecules, to connect two or more polymer chains, increasing thus the molecular weight [14, 15]. Quite surprisingly, only few publications on PA up-grading through chain-extenders can be found in literature, and the greatest part of them deals with the use of different bisoxazoline coupling agents. Some papers reported the chemical modification of PA6 by chain extension with bis(2-oxazoline) [16], with biscaprolactam molecules [17], and with their combination [18, 19]. It was shown how the intrinsic viscosity of PAs increased with the chain-extender amount. It was also reported that during up-grading process the degradation of PAs is likely to proceed simultaneously with the chain-extension reactions. The chain extension potential of 2,2′-(1,4-phenylene)bis(2-oxazoline) on carboxy-terminated aliphatic PAs and polyesters was investigated by Nery et al. [20]. It was found that arylene and pyridylene bisoxazolines reacted with carboxy-terminated aliphatic PAs and polyesters without noticeable side reactions, and the highest reactivity could be reached within 20 min at 200°C. A strict control of critical parameters (i.e., starting oligomer molar mass, bisoxazoline structure, oligomer/coupling agent molar ratio, reaction temperature) revealed necessary to control reaction kinetics, the thermal properties and the molar mass of the final copolymer. The chain extension of oligoamide or PA by using oxazoline was investigated by Schacker et al. [21]. In that article, it was shown how during extrusion process bisoxazoline reacted with PA macromolecules by extending them linearly or by leading to branched polymers. A Monte Carlo simulation was utilized by Yan et al. to study the carboxyl terminated polymers chain extension by using a bisoxazoline coupling agent [22]. Qian et al. [23] performed a detailed investigation on the chain extension of PA1010 by using two different diepoxides as chain-extenders, investigating also the rheological, thermal and the mechanical properties of the chain-extended materials.

In a previous work of our group [24], a polycarbonate/polyamide blend (PCPA) was melt compounded with a PA6 matrix to evaluate the chain extension behavior of the resulting materials. Dynamic rheological tests on the compounded pellets and relative viscosity measurements on the solubilized materials evidenced an interesting increase of the molecular weight with the PCPA loading. Interestingly, a prolonged thermal treatment at high temperature produced a further progression of the chain extension reaction. Moreover, the decrease of the crystallinity degree due to chain extension was found to be responsible of an interesting improvement of the strain at break values in the up-graded materials.

Starting from these considerations, in this article, the efficacy of a 1,1′-Carbonyl-Bis-Caprolactam (CBC) in increasing the molecular weight of commercial PA6 was investigated. This work represents the preliminary step of a wider research with the final goal to recycle post-industrial and post-consumer polymers. The chain extension behavior of the compounded materials was evaluated through capillary rheological tests, relative viscosimetry measurements, and end group analysis on solubilized chips. Thermal and mechanical properties of chain extended materials were determined through differential scanning calorimetry (DSC) and quasi-static tensile tests. Finally, a comparison between the mechanical properties of the compounded samples and those of the corresponding virgin polymers at the same molecular weight was carried out.

EXPERIMENTAL PART

Materials

Polymeric chips of four kinds of virgin PA6 grades, differing for their molecular weight, were supplied by Aquafil S.p.A (Arco, Italy): Aquamid AQ24000, Aquamid AQ27000, Aquamid AQ34000 and Aquamid AQ40000. A powder of CBC, supplied by DSM (Urmond, NL), was utilized as chain-extender. All the materials were used as received. The properties of the different PA6 grades and of the chain-extender are summarized in Table 1.

TABLE 1. Properties of the different virgin PA6 grades and of the chain extender used in this work.

Property	AQ 24000	AQ 27000	AQ 34000	AQ40000
η_{rel}[a]	2.4	2.7	3.4	4.0
T_m (°C)[b]	222	222	222	222
ΔH_m (J g^{-1})[b]	73	70	66	66

[a] Measured through a Ubbelohde viscometer at 25°C on sulfuric acid solutions (concentration = 10 g L^{-1}).

[b] Evaluated from DSC tests.

Sample Preparation

Aquamid AQ27000 grade was chosen as reference material to be melt compounded with different chain-extender amounts, while the other PA6 grades were processed without the CBC addition, to compare the properties of the chain extended products with those of the virgin materials having the same molecular weight (i.e., the same relative viscosity). Therefore, different amounts (from 0.1 to 0.4 wt %) of CBC powder were melt compounded with AQ27000 chips in an industrial twin screw extruder, having a screw diameter of 42 mm and a L/D ratio between 32 and 48. The process parameters were optimized as follows: rotational speed = 300 rpm, feed rate = 120 kg h^{-1}, barrel temperature profile = 80/230/245/245/245/245/245/245/250/260°C. The extrudate was immediately cooled down in a water bath and pelletized. The resulting pellets were utilized for rheological tests at the molten state, for relative viscosity measurements and end group analysis on solubilized chips, and for DSC tests. The pellets were then injection molded through a Battenfield Plus 350/075 machine, to prepare ISO 527 1A dumbbell specimens for quasi-static tensile tests. The following process parameters were set: screw temperature = 255°C, die temperature = 260°C, mold temperature = 80°C, filling time = 0.4 s, injection pressure = 35 bar. About 30 specimens were prepared for each composition. In the Results and Discussion section, the neat AQ27000 sample was designated as PA-2.7, while the chain extended materials were denoted indicating the matrix (PA6), the chain-extender (CBC) and its weight amount. As an example, PA-CBC-0.1 indicates the AQ27000 sample chain extended with a CBC content of 0.1 wt %. To have a direct comparison, samples of PA6 grades without any chain-extender addition were prepared with the same procedure.

Experimental Methodologies

Dynamic rheological measurements were performed by using a Dynisco Polymer LCR 52M capillary rheometer, setting a chamber temperature of 260°C and a shear rate ($\dot{\gamma}$) interval between 100 and 10000 s^{-1}. Before testing, pelletized samples were dried in vacuum oven at 120°C for 12 h. The samples were maintained in the rheometer for two different residence times (3 and 13 min), to evaluate the time dependency of the chain extension process and the thermal stability of the compounded materials. These times were chosen according to the requirements of the industrial processing of PAs. In particular, a time of 3 min is required to completely melt PA6 in the rheometer oven at 260°C, while an interval of 13 min is the typical residence time at elevated temperature for a melt spinning process.

Relative viscosity tests were carried out through an Ubbelohde viscometer according to ISO 307. Both extruded pellets and samples deriving from dynamic rheological measurements at 3 and 13 min were tested, to evaluate the influence of the residence time at high temperature on the chain extension of the compounded materials. About 0.4 g of samples were previously dried for 30–60 min in oven at 90°C and solubilized at 50°C with sulfuric acid (purity 95.7%), at a concentration of 10 g L^{-1}. The solution was then put in a water bath at 25°C for about 20 min and then tested at the same temperature.

End groups analyses were performed both on extruded pellets and on the samples obtained from dynamic rheological measurements at different residence times (3 and 13 min), to better investigate the reactivity of CBC toward carboxylic and amminic groups of PA6. These tests were performed by using a Mettler DL50 automatic titrator coupled with an electronic voltmeter. About 0.8 g of samples were solubilized in 20 mL of 2,2,2 trifluoroethanol (TFE) at 55°C. —NH_2 groups titration was performed at 25°C through a HCl 0.02 N solution, while —COOH titration was carried out with a NaOH 0.02 N solution. The adopted testing methods and the relative parameters have been optimized, and the absolute error associated to each measurement is in the order of 1 $mmol_{eq} \cdot g^{-1}$.

DSC tests were performed through a TA Instrument DSC Q20 calorimeter on extruded pellets. The samples were first heated from 0°C to 260°C at 20°C min^{-1}, cooled to 0°C at the same rate and finally re-heated up to 350°C. About 10 mg were tested for each sample under a nitrogen flow of 100 mL min^{-1}. In this way, the glass transition (T_g), the melting (T_m) and the crystallization temperature (T_c) of the compounded materials was determined. The relative crystallinity degree (χ) was computed dividing the specific melting enthalpy of the polymer (ΔH_m) with that of the fully crystalline PA6 (ΔH_0), taken as 190 J g^{-1} [25], as reported in *Eq. 1*:

$$\chi = \frac{\Delta H_m}{\Delta H_0} \cdot 100 \quad (1)$$

Quasi-static tensile tests were performed at 25°C by using an Instron 4502 tensile testing machine, equipped with a load cell of 1 kN, at a crosshead speed of 50 mm min^{-1}. ISO 527 1A dumbbell specimens (width = 10 mm, thickness = 4 mm, gage length = 80 mm) were utilized, and at least five specimens were tested for each sample. The

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most important tensile properties of the samples were evaluated: elastic modulus (E), stress at yield (σ_y), deformation at yield (ε_y), and deformation at break (ε_b).

RESULTS AND DISCUSSION

In Fig. 1a and b, the results of dynamic rheological tests performed on neat PA-2.7 sample and of the relative chain extended products, after a residence time at 260°C of 3 min and 13 min are respectively reported. All the tested samples show the typical pseudoplastic behavior of PAs [26]. The first region at low shear rate, called Newtonian plateau, is characterized by a constant value of the apparent viscosity (η_{app}) while at higher $\dot{\gamma}$ the viscosity rapidly decreases with the shear rate (shear thinning region). First of all, neat PA sample shows a slight enhancement of η_{app} by increasing the residence time at 260°C from 3 to 13 min. As suggested by La Mantia et al. [27], this is due to the fact that at low humidity contents and under equilibrium conditions, reprocessing operations promote post-condensation reactions with a consequent increase of the molecular weight.

The apparent viscosity increases proportionally to the CBC content over the whole shear rate interval. At low $\dot{\gamma}$ the increment of the shear viscosity is more pronounced, while at higher shear rates η_{app} curves are very near to that of the neat PA. It is well known that above a certain molecular weight strong physical entanglements between the macromolecules are formed, and in these conditions the shear viscosity is proportional to the molecular weight [28]. Therefore, the increase of the shear viscosity values induced by CBC can be related to an increase of the molecular weight of the compounded PAs. At higher $\dot{\gamma}$, the physical bonds between the macromolecules are partially destroyed by the shear flow and the viscosity increase due to CBC is less evident. These results demonstrate the up-grading effectiveness of CBC in increasing the molecular weight of PA6. Another important aspect can be drawn from Fig. 1c, where a general comparison between apparent viscosity values at a shear rate of 1000 s^{-1} was reported for the two residence times (3 and 13 min). While for PA-2.7 sample the apparent viscosity increases with the residence time, for chain extended products apparent viscosity values at 13 min are lower than that obtained at 3 min, and the relative decrease is more

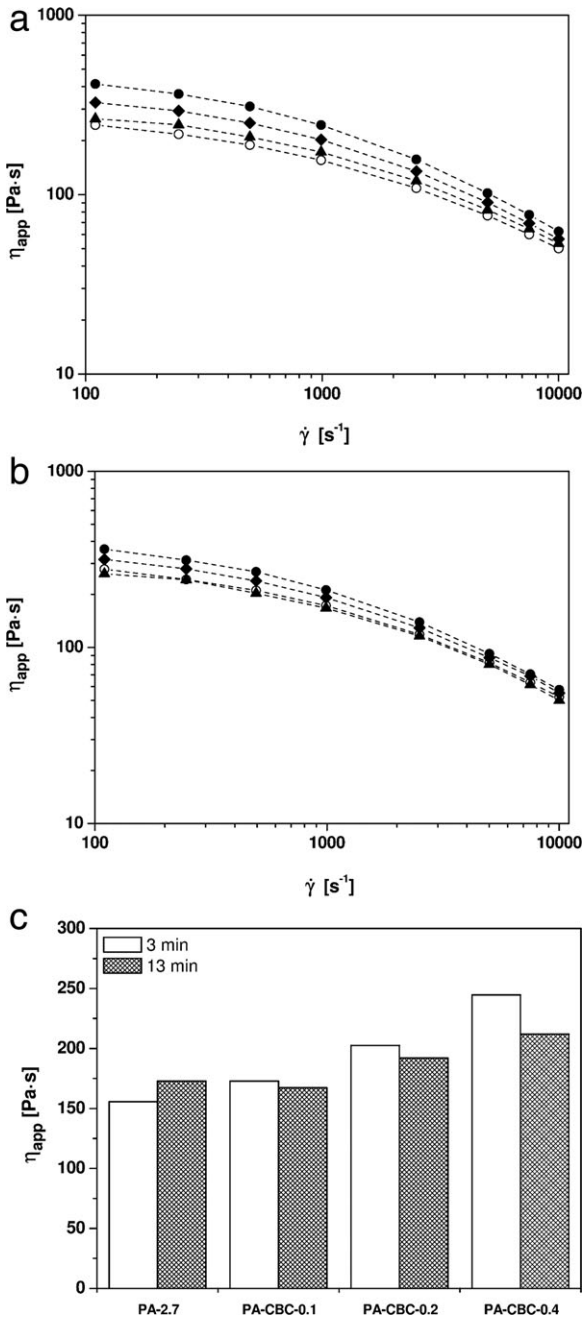

FIG. 1. Apparent shear viscosity of neat PA-2.7 and of the relative CBC chain-extended products from rheological tests at $T = 260$°C. (a) Residence time 3 min, (b) residence time 13 min. (○) PA-2.7, (▲) PA-CBC-0.1, (◆) PA-CBC-0.2, (●) PA-CBC-0.4, (c) comparison of shear viscosity values at a shear rate of 1000 s^{-1}.

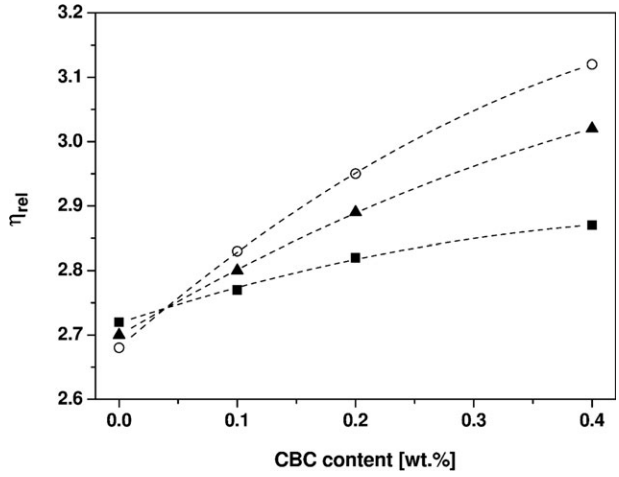

FIG. 2. Relative viscosity values of neat PA-2.7 and of the relative CBC chain-extended products from rheological tests on H_2SO_4 solubilized chips, at different residence times in the rheometer. (○) Chips, (▲) 3 min, (■) 13 min.

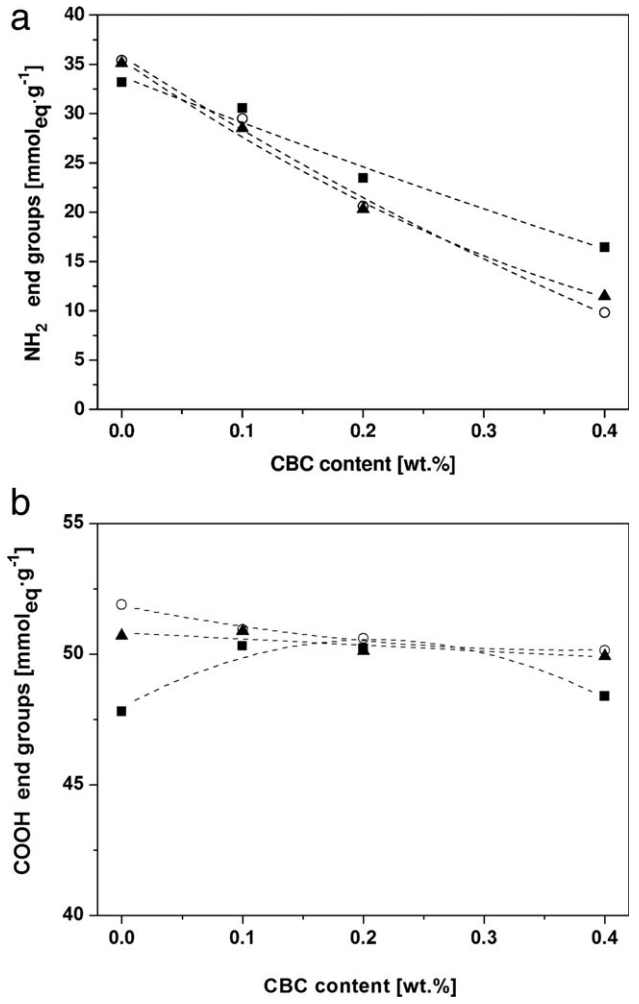

FIG. 3. (a) $-NH_2$ and (b) $-COOH$ end groups analysis on neat PA-2.7 and relative CBC chain extended products at different residence time in the rheometer. (○) Chips, (▲) 3 min, (■) 13 min.

pronounced at elevated CBC amounts. It can be, therefore, hypothesized that, when CBC is added to PA6, a prolonged residence time at elevated temperature could lead to a partial degradation of the matrix, with a decrease of its molecular weight.

Solution viscosimetry measurements on solubilized samples were carried out both on extruded chips and on samples tested in dynamic rheological measurements at two different times (3 and 13 min). In Figure 2 relative viscosity values (η_{rel}) of neat PA-2.7 and of the corresponding chain extended products are reported. Accordingly to dynamic rheological measurements, relative viscosity values of neat PA-2.7 slightly increase with the residence time because of the effect of post-condensation reactions, while η_{rel} values of the up-graded materials increase with the CBC content both at residence times of 3 and 13 min. Even in this case, η_{rel} values of chain extended samples at 3 min are higher than that of the corresponding samples at 13 min for all the tested compositions, and the difference is more evident at elevated CBC amounts. Therefore, relative viscosity measurements confirm the up-grading capability of CBC during reactive extrusion, but a prolonged permanence at elevated temperatures seems to produce a partial degradation of the polymer, with a consequent decrease of the molecular weight.

To analyze the up-grading capability of CBC from a chemical point of view, end group analysis was performed. In Fig. 3a and b, the trends of the amminic and of the carboxylic groups as a function of the chain-extender amount for the neat PA-2.7 and for the relative CBC chain extended products are respectively reported. The number of amminic end groups rapidly decreases with the CBC content, while the concentration of carboxylic functionalities is substantially unaffected by the chain-extender introduction. This means that chain extension reaction really occurred in these systems, and that the observed increase of the relative viscosity values (see Fig. 2) can be surely attributed to the increase of the molecular weight promoted by chain extension. Moreover, end group analysis highlights that the increment of molecular weight is mainly due to the reaction between CBC and amminic end groups. According to the literature references [19], it can be hypothesized that CBC molecules react mainly with the amminic end groups of PA in two different ways. The first mechanism (Fig. 4a) is characterized by nucleophilic substitution reaction with the

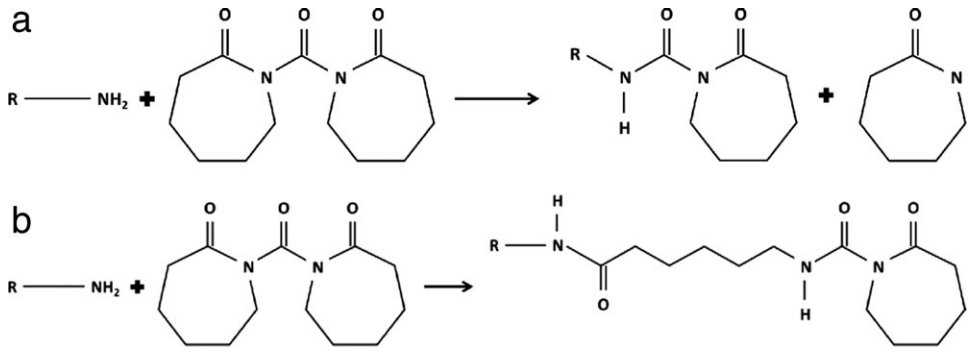

FIG. 4. Reaction scheme of CBC with amminic end groups of PA6. (a) nucleophilic substitution with CPL formation, (b) ring-opening reaction.

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TABLE 2. Results of DSC tests on neat PA-2.7 and on the relative CBC chain extended products.

Sample	First heating		Cooling			Second heating		
	T_m (°C)	ΔH_m (J g^{-1})	T_c (°C)	ΔH_c (J g^{-1})	χ (%)	T_g (°C)	T_m (°C)	ΔH_m (J g^{-1})
PA-2.7	228	69	184	70	37.1	55	223	70
PA-CBC-0.1	225	65	182	71	37.2	55	222	70
PA-CBC-0.2	226	67	180	67	35.5	54	222	68
PA-CBC-0.4	226	63	179	66	34.6	53	222	66

T_m: melting temperature; ΔH_m: specific melting enthalpy; T_c: crystallization temperature; ΔH_c: specific crystallization enthalpy; χ: relative crystallinity degree; T_g: glass transition temperature.

formation of a CPL molecule as by-product, while the second mechanism (Fig. 4b) involves a ring opening reaction, without any by-product formation. The elimination of CPL is promoted at low temperature, while at high temperature (i.e. above 200°C) both reactions take place. It is important to point out that spectroscopic measurements (i.e. NMR spectroscopy) could give further insights on the chemical aspects involved in the chain extension behavior of the investigated materials. However, a more detailed analysis of the chemical mechanisms involved in the up-grading process of these samples will be reported in a future article.

Even in this case, an increase of the residence time from 3 min to 13 min produces an enhancement of —NH_2 end groups, while —COOH end groups concentration remains at a stable level. According to dynamical rheological tests and relative viscosity measurements, it can be concluded that a prolonged heat treatment leads to a degradative action with the reduction of the molecular weight of the resulting polymers. It could be interesting to compare these results with those reported in a previous work of our group [24], in which a PCPA was used as chain-extender for the same PA6 matrix. In that article, the increase of the relative viscosity values and the consequent decrease of —NH_2 end groups resulted to be proportional to the high temperature residence time. This means that a prolonged heat treatment promoted a further enhancement of the molecular weight. An opposite conclusion was found in this case. A processing time of 3 min is probably sufficient to obtain a complete chain extension reaction, and a further thermal treatment leads to a partial degradation of the material with an important reduction of its molecular weight. It can be therefore concluded that CBC powder can be utilized as chain-extender agent only in one-step reprocessing operations, in which the permanence of the material at elevated temperature is rather limited, while its efficacy noticeably decreases in two-step up-grading recycling operations or under long lasting thermal processing conditions.

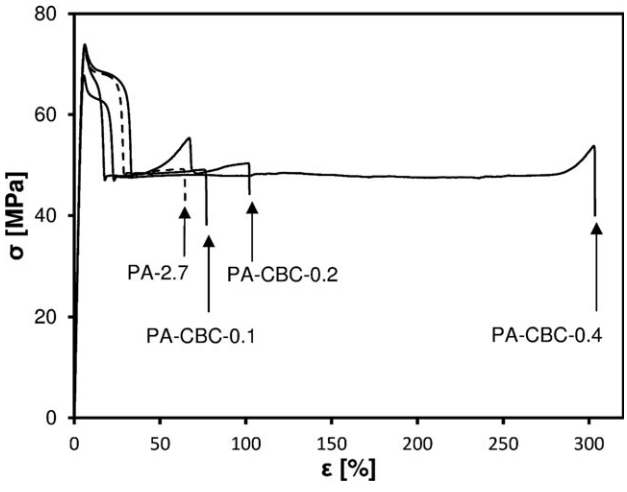

FIG. 5. Representative stress–strain curves from quasi-static tensile tests on neat PA-2.7 and relative CBC chain extended products.

It can be now interesting to analyze the effect of the CBC on the thermal and mechanical properties of the resulting materials. In Table 2, the main results from DSC tests performed on extruded pellets of neat PA-2.7 and on the relative chain extended products are summarized. Both melting (T_m) and glass transition temperature (T_g) decrease with the chain-extender amount. Also crystallization temperature (T_c), melting (ΔH_m), and crystallization (ΔH_c) enthalpy values show the same trend. This means that the crystallization process of PA6 is partially hindered by chain extension reaction. Similar results were obtained by Lu et al. in their works on the chemical modification of PA6 by chain extension with different kinds of bisoxazolines [16–18]. In those articles, the crystallinity drop was attributed to the increase of the molecular weight of PA6 and to the introduction of the ester-amide groups in the PA6 main chains upon the chain extension reaction. In this case, it can be hypothesized that crystallinity reduction is mainly due to the increase of the molecular weight that hinders the arrangement of the macromolecules in a crystalline structure. Also the presence of free CPL by-products due to chain extension reaction (see Fig. 4a) could negatively affect the crystallization properties of the up-graded materials.

The crystallinity drop detected in chain extended products may affect their tensile behavior. In Fig. 5, representative stress–strain curves from quasi-static tensile tests on neat PA-2.7 and on the relative CBC chain extended products are reported, while Table 3 summarizes the most important tensile properties. The elastic modulus slightly decreases with the CBC content, probably because of the reduction in crystallinity degree. For the same reason, stress at yield (σ_y) decreases upon CBC introduction.

TABLE 3. Quasi-static tensile mechanical properties of neat PA-2.7 and relative CBC chain-extended products.

	E (MPa)	σ_y (MPa)	ε_y (%)	ε_b (%)
PA-2.7	1815 ± 18	72.6 ± 0.5	5.8 ± 0.1	72 ± 15
PA-CBC-0.1	1776 ± 11	74.2 ± 0.5	6.1 ± 0.1	76 ± 6
PA-CBC-0.2	1718 ± 14	73.6 ± 0.6	6.0 ± 0.1	99 ± 6
PA-CBC-0.4	1704 ± 33	67.9 ± 1.1	5.7 ± 0.3	323 ± 17

Interestingly, the strain at break (ε_b) noticeably increases with the CBC amount, passing from 72% for the neat PA-2.7 to 323% for the PA-CBC-0.4 sample. Similar effects were described by Lu et al. for PA6 systems chain extended with different kinds of bisoxazolines [16, 18].

In Fig. 6a–d, a direct comparison between the relative tensile properties (Fig. 6a–c) and the crystallinity degree (Fig. 6d) of the up-graded samples and of the virgin materials at different relative viscosity values are reported. In all these plots, the neat PA-2.7 sample was taken as reference. Considering standard deviation values associated to each measurement, it can be noticed that for virgin PA6 samples both the elastic modulus and the stress at yield do not substantially change with the relative viscosity values (Fig. 6a and b). Interestingly, while a limited strain at break enhancement can be registered for virgin PA6 having elevated η_{rel} values, the increase of the strain at break (ε_b) is more pronounced for chain extended materials (Fig. 6c). It is interesting to underline that the observed increase of the strain at break values observed in the present work is even more evident than that obtained in a previous work by using a PCPA blend, if samples with the same η_{rel} values are considered [24].

Moreover, from Fig. 6d, it can be inferred that the crystallinity drop due to the increase of the relative viscosity value (i.e. of the molecular weight) experienced for virgin PAs is less intense than that reported for the corresponding chain extended products. It can be therefore hypothesized that, while for virgin materials the observed crystallinity decrease is exclusively due to an increase of the molecular weight, in chain extended samples other factors can affect the crystallization behavior of the materials. As reported in Fig. 4a, the chain extension reaction by nucleophilic substitution reaction leads to the formation of a CPL molecule as by-product. This molecule can negatively affect the crystallization capability of the samples and can also have a plasticizing effect within the material, contributing thus to the increase of the strain at break values observed in chain extended samples.

It can be therefore concluded that chain extension upgrading reaction of PA6 through CBC can lead to the production of new materials having higher strain at break

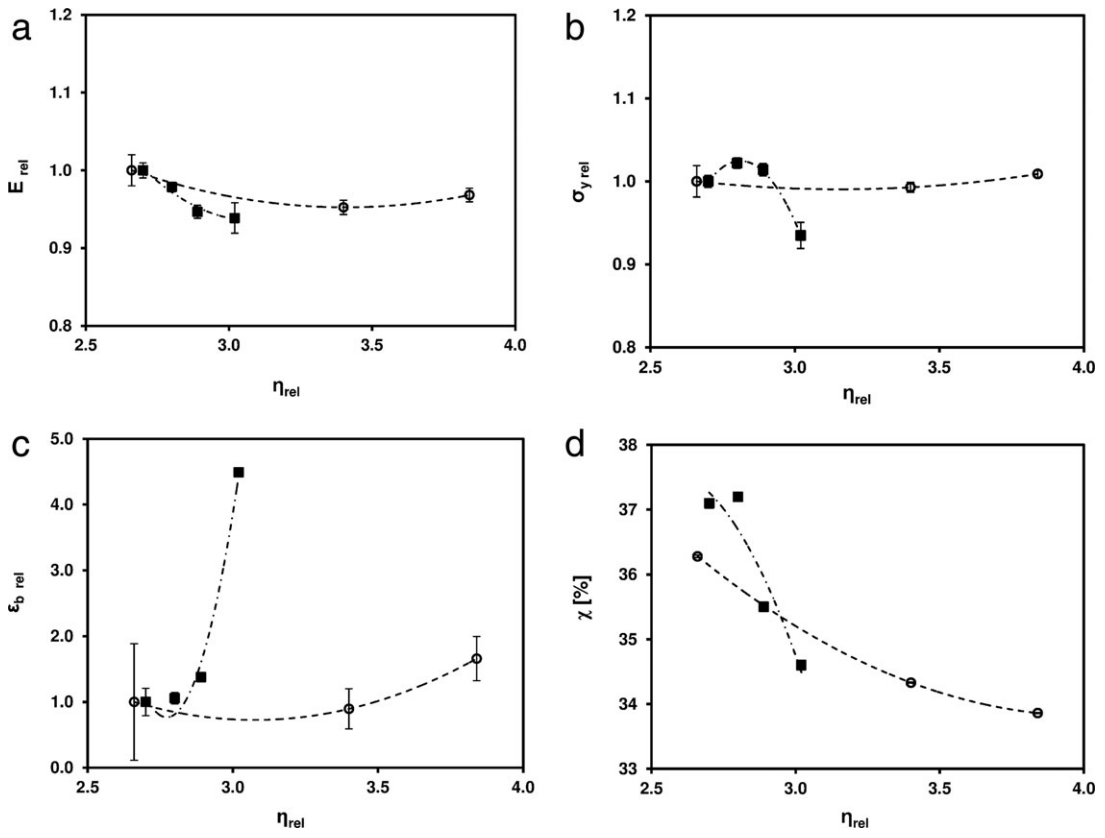

FIG. 6. Mechanical properties of (○) virgin and of (■) chain extended products as a function of the relative viscosity values. (a) Relative elastic modulus, (b) relative stress at yield, (c) relative strain at break, (d) relative crystallinity.

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values with respect to the corresponding virgin materials at the same molecular weight.

CONCLUSIONS

Different amounts of a CBC powder were melt compounded with commercial PA6 granules, to evaluate the chain extension behavior of the resulting materials through rheological, thermal, and quasi-static tensile tests. An interesting increase of the shear viscosity values (i.e. of the molecular weight) with the CBC loading was determined through dynamic rheological tests on the compounded pellets and relative viscosity measurements on the solubilized materials. Terminal groups analysis evidenced how chain extension process was related to the reaction of CBC with the $—NH_2$ functionalities of PA6, while the concentration carboxylic functionalities was practically unaffected by CBC introduction. Interestingly, a prolonged thermal treatment at elevated temperature produced a partial degradation of polymer with a reduction of its molecular weight. While elastic modulus and stress at yield were only marginally affected by CBC addition, the decrease of the crystallinity degree due to chain extension reaction was responsible of an important improvement of the strain at break values. Therefore, the addition of CBC powder to commercial PA6 matrices could represent an effective way to increase their molecular weight, leading to up-graded products with improved strain at break values.

ABBREVIATIONS

CBC	1,1′-Carbonyl-Bis-Caprolactam
CPL	Caprolactam
DSC	Differential Scanning Calorimetry
PA	Polyamide
PCPA	Polycarbonate/Polyamide blend
ROP	Ring Opening Polymerization
TFE	2,2,2 Trifluoroethanol

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