J Polym Res (2012) 19:9935
DOI 10.1007/s10965-012-9935-0

ORIGINAL PAPER

Thermo-mechanical properties of Polyamide 6 chemically modified by chain extension with Polyamide/Polycarbonate blend

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Received: 27 March 2012 / Accepted: 5 July 2012

Abstract A Polycarbonate/Polyamide (PCPA) blend was used as chain extender in a melt compounding process with a Polyamide 6 (PA6), by using a twin screw extruder. The chain extension capability of the PCPA blend was evaluated through rheological, thermal and mechanical tests. 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 and with the high temperature residence time. Terminal group analysis confirmed the increase of the molecular weight with the PCPA content and highlighted a preferential reactivity of the chain extender with amminic end groups. DSC tests showed a slight crystallinity decrease with the PCPA content, while both melting and crystallization temperatures were unaffected. Elastic and yield properties of chain-extended PA6 were similar to that of neat PA6 at different molecular weights, while crystallinity drop due to chain extension produced an increase of the strain at break values.

Keywords Polyamide · Chain extension · Viscosity · Crystallinity · Mechanical properties

Introduction

Due to the increasing consumption of plastic materials and the environmental pollution, recycling has gained an increasing importance in many areas of the human activities. Plastics production is directly linked to oil and natural resources consumption, with a negative impact on the environment and the climate [1]. It was therefore widely recognized that collection and recycling of plastic wastes is the only feasible way to avoid environmental pollution [2, 3]. Generally speaking, four main methods are actually utilized for the plastic waste recycling: energy recovery (incineration), landfilling, chemical processing (de-polymerization) and material recycling [4]. It was demonstrated that incineration and landfilling are increasingly unsatisfactory and unsafe, while landfilling is relatively expensive and incineration is not environmentally viable [5]. Also biodegradation can be hardly performed, because of the non degradable nature of the polyolefins and of the most common polymers. Therefore, recycling is the most feasible option to operate the disposal of plastic wastes in a convenient way [6]. Reprocessing wastes into a new material is the most convenient way, but it is also evident that material recycling can be successfully applied to a single-sort industrial plastic waste. Recycling plastics deriving from a mixture of several commodity polymers with various degrees of damage is a more difficult task. Materials obtained by this technology can be bulky but possess mediocre mechanical performances, because of the relative incompatibility of most polymer pairs [7]. The mechanical properties of immiscible polymer blends can be strongly improved by compatibilization, but this process is complicated and expensive, because simultaneous compatibilization of several damaged polymers is needed [8]. However, it is clear that the possibility of recycling polymers deriving from a specific product with a precise chemical composition represents the best way to process plastics wastes.

Polyamides, also called Nylon, are one of the most important commercial engineering resins [9]. Due to their good drawability and their similarity with silk fibers, they were

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initially used in the field of socks, carpets, rugs. Only subsequently they were utilized for engineering purposes, because of their excellent mechanical and chemical properties. Today Polyamides are widely used in fiber, film, packaging and moulding applications [10]. From a chemical point of view, Polyamide 6 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 Caprolactam are produced worldwide to synthesize Nylon-6. Approximately 1.3 million tons are consumed in Europe for textile yarns, industrial yarns and flooring [11]. In 2010, according to the last CARE Report, only the 4.5 % by wt. of post-consumer US carpet discards has been recycled [11]. In particular, polyamide fibers appear to predominate the scenario of recycled carpet materials. For these reason, appears evident the strategic interest in polyamide carpet recycling.

In the last decades, particular attention was devoted to downgrading plastics recycling technology. In these processes the material is recovered after use and re-utilized for less noble applications. However, this operation leads to a progressive loss of the material properties, up to the final disposal by landfill or incineration. On the contrary, in the upgrading process plastic wastes are recovered to their original inherent quality through chemical processes [12]. Even if there is necessarily a partial share of reinstatement with source material as the returns may not always be equal to 100 %, recycling through plastics upgrading has no limit and can be repeated several times. Generally speaking, post-industrial and post-consumed polymers have a lower molecular weight and mechanical performances with respect to the virgin polymers, because the degradative action of the UV radiation and of the thermal and mechanical stresses lead to a sensible drop of their physical properties. Different chain-extenders, specifically designed to restore the original properties of the degraded polymers, can be synthesized for the up-grading recycling. Generally speaking, chain-extenders are low molecular weight compounds that can be found on the market like additives in the form of blends. These additives can be used either during polymerization or during reactive extrusion processes. The optimal choice of the additive is very complex and depends from the processing technology. In the case of injection moulded products, a chain-extender having 2 or more functionalities may leads to a partial curing after moulding, thus increasing the stiffness of the material. On the other hand, chain extenders for polymers processed by spinning operations must be as linear as possible, to promote chain alignment and crystallization of drawn fibers. The most important 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].

In the case of polyamide chemical upgrading, the basic principle of the chain-extension lies in exploiting the reactivity of amino and carboxyl end groups of the PA macromolecules, in order to connect two or more polymer chains through a multifunctional agent [14, 15]. Quite surprisingly, only few publications on polyamide upgrading through chain-extenders can be found in literature. The greatest part of them are generally related to the use of different bisoxazoline coupling agents. For instance, Lu et al. carried out detailed studies on the chemical modification of PA6 by chain extension with 2,2′-Bis(2-oxazoline) [16], with Terephthaloyl-biscaprolactam [17] and with their combination [18]. When the optimum amount of chain extenders was added in PA6, the intrinsic viscosity of the polyamide considerably increased. The chain-extended PA6 dissociated at high temperature, and the degradation was suggested to proceed simultaneously from the onset of the chain extension reaction. Nery et al. [19] investigated the chain extension of carboxy-terminated aliphatic polyamides and polyesters by arylene and pyridylene bisoxazolines. It was found that 2,2′-(1,4-phenylene)bis(2-oxazoline) presented the highest reactivity and led to high-molar-mass polymers within 20 min at 200 °C without noticeable side reactions. The control of critical parameters (i.e. starting oligomer molar mass, bisoxazoline structure, oligomer/coupling agent molar ratio, reaction temperature) revealed necessary in order to control reaction kinetics, final copolymer molar mass, and thermal properties. Schacker et al. [20] investigated the chain extension of oligoamide or polyamide by using oxazoline. In particular, the melt viscosity of polyamides resulted to be enhanced in the extruder both by extending them linearly with a bisoxaline, and by bundling polyamide chains by grafting them onto a functionalized backbone chain (i.e. maleinated polystyrene), thus leading to branched chain extension. Yan et al. [21] analyzed carboxyl terminated polymer chain extension using bisoxazoline coupling agent by Monte Carlo simulation, while Qian et al. [22] have carried out studies on the chain extension of PA1010 by reactive extrusion by two different diepoxides as chain extenders, investigating also the rheological, thermal and the mechanical properties of the chain-extended materials.

Considering the limited number of papers regarding chain extension reaction with products different by Bisoxazolines, in this paper we investigated the efficacy of another kind of chain extender (i.e. a PCPA blend) in increasing the molecular weight of a commercial PA6 system. This chain extender was selected after a preliminary selection based on the thermal degradation stability through thermogravimetric (TGA) analysis. A detailed investigation on the rheological and mechanical properties of chain extended PA6 was carried out, in order to determine the appropriate chain extender amount and right set of process parameters to increase the properties of the pristine polymer in a controlled way. This investigation, conducted on virgin polymers, represents the preliminary step of an extended researched activity, with the objective to transfer these results to post-industrial and finally to post-consumer polymers. The chain extension behaviour was monitored through capillary rheological tests on the compounded materials at the molten state, through viscosimetry measurements and end group analysis on solubilized chips. The thermal properties of chain extended materials were investigated through DSC tests and correlated with their quasi-static tensile properties. Finally, a comparison between the mechanical properties of the compounded samples with that of the virgin polymers at different molecular weight was carried out.

Experimental part

Materials

Four kinds of virgin PA6 grades, different for their molecular weight, were supplied by Aquafil S.p.A (Arco, Italy) in the form of polymeric chips: Aquamid AQ24000, Aquamid AQ27000, Aquamid AQ34000 and Aquamid AQ40000. Polymeric chips of a Bruggolen® M1251 commercial masterbatch, supplied by Bruggemann Chemical KG (Heilbronn, Germany), were utilized as chain extender (designated as PCPA). All the materials were utilized as received. The properties of the different PA6 grades and of the chain extender are summarized in Table 1.

Sample preparation

Aquamid AQ27000 grade was chosen as reference material and melt compounded with different amounts of the chain extender, while the other PA6 grades were processed without the PCPA addition, in order to directly compare the mechanical properties of the chain extended products with those of the virgin materials having the same molecular weight (i.e. relative viscosity). Therefore, PCPA were melt compounded with AQ27000 chips at different amounts (ranging from 0.5 to 2 wt.%) in an industrial twin screw extruder, having a screw diameter of 42 mm and a L/D ratio between 32 and 48. After some preliminary trials, the following process parameters were selected: 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. These 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. In order to prepare ISO 527 1A dumbbell specimens for quasi-static tensile tests, the pellets were injection molded through a Battenfield Plus 350/075 machine. The following process parameters were set : screw temperature =255 °C, die temperature =260 °C, mould temperature =80 °C, filling time =0.4 s, injection pressure =35 bar. In this way about 30 specimens for each composition were prepared.

In the Results and Discussion section, the neat AQ27000 sample was denoted as PA-2.7, while the chain extended materials were designated indicating the matrix (PA6), the chain extender (PCPA) and its weight amount. As an example, PA-PCPA-1 indicates the AQ27000 sample chain extended with a PCPA content of 1 wt.%. In order to have a direct comparison, samples of PA6 grades without any chain extender addition were prepared with the same procedure.

Table 1 Properties of PA6 and of the chain extender used in this work

Property	AQ 24000	AQ 27000	AQ 34000	AQ 40000	PCPA
density (g·cm^{-3})	1.14	1.14	1.14	1.14	1.18
PA6 content (wt%)[a]	100	100	100	100	70.0
$\eta_{\mathbf{rel}}^{\mathbf{b}}$	2.4	2.7	3.4	4.0	–
T$_m$ (°C)	222	222	222	222	223
ΔH$_m$ (J·g^{-1})	73	70	66	66	29

[a] evaluated from FT-IR tests through a comparison with theoretical spectra of PC/PA blends at different relative compositions elaborated starting from the plots of the single constituents (PC, PA) through the software of a Perkin Elmer Spectrum 100 FT-IR spectrometer

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

Experimental methodologies

Dynamic rheological tests were performed by using a Dynisco Polymer LCR 52 M capillary rheometer, setting a chamber temperature of 260 °C and a shear rate interval between 100 and 1000 s^{-1}. Before testing, pelletized samples were dried in vacuum oven at 120 °C for 12 h. In order to evaluate the time dependency of the chain extension process and the thermal stability of the compounded materials, two different residence times (3 and 13 min) were utilized. These times were chosen according to the requirements of the industrial processing of polyamides. In particular, a time of 3 min is required at 260 °C to completely melt PA6 in the rheometer oven, while a period of 13 min represents the typical residence time at elevated temperature for a melt spinning process.

Relative viscosity tests were performed through an Ubbelohde viscometer according to ISO 307. In order to evaluate the effect of the residence time at high temperature on the chain extension process of compounded materials, both extruded pellets and samples deriving from dynamic rheological measurements at 3 and 13 min were tested. 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 were then put in a water bath at 25 °C for about 20 min and then tested at the same temperature.

In order to have a more detailed analysis about the reactivity of PCPA towards carboxylic and amminic groups of PA6, end groups analyses were performed both on extruded pellets and the samples obtained from dynamic rheological measurements at different residence times (3 and 13 min). 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 ambient temperature through a HCl 0.02 N solution, while COOH titration was carried out with a NaOH 0.02 N solution. End group analysis was performed by using the experimental equipment present in quality control laboratories of Aquafil group Spa. The adopted testing methods and the relative parameters have been optimized by this company through an experimental experience of 30 years, and the absolute error associated to each measurement is in the order of 1 $\text{mmol}_{eq}\ g^{-1}$. Differential scanning calorimetry (DSC) tests were performed on extruded pellets through a TA Instrument DSC Q20 calorimeter. 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 it was possible to determine the glass transition (T_g), the melting (T_m) and the crystallization temperature (T_c) of the compounded materials. 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} [23], as reported in the following expression:

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

Quasi-static tensile tests were performed at room temperature by using an Instron 4502 tensile testing machine, equipped with a load cell of 1 kN, imposing a crosshead speed of 50 mm min^{-1}. ISO 527 1A dumbell specimens, 10 mm wide and 4 mm thick, with a gage length of 80 mm, were tested. In this way it was possible to evaluate the most important tensile properties of the samples: elastic modulus (E), stress at yield (σ_y), deformation at yield (ε_y) and deformation at break (ε_b). At least five specimens for each sample were tested.

Results and discussion

The trends of the apparent shear viscosity of the 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 in Fig. 1a and in Fig. 1b. On a general level, it can be noticed for all the tested samples the typical pseudoplastic rheological behavior of unfilled thermoplastic materials [24]. After a plateau region at low shear rates, the

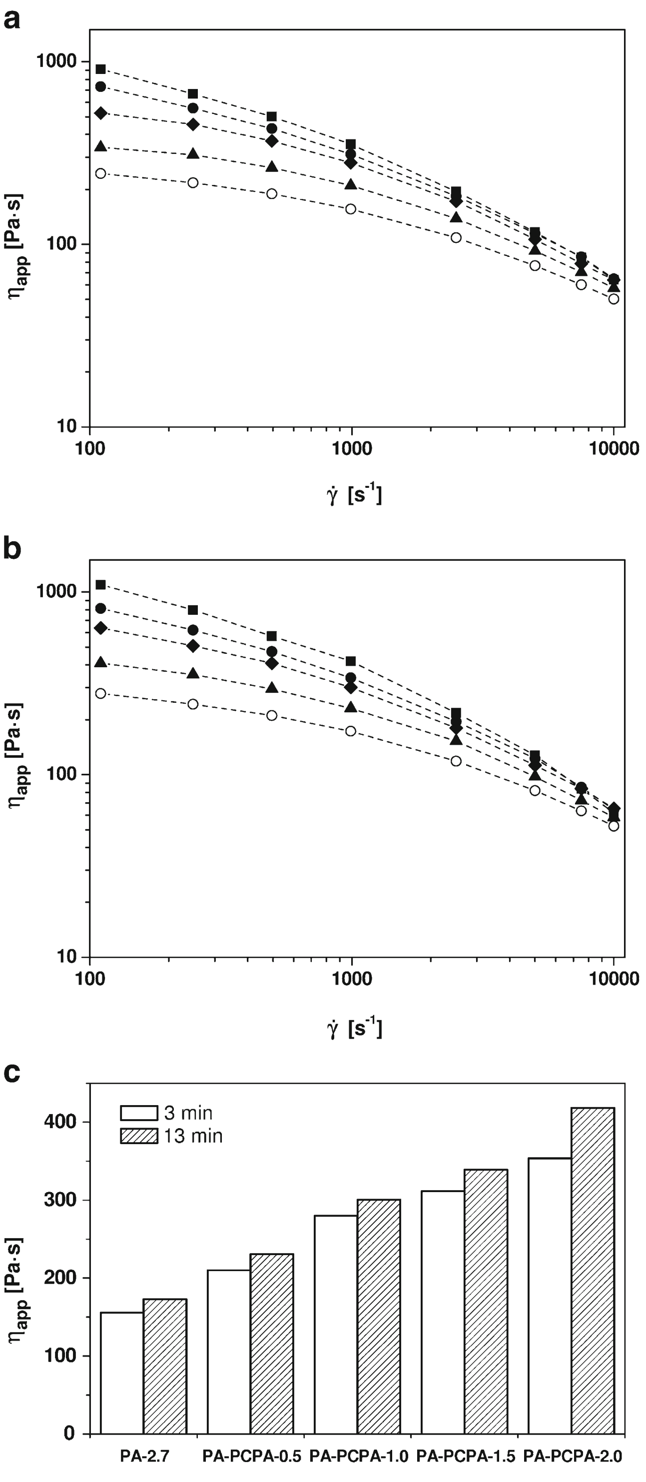

Fig. 1 Apparent shear viscosity of neat PA-2.7 and of the relative PCPA chain-extended products from rheological tests at T=260 °C. **a** Residence time 3 min, **b** residence time 13 min. (○) PA-2.7, (▲) PA-PCPA-0.5, (♦) PA-PCPA-1, (●) PA-PCPA-1.5, (■) PA-PCPA-2, **c** comparison of shear viscosity values at a shear rate of 1000 s^{-1}

apparent viscosity rapidly decreases with the shear rate (shear-thinning fluids). It can be noticed that the apparent viscosity increases proportionally to the PCPA content over the whole range of shear rates. The increase of the shear viscosity is more pronounced at low shear rates, while at higher shear rates η_{app} curves approach to that of the neat PA-2.7. Considering that above a certain molecular weight the shear viscosity is proportional to the molecular weight as a consequence of the formation of strong physical entanglements between the macromolecules [25], the observed increase of the shear viscosity values induced by PCPA can be directly related to an increase of the molecular weight. At elevated shear rates, the physical entanglements between the macromolecules are partially destroyed by the viscous flow and the viscosity increase due to PCPA is less pronounced. Similar conclusions were reported by Qian et al. for a PA1010 system chain extended by different kinds of diepoxides [22]. These results demonstrate the upgrading effectiveness of PCPA blends in increasing the molecular weight of PA6. Comparing Fig. 1a and b, it can be noticed that increasing the residence time at 260 °C from 3 min to 13 min η_{app} slightly increases, both for the neat PA-2.7 and for the chain extended materials. As suggested by La Mantia et al., if a careful drying is carried out before melt reprocessing operations, an interesting increase of the molecular weight can be obtained in polycondensation polymers, because of post-condensation reactions [26]. Considering that the increase of the shear viscosity provided by PCPA blends is not constant over the considered shear rate interval, in Fig. 1c a general comparison between apparent viscosity values at a shear rate of 1000 s^{-1} was reported. It can be observed that for elevated PCPA contents (2 wt.%) the viscosity increase registered passing from 3 min to 13 min cannot be explained as an effect of the post-condensation reaction. Therefore, this probably means that the chain extender did not totally react during extrusion process and it could further react with PA6 once exposed to high temperatures.

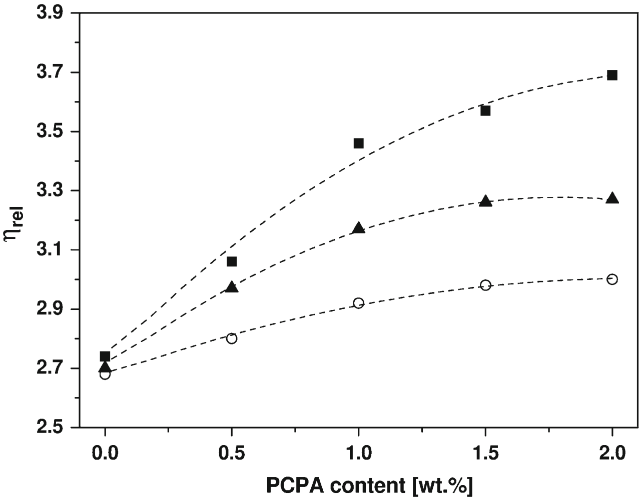

Fig. 2 Relative viscosity values of neat PA-2.7 and of the relative PCPA chain-extended products from rheological tests on H_2SO_4 solubilized chips, at different residence times in the rheometer. (○) Chips, (▲) 3 min, (■) 13 min

In order to confirm the upgrading capability of PCPA blends, capillary viscosimetry measurements were carried out on solubilized samples. Both extruded chips and samples tested in dynamic rheological measurements at two different times (3 and 13 min) were tested. In Fig. 2 relative viscosity values (η_{rel}) of neat PA-2.7 and of the relative chain extended products are reported. Even in this case an interesting increase of the relative viscosity values with the PCPA content can be observed for all the tested specimens. Even if η_{rel} values of neat PA-2.7 slightly increase with the residence time because of the effect of post-condensation reactions, the enhancement observed for PCPA chain extended products is more pronounced, especially at elevated PCPA amounts. Therefore, also relative

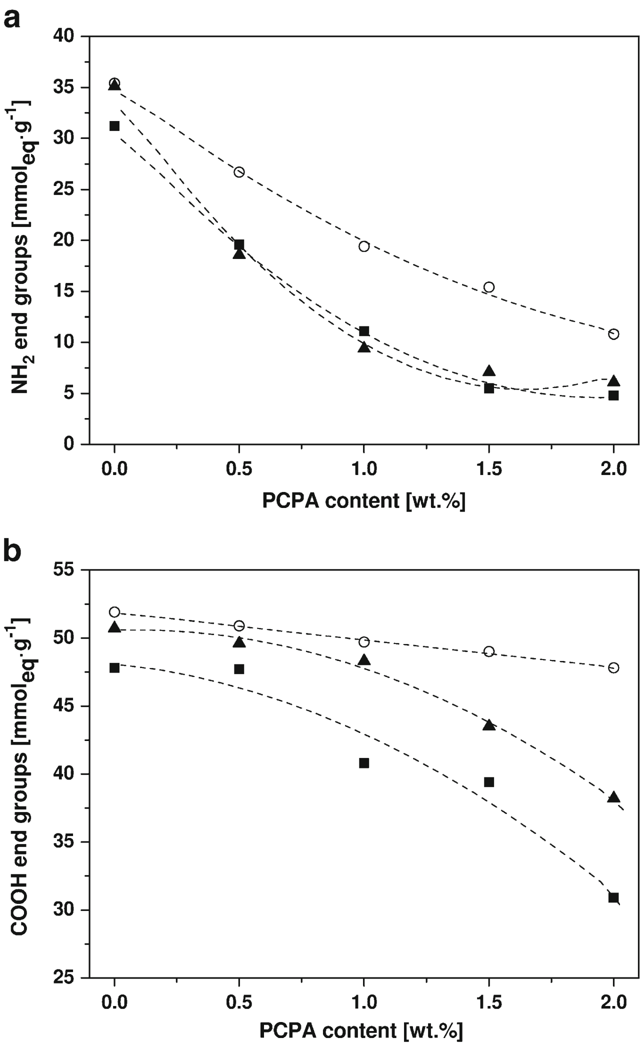

Fig. 3 **a** -NH_2 and **b** -COOH end groups analysis on neat PA-2.7 and relative PCPA chain extended products at different residence time in the rheometer. (○) Chips, (▲) 3 min, (■) 13 min

Table 2 Results of DSC tests on neat PA-2.7 and on the relative PCPA chain extended products

	First heating		Cooling			Second heating		
Sample	T_m (°C)	ΔH_m ($J \cdot g^{-1}$)	T_c (°C)	ΔH_c ($J \cdot g^{-1}$)	χ (%)	T_g (°C)	T_m (°C)	ΔH_m ($J \cdot g^{-1}$)
PA-2.7	228	69	184	70	37.1	55	223	70
PA-PCPA-0.5	228	65	183	65	34.3	54	222	64
PA-PCPA-1.0	226	65	181	66	34.6	53	222	67
PA-PCPA-1.5	228	63	180	64	33.8	53	222	64
PA-PCPA-2.0	226	65	181	64	33.7	53	221	64

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

viscosity measurements confirm that the upgrading capability of PCPA blends is proportional to its relative amount, and that a second thermal treatment can re-activate chain extension to an higher extent with respect to post-condensation reactions observed for neat PA6 chips.

The plots of the amminic and the carboxylic groups as a function of the chain extender amount from end group analysis on neat PA-2.7 and relative PCPA chain extended products are respectively reported in Fig. 3a and b. Even in this case both extruded pellets and samples obtained from dynamic rheological tests after different residence times were tested. As expected, the number of both amminic and carboxylic end groups decreases with PCPA content. Comparing Fig. 3a and b it can be seen that the reduction of amminic end groups due to PCPA introduction is more pronounced with respect to that observed for carboxylic groups. This probably means that the increase of molecular weight due to PCPA addition is mainly due to a reaction with PA6 amminic groups. From Fig. 3a it can be seen that an enhancement of the residence time from 3 min to 13 min does not leads to a further reduction of $-NH_2$ end groups. This means that a second thermal treatment of 3 min at 260 °C is sufficient to complete the chain extension reaction with amminic groups. On the contrary, Fig. 3b evidences that an increase of the thermal treatment up to 13 min leads to a further reduction of carboxylic end groups. This is not surprising, and in literature is widely reported that for dried polyamides an important increase of the molecular weight due to post-condensation reactions is possible at elevated temperatures [26]. The differential reactivity observed for PCPA chain extender can be probably explained considering that acid terminations preferentially react with amminic groups through nucleophilic substitution reactions [27]. From Fig. 3b it is evident that the relative reduction of carboxylic end groups due to the increase of the thermal treatment time is slightly influenced by the PCPA amount. Moreover, Fig. 2 showed how an increase of the residence time at elevated temperatures produces an increase of the molecular weight, more pronounced at elevated chain extender contents. This probably indicates that a processing time of 3 min is not sufficient to obtain a complete chain extension reaction, and more time is required to obtain an efficient diffusion of the reactants through the polymers and

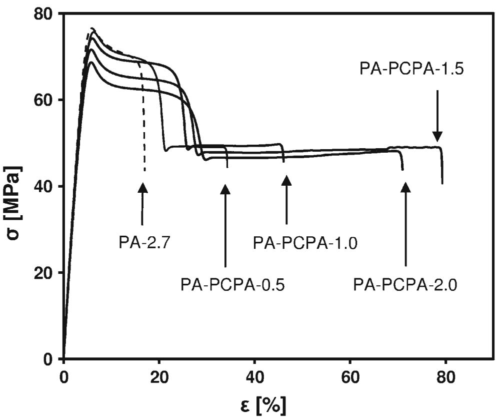

Fig. 4 Representative stress–strain curves from quasi-static tensile tests on neat PA-2.7 and relative PCPA chain extended products

Table 3 Quasi-static tensile mechanical properties of neat PA-2.7 and relative PCPA chain-extended products

	E (MPa)	σ_y (MPa)	ε_y (%)	ε_b (%)
PA-2.7	1780±79	74.2±2.3	5.6±0.5	19±10
PA-PCPA-0.5	1879±101	76.3±5.4	6.0±0.4	31±6
PA-PCPA-1.0	1783±45	74.0±0.8	5.8±0.2	46±7
PA-PCPA-1.5	1792±43	72.8±1.2	5.8±0.1	78±12
PA-PCPA-2.0	1759±32	71.1±1.3	5.7±0.1	77±11

a further enhancement of the molecular weight. Therefore, end groups analysis demonstrates how chain extension reaction really occurred in these systems, and 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. It is also possible to hypothesize that the presence of stiff polycarbonate macromolecules could contribute to the increase of relative viscosity values. However, the PC fraction in chain extended materials is very low at all the tested compositions (less than 1 wt.%). This means that the effect of PC on the rheological properties of the tested samples, if present, is probably very limited. A better comprehension of this aspects could be reached through the determination of intrinsic viscosity or through Gas Permeation Chromatograpy (GPC) measurements, and further efforts will be made in the future to get deeper insights on these open questions.

In Table 2 the main results from DSC tests conducted on extruded pellets of neat PA-2.7 and on the relative PCPA chain extended products are summarized. While both melting and glass transition temperatures are marginally affected by PCPA addition, both melting and crystallization enthalpy values progressively decrease with the chain extender amount. This means that the crystallization process of PA6 is partially hindered by chain extension reaction. Similar observations were reported by Lu et al. in their studies on the chemical modification of PA6 by chain extension with different kind of bisoxazolines [16–18]. In these works the depression of crystallinity 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 after the chain extension reaction. In our case it can be hypothesized that crystallinity reduction is due both to an increase of the molecular weight and to the steric hindrance produced by amorphous polycarbonate chains present in the PCPA blend. The crystallinity drop observed in chain extended products may affect their tensile behaviour.

Representative stress–strain curves from quasi-static tensile tests on neat PA-2.7 and on the relative PCPA chain extended

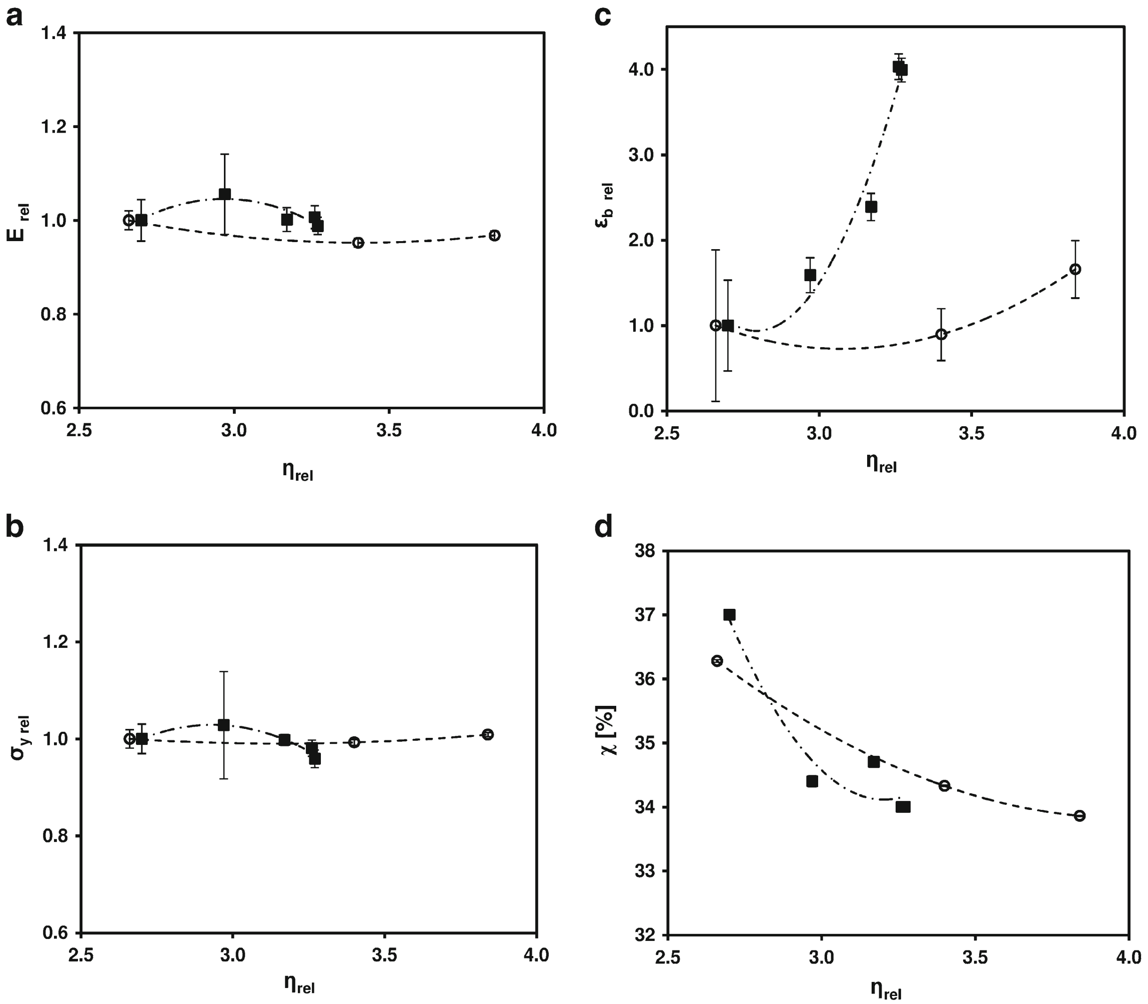

Fig. 5 Mechanical properties of (○) virgin and of (■) chain extended products as a function of the relative viscosity values. **a** Relative elastic modulus, **b** relative stress at yield, **c** relative strain at break, **d** relative crystallinity

products are shown in Fig. 4, while the most important tensile properties are summarized in Table 3. The elastic modulus of the neat PA-2.7 is not altered by PCPA addition, neither at elevated chain extender amount. This is probably due to the balance between two concomitant and contrasting effects: the stiffening effect due to the increase of the molecular weight and the decrease of the crystallinity degree at elevated PCPA amounts. For the same reason, the tensile properties at yield (σ_y, ε_y) are marginally affected by PCPA introduction. Interestingly, the strain at break (ε_b) noticeably increases with the PCPA amount, passing from 19 % for the neat PA-2.7 to 77 % for the PA-PCPA-2.0 sample. As mentioned before, this ε_b increase can be explained considering that the crystallinity drop induced by PCPA can positively affect the fracture toughness of the material. Similar conclusions were reported by Lu et al. for PA6 systems chain extended with different kinds of bisoxazolines [16, 18].

Considering that chain extension process should lead to new products having similar properties to those of virgin polymers at the same molecular weight, it can be interesting to compare the tensile properties of the up-graded products with those of virgin materials at different relative viscosity (Fig. 5a–d), taking the sample at η_{rel}=2.7 as reference. If standard deviation values are considered, it can be noticed that also for virgin PA6 samples both the elastic modulus and the stress at yield do not substantially change with the relative viscosity (Fig. 5a and b). Interestingly, while a limited strain at break enhancement can be registered for virgin PA6 having elevated η_{rel} values, ε_b increase is more pronounced for chain extended materials (Fig. 5c). In order to explain these results, from Fig. 5d it can be noticed that crystallinity drop for virgin PA6 at high molecular weight is less intense than that experienced for the corresponding chain extended products. In Fig. 3a and b a decrease of both NH_2 and COOH end groups due to the addition of PCPA compound was reported. This demonstrates how the chemical reaction between polyamides end groups and the chain extender, with a consequent increase of the molecular weight, effectively occurred. Moreover, in Fig. 4d a decrease of the crystallinity due to the increase of the relative viscosity value (i.e. molecular weight) for the virgin polyamides was reported. This indicates that an increase of the molecular weight in these systems could lead to a decrease of the crystallinity values. However, from Fig. 5d it is evident how the decrease of the crystallinity experienced in chain extended polyamides is slightly higher than that reported for virgin polymers with the same relative viscosity values. It is probable that the presence of small amounts of amorphous polycarbonate chains and of some lateral ramifications due to PCPA extension could represent a steric hindrance for the alignment and the subsequent crystallization of PA macromolecules. Therefore, it is possible to conclude that the observed decrease of crystallinity in chain extended materials is related both to an increase of the molecular weight and to a steric hindrance provided by polycarbonate component in the blends. However, a neat separation between these two effects is very difficult from an experimental point of view, and further investigations will be performed in the future to get a better comprehension of these phenomena.

Concluding, PA6 up-grading through chain extension with PCPA leads to new materials having the same elastic and yield properties with respect to the corresponding virgin materials at the same molecular weight, but with strongly improved strain at break values.

Conclusions

A Polycarbonate/Polyamide blend was melt compounded with a Polyamide 6 matrix in order to evaluate the chain extension behaviour of the resulting materials through rheological, thermal and quasi-static tensile tests.

Dynamic rheological tests on the compounded pellets and relative viscosity measurements on the solubilized materials evidenced an interesting increase of the shear viscosity values (i.e. of the molecular weight) with the PCPA loading. A second thermal treatment at high temperature produced a further progression of the chain extension reaction. Furthermore, terminal group analysis evidenced how PCPA preferentially reacted with amminic groups rather than carboxylic functionalities. While both melting and crystallization temperatures were not affected by chain extension, PCPA addition produced a decrease of the crystallinity degree, that was responsible of an improvement of the strain at break values.

Therefore, addition of PCPA blends could represent an effective way to increase the molecular weight of PA6 matrix, leading to upgraded products having the same stiffness of the corresponding virgin materials at the same molecular weight, but with much higher strain at break values.

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